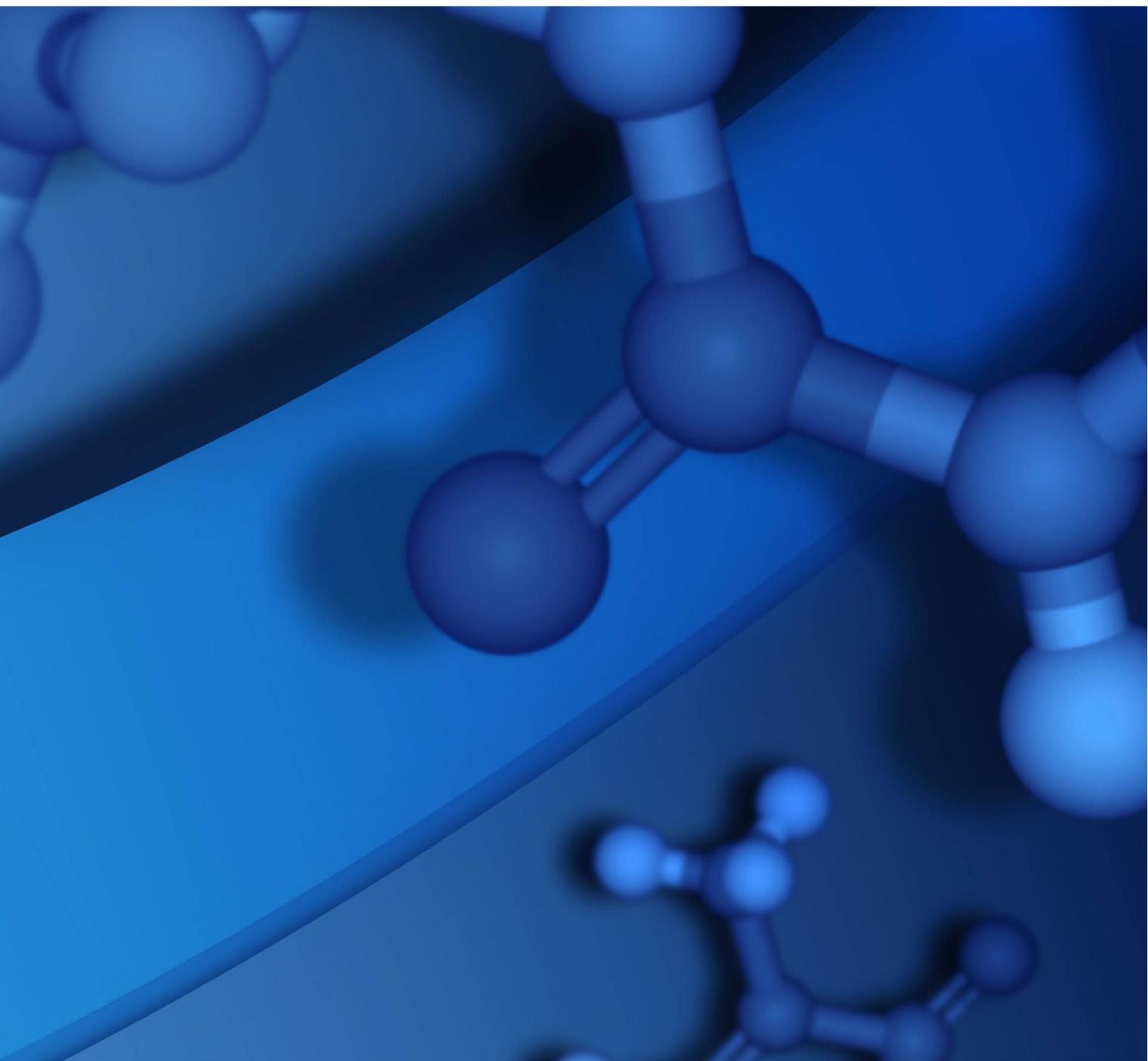


MODULES TUTORIALS

MATERIALS STUDIO 2025



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Acknowledgments and References

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Tutorials

This section contains tutorials for the modules you have installed.

Note: Numbers in the tutorials are shown in American English format. If your system is configured for a different locale, you should "translate" the numbers to the format appropriate to your locale before entering them.

For example, if your system is configured for the German locale, and a tutorial asks you to enter a value of 5,000 (five thousand), you should enter 5.000.

Chapter 1: Adsorption Locator tutorials

The following tutorials illustrate how to utilize the Adsorption Locator's capabilities.

- [Determining the location of SO₂ on the Ni\(111\) surface with Adsorption Locator](#)
- [Modeling inhibitor adsorption onto a Pigment Red crystal face](#)

Determining the location of SO₂ on the Ni(111) surface with Adsorption Locator

Purpose: Introduces the use of Adsorption Locator to study the adsorption of different types of adsorbates onto substrates of different nature.

Modules: Materials Visualizer, Adsorption Locator, Forceite

Time:   

Prerequisites: Sketching a benzamide molecule Visualizer Tutorial

Background

A paper on "Density functional theory investigation of the structure of SO₂ and SO₃ on Cu(111) and Ni(111)" by Harrison et al. ([2006](#)) inspired this tutorial. The importance of the adsorption of SO₂ and SO₃ molecules relates to the necessity of scrubbing such environmental pollutants from power station emissions. The paper presents DFT calculations on a number of geometries of the adsorbed SO₂ molecules.

You can use Adsorption Locator as a preparatory and screening tool in two ways:

- to generate adsorbed configurations automatically, which you can then use as starting points for further DFT studies such as in the above paper.
- to use the forcefield method to obtain a ranking of the energies for each generated configuration, which indicates the preferred adsorption sites.

This tutorial concentrates on the case of SO₂ on Ni(111), and covers:

- [Getting started](#)
- [To prepare the structures](#)
- [To set up the Adsorption Locator calculation](#)
- [To analyze the results](#)
- [Summary](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

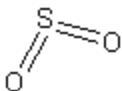
Open the **New Project** dialog and enter **Ni_SO2** as the project name, click **OK**.

This creates the new project with *Ni_SO2* listed in the Project Explorer.

2. To prepare the structures

In this section of the tutorial, prepare the structures of the Ni(111) surface and the SO₂ adsorbate. First prepare the SO₂ molecule.

Adsorption Locator: Determining the location of SO₂ on the Ni(111) surface with Adsorption Locator



Select **File | New...** from the menu bar to open the New Document dialog, double-click **3D Atomistic**. Using the sketching tools, **build an SO₂ molecule** defining both S-O bonds as double bonds, click **Clean** . Select **File | Save** from the menu bar and save the structure as **SO2.xsd**.

Optimize the SO₂ molecule before adsorbing it onto the Ni surface that you will construct.

Select **Modules | Forceite | Calculation** from the menu bar to open the Forceite Calculation dialog. On the **Setup** tab, change the *Task* to **Geometry Optimization** and the *Quality* to **Fine**.

Select the **Energy** tab and change the *Forcefield* to **COMPASSIII**. Click **Run**.

When the job has completes, this creates the optimized structure in **SO2_Forceite_GeomOpt/SO2.xsd**.

Now, construct a Ni(111) surface.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Structures/metals/pure-metals** and import **Ni.xsd**.

Select **Build | Surfaces | Cleave Surface** from the menu bar to open the Cleave Surface dialog. Change the *Cleave plane (h k l)* to **1 1 1** and press **TAB**. Increase the *Fractional Thickness* to **6.0** and press **TAB**. Click **Cleave** and close the dialog.

Choose the number of layers in the structure so that the depth of the surface is greater than the non-bond cutoff used in the calculation. The choice of the cutoff is always a trade-off between the accuracy and the time required for the calculation. Using 6 layers of Ni atoms gives a sufficient depth that the SO₂ molecule can only be involved in non-bond interactions with Ni atoms in the layers of the surface, without increasing the calculation time unreasonably.

Next, build a 2×2 supercell to expose a more realistic surface area for docking the SO₂ molecules.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase the values of **U** and **V** to **2** and click **Create Supercell**. **Close** the dialog.

Convert this structure to have 3D periodicity. As the calculation uses 3D periodic boundary conditions, it is important that the size of the vacuum is great enough that the non-bond calculation for the sorbate does not interact with the periodic image of the bottom layer of atoms in the surface. Base the vacuum depth on the non-bond cutoff and the shape of sorbate molecule, an over-estimation ensures that the sorbate interacts only with the surface.

In this case, a distance of 15 Å between the Ni surface layer and the next layer beyond the vacuum is sufficient. This prevents any non-bond interactions between the next repeat unit and either the Ni surface or the SO₂ molecule.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. Specify the value of **Vacuum thickness** as **15.0** and click **Build**.

To display the Ni atoms more clearly, use the ball and stick display style.

Select **View | Display style** from the menu bar to open the Display Style dialog. On the **Atom** tab, change the *Display style* to **Ball and stick**, then close the dialog.

3. To set up the Adsorption Locator calculation

You can now set up the Adsorption Locator calculation. Define the settings for the quality and the forcefield and the method for selecting the location of the sites to probe in the calculation.

Click the **Adsorption Locator** arrow  on the **Modules** toolbar and select **Calculation** from the dropdown list to open the Adsorption Locator Calculation dialog. Ensure that **Ni (1 1 1).xsd** is the active document.

On the **Setup** tab, select **Fine** as the *Quality*. Select **SO₂ Forceit GeomOpt/SO₂.xsd** from the **Adsorbate** dropdown list. Specify the value of **Loading** as **1**.

On the **Energy** tab, select **COMPASSIII** from the **Forcefield** dropdown list.

On the **Location** tab, select the **Surface region defined by atom set** checkbox.

When you select **Fine** as the *Quality* of the calculation, this uses many simulated annealing cycles with many steps per cycle, to obtain good statistics.

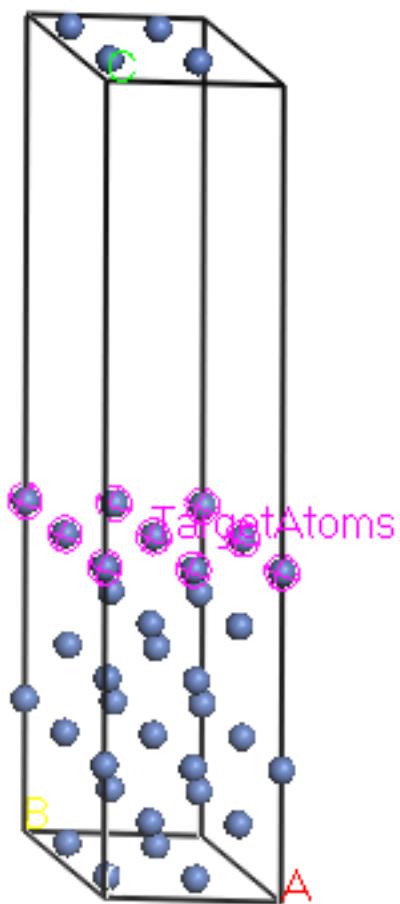
Next select the atoms that define the surface region.

Select the **top layer of Ni atoms**, this displays them in yellow.

Tip: If you are not familiar with selecting atoms, refer to the Opening and Viewing 3D Atomistic Documents visualizer tutorial.

On the **Location** tab of the Adsorption Locator Calculation dialog, click **Add** to include the selected atoms in the *TargetAtoms* set for the adsorption calculation. Select the **Set maximum adsorption distance** checkbox, and enter a value of **5.0**.

This samples the region defined by the specified maximum distance from the selected target atoms for adsorbate inclusion. A value of **5.0** allows the system to develop new configurations of SO₂ adsorbed onto the Ni surface. If the maximum adsorption distance is too short some configurations are not accessible, and if it is too long no new configurations are added.



Ni(111) after defining the TargetAtoms set

The fixed energy window is used to select which configurations are reported. In this case, this returns all configurations that differ from the lowest configuration by less than 100 kcal/mol. In initial calculations, it is useful to use a wider energy window, as this ensures that no significant configurations are missed.

On the **Properties** tab, select the checkboxes for **all properties**. Select the option for **Fixed energy window** and enter a value of **100** kcal/mol.

You are now ready to run the calculation.

Click **Run** and close the dialog.

4. To analyze the results

When the calculation begins Materials Studio, this creates a new folder called *Ni (1 1 1) Adsorption Anneal*. Once the calculation complete, this returns all results to this folder.

Open the 3D Atomistic document **Ni (1 1 1) Fields.xsd**.

This file displays a field of adsorption sites, the higher density of points showing more likely locations.

Adsorption Locator: Determining the location of SO₂ on the Ni(111) surface with Adsorption Locator

Right-click in the document and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Field** tab, select the **Color by field values** option and the **Volume** display style. Close the dialog.

This shows the more likely adsorption areas in green and the less likely sites in red.

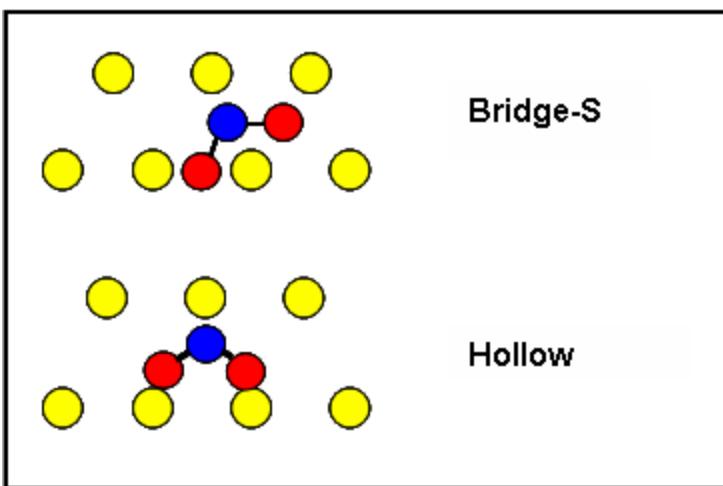
Open the study table **Ni (1 1 1).std**.

This contains the structures and energies of the lowest energy configurations. Compare the one found here with the lowest one found in the paper.

Repeat the Adsorption Locator calculation using Cu in place of Ni.

5. Summary

Your Adsorption Locator calculations yield results similar to the following.



Schematic view of two possible bonding sites

Tip: To improve the view of the energy fields over the Ni surface, select all the non-surface Ni atoms and choose *None* for their display style.

Because the Monte-Carlo approach has a statistical component, your results might be slightly different. To obtain results that are consistent between repeated calculations, run longer, more accurate simulations.

For SO₂ on Ni, the bridge site is lowest in energy, in agreement with the [paper](#) by Harrison et al. That paper also reports no appreciable difference in energy between the bridge and the hollow sites for SO₂ on Cu.

This is the end of the tutorial.

M. J. Harrison; D. P. Woodruff; J. Robinson, "Density functional theory investigation of the structure of SO₂ and SO₃ on Cu(111) and Ni(111)" by , *Surface Science*, **600**, 1827, (2006).

Modeling inhibitor adsorption onto a Pigment Red crystal face

Purpose: Illustrates how to calculate binding energies to evaluate the potential of an additive using Adsorption Locator.

Modules: Materials Visualizer, Adsorption Locator, Forcite, COMPASS

Time:  

Prerequisites: Using the Crystal Builder Visualizer Tutorial

Background

The bulk shape of crystals is critically important to many industrial processes. There are numerous examples of processes in the chemical and pharmaceutical industries where crystal shape is an important factor, including:

- Dissolution rate of chemicals and biological availability of drugs
- Handling, packaging, and storage of crystalline products
- Slurry handling, caking, and filtration during processing
- Milling, grinding, fragmentation, and dusting
- Density and texture optimization
- Wax and scale formation in petrochemicals

The relationship between the crystal morphology and the internal arrangement of atoms in the crystal is therefore of great interest to chemists, chemical engineers, and process engineers. Rationalization of this relationship allows prediction of crystal shape, development of tailor-made additives, and control of solvent and impurity effects. The effect of additives on crystal growth and the resultant morphology is therefore of great interest. Adsorption Locator can model the adsorption of an additive onto a crystal face and thus provide access to the energetics of the adsorption and its effects on crystal growth.

Introduction

Pigment Red (a diphenyl derivative of 1,4-diketopyrrolo(3,4-c)pyrrole, DPP) is a high-quality heterocyclic pigment, offering good heat stability, high coloring strength and hiding power, and excellent light and weather fastness. It can be produced as transparent or opaque color by controlling the particle size during manufacture.

In this tutorial, you study the distances between functional groups on surfaces. The results suggest that an amino acid derivative that could act as a growth inhibitor, slowing down the growth rate of the fast growing faces. You model the binding of this additive to one fast growing face using the Adsorption Locator module and the COMPASS forcefield.

This tutorial covers:

- [Getting started](#)
- [To prepare a crystal surface](#)
- [To create an additive](#)
- [To study interactions between the surface and the additive](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Pigment Red Additive** as the project name, click **OK**.

This creates the new project with *Pigment Red Additive* listed in the Project Explorer. Now, import the input file to study.

In the Project Explorer, right-click the project root and select **Import...** to open the Import Document dialog. Navigate to **Examples/Documents/3D Model**, select **pigment_red_010.xsd**, and click **Open**.

2. To prepare a crystal surface

In this section, you build a slab (a surface with a region of vacuum) from the (0 1 0) Pigment Red surface. The crystal is constructed by repeating the surface in a given direction using a repeat distance that is greater than the surface thickness. This introduces a region of vacuum between the surface blocks.

The surface needs to be big enough to accommodate the particular inhibitor being studied.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase the **Supercell range** to **4** for **U** and **6** for **V**. Click **Create Supercell** and **close** the dialog.

This displays an enlarged surface. You can now construct a 3D slab from the 2D surface model.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. On the **Vacuum Slab** tab, change the **Vacuum thickness** to **50 Å** and click **Build**.

Click **Display Style**  on the **3D Viewer** toolbar to open the Display Style dialog. On the **Lattice** tab, specify the **Max** value for **C** as **2.00**.

This orients the vacuum along the c-axis.

Later on in the tutorial, you will add an additive to the surface. The additive could potentially interact with both the surfaces because of the periodic boundary conditions. Therefore, you have added a large region of vacuum above the surface so that the additive can only interact with one of the surfaces. In this case, the thickness of the (0 1 0) surface is about 20 Å, so a vacuum region thickness of 50 Å is sufficient.

Change the **Max** value for **C** back to **1.00** and **close** the Display Style dialog.

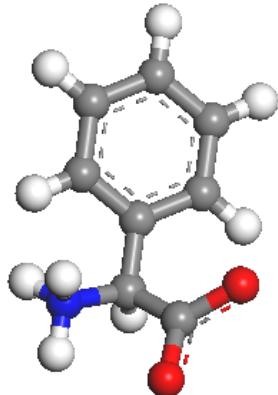
Select **File | Save Project** from the menu bar, followed by **Window |Close All**.

3. To create an additive

The inhibitor used in this tutorial, 2-phenylglycine, is an amino acid derivative that exists as a zwitterion.

Click the **New** arrow  and select **3D Atomistic Document** from the dropdown list. In the Project Explorer, right-click **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Change the name of the document to **inhibitor.xsd**.

Use the tools on the **Sketch** toolbar to construct the 2-phenylglycine molecule (shown below) and then tidy up the structure using the **Clean** tool .



Molecular structure of the inhibitor, 2-phenylglycine

Now, optimize the molecular structure of the inhibitor using Forcite and the COMPASS forcefield.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog.

Select **Geometry Optimization** from the **Task** dropdown list. On the **Energy** tab, choose **COMPASSIII** as the **Forcefield**. Specify **Atom Based** for both the **Summation methods**.

On the **Job Control** tab, select **My Computer** as the **Gateway location** and click **Run**.

This creates a new folder called **inhibitor Forcite GeomOpt**, in the Project Explorer. The calculation takes less than a minute to complete. When the calculation has finished, this saves the minimized structure in a new folder as **inhibitor . xsd** and displays it in the Materials Visualizer.

Select **File | Save Project** from the menu bar and close all the open documents.

4. To study interactions between the surface and the additive

Now that you have constructed a 3D slab of the Pigment Red (0 1 0) surface and optimized the structure of the inhibitor, position the inhibitor over the surface.

In the Project Explorer, double-click **pigment_red_010.xsd**.

Next, run an adsorption calculation to explore the likely binding site and the orientation of the inhibitor molecule on the surface. Then run a geometry optimization of the inhibitor molecule on the crystal surface to obtain the global minimum energy orientation.

Select **Modules** | **Adsorption Locator** | **Calculation** from the menu bar to display the Adsorption Locator Calculation dialog.

On the **Setup** tab, select **Simulated annealing** from the **Task** dropdown list. Choose the optimized **inhibitor.xsd** as the **Adsorbate** and select **Coarse** as the **Quality**.

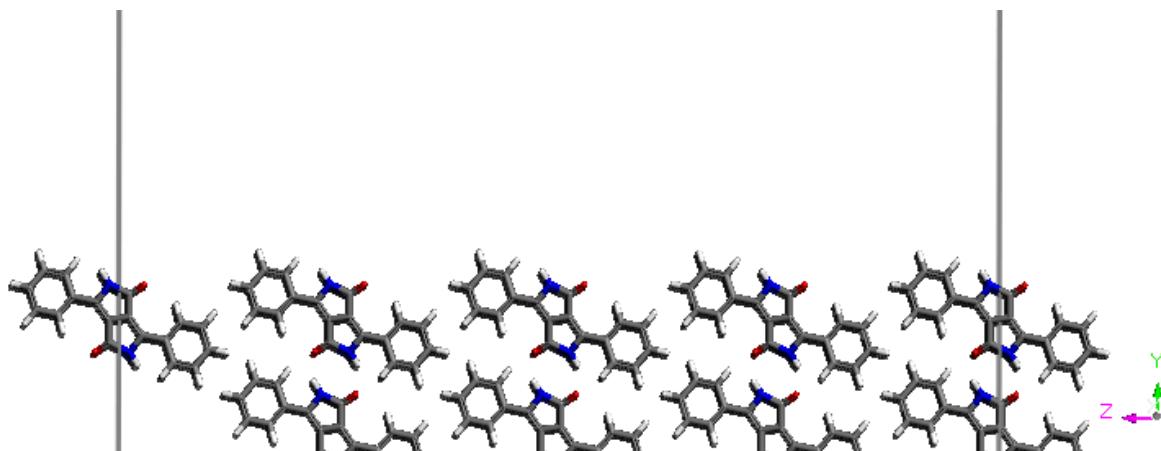
On the **Energy** tab, choose **COMPASSIII** as the **Forcefield**. In the *Summation method* section, select **Ewald** for **Electrostatic** and **Atom Based** for **van der Waals**.

You can restrict the search space used in the sampling in a number of ways. In this tutorial, define the search to be within 10 Å of the hydrogen bond donors and acceptors on the surface.

On the **Location** tab, select the **Surface region defined by atom set** checkbox.

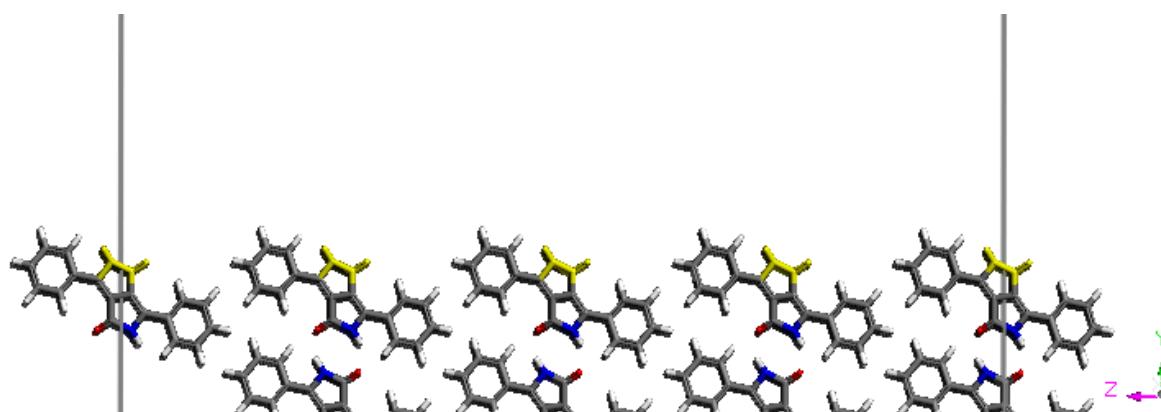
Define the hydrogen bonding moieties on the surface as sites where adsorption of the potential inhibitor can occur.

In **pigment_red_010.xsd** rotate and zoom in on the surface of one of the crystal layers.



Pigment Red 010 surface oriented to view the structures side-on.

Hold down the **Q + SHIFT** keys and lasso all the **amide** groups in the top layer of molecules.



Pigment Red 010 surface with surface amides selected

Adsorption Locator: Modeling inhibitor adsorption onto a Pigment Red crystal face

On the **Location** tab of the Adsorption Locator Calculation dialog, click **Add selected atoms to TargetAtoms set**. Select the **Set maximum adsorption distance** checkbox and enter a value of **10.0**.

Click **Run** and close the dialog.

This creates a new folder called **pigment_red_010 Adsorption Anneal** in the Project Explorer. The calculation might take some time to complete, depending on the speed of the processor in your computer.

As the calculation runs, this updates a chart containing various energy contributions. The text document **Status.txt** reports the computation time and the number of steps completed so far. When the calculation is complete, the **pigment_red_010.xsd** document reports the results.

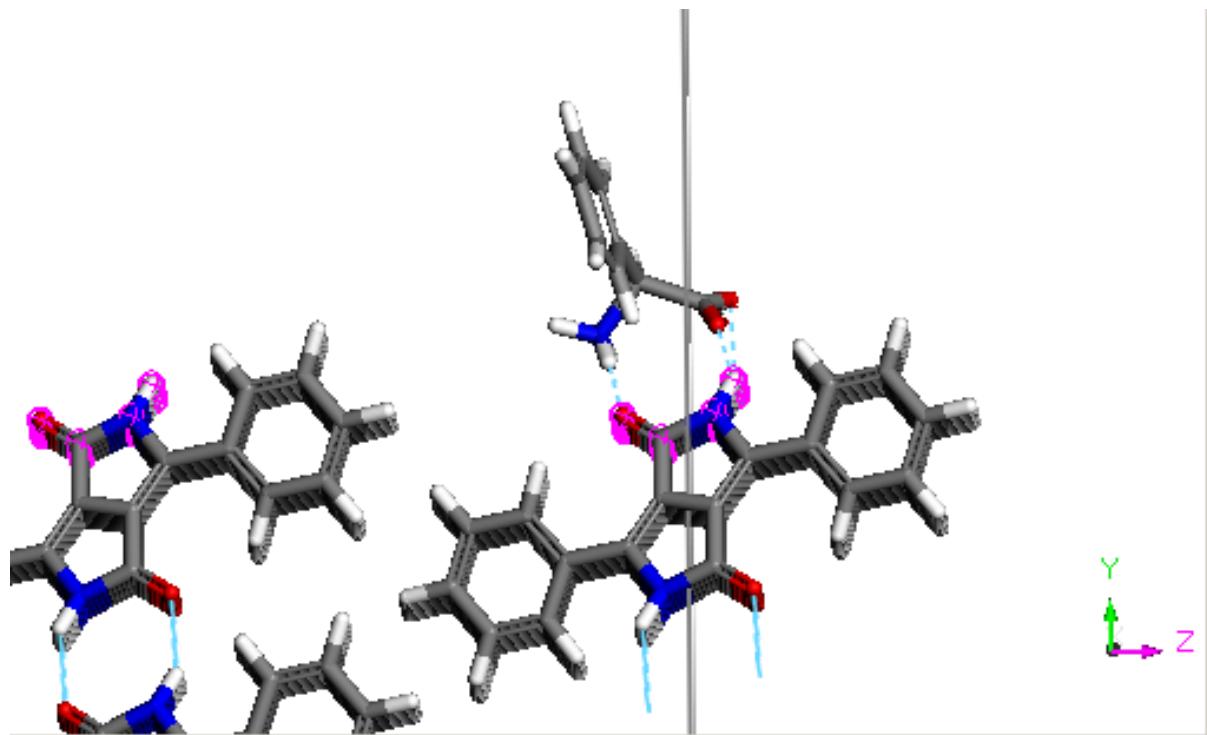
Wait until the job finishes before proceeding. On completion, this returns a study table containing a number of low energy configurations, together with the energetic properties of each configuration.

Open the study table **pigment_red_010.std** and double-click the structure in the first row.

You can observe the interaction between the inhibitor and the surface amide groups by displaying the hydrogen-bonding patterns.

Click **Calculate Hydrogen Bonds** .

Your result might vary slightly from the image below.



Crystal surface with attached inhibitor

The third column *Adsorption energy* contains the most relevant energy parameter for adsorption. This comprises two parts:

- The energy of adsorbing the sorbate onto the surface in its input conformation, listed in column *D*.
- A small deformation energy because of the relaxation of the sorbate in the presence of the surface, listed in column *E*.

The second column, *Total energy* contains the adsorption energy plus the internal energy of the sorbate. It does not include the energy of the framework.

The last column *F* is the differential adsorption energy, which is the energy of adding a sorbate of a particular component. Since in this case there is only 1 molecule and 1 component, this is the same as column *C*.

The *attachment* energy for the (0 1 0) face was previously calculated as around -27 kcal/mol. If you want to obtain this energy using Materials Studio, the procedure in the *Morphology prediction for Pigment Red* tutorial for the Morphology module describes the steps in detail.

For the (0 1 0) face, the adsorption energy as calculated by Adsorption Locator is more negative than the attachment energy. Therefore, 2-phenylglycine is a good candidate to inhibit the growth of the fast growing (0 1 0) face of Pigment Red crystals, which produces a more isometric crystal morphology.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

- Hartman, P.; Perdok, W. *Acta Crystallogr.*, **8**, 521 (1955).
Bennema, P. *J. Cryst. Growth*, **166**, 17 (1996).

Chapter 2: Amorphous Cell tutorials

The following tutorial illustrates how to utilize Amorphous Cell's capabilities.

Amorphous Cell is also used to construct starting structures in several [Forcite Plus](#) tutorials.

Packing molecules into existing structures

Purpose: Demonstrates how to pack molecules into existing structures using Amorphous Cell

Modules: Materials Visualizer, Amorphous Cell

Time:  

Prerequisites: Sketching organometallic structures, Using the polymer builder, Field segregation and analysis Visualizer Tutorial

Background

The Amorphous Cell module enables the construction of 3D periodic boxes of amorphous polymers and other amorphous materials. However, it can also be used as a fast method to soak a pre-existing structure such as a nanocluster with a small molecule or polymer. The Packing task can also be used to build non-orthorhombic amorphous cells by allowing you to pack into an empty cell.

Introduction

In this tutorial you will build a carbon nanotube in a box and then soak the nanotube with water. Using the same nanotube structure, you will use field segregation to pack ferrocenes into the nanotube and polymer around the outside of the nanotube. Such systems have potential commercial applications as nanotube conductors.

This tutorial covers:

- [Getting started](#)
- [To create the nanotube](#)
- [To soak the nanotube with water](#)
- [To set up the structures and isosurfaces](#)
- [To pack into isosurface enclosed volumes](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **packing** as the project name, click the **OK** button.

The new project is created with *packing* listed in the Project Explorer.

2. To create the nanotube

The first step is to build a carbon nanotube using the Nanotube building tools.

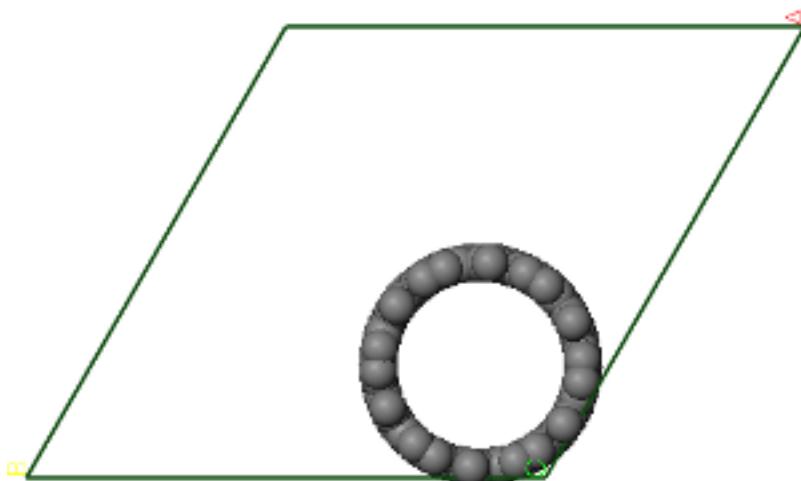
Select **Build | Build Nanostructure | Single-Wall Nanotube** from the menu bar to open the Build Single-Wall Nanotube dialog. Change **N** to **12** and click the **Build** button. Close the dialog.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase **C** to **2** and click the **Create Supercell** button. Close the dialog.

A periodic nanotube is created. You will need some space to pack the polymer so you should increase the size of the lattice, keeping the position of the nanotube constant.

Right-click in the 3D viewer and select **Lattice Parameters** from the shortcut menu to open the Lattice Parameters dialog. On the **Advanced** tab uncheck the **Keep fractional coordinates fixed during changes to the lattice** checkbox. On the **Parameters** tab double the **A** and **B** lengths to **31.55**. Close the dialog.

You should have a structure which looks similar to the one below.



Initial structure containing a single nanotube, displayed in CPK style.

You will use this structure twice so you should make a copy of it.

Select **File | Save As...** to open the Save As dialog. Set the **File name** to **SWNT_water.xsd** and click the **Save** button. Repeat this, naming the second copy **SWNT_polymerFe.xsd**.

You are now ready to pack the first nanotube with water.

3. To soak the nanotube with water

Before soaking the nanotube with water, you need to sketch a molecule of water.

Create a new **3D Atomistic document** and rename the new document **water.xsd**. Use the sketching tools to sketch a molecule of water.

Now you are ready to soak the nanotube with water.

Change focus to **SWNT_water.xsd**. Select **Modules | Amorphous Cell | Calculation** from the menu bar to open the Amorphous Cell Calculation dialog.

The packing task is used to pack molecules into an existing structure.

[Amorphous Cell: Packing molecules into existing structures](#)

Change the **Task** to **Packing**.

For the Packing task the components in the system are specified according to their molar ratio. This gives you the option to pack with combinations of molecules. However, in this case, you will pack with water only.

In the **Composition** table, click in the **Molecule** column and select **water.xsd** from the dropdown list.

You can set the density of the packed structure. Note that this is the density of all atoms inside the volume available for packing, which may or may not include the framework atoms. In this tutorial you will explore how to control the packing volume.

The output option allows you to build multiple frames so you can review the building process later. However, in this case, you will just build one frame.

Click the **Options...** button to open the Amorphous Cell Options dialog.

On this dialog, you can control how torsions are defined, the building steps, and whether energies are used in the calculation. For this small molecule, you could switch off energies for the build and just pack with a scaled van der Waals radius penalty. This significantly increases the speed of the packing task. However, you will get a more optimal structure if you build with energies and optimize geometry. In this tutorial you will use the default settings.

Close the **Amorphous Cell Options** dialog. On the **Setup** tab, click the **More...** button to open the Amorphous Cell Packing dialog.

You can choose whether to pack into an isosurface enclosed volume. If you pack into a structure which does not have an isosurface, the density that you specify on the Amorphous Cell Calculation dialog will be the overall density of the cell. If you pack into an isosurface, the density on the Amorphous Cell Calculation dialog is the density of the volume you are packing into. You will perform two packing calculations, one with and one without the isosurface so that you can see the difference. Initially, you will just pack into the structure without an isosurface.

Close the **Amorphous Cell Packing** dialog. Select the **Energy** tab on the Amorphous Cell Calculation dialog.

You can choose which forcefield and energy settings will be used when building the structure. For this tutorial, you can use the default settings.

Click the **Run** button.

A new folder called **SWNT_water AC Packing** is created. This has a subfolder named **Input** which contains a copy of the input documents. When the job completes, the packed structure is called **SWNT_water.xtd**.

Change focus to the results **SWNT_water.xtd**.

You should see that the nanotube is now packed both inside and outside with water.

Change focus to **SWNT_water.txt**. Scroll down to the **Amorphous Cell calculation** section.

Here you can see the components and their loadings. You should see that 426 molecules of water were packed into the box.

Make **SWNT_water.xtd** the active document and, in the **Properties Explorer**, change the **Filter** to **Symmetry System**.

You should see that the density is about 1.0 g cm^{-3} , the value you set in the Amorphous Cell Calculation dialog. Now you will pack into an isosurface and examine the difference. You will pack into a Connolly surface.

Make **SWNT_water.xsd** the active document. Use the **Atom Volumes & Surfaces** tool to create a **Connolly surface**.

The isosurface describes the volume where the atoms are located, this is volume that is already occupied. If you try to pack into this isosurface, you will find that the calculation terminates with the error: "The density in the isosurface enclosed volume is greater than the requested density." To enable the packing into a Connolly surface, you need to invert the definition of the isosurface. You can do this using the Display Style dialog.

Select the isosurface and right-click on the selection, choose **Display Style** from the shortcut menu to open the Display Style dialog. On the **Isosurface** tab check the **High values inside** checkbox and close the dialog.

You can now pack into this isosurface.

Tip: If you are using MaterialsScript, you should use `HasFlippedNormals` to control the definition of the isosurface.

On the **Amorphous Cell Calculation** dialog, click the **More...** button for the **Task** to open the Amorphous Cell Packing dialog. Check the **Pack in isosurface enclosed volume** checkbox and close the dialog. Click the **Run** button on the Amorphous Cell Calculation dialog.

When the calculation completes, you can examine the density and the loading.

Open the **SWNT_water.txt** file.

You should see that the loading for water is now 558 molecules.

Make **SWNT_water.xtd** the active document and, in the **Properties Explorer**, change the **Filter** to **Symmetry System**.

The overall density of the cell should be about 1.2 g cm^{-3} .

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

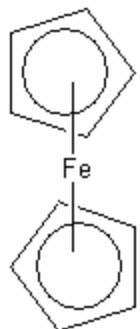
4. To set up the structures and isosurfaces

Before packing the second nanotube that you created earlier, you need to sketch the ferrocene structure to pack inside the nanotube and build a polymer to pack around the outside.

Open a new **3D Atomistic Document** and rename the document to **ferrocene.xsd**. Use the **Fragment** tools to create a ferrocene structure.

Alternatively, you can use the example document **ferrocene.xsd** in the **Example\Documents\3D Model** folder and continue with the tutorial.

[Amorphous Cell: Packing molecules into existing structures](#)



Now you need to build the polymer. In this tutorial, you will just build a 5-mer of polyoxyethylene.

Use the **Homopolymer** building tools to create a 5-mer of **oxyethylene** from the **oxides** library. Rename the structure **peo5.xsd**.

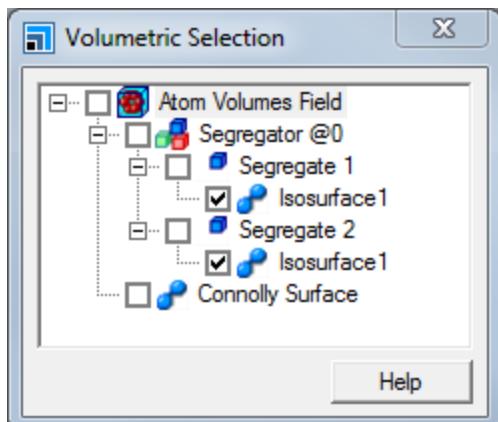
Alternatively, you can use the example **polyoxyethylene5.xsd** document in the **Examples\Documents\3D Model** folder and rename the file to **peo5.xsd**.

You are going to use fields and isosurfaces to indicate what you want to pack. To create the initial fields, you will use Connolly surfaces.

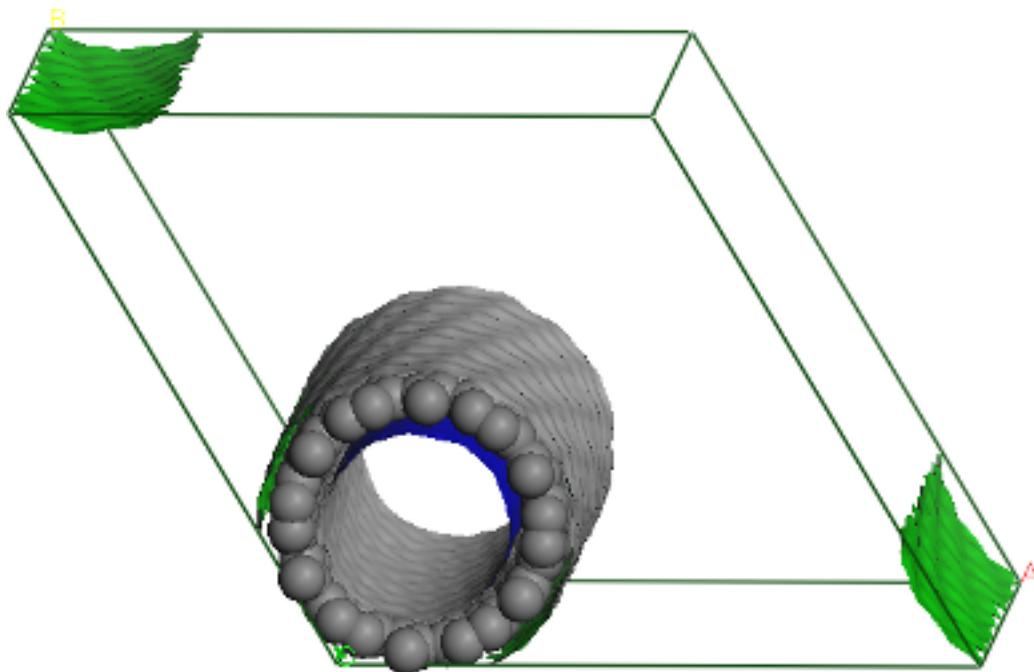
Change focus to **SWNT_polymerFe.xsd** and create a **Connolly surface**. Click the **Create Segregates** button . Click the **Volumetric Selection** button to open the Volumetric Selection dialog. Select each of the **Segregates** by clicking their names and then click **Create Isosurfaces** .

On the Volumetric Selection dialog, **uncheck** the **Connolly Surface**, **Segregate 1**, and **Segregate 2** checkboxes.

You should now have a blue and a green isosurface displayed in **SWNT_polymerFe.xsd**.



Volumetric selection dialog with the isosurfaces of the segregates displayed



Nanotube with segregated isosurfaces colored green and blue

Note: As the segregated isosurfaces show volumes of free space, you do not have to invert the isosurface as you did for the Connolly surface.

You will pack the ferrocene into the blue isosurface enclosed volume and the polymer into the green isosurface enclosed volume.

5. To pack into isosurface enclosed volumes

The final step is to pack into the two isosurface enclosed volumes using two separate packing calculations. You will pack ferrocene first (the order is not important). However, you can only pack into a single visible isosurface so you need to ensure that the isosurface for Segregate 2 is the only one that is visible.

Ensure that **SWNT_polymerFe.xsd** is in focus. On the Volumetric Selection dialog **uncheck Segregate 1 -> Isosurface1**.

Open the **Amorphous Cell Calculation** dialog. Change the **Composition** to **ferrocene**. Set the **Density** to **0.9** and click the **More...** button, check the **Pack in isosurface enclosed volume** checkbox.

You will leave the default values for all other options.

Click the **Run** button.

When the job completes, you should have a 3D atomistic trajectory containing the nanotube with ferrocenes packed in the core of the nanotube. First, make a copy of the output trajectory frame in a new structure document.

[Amorphous Cell: Packing molecules into existing structures](#)

Make **SWNT_polymerFe AC Packing/SWNT_polymerFe.xtd** the active document.

On the **Volumetric Selection** dialog, **uncheck Segregate 2 -> Isosurface1** and **check Segregate 1 -> Isosurface1**.

You should now see the blue isosurface become invisible and the green isosurface is visible again. This time, you will build into the output trajectory from the previous calculation.

Note: If you are doing a multistep packing as in this exercise and you generate multiple frames for the first pack, the second packing will only pack into the current frame in the trajectory not into all the frames.

On the Setup tab of the Amorphous Cell Calculation dialog, change the **Composition** to **peo5** and **Density** to **0.85**. Click the **Run** button.

When the calculation completes, you should have a structure containing a nanotube that is packed with ferrocene and the space between the nanotubes is packed with polymer.

This is the end of the tutorial.

Chapter 3: Blends tutorials

The following tutorial illustrates how to utilize Blends' capabilities.

Screening for compatibility in polymer blends

Purpose: Demonstrates the use of Blends for screening molecular interactions.

Modules: Materials Visualizer, Blends, Forcite (optional)

Time: 

Prerequisites: Using the polymer builder Visualizer Tutorial

Background

There are many industrial situations where formulators routinely mix two polymers to produce a blend with improved physical properties. The same is true for surfactants, solvents, and fine chemical intermediates. Generally, the goal is to produce a blended product with optimized physical or chemical properties, at the lowest possible cost. The usual experimental approach involves the screening of a large number of different formulations to find a final formulation that meets all the requirements. Hence, preparing and testing formulations consumes much of the development time. Formulation stability problems may take weeks or months to become apparent, by which point, a considerable investment in resources and materials may well have been made.

The Blends module in Materials Studio provides a solution that reduces the need for laboratory experimentation and, more importantly, the risk of product failure.

Introduction

In this tutorial, you use Blends to predict the miscibility of a polymer with two others. You import the structures of monomers for poly(oxyethylene), polypropylene, and poly(acrylic acid). You then prepare a Blends calculation to examine the compatibility of poly(oxyethylene) with both polypropylene and poly(acrylic acid).

You analyze the run to predict properties such as the temperature dependence of the Flory-Huggins chi parameter and the phase diagrams for the two blends. Finally, you use a study table to examine the 50 lowest energy pairs from each run and overlay these to examine low energy absorption sites.

This tutorial covers:

- [Getting started](#)
- [To prepare the input structures](#)
- [To configure and run the Blends calculation](#)
- [To analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Polyoxyethylene** as the project name, click the **OK** button.

Materials Studio has an extensive library of pre-defined monomer repeat units, you can use some of them in this tutorial.

In this tutorial, you are going to screen poly(oxyethylene) against polypropylene and poly(acrylic acid).

Select **File | Import...** from the menu bar or click the **Import** button  to open the Import Document dialog. Navigate to and select **Structures/repeat-units/oxides/oxyethylene.xsd**. Click the **Open** button.

The structure of oxyethylene imports into the project. The head and tail atoms in the structure are indicated by cyan and magenta cages around the respective atoms.

Repeat the procedure above to import **Structures/repeat-units/olefins/propylene.xsd** and **Structures/repeat-units/acrylates/acrylic_acid.xsd** into the project.

2. To prepare the input structures

In a Blends calculation, you can screen for polymer-polymer, polymer-solvent, or solvent-solvent interactions. You can define a polymer by specifying head and tail atoms on a monomer repeat unit.

As part of the preparation procedure, optimize the geometries of the repeat units before submitting them for the Blends calculation. This requires the Forcite module. If you do not have a license for this module, proceed to [section 3](#).

Make **oxyethylene.xsd** the active document. Choose **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog.

On the **Setup** tab, change the **Task** to **Geometry Optimization**.

On the **Energy** tab, select **COMPASS III** from the **Forcefield** list and change the **Charges to Charge using QEq**. Click **Run**.

A job launches and its progress displays in the Job Explorer. A new folder, **oxyethylene Forcite GeomOpt**, displays in the Project Explorer. When the calculation is complete, a dialog notifies you.

The **oxyethylene Forcite GeomOpt** folder contains six results files:

- **oxyethylene.xsd**: A 3D Atomistic document containing the optimized geometry of the initial structure.
- **oxyethylene - Calculation**: An **.xml** file containing the settings for the Forcite job. Clicking on this file opens the Forcite Calculation dialog with the settings that you specified for the calculation.
- **oxyethylene Convergence.xcd**: A chart file containing plots of the evolution of the energy change and gradient normal change.
- **oxyethylene Energies.xcd**: A chart file containing a plot of the evolution of the energy.
- **Status.txt**: A text file containing the live update status.
- **oxyethylene.txt**: A file containing the initial job settings and a breakdown of energies for the initial and final structures.

Repeat the geometry optimization calculation for **acrylic_acid.xsd** and **propylene.xsd**. Close the Forcite Calculation dialog.

You now have a large number of documents open in the workspace area.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

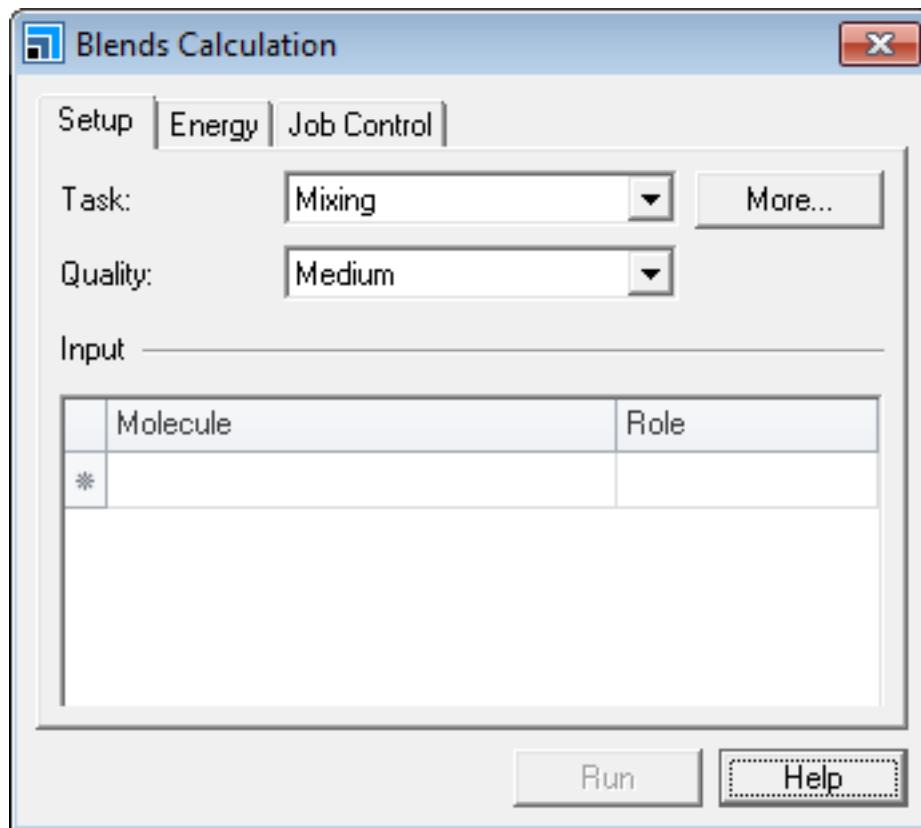
In the Project Explorer, double-click **oxyethylene.xsd** in the folder **oxyethylene Forcite GeomOpt**, **acrylic_acid.xsd** in the folder **acrylic_acid Forcite GeomOpt**, and **propylene.xsd** in the folder **propylene Forcite GeomOpt**.

3. To configure and run the Blends calculation

A Blends calculation is very simple to configure and consists of defining your molecules, choosing the task, and choosing the calculation quality level.

Click **Blends**  on the **Modules** toolbar and select **Calculation**.

This opens the Blends Calculation dialog.



Blends Calculation dialog, Setup tab

The first step is to define the input molecules.

In the **Input** section of the **Setup** tab, click in the empty **Molecule** cell and select **oxyethylene Forcite GeomOpt/oxyethylene.xsd** from the list.

Blends: Screening for compatibility in polymer blends

The first row of the *Input* grid now contains `oxyethylene.xsd` in the *Molecule* column and this structure automatically has the *Role* of `Base` assigned. A new empty row appears below the first one in the dialog table.

Click in the **Molecule** cell in the new empty row and select `acrylic_acid.xsd` in the folder `acrylic_acid` **Forcite GeomOpt**. Repeat this for **propylene** **Forcite GeomOpt/propylene.xsd** in the third row of the grid.

Both `propylene.xsd` and `acrylic_acid.xsd` are automatically assigned `Screen` roles. Any molecule with a screen role will be screened against molecules with a base role. In this tutorial, you obtain interaction energies for oxyethylene-propylene and oxyethylene-acrylic acid mixtures. This is an example of a one-to-many screening calculation.

Click in the **Role** cell for `oxyethylene`.

The role options are `Base+Screen`, `Base`, and `Screen`. If you want to calculate interaction energies for all possible combinations of the polymers, assign all three input structures a `Base+Screen` role. Choosing the `Base+Screen` role for all the molecules enables a many-to-many screen. For example: poly(oxyethylene)-poly(oxyethylene), poly(oxyethylene)-polypropylene, poly(oxyethylene)-poly(acrylic acid), polypropylene-polypropylene, polypropylene-poly(acrylic acid), and poly(acrylic acid)-poly(acrylic acid). In this tutorial, run a one-to-many screening calculation.

For the **Role** for `oxyethylene.xsd`, specify `Base`.

The next step is to choose the task. There are three tasks in Blends.

- **Mixing** - Performs both binding energy and coordination number calculations. Predicts mixing energy, interaction energy, and chi parameter values.
- **Binding energies** - Calculates binding energies only. This gives a fast screen on interaction energy
- **Coordination numbers** - Calculates the coordination numbers for a pair of molecules.

For the **Task**, select **Mixing**, and click **More....**

This opens the Blends Mixing Options dialog, which allows you to fine-tune the mixing energy calculation.

On the **Setup** tab on the Blends Calculation dialog, change the **Quality** to **Fine**.

The *Quality* selected affects the number of pairs sampled, the energy bin width, and the cluster samples. As you change the *Quality* setting, the values on the Blends Mixing Options dialog change in response. The *Quality* setting also propagates to the *Energy* tab and affects the non-bond cutoff settings on the Blends Non-Bond Options dialog.

On the Blends Mixing Options dialog, for **Energy samples** specify **200000**.

By changing the number of energy samples from the default value for Fine quality, the *Quality* changed to `Customized`.

In the Blends calculation, you can exclude specific atoms in a molecule from being in contact with other atoms, by adding them to a set named `NONCONTACT`. This is useful if a part of the molecule is sterically hindered, for example the area around the head and tail atoms in a repeat unit. When requested, Blends automatically creates a set containing the head and tail atoms in a repeat unit.

Make sure that you select **Head and tail atoms are non-contact**.

Note: If you want to define more than two atoms as non-contact, select the atoms and define them as a set with the name NONCONTACT.

You can also request that Blends saves the lowest energy configurations for each base and screen combination in a 3D Atomistic Trajectory document. For each such combination, Blends returns three trajectory documents containing the configurations of the base-base, base-screen, and screen-screen pair. Then, you can further analyze or optimize those conformations.

Select **Return lowest energy frames** and change the **Number of frames** to **50**. Close the Blends Mixing Options dialog.

Before running the Blends calculation, change the energy options to reflect the options you used to minimize the input molecules. As you already calculated charges using QEq in the previous step, you can use the current charges on the model.

On the Blends Calculation dialog, select the **Energy** tab. For the **Forcefield**, select **COMPASS III**, and for the **Charges**, choose **Use current**.

Finally, configure the job control options and change the live update frequency.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click **More...** to open the Blends Job Control Options dialog. Select **Update structure** and change **Update every** to **2 seconds**. Close the Blends Job Control Options dialog.

You are now ready to run the calculation.

In the Project Explorer, the project root. On the Blends Calculation dialog, click **Run** and close the dialog.

A new folder, **oxyethylene Blends Mixing** displays in the Project Explorer. When the calculation completes, this folder contains the following documents:

- **Input:** A folder containing the input structures.
- **Lowest energies:** A folder containing 3D Atomistic Trajectory documents comprising the lowest energy configurations for each base and screen combination. For each such combination, Blends returns three trajectory documents containing the configurations of the base-base, base-screen, and screen-screen pair. Blends omits any pair that is a duplicate of an existing pair.
- **oxyethylene - Calculation:** An xml file containing the settings for the Blends job. Clicking this file opens the Blends Calculation dialog with the settings that you specified for the calculation.
- **oxyethylene.txt:** A text document containing information about the job run and any warnings.
- **Configurations .xsd:** A 3D Atomistic document containing the sampled structures. This file receives live updates as the job progresses.
- **Energies .xcd:** A chart document containing plots of the sampled energies . This file receives live updates as the job progresses.
- **Status .txt:** A text document containing the status of the run. This file receives live updates as the job progresses.
- **oxyethylene .std:** A study table containing the results of the Blends run.

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4. To analyze the results

The study table document, `oxyethylene.std`, contains a summary of the screening results, with each row representing a single pair calculation.

Note: Due to the nature of Blends calculations, you can expect some variation in results. Therefore, it is entirely possible that your results do not precisely match those shown below.

	A	B	C	D	E	F	G	H	I	J	K
	Base	Screen	Energies	Chi (298 K)	Emix (298 K)	Ebb avg (298 K)	Ebs avg (298 K)	Ess avg (298 K)	Ebb min	Ebs min	Ess min
1				-0.13011286	-0.07705121	-1.43261148	-1.52510183	-1.59252071	-3.51591432	-3.46908408	-3.72487326
2				3.39513974	2.01055944	-1.43261148	-0.58740323	-0.57634964	-3.51591432	-1.50166069	-1.19132661

Blends study table output

Columns A and B contain the structures of the base and screen molecules used in the screening calculation. Column C contains a chart document comprising plots of the interaction energies for the base-base, base-screen, and screen-screen combinations. Columns D and E contain predicted values for the chi parameter and the energy of mixing. Columns F-Q contain a breakdown of the interactions energies giving average, minimum, and maximum values. Columns R-U contain coordination numbers for each base and screen combination.

Double-click cell **B2** to open the Study Table Detail View of the propylene monomer.

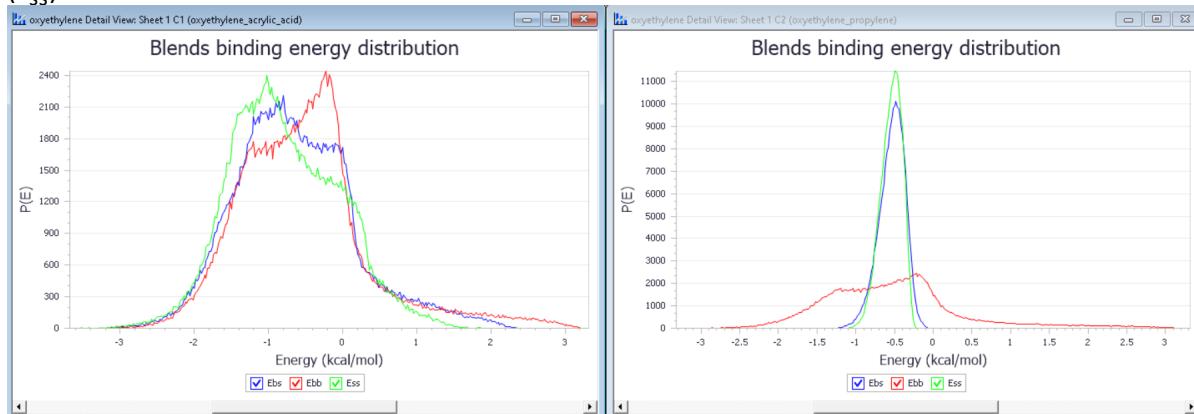
The head and tail atoms have labels indicating them as non-contact groups called NONCONTACT.

Close the detail view.

The energy charts in the study table contain the binding energy distributions for the base and screen pairs.

Double-click the charts in cells **C1** and **C2**.

Two charts appear with graphs for the combination base-base (E_{bb}), base-screen (E_{bs}), and screen-screen (E_{ss}).



Binding energy distributions for the two base-screen pairs: oxyethylene-acrylic acid (left) and oxyethylene-propylene (right).

The base-base binding energies in both charts look similar as they correspond to the oxyethylene-oxyethylene pair in both cases. The screen-screen binding energies will be very different. The one for acrylic acid is more similar to oxyethylene. This is a good indicator of the structures' compatibility. In contrast, the propylene interaction is very different, indicating poor miscibility.

Close the two detail views.

The next indicators as to miscibility are the χ and E_{mix} values.

Examine the values in columns **D** and **E**.

A χ (chi) value close to zero indicates miscibility, as does an E_{mix} value that is close to zero. The higher the value of χ and E_{mix} , the less miscible the pair is. These values reinforce the conclusions from the energy distributions, poly(oxyethylene) is miscible with poly(acrylic acid), but less with polypropylene.

Besides reporting these initial results, Blends also provides tools for further analysis. You can perform analyses by selecting the row in the study table containing the polymer pair of interest and choosing an analysis task from the Blends Analysis dialog.

In the study table, select row **1**.

From the menu bar, select **Modules | Blends | Analysis** to open the Blends Analysis dialog. With the default analysis mode selected, **Chi parameter**, click **Analyze**.

A chart document, **Chi parameter.xcd**, displays showing the temperature dependence of χ for poly(oxyethylene) mixed with poly(acrylic acid). You can also perform analysis on more than one study table row at a time, where appropriate.

Close **Chi parameter.xcd** and click **No** when prompted to save the file as part of the project.

Hold down **SHIFT**, click row **2** in the study table to select both rows.

On the Blends Analysis dialog, click **Analyze**.

This time, the chart shows the temperature dependence of χ for both base-screen pairs. Both graphs approach 0 as temperature increases, but differ at low temperatures.

For mixtures of polymer with the same degree of polymerization N , there is a critical value $\chi_{\text{crit}} = 2/N$. At temperatures where χ is above the critical value at which the mixture separates in two phases. The concentrations in the two phases lie on the binodal in the phase diagram. You can obtain the binodal using the Phase diagram analysis.

Calculate the phase diagram for $N = 25$, such that $\chi_{\text{crit}} = 0.08$.

Select **Phase diagram** on the Blends Analysis dialog and change the **Degree of polymerization** to **25** for both **Base** and **Screen**. Click **Analyze**.

The phase diagram for oxyethylene-propylene contains a critical point at the temperature for which $\chi = \chi_{\text{crit}} = 0.08$. Below this temperature the system separates into two phases, whose concentrations are given by the binodal lines. This phase separation is spontaneous if the concentration and temperature are within the spinodal lines. In between the binodal and spinodal, the system is metastable; only processes far from equilibrium enable phase separation in that case.

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The critical point for oxyethylene-acrylic acid is either absent, or much smaller than oxyethylene-propylene, indicating the components are miscible at any composition. If the $\chi(T)$ curve is below 0.08 for any temperature, the critical point, and hence the binodal and spinodal, is absent. If the curve crosses χ_{crit} twice, the phase diagram has two critical points on either side of a two phase region.

In the final part of this tutorial, examine the lowest energy conformations trajectories. You can play the trajectories.

Double-click **oxyethylene_acrylic_acid.xtd** in the **Lowest energies** folder. Choose **View | Toolbars | Animation** from the menu bar. Click **Play**  on the **Animation** toolbar.

The frames play very quickly. An alternative approach is to use the Forcite Analysis dialog to analyze the trajectory. You do not need a Forcite license to use Forcite Analysis in this way.

On the **Modules** toolbar, click **Forcite**  and select **Analysis** to open the Forcite Analysis dialog. Choose **View in study table** and select **Include structures**. Click **View**.

The trajectory, along with related energy data, displays in a study table document. You can use the study table tools to sort by energies other than the total energy.

Select column **E, van der Waals energy**. Click **Sort Ascending**  on the **Study Table** toolbar.

The rows are ordered with the lowest van der Waals energy conformation at the top of the study table. You can also extract structures from the study table and overlay them in a 3D Atomistic Collection document.

Select column **A**, right-click in one of the selected cells, and choose **Extract To Collection**. A warning dialog appears, informing you that this action may take some time. Click **OK**.

A new 3D Atomistic Collection document, **Extracted From oxyethylene_acrylic_acid.xod**, displays. You can remove the NONCONTACT labels.

Right-click in the collection document and select **Label** to open the Label dialog. Click **Remove All** and close the Label dialog.

In the collection document, you can observe three areas along one half of the molecule where binding is concentrated.

Repeat the above steps to view **oxyethylene_propylene.xtd** as a collection document.

In this case, there are two main interaction sites and they are not as spread out around the molecule as they were for the poly(oxyethylene)-poly(acrylic acid) pairs.

This is the end of the tutorial.

Chapter 4: Cantera tutorials

The following tutorials illustrate how to utilize Cantera's capabilities.

- [Continuous stirred-tank reactor](#)
- [Laminar premixed flame](#)
- [Using the Cantera Reaction Editor](#)
- [Surface reactions in Cantera](#)
- [Mechanism reduction using sensitivity analysis](#)
- [Temperature programmed desorption](#)

Continuous stirred-tank reactor

Purpose: Introduces the use of Cantera for simulating a solution of hydrogen and oxygen in a Continuous Stirred-Tank Reactor.

Modules: Materials Visualizer, Cantera

Time:  

Prerequisites: None

Background

A Continuous Stirred-Tank Reactor (CSTR) is a type of ideal reactor which consists of a perfectly mixed gas. This means it is assumed that the solution within the CSTR is identical at all points, and that no mass accumulates inside the reactor.

Real CSTRs do not match this theoretical ideal, but the concept is used throughout the biological and chemical industries, for example in brewing, antibiotic production, and biodiesel production. The model you will solve here can be used to estimate yields and operating conditions for such processes. One particular usage to consider in this tutorial is the simulation of combustion processes. Experimental determination of ignition delay time in gaseous mixtures can be difficult, not to mention dangerous, but detailed simulations match well with experimental results [Maas & Warnatz, 1988](#). A detailed simulation can be used to ensure that the ignition delay of a mixture is significantly longer than the residence time (or the opposite, if combustion is desired). This tutorial considers the combustion of a stoichiometric mixture of hydrogen and oxygen - quite safe to simulate but highly dangerous experimentally.

In Cantera this type of reactor is modeled using the ideal gas law and may be considered isothermally or adiabatically.

Introduction

In this tutorial, you will learn how to use Cantera to simulate a solution of hydrogen and oxygen in a Continuous Stirred-Tank Reactor (CSTR) both isothermally and adiabatically.

This tutorial covers:

- [Getting started](#)
- [Cantera input data](#)
- [To set up the Cantera reaction dynamics calculation](#)
- [To run and analyze an isothermal simulation](#)
- [To run and analyze an adiabatic simulation](#)
- [To run a refined simulation at a higher resolution](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **cstr** as the project name, click the **OK** button.

The new project is created with *cstr* listed in the Project Explorer. In this tutorial you will be working with a solution of hydrogen and oxygen.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples/Cantera** folder, change the file type filter to **All Materials Studio Files**, and double-click on **MS_h2o2.std**.

A study table displaying the data required by Cantera is displayed. This study table contains a subset of the reactions from the *GRI Mechanism 3.0* ([GRI-MECH 3.0](#)), reference species using standard enthalpies from the [NIST Chemistry WebBook](#), and species data calculated in Materials Studio.

2. Cantera input data

The *Species* tab contains data for elemental hydrogen and oxygen and the compounds they form, both by themselves and together. Data is also included on argon, which plays a role in some three-body reactions. There are nine columns on the *Species* tab in *MS_h2o2.std*:

- *Structure* stores atomistic documents representing each species. Cantera uses this information for species recognition (if available) and it is also useful for visualization.
- *Name* contains an identifying string for each species. This is how Cantera differentiates between species, so each name must be unique.
- *Phase* describes the phase of the species.
- *Atoms* contains the atomic components of each species in the format *A:n B:m*.
- *Standard enthalpy of formation* contains the enthalpy of formation for the species, as determined by the NASA polynomial for enthalpy evaluated at [298.15 K](#).
- *Duplicate* contains a string if the species is intentionally duplicated, for example if you have the same species in different spin states. Any string can be used to ensure the table validates successfully, but it is recommended that something descriptive is used.
- *Thermo* contains the *NASA polynomial* which Cantera uses to calculate thermodynamic properties during the simulation.
- *Transport* contains data on gaseous transport properties of the species, used when simulating a reactor network.
- *Note* may contain any additional information – in *MS_h2o2.std* it contains the settings used to optimize the structure in *DMol³*.

Investigate the content of the *Note* column on the *Species* tab. This column contains the computational details for the *DMol³* calculations used to calculate each particular species.

Click on the **Reference** tab.

The *Reference* tab contains a selection of species with known standard enthalpies of formation, and which include every element used in the reaction mechanism.

- *Column D* contains the result of evaluating the uncorrected NASA polynomial at [298.15 K](#).
- *Column E* contains an experimentally obtained value for the enthalpy of formation at [298.15 K](#).
- *Column F* contains the enthalpy of formation after it has been corrected by fitting to the reference energies.

The difference between *Column E* and *Column F* gives you an idea about the quality of your reference.

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The purpose of the reference species is to ensure that the NASA polynomials on the *Species* tab, which are used to calculate thermodynamic properties of each species, are evaluated on a common energy scale.

Click on the **Reactions** tab.

The *Reactions* tab contains data on possible reactions between the species listed in the *Species* tab. Specifically, the data in this tab is used to calculate the reaction rates.

Investigate the content of the *Note* column on the *Reactions* tab. This column lists literature and methodical references for the data used to obtain the reaction rate coefficients.

In general, it is a good idea to keep track of the history of a particular data set during a calculation. The *Note* column in the reaction mechanism documents provides an opportunity to do so.

Click on the **Species** tab.

Click on the column heading **G** to select the entire **Thermo** column.

Right-click on the column heading **G** and select **Size to Contents** from the shortcut menu.

The *NASA polynomials* are calculated empirically and are only valid over a certain temperature range, which may be different for each species and it is important to check as calculating outside the range of the polynomials will invalidate the simulation.

Each *NASA polynomial* consists of two sets of two arrays (as seen in `MS_h2o2.std`). The first array in each contains only two entries, which are the lower and upper temperature bounds for the polynomial. The second array consists of seven numbers, which are the polynomial coefficients.

The third row in `MS_h2o2.std` contains hydrogen (H_2) and the first *NASA polynomial* has the temperature range [200.00, 1000.00], and the second *NASA polynomial* has the temperature range [1000.00, 6000.00], so H_2 can be reliably simulated in the range 200 - 6000 K. In fact all of the species in `MS_h2o2.std` have this range.

3. To set up the Cantera reaction dynamics calculation

The data contained in `MS_h2o2.std` will be used as input to Cantera.

Click the **Cantera** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | Cantera | Calculation** from the menu bar.

This opens the Cantera Calculation dialog.

Select **CSTR** from the **Task** dropdown list and make sure that **Mole fraction** is selected in the **Gas** section.

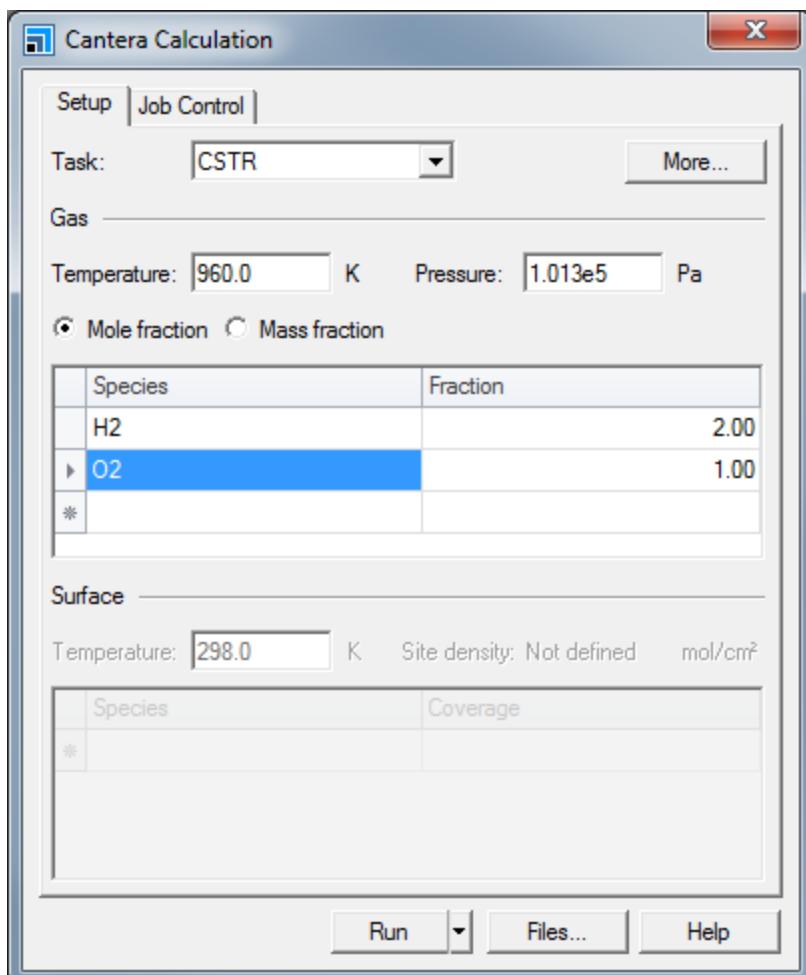
Select **H₂** from the **Species** dropdown list and then in the next, newly created, row select **O₂**.

Set the **Fraction of H₂** to **2**, and the **Fraction of O₂** to **1**.

Set the **Temperature** to **960 K** and change the **Pressure** to **101325 Pa**.

Click the **More...** button to open the Cantera CSTR dialog, set the **Output time window** to finish at **50 s** and the **Time step** to **0.5** and close the dialog.

The Cantera Calculation dialog will look like this.



4. To run and analyze an isothermal simulation

Next, run a default CSTR calculation using these inputs.

Select the **Job Control** tab and review the settings, select an appropriate **Gateway location** and **Queue**. Click **Run** and close the dialog.

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A new folder, named **MS_h2o2 Cantera CSTR**, opens in the Project Explorer and a Cantera job is run by the server which will only take a few seconds. Wait until the job completes and the results are downloaded before moving on to the next step.

In the **Project Explorer** right-click on **MS_h2o2 Cantera CSTR** and select **Rename** from the shortcut menu. Change the name to **Isothermal**.

Select **File | Save Project** from the menu bar.

A text document called **MS_h2o2.txt** is opened when the job completes. It contains a notification that Python has started, and that it completed successfully, and summary reports on the thermodynamic properties of the initial and final states of the hydrogen-oxygen solution. It can be seen from these reports that the temperature of the solution did not change from **960 K**. By default, Cantera assumes that the system is embedded in a thermal bath of a fixed temperature.

Three other files were created in the **Isothermal** directory, not including the calculation file, **MS_h2o2 - Calculation** and the input study table. The other files are **MS_h2o2.cti**, **MS_h2o2.py**, and a study table **MS_h2o2 Results.std**.

Double-click on **MS_h2o2.cti** in the **Project Explorer** to open it.

The **.cti** file contains the input data from the Cantera Calculation dialog in a format readable by Cantera itself. It is kept as a record of the inputs to a particular calculation.

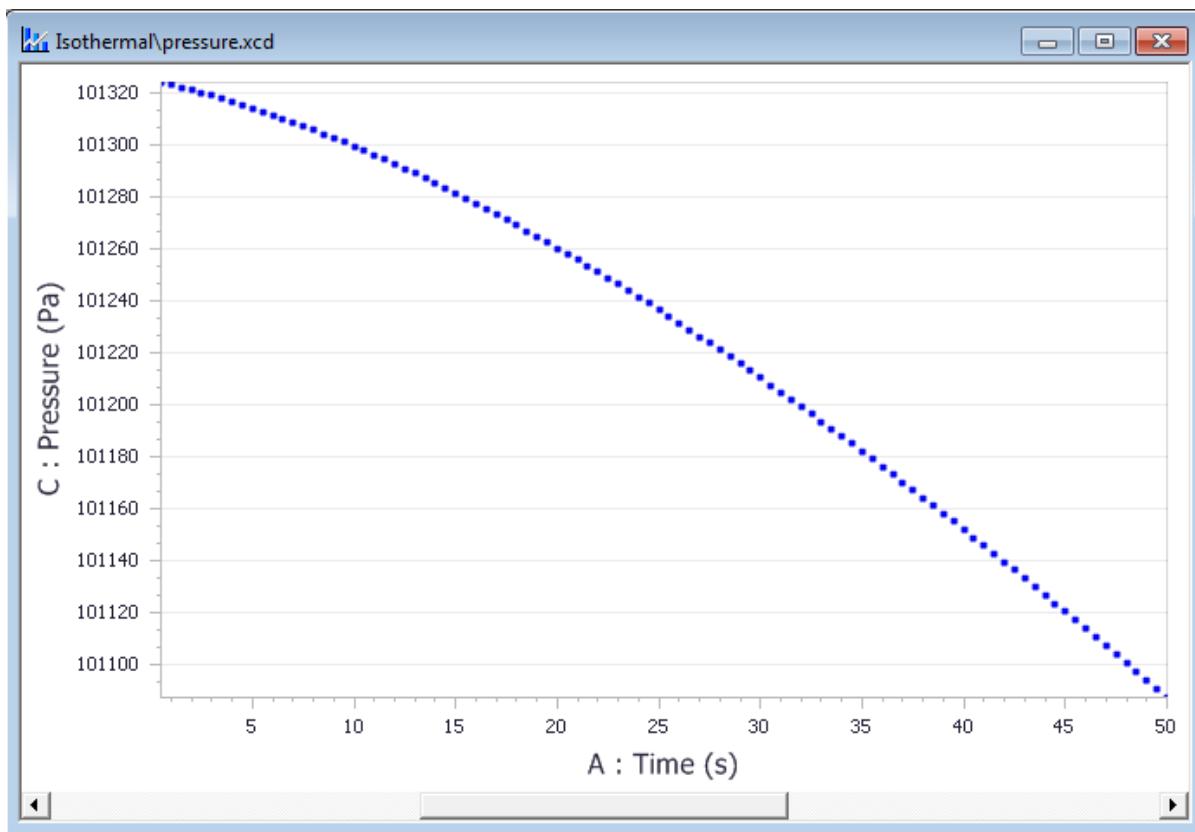
Close **MS_h2o2.cti** and double-click on **MS_h2o2.py** in the **Project Explorer** to open it.

This Python script and the Cantera input file **MS_h2o2.cti** were created for you by Materials Studio. Materials Studio includes a full Python interpreter and runs Cantera inside that environment. The file **MS_h2o2.txt** is the **stdout** stream from the interpreter.

Double-click on **MS_h2o2 Results.std** in the **Project Explorer** to open it.

Select column **A Time (s)**, press CTRL and select column **C Pressure (Pa)**. Click the **Quick Plot** button . Right-click on **MS_h2o2 Results Scatter plot.xcd** in the **Project Explorer** and rename it **pressure.xcd**.

A plot of time and pressure will open, for example:



The calculation used the ideal gas law:

$$pV = nRT$$

With fixed volume and temperature.

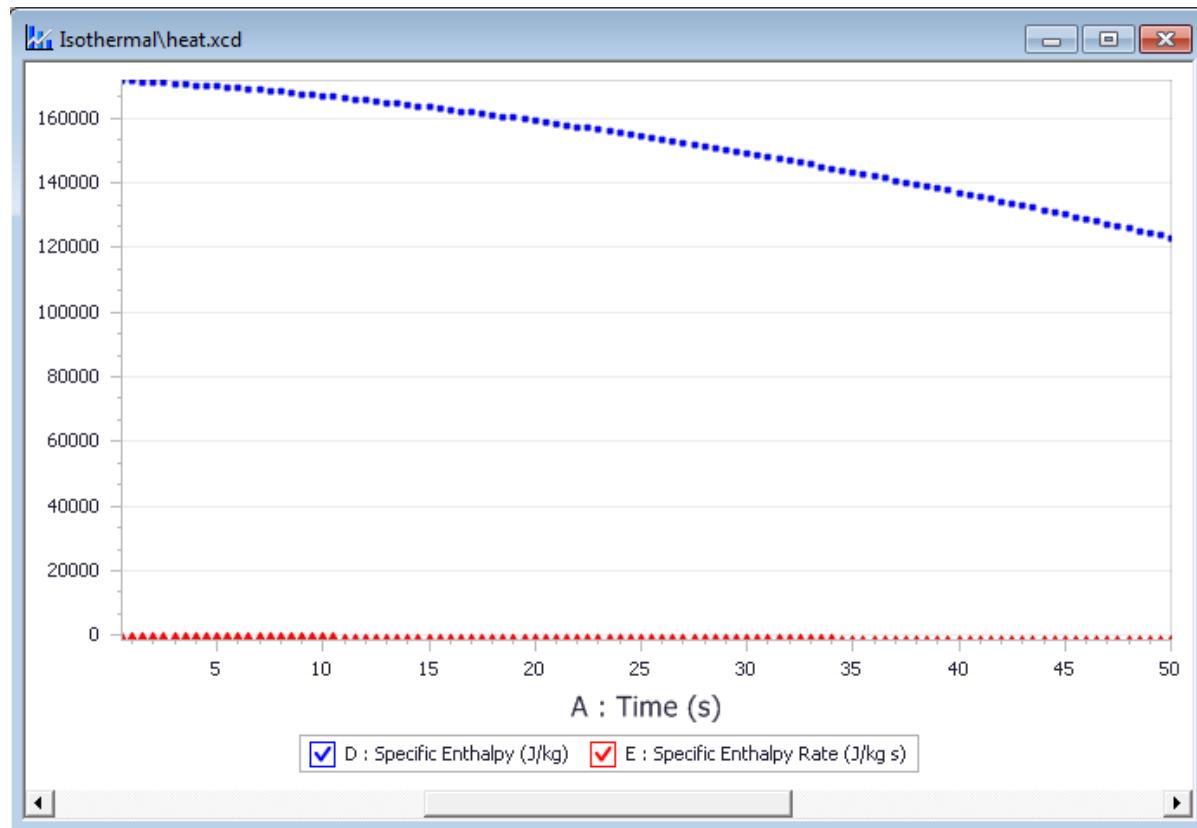
So the drop in pressure is caused by the fact that 2 moles of H₂ plus 1 mole of O₂ creates only 2 moles of H₂O.

Double-click on **MS_h2o2 Results.std** to make it the active document, and select columns: **A Time**, **D Specific Enthalpy (J/kg)**, and column **E Specific Enthalpy Rate (J/kg s)**.

Click the **Quick Plot** button . Right-click on **MS_h2o2 Results Scatter plot.xcd** in the **Project Explorer** and rename it **heat.xcd**.

A plot of time and the enthalpy and enthalpy rate will open, for example:

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It can be seen from this plot that the net reaction was exothermic, but not rapid.

Double-click on **MS_h2o2 Results.std** to make it the focus again, and select column **N Mass fraction AR**, then hold down **SHIFT** and click to select all columns from **N** to **F Mass fraction O2**. Press **CTRL** and click to additionally select column **A Time (s)**.

Click the **Quick Plot** button .

A plot of time and the fractions of the selected species will be displayed, for example:



This plot shows the mass fraction of every species considered in the `MS_h2o2.std` dataset. It confirms the observations from `heat.xcd`, that the H₂ and O₂ slowly react to steadily produce H₂O. If you have seen this type of reaction in a chemistry experiment, for example in high school you will remember a very different effect than the slow and measured reaction dynamics found here.

Right-click on **MS_h2o2 Results Scatter plot.xcd** in the **Project Explorer** and rename it **fractions.xcd**.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

5. To run and analyze an adiabatic simulation

The previous calculation resulted in the slow and steady production of water, but no sign of any explosive combustion due to the boundary conditions used in that calculation. The temperature is held constant such that any heat produced by the reaction is instantaneously drawn off from the tank. As such, the mixture cannot reach the autoignition temperature and will not combust explosively as one would expect from experiments. This boundary condition can be relaxed in Cantera by ensuring that all the heat stays in the system and the tank behaves adiabatically.

Double-click on **MS_h2o2.std** in the **Project Explorer** to open it. Open the **Cantera Calculation dialog** and verify that the settings are the same as before: **Temperature** is **960 K**, **Pressure** is **101325 Pa**. Click **More ...** and ensure that the **Output time window** goes from **0** to **50 s**, and that the **Time step** is **0.5 s**.

On the **Cantera CSTR** dialog uncheck **Isothermal** and close the dialog.

Click **Run**.

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A new folder **MS_h2o2 Cantera CSTR** will be created and the simulation will complete after a few seconds.

Once the calculation has finished, right-click on the folder **MS_h2o2 Cantera CSTR** in the **Project Explorer** and rename it **Adiabatic_Coarse**.

Double-click on **Adiabatic_Coarse\MS_h2o2.txt** in the **Project Explorer** to make it the active document.

Inspecting the thermodynamics report on the initial and final states of the hydrogen and oxygen solution contained in this file will reveal that the temperature increases to around **3220 K** through the course of this simulation. Rename the folder containing the first adiabatic simulation to avoid confusion with later results.

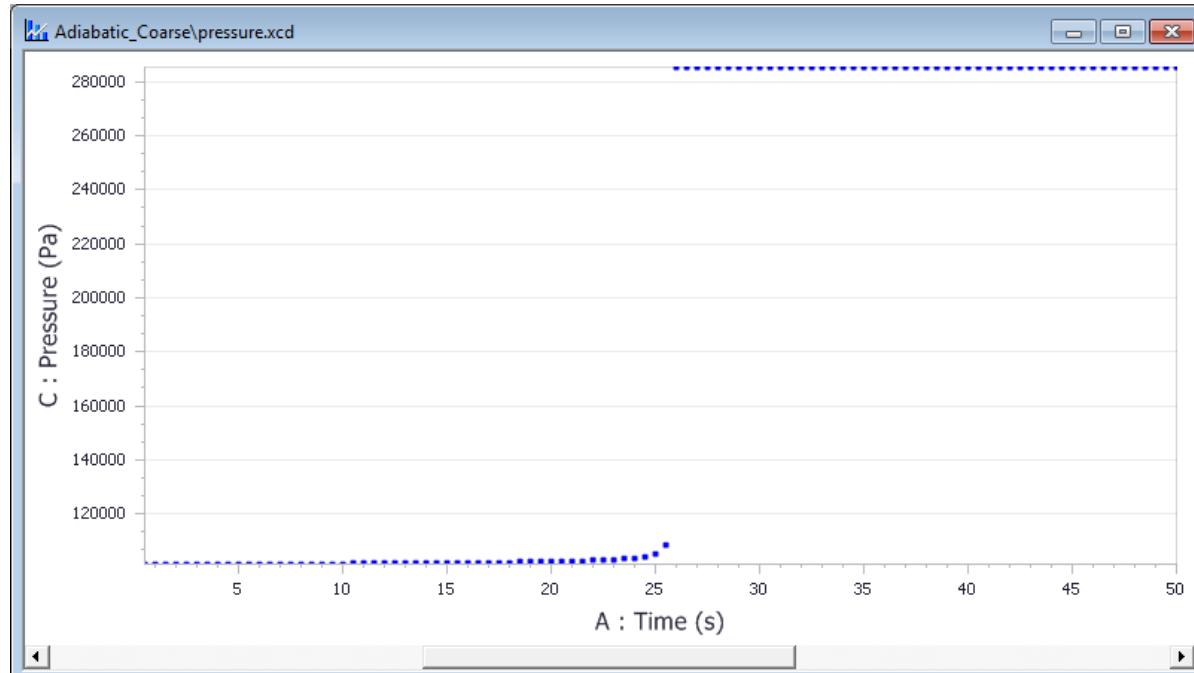
Double-click on **Adiabatic_Coarse\MS_h2o2 Results.std** in the **Project Explorer** to open it.

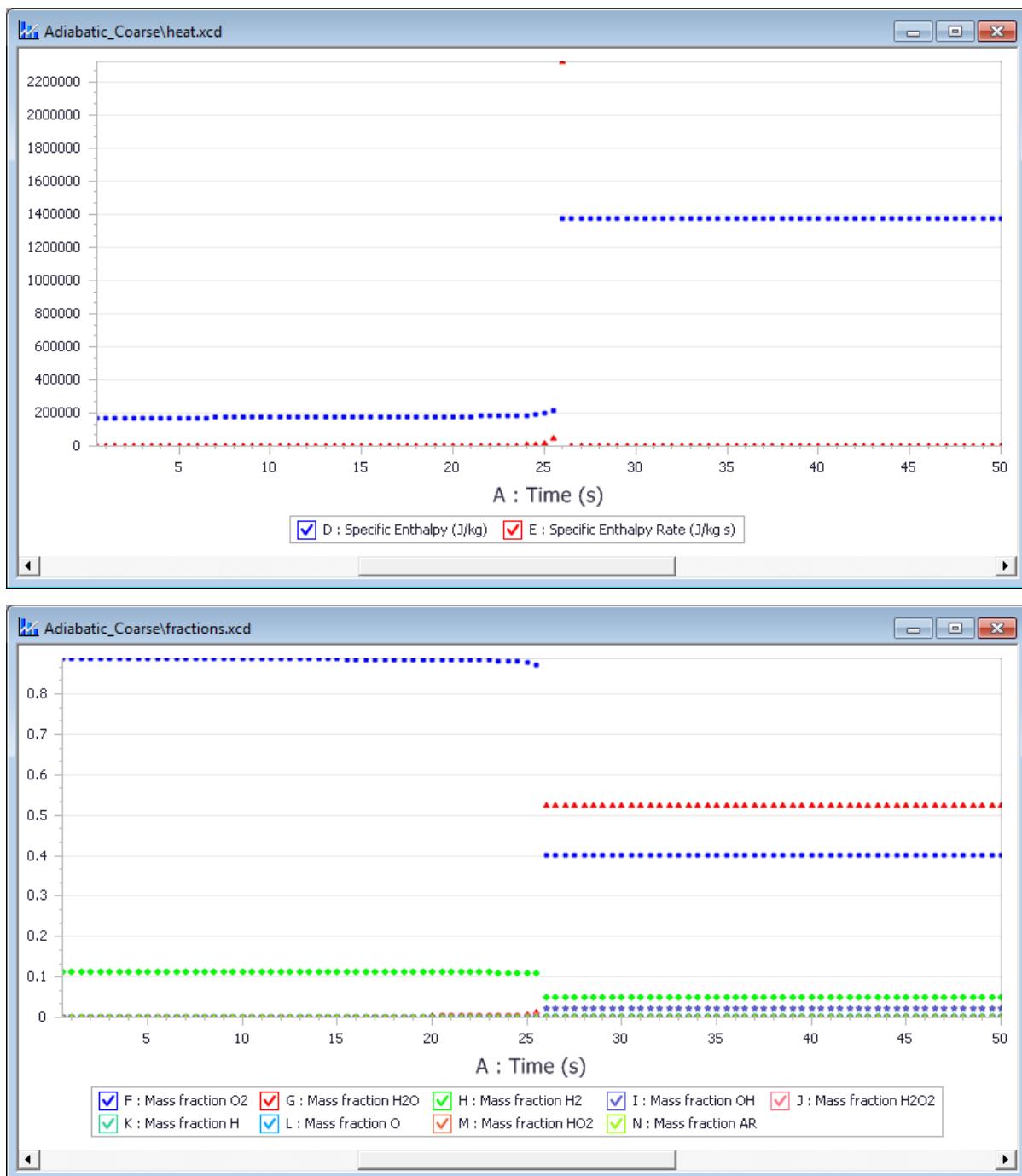
Using the same procedure as above create plots of the Pressure, Specific Enthalpy and Specific Enthalpy Rate, and Mass Fractions, and rename them appropriately.

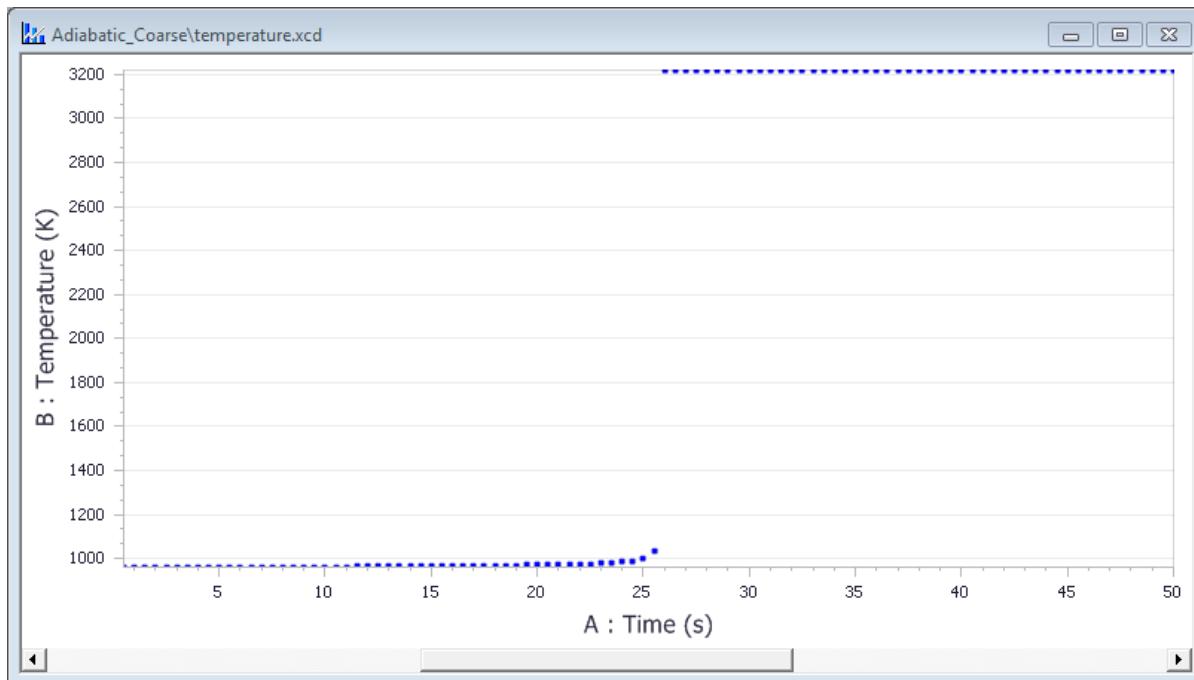
Additionally, on **Adiabatic_Coarse\MS_h2o2 Results.std** select column **A Time**, and column **B Temperature (K)**.

Rename the plot **temperature.xcd**.

Plots like the ones below are displayed.







It can be clearly seen from these plots that ignition occurs just before 26 seconds, much more consistent with expectation that a mixture of H₂ and O₂ explodes when lit. Cantera uses a variable time step integrator, which means the final state presents an accurate representation of the system. However, in the present calculation there is no useful information about the actual time scale of the reaction.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

6. To run a refined simulation at a higher resolution

In this section, we will use the controls on the CSTR dialog to zoom into the ignition point and analyze it in detail while running the same overall simulation as before. Cantera performs time integration using an adaptive step integration method, which allows us to start the output after some initial time, and to get results at whatever time resolution is required. Looking at the plot above, an initial time around 25.5 s with a runtime of 1 s and a time step of 0.001 s seems a sensible starting point to zoom in on the step change in the reaction.

Reopen the **MS_h2o2.std** study table.

Open the **Cantera Calculation** dialog, and click **More ...** to open the **Cantera CSTR** dialog.

Change the **Output time window** to run from 25.5 s to 26.5 s and select a time step of 0.001 s.

Click **Run**.

When the calculation completes, explore the results by plotting the same quantities as above. You should still see a drastic step-like change in the temperature and reactant behavior, just as before. By successively zooming in the time interval, you should be able to actually resolve the reaction dynamics to the sub-microsecond time scale on which the explosion occurs.

Repeatedly modify the starting and ending time of the Cantera run as well as the time step to find the interval at which most of the reaction occurs. You should be able to resolve everything down to a time step of around 1e-7 s.

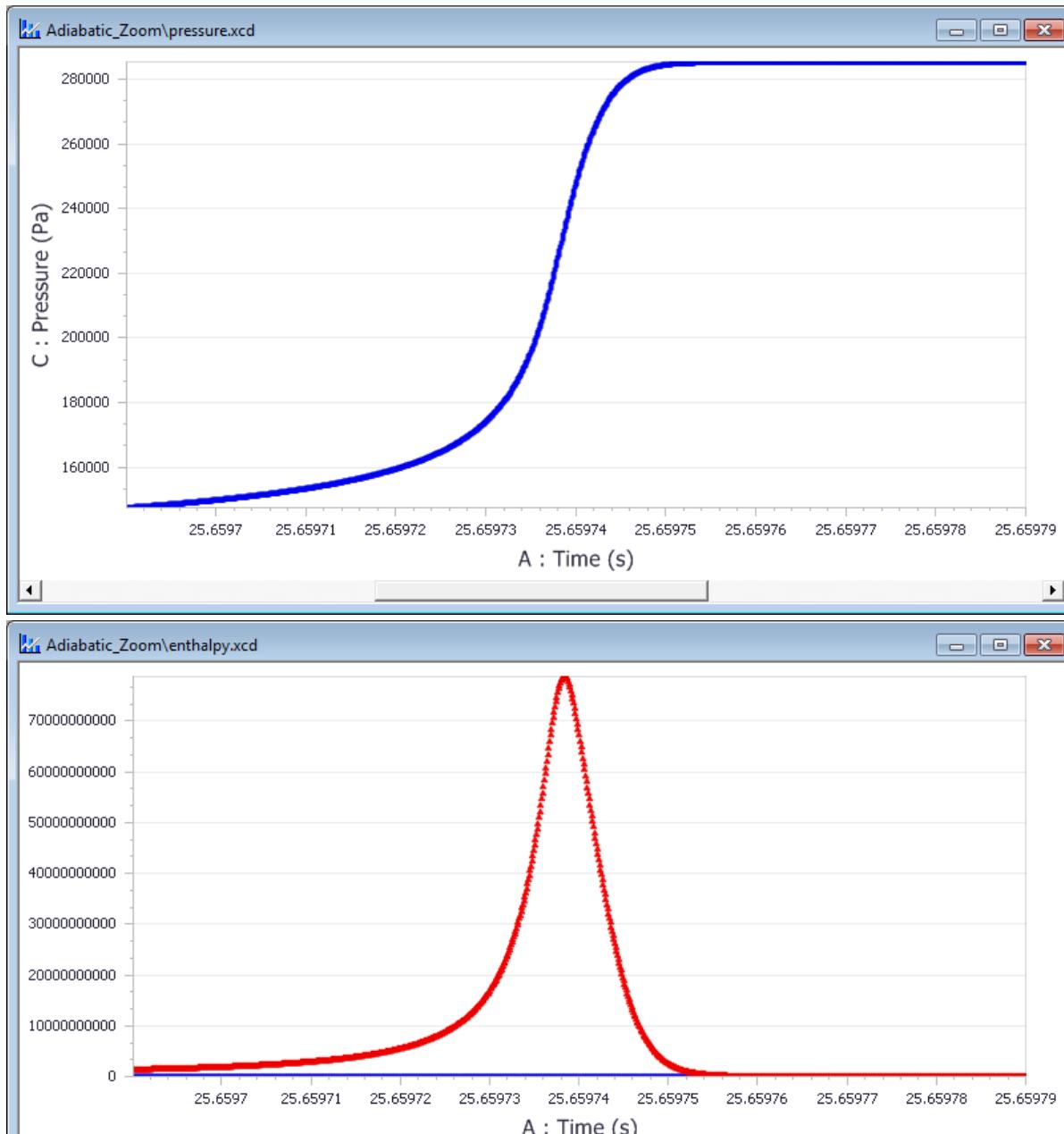
You should see the main reaction occur in an interval close to 25.65969- 25.65979 s, which can be resolved with a time step of 1e-7 s.

Right-click on the final results folder in the **Project Explorer** and rename it **Adiabatic_Zoom**.

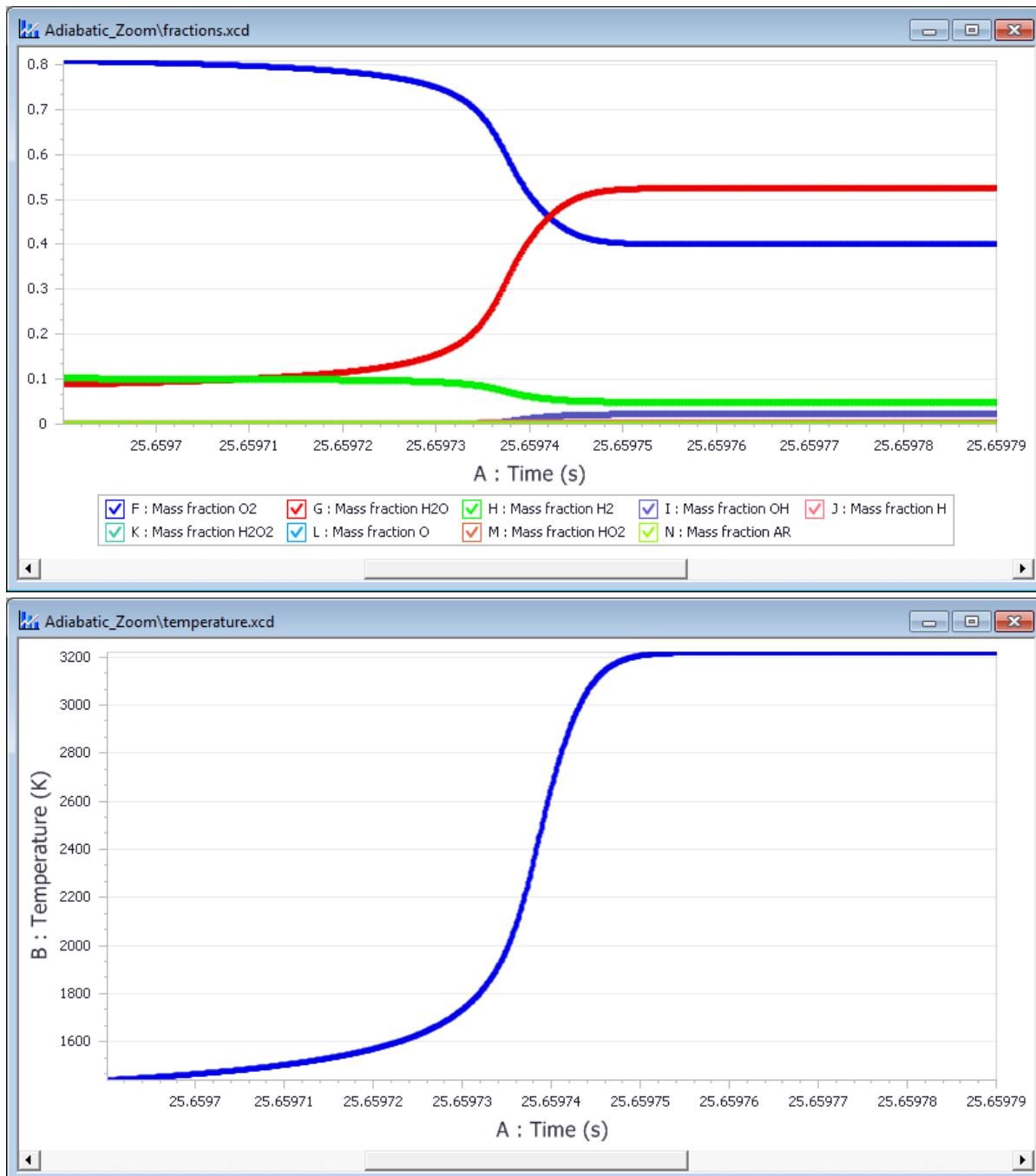
Double-click on **MS_h2o2 Results.std** in the **Project Explorer** to open it.

Using the same procedure as before, create plots of the **temperature**, **pressure**, **specific enthalpy**, and **specific enthalpy rate**, and **mass fractions**, and name them appropriately.

Your plots should look like those shown below.



Cantera: Continuous stirred-tank reactor



In this new data, the ignition point of the hydrogen-oxygen mixture can be very clearly seen, especially by looking at the maximum specific enthalpy rate.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

[1] U. Maas & J. Warnatz, *Ignition processes in hydrogen-oxygen mixtures*, Combustion and Flame, **74**, 1, (1988), 53–69, doi:10.1016/0010-2180(88)90086-7

[2] [GRI-MECH 3.0](#)

[3] [NIST Chemistry WebBook](#)

Laminar premixed flame

Purpose: Introduces the use of Cantera for simulating the burning of a premixed laminar flow of oxygen and hydrogen.

Modules: Materials Visualizer, Cantera

Time: 

Prerequisites: Continuous stirred-tank reactor

Background

A laminar premixed flame is a flame in which the fuel and oxidizer are assumed to be perfectly mixed and forming a laminar flow, before reaching the flame front. We will look at the situation in which the flame front is then allowed to freely propagate in one dimension. This model can, for example, be used to describe the combustion process in a Bunsen burner, or a stationary gas turbine. It can be used to calculate properties such as the unburned and burned laminar flame speed, and the burn temperature.

Introduction

In this tutorial, you will learn how to use Cantera to simulate the burning of a laminar gas mixture of methane and air.

This tutorial covers:

- [Getting started](#)
- [To set up the Cantera reaction](#)
- [To run and analyze a laminar premixed flame simulation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **flame1D** as the project name, click the **OK** button.

The new project is created with *flame1D* listed in the Project Explorer. In this tutorial you will be working with a mechanism to model a hydrogen flame.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples/Cantera** folder and double-click on **MS_gri30.std**.

A study table containing the reaction mechanism is displayed. The reference standard enthalpies are from the [NIST Chemistry WebBook](#), and the NASA polynomials have been calculated in Materials Studio.

2. To set up the Cantera reaction

We will now use data contained in **MS_gri30.std** as an input to Cantera.

Cantera: Laminar premixed flame

Click the **Cantera** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | Cantera | Calculation** from the menu bar.

This opens the Cantera Calculation dialog.

Select **Flame 1D** from the **Task** dropdown list.

Ensure that the **Mole fraction** radio button is selected under **Composition**. Use the **Species** dropdown list to add **AR**, **N2**, **O2**, and **CH4** to the dialog.

Set the molar fractions as follows:

- **AR** to **0.009**
- **N2** to **0.707**
- **O2** to **0.189**
- **CH4** to **0.095**

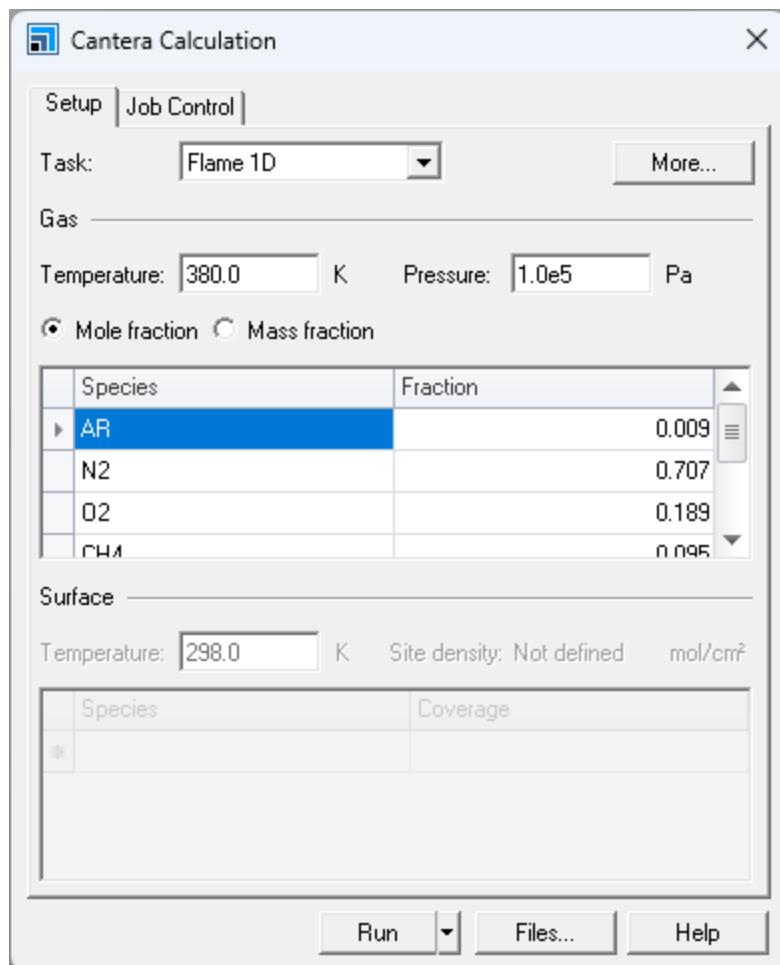
This is a stoichiometric mixture of air and methane.

Set the **Temperature** to **380 K**, ensure that the **Pressure** is **100000 Pa**.

Click the **More...** button to open the Cantera Flame 1D dialog. Select **Burner flame** from the **Flame type** dropdown list. Set the **System length** to **0.1 m** and the **Input flow rate** to **0.005 kg/m²/s**.

The Cantera Calculation dialog is configured. The two available flame types are:

- *Free flame* in which the flame front propagates freely through a uniformly mixed gas in one dimension
- *Burner flame* in which the flame front is held at a fixed point in space and requires a steady input flow



3. To run and analyze a laminar premixed flame simulation

We will now run the Flame 1D task.

Ensure that **MS_gri30.std** is open and in focus, click **Run** on the Cantera Calculation dialog and close the dialog.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

The calculation will run and complete in a few seconds.

Cantera: Laminar premixed flame

Double-click on **MS_gri30 Cantera Flame1D/MS_gri30 Results.std** to open it.

Select columns **A z (m)** and **B u (m/s)** and click **Quick Plot** . Rename the plot **velocity.xcd**.

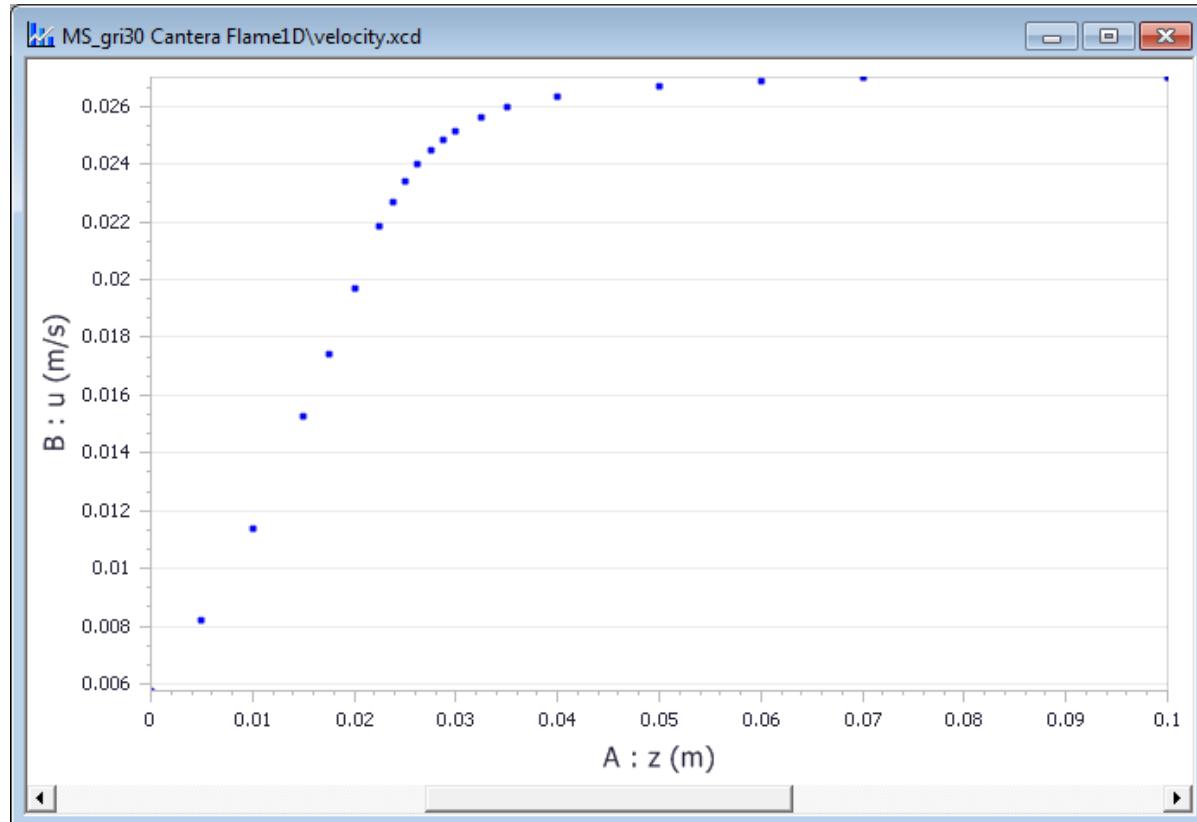
In **MS_gri30 Results.std** select columns **A z (m)** and **D T (K)** and click **Quick Plot** . Rename the plot **temperature.xcd**.

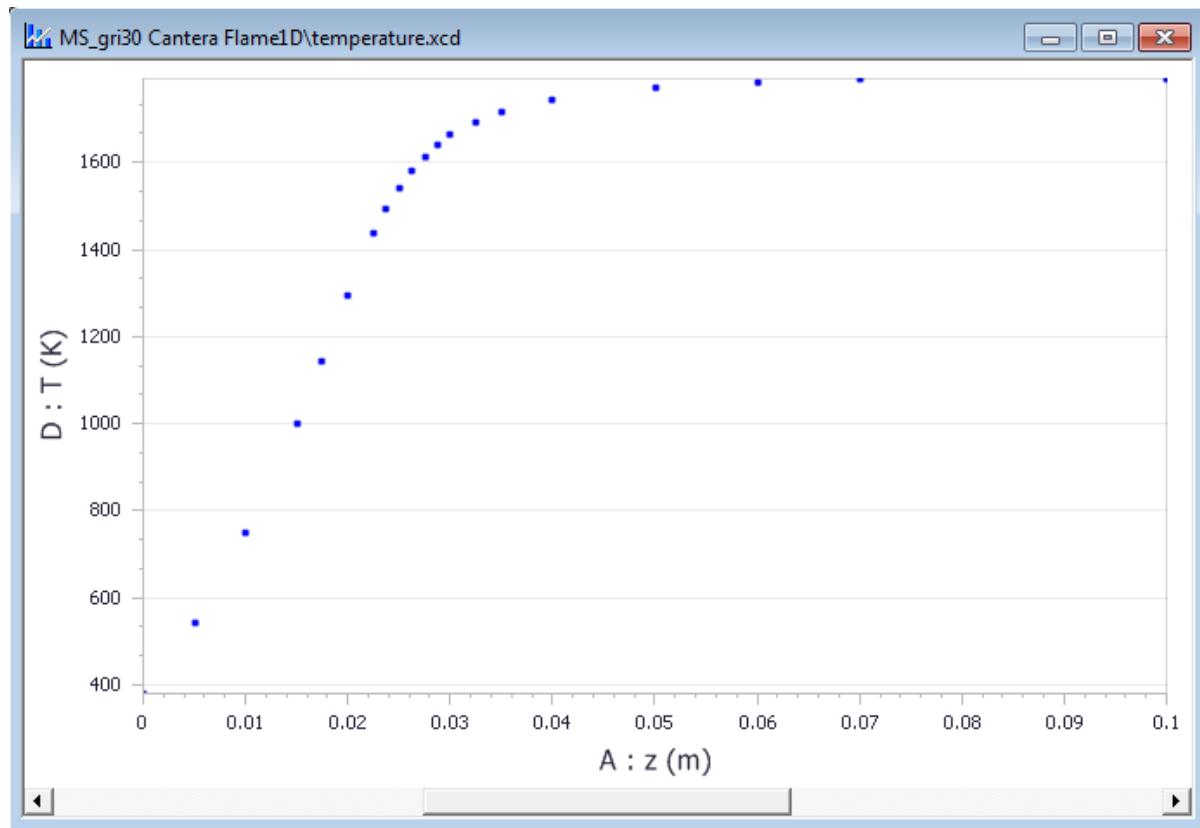
In **MS_gri30 Results.std** select column **A z (m)**, **G to K**, and click **Quick Plot** . Rename the plot **fractions.xcd**.

This produces the three plots shown below. The flame extends across the whole system and the mixture combusts rapidly. The computed unburned laminar flame speed is around **0.005 m/s**, and the mixture burns at around **1700 K**. The unburned laminar flame speed $s_{L,u}$ is the velocity at which the fuel mixture approaches the flame front, and is dependent on the temperature, pressure, density, and diffusivity of the mixture. The burned laminar flame speed is the velocity at which the reaction products leave the flame front and is related to the unburned flame speed by the equation:

$$s_{L,b} = \frac{\rho_u}{\rho_b} s_{L,u}$$

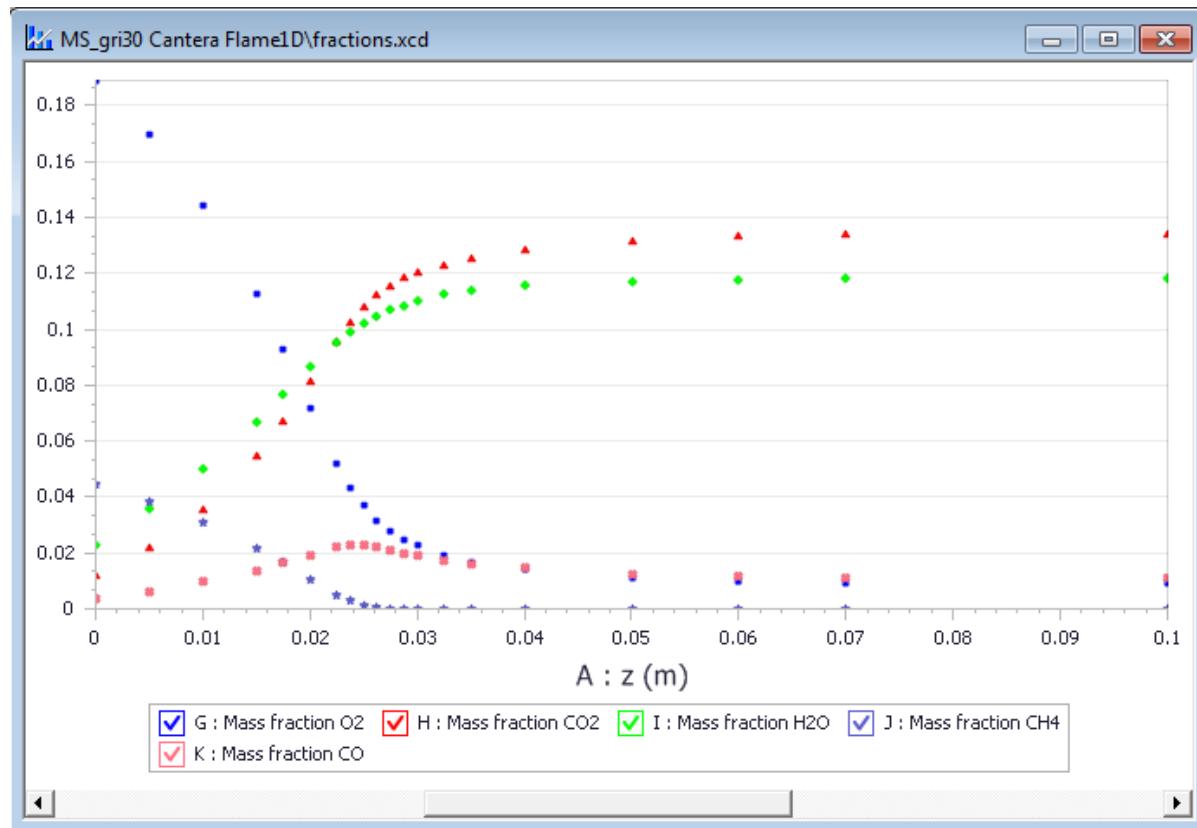
Where ρ_u is the unburned mixture density and ρ_b is the burned mixture density.





The plot of the mass fractions of the oxidation reactants and products shows that the CH_4 is completely depleted while a little molecular oxygen remains, the major products are CO_2 , H_2O , and CO .

Cantera: Laminar premixed flame



The temperatures in this flame are high enough to oxidize some of the nitrogen molecules. You can investigate how much NOx (that is, NO, NO₂) is formed during the reactions and how much nitrogen is still present in the gas stream at the end of the reactor.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

[1] [GRI-MECH 3.0](#)

[2] [NIST Chemistry WebBook](#)

Using the Cantera Reaction Editor

Purpose: Introduces the use of the Cantera Reaction Editor for creating or modifying a reaction mechanism.

Modules: Materials Visualizer, Cantera, DMol³

Time:  

Prerequisites: Continuous stirred-tank reactor

Background

Cantera requires information on the reactions that can occur between species in a mixture to be held in a study table, along with the species. Any species which may be a product or catalyst to a reaction should also be included. Together this information constitutes a *reaction mechanism*. The *Cantera Reaction Editor* allows you to create or modify a reaction mechanism using data generated by calculations performed in Materials Studio. In particular, we use the output from a single Reaction Kinetics calculation performed using the DMol³ module on the Diels-Alder cycloaddition of 1,3-butadiene and ethene to form cyclohexene.

Introduction

In this tutorial, you will learn how to use the results of a DMol³ Reaction Kinetics calculation to enhance a pre-existing reaction mechanism.

This tutorial covers:

- [Getting started](#)
- [Calculating reaction data](#)
- [Importing species and reaction data](#)
- [Running a calculation with a modified reaction mechanism](#)
- [Augmenting an experimental reaction mechanism](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **reaction_editor** as the project name, click the **OK** button.

The new project is created with *reaction_editor* listed in the Project Explorer. In this tutorial you will add the Diels-Alder reaction of 1,3-butadiene with ethene to a modified version of the *GRI Mechanism* ([GRI-MECH 3.0](#)).

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples/Cantera** folder and double-click on **MS_gri30.std**.

Use the same procedure to import **Diels-Alder.xod**.

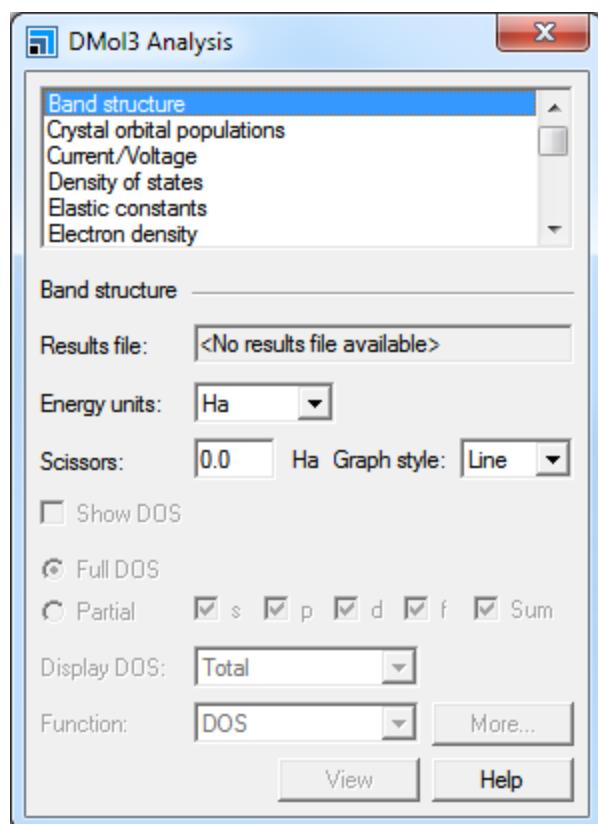
A Cantera study table containing the *GRI Mechanism* and a collection document containing the results of a DMol³ Reaction Kinetics calculation of the Diels-Alder reaction are displayed.

2. Calculating reaction data

First the reaction rate must be calculated from the structural data. This is done using the DMol3 Analysis dialog.

Click the **DMol3** button  on the **Modules** toolbar and choose **Analysis** or select **Modules | DMol3 | Analysis** from the menu bar.

This opens the DMol3 Analysis dialog.



Select **Reaction kinetics** from the list.

Set the temperature range **From: 200 K To: 6000 K**.

Ensure that **Diels-Alder.xod** is in focus, click **Calculate**, and close the dialog.

A study table called `Diels-Alder.std` is opened when the calculation completes. This study table contains the information needed to add the reaction to a mechanism study table for use in Cantera, and any available information about the DMol³ settings used to calculate the structures contained in `Diels-Alder.xod`. To make sure that this data is physically sensible, you can verify that the forward and reverse Arrhenius parameters listed on the Summary tab of the `Diels-Alder.std` study table have the right size. You can also plot the reaction rate and the corresponding fit quality of the Arrhenius representation visually.

Select the **Graphs** tab on the `Diels-Alder.std` study table and highlight the columns **1000/Temperature**, **log(Forward reaction rate)**, **log(modified Arrhenius fit) forward reaction rate**, and **log(standard Arrhenius fit) forward reaction rate**.

Click the **Quick Plot** button .

The resulting scatter plot shows that the modified Arrhenius form provides an excellent fit to the raw data computed by Materials Studio. The standard Arrhenius fit is substantially worse, particularly at high temperatures. Cantera consistently uses the modified Arrhenius forms.

Tip: In some instances, you might only have the transition state, reactants, and products available as separate 3D atomistic documents. These can still be imported into Cantera study tables if you follow the instructions on how to create a collection document from atomistic data in the DMol³ section of the online help.

3. Importing species and reaction data

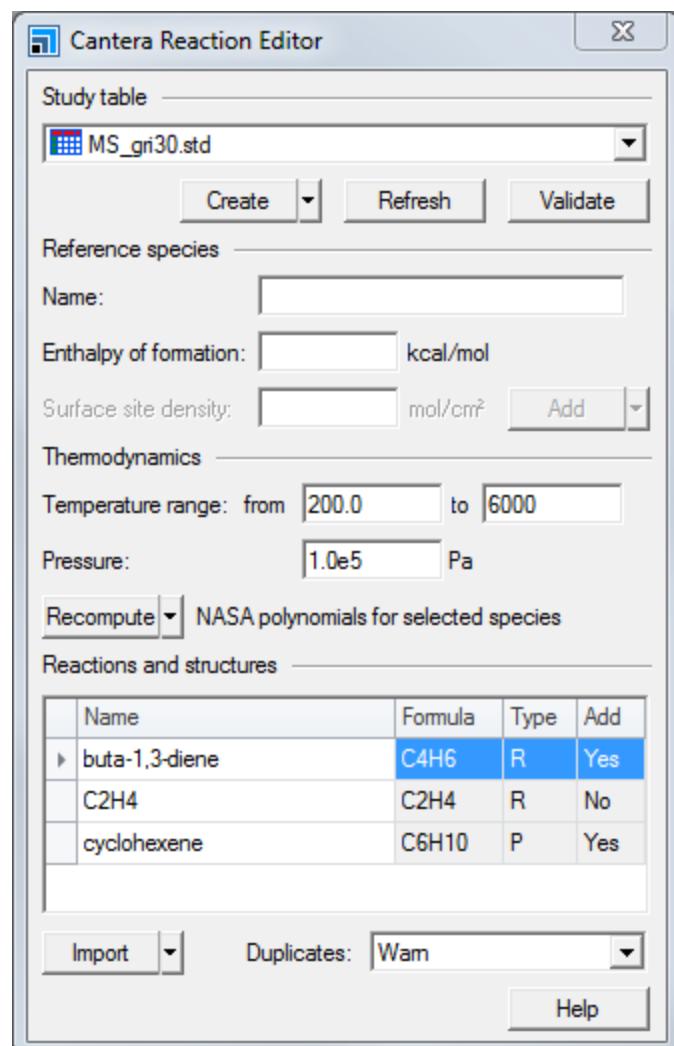
The Cantera Reaction Editor is used to extract species data and reaction rates from a study table containing the output from a DMol³ Reaction Kinetics analysis. It also calculates the NASA polynomials required for representing thermochemical data.

Click the **Cantera** button  on the **Modules** toolbar and choose **Reaction Editor** or select **Modules | Cantera | Reaction Editor** from the menu bar.

This opens the Cantera Reaction Editor dialog.

Select **MS_gri30.std** from the **Study table** dropdown list and click on the `Diels-Alder.std` study table to make it the active document.

Cantera: Using the Cantera Reaction Editor



Three species will appear in the *Reactions and structures* grid in the Cantera Reaction Editor dialog: buta-1,3-diene, C₂H₄, and cyclohexene. The last column in this grid is the *Add* column, which specifies whether or not the species will be added to the selected study table.

Note: The *Add* column has a value of *Yes* for buta-1,3-diene and cyclohexene, but *No* for C₂H₄. This is because the Cantera Reaction Editor has identified that C₂H₄ is already present in MS_gri30.std so it does not need to be imported again. This behavior can be overridden by modifying the *Name* of a species. This is useful for adding different conformers or different spin states of the same molecule for example - as long as they are given different names they can all be included in the study table.

By default, the Cantera Reaction Editor dialog will prevent addition of the same reaction twice. To include a reaction twice (and mark it as a duplicate) select *Include* instead of *Warn* from the *Duplicates* dropdown list.

In the **Name** column change **buta-1,3-diene** to **butadiene**.

Ensure that the **Temperature range** is set from **200 K** to **6000 K**.

Click **Import**.

The *Reactions* tab of `MS_gri30.std` is displayed.

The Diels-Alder reaction has been added at the bottom of the list of reactions in the mechanism:



Information about the calculation used to find the reaction rate is stored in the *Note* column.

Click the **Species** tab and scroll to the bottom of the study table. Save the study table `MS_gri30.std`.

Butadiene and cyclohexene have been added to the species included in the mechanism study table, including the NASA polynomials. The *Note* column contains the NASA Polynomial fit RMS, as well as information about the calculation used to optimize the structure. The enthalpy of formation for each species has been evaluated at $T = 298.15$ K, and is displayed in column *E*. These can be compared against experimental values, found for example in the [NIST Chemistry WebBook](#), and used to check how well the NASA polynomials are fitted. NIST gives the standard enthalpy of formation as **-1.03** kcal/mol for cyclohexene and **29.95** kcal/mol for 1,3-butadiene. NIST gives data for trans-butadiene but the Diels-Alder reaction contains cis-butadiene, so we should adjust the standard enthalpy accordingly. You can use DMol³ to optimize both conformers and will find that the enthalpy of formation is **3.95** kcal/mol higher for cis-butadiene, so we shall use a standard enthalpy of **29.95** kcal/mol. The NASA polynomials for butadiene and cyclohexene give enthalpies in reasonable agreement with the standard reference data, but we can improve this fit by adding both species as reference molecules.

On the **Cantera Reaction Editor** dialog ensure that `MS_gri30.std` is selected in the **Study table** dropdown list.

Focus on the `Diels-Alder.std` study table and select the **Structures** tab.

Double-click on **buta-1,3-diene** in the **Structure** column to open it.

The *Reference species* section in the Cantera Reaction Editor dialog will recognize this molecule as butadiene which is already present in the *Species* tab of `MS_gri30.std`. It also evaluates the NASA polynomial on the species tab to give the standard Enthalpy of formation. We will enter the accepted standard enthalpy of formation for this conformer to create an improved reference.

In the **Cantera Reaction Editor** dialog change **Enthalpy of formation** to **29.95** kcal/mol.

Click **Add**.

Repeat the process with **cyclohexene** from the **Structures** tab of the `Diels-Alder.std` study table, this time changing **Enthalpy of formation** to **-1.03** kcal/mol.

Close the two atomistic documents.

The two new species have been added at the bottom of the *Reference* tab. Since we have added new references to the table, we should recalculate the NASA polynomials for all species to ensure consistency.

Click the **Species** tab, and select any cell in the table.

Press **CTRL + A** to select the whole table.

Click **Recompute NASA polynomials for selected species** on the **Cantera Reaction Editor**.

The standard enthalpies for butadiene and cyclohexene should now be much closer to their reference values than they were before. The Cantera Reaction Editor can also validate a study table. The validation tool looks for missing species, duplicate species and reactions, and checks that reactions are balanced.

Note: The initial reasonably good agreement between the predicted enthalpy of formation of butadiene and cyclohexene with respect to the accepted standard values is due to the fact that all the NASA polynomials present in the study table were computed with the same computational settings as the Diels-Alder reaction in this particular document. If you are extending a reaction mechanism with an unknown source of all the species, this cannot be expected in general and the reference state for the added species must be handled very carefully.

On the Cantera Reaction Editor dialog ensure that **MS_gri30.std** is selected in the **Study table** dropdown list.

Click the **Validate** button.

A message appears saying *Validation of study table successful*. This means that no information is missing from the reaction mechanism, and you are ready to proceed with a calculation.

Click **OK** and close the Cantera Reaction Editor dialog.

4. Running a calculation with a modified reaction mechanism

You will use the modified reaction mechanism in Cantera to examine the production of cyclohexene in a continuous flow stirred-tank reactor.

Click the Cantera button  on the **Modules** toolbar and choose **Calculation** or select **Modules | Cantera | Calculation** from the menu bar.

Ensure that the study table **MS_gri30.std** is in focus.

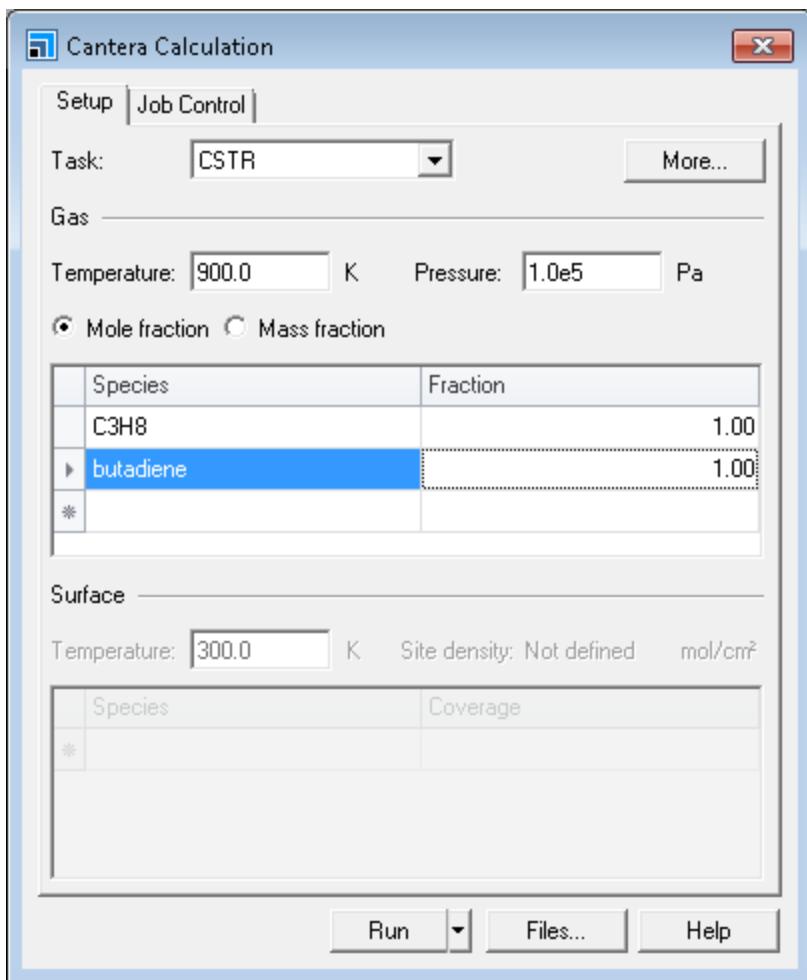
Select **CSTR** from the **Task** dropdown list. Ensure that the **Mole fraction** radio button is selected in the **Composition** section. Use the **Species** dropdown list to add **C3H8**, and **butadiene** to the dialog. Set the molar fractions as follows:

- **C3H8** to 1
- **butadiene** to 1

Set **Temperature** to **900 K**, and ensure that the **Pressure** is set to **1e5 Pa**.

Click the **More...** button to open the Cantera CSTR dialog, and uncheck the **Isothermal** checkbox. Set the **Output time window** to finish at **1000 s** and set a **Time step** of **1 s**.

The Cantera Calculation dialog will look like this.



Use the **Job Control** tab to select a **Gateway location** and **Queue** if necessary.

Click **Run** and close all dialogs.

A new folder, **MS_gri30_Canterac** CSTR will be created in the Project Explorer. Once the calculation has finished the file **MS_gri30.txt** will open. The final state presented in this text file should show substantial mole fractions of ethylene (C_2H_4) and methane (CH_4) along with the input reactants. Any possible formation of cyclohexene from this reaction can be investigated by plotting the mass fraction of some of the reactants as a function of time.

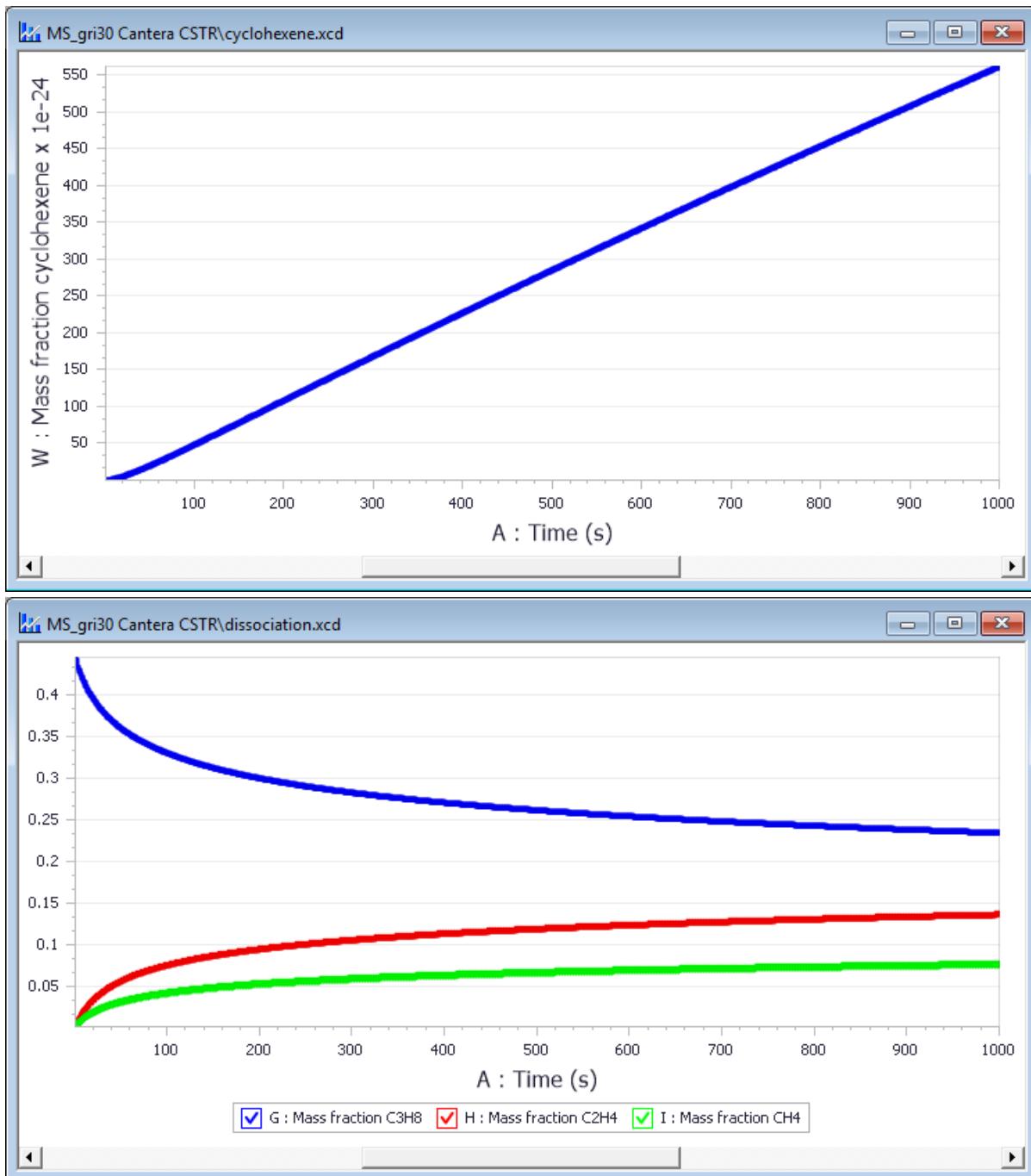
Double click on **MS_gri30_Canterac CSTR\MS_gri30 Results.std** to open it.

Select column **A Time (s)** and column **W Mass fraction cyclohexene**, and click **Quick Plot** . Rename the newly created plot **cyclohexene.xcd**.

Select columns **A Time (s)**, **G Mass fraction C3H8**, **H Mass fraction C2H4**, and **I Mass fraction CH4**.

Click **Quick Plot** and rename the newly created plot **dissociation.xcd**.

Cantera: Using the Cantera Reaction Editor



These plots show that butane (C3H8) partially dissociates at such an elevated temperature and produces ethylene and methane, as expected. At the same time, a minuscule fraction of the ethylene reacts with the butadiene present in the tank reactor to give cyclohexene.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

5. Augmenting an experimental reaction mechanism

A reaction mechanism which has not been created in Materials Studio will have an implicit reference state associated with it. Most often this reference state will be based on the commonly accepted standard enthalpies of formation, but this can not be guaranteed. If you want to amend and modify

such a reaction mechanism, great care must be taken to ensure that the species added with the Cantera Reaction Editor correspond to the reference state that is already implicit in the reaction mechanism.

In this section, we will therefore illustrate how to amend a study table where there is no known reference state. For this purpose, we have created a version of the *GRI 3.0 Mechanism* which has no entries on the Reference tab.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples/Cantera** folder and double-click on **MS_gri30v2.std**.

The study table containing the *GRI 3.0 Mechanism* without any reference species is displayed. Before you can import the Diels-Alder reaction, the study table *must* contain reference standard enthalpies for new species. We will, once again, use values from the [NIST Chemistry WebBook](#). In general it is best to use the same source as the original authors of the reaction mechanism, if possible.

Click the **Cantera** button  on the **Modules** toolbar and choose **Reaction Editor** or select **Modules | Cantera | Reaction Editor** from the menu bar.

Select **MS_gri30v2.std** from the **Study table** dropdown list.

Double-click on **Diels-Alder.std** in the **Project Explorer** to open it, and click the **Structures** tab.

Now we need to follow the same procedure as before to add butadiene as a reference species.

Double-click on **buta-1,3-diene** in the **Structure** column to open it.

In the **Cantera Reaction Editor** dialog change **Enthalpy of formation** to **29.95 kcal/mol**.

Click **Add**.

Repeat this procedure to add cyclohexene as a reference species with an Enthalpy of formation of **-1.03 kcal/mol**.

Now that reference species exist for butadiene and cyclohexene you will be able to import the Diels-Alder reaction as before. When the new species are added, only they will have new NASA polynomials calculated, and they will be quite precisely fitted to the reference enthalpies of formation. All of the existing species data will remain unchanged.

Double click on **Diels-Alder.std** in the **Project Explorer** to make it the active document.

Change **buta-1,3-diene** to **butadiene** in the **Name** column of the **Reactions and structures** grid.

Click **Import**.

The Diels-Alder reaction, cyclohexene, and butadiene are now added to the study table. You can validate the study table to check that it is ready to be used in a calculation.

Ensure that **MS_gri30v2.std** is selected in the **Study table** dropdown list.

Click **Validate**.

[**Cantera: Using the Cantera Reaction Editor**](#)

A message appears saying *Validation of study table successful.*

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

[1] [GRI-MECH 3.0](#)

[2] [NIST Chemistry WebBook](#)

Surface reactions in Cantera

Purpose: Introduces the use of Cantera for heterogeneous catalysis on surfaces and demonstrates the generation of reaction mechanisms for surface systems.

Modules: Materials Visualizer, Cantera, DMol³ (Analysis only, optional)

Time:  

Prerequisites: None

Background

Heterogeneous catalysis is one of the most essential processes in chemistry. To understand it, one requires atomic-level understanding of the underlying reaction rates, as well as a tool to integrate the reaction mechanisms on the surface and in the gas phase. Materials Studio Cantera provides such a tool in conjunction with the DMol³ module.

In this tutorial, we provide the results from a range of density functional theory calculations performed with DMol³ and demonstrate how to use them in Cantera. We use an approximate model for the well-studied catalytic oxidation of CO on the (110) surface of RuO₂ ([Reuter et al., 2004](#)). We will focus on adsorption and desorption processes, but will neglect any diffusion processes on the surface.

The reactions on this surface occur on the ruthenium atoms, which are aligned in separate rows. There are two distinct types of Ru atoms on the surface (called bridge and cus), leading to two sets of adsorption sites and a number of different reactions with similar reactants and products. We will discuss in detail how to handle this type of situation in the Materials Studio Cantera framework.

At the start of the tutorial, you will be working with a partially complete reaction mechanism in a Cantera study table and learn how to generate a reaction mechanism for surfaces. Then you will use this mechanism to perform calculations on two different reactor models.

Introduction

This tutorial covers:

- [Getting started](#)
- [Modifying Cantera input data using the Reaction Editor](#)
- [Setting up the Cantera Equilibrium calculation for surfaces](#)
- [Setting up the Cantera plug flow reactor calculation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **surface** as the project name, click the **OK** button.

The new project is created with *surface* listed in the Project Explorer.

The first two sections in this tutorial provide information on how to use the Cantera Reaction Editor. Optionally, you could also skip straight to section 3 and import a complete version of the study table to learn how to run surface reaction simulations.

Import the initial surface study table.

Click the **Import** button  to open the **Import Document** dialog. Navigate to the **Examples\Cantera\Surface Reactions** folder and import the **RuO₂_surface_incomplete.std** study table document.

Click the **Cantera** button  on the **Modules** toolbar and choose **Reaction Editor** or select **Modules | Cantera | Reaction Editor** from the menu bar. Select **RuO₂_surface_incomplete.std** from the Study table dropdown list.

Select the **Reference** sheet of the study table and double-click the **O₂Ru_surface** cell in the **Structure** column.

A model of the ruthenium oxide surface is displayed.

On the RuO₂(110) surface, there are two distinct rows of non-equivalent ruthenium atoms on the top layer of the surface. Five-fold coordinated Ru atoms are located directly above an oxygen atom and bonded to four additional O atoms in the top layer. We will call this adsorption position the *cus* site. Four-fold coordinated Ru atoms are bonded to two O atoms in the top layer and two more O atoms in the layer beneath. We will call these bridge sites. There is one site of each type in each surface unit cell. Throughout this tutorial, we will ensure that Materials Studio and Cantera are aware of this distinction and that the reaction mechanism and simulations contain and retain the correct surface structure.

The Cantera Reaction Editor dialog automatically interprets the content of the study table detail view when it is opened. In the *Reference species* section, it reports a *Surface site density* of 8.41×10^{-10} mol/cm², which has been calculated from the surface area of the irreducible unit cell of the system. In this particular case, there are two adsorption sites per surface unit cell. This means that the *Surface site density* on the *Reference* tab of the **RuO₂_surface_incomplete.std** study table should be exactly double the value found automatically by the Reaction Editor.

Select the **Reference** sheet of the study table and locate the **Surface site density (mol/cm/cm)** column. Check that the value in this column is twice that of the value reported in the Cantera Reaction Editor dialog.

In the *Reactions and structures* section on the *Cantera Reaction Editor* dialog, the system is recognized as a substrate and is named as *bridge* site. The study table actually contains two copies of the same structure in the species tab (*bridge* and *cus*), corresponding to both available adsorption sites on the RuO₂ surface. One of these two structures is chosen as a suggested name for the species.

Note: The *Add* column in the *Reactions and structures* grid contains the value **No**, this is because the species is already present in the study table.

Close the study table detail view.

2. Modifying Cantera input data using the Reaction Editor

The study table is missing the reaction:



Open the **Import Document** dialog and import the file **COcus+Obridge.xod**.

The imported collection document contains the missing reaction. First, we need to generate the rate constants.

Click the **DMol3** button  on the **Modules** toolbar and choose **Analysis** or select **Modules | DMol3 | Analysis** from the menu bar.

Select **Reaction kinetics** from the list.

Set the temperature range **From: 200 K To: 6000 K**.

Click **Calculate** and close the dialog.

A study table called **COcus+Obridge . std** containing information about the reaction is created.

Inspect the new study table to make sure the fitted values for the reaction rate parameters make sense. For example, the fitted activation energies, E_a , for the modified Arrhenius equation should be positive and have the correct scale, close to 20 kcal/mol.

On the **Graphs** tab highlight columns **F-H**, **K**, and **L**. Click the **Quick Plot** button  to obtain a graph of the computed and fitted rates derived for this reaction.

Select the **Structures** tab in the study table and inspect the different documents in the **Structure** column.

The top row contains a copy of the original collection document, while the second and third rows contain the separate *Reactant* and *Product* structures. Neither of these can be imported directly by the Cantera Reaction Editor: the reactant is a surface with two motion groups while the product is a gas phase molecule above the surface. Either of these require a separate calculation of the species.

Tip: In some instances, you might only have the transition state, reactants, and products available as separate 3D atomistic documents. These can still be imported into Cantera study tables if you follow the instructions on how to create a collection document from atomistic data in the DMol³ section of the online help.

Inspect the **Reactions and structures** grid in the Cantera Reaction Editor dialog.

This contains a list of the structures required for the reaction. The **Add** column in the grid contains the value **NA**, reflecting the fact that the species can not be imported as part of the reaction import.

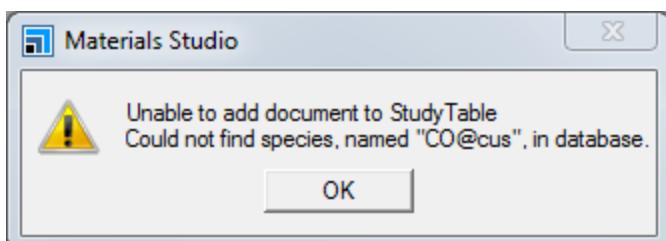
Note: The adsorbed carbon monoxide molecule is named *CO@bridge*, corresponding to what the *Cantera Reaction Editor* dialog already found in the study table. The *Cantera Reaction Editor* dialog can detect molecules on surfaces, but is unable to differentiate between different adsorption sites. This will have to be corrected by hand prior to importing the reaction.

In the **Reactions and structures** grid on the Cantera Reaction Editor dialog change the **Name** of the carbon monoxide species from *CO@bridge* to *CO@cus*.

Click **Import**.

[Cantera: Surface reactions in Cantera](#)

Cantera will show an error message.



As provided, the study table does not contain the species CO@cus required to describe the full reaction mechanism. Before we can import our reaction we need to import the missing CO on the surface document. The document must contain vibrational data for the molecule. The required file is most likely created during the process of finding the reaction transition state. This structure could be automatically included in the DMol³ Reaction Kinetics calculation task by checking the *Calculate subsystems* checkbox on the *DMol³ Reaction Kinetics dialog*, but that might incur substantial computational costs. In this particular case we will provide the adsorbed species as a single document.

Click the **Import** button  to open the Import Document dialog and import the file **CO@RuO2_110_cus.xsd**.

A HessianAtoms set is defined in the atomistic document which corresponds exactly to the adsorbate. On the Cantera Reaction Editor dialog, the species is recognized as a surface with the name [CO25Ru12_surface](#), which you could add to the study table as a new substrate. However, there is no indication that Cantera recognizes this as an adsorbate on a surface, which means that it will not interpret the chemical formula or the free energy correctly. To clearly distinguish the adsorbate, you must define a motion group for the CO molecule.

Rotate the structure and select the **CO** atoms in the **HessianAtoms** set.

Select **Modify | Motion Groups** to open the **Motion Groups** dialog and click **Create** from selection. Close the dialog.

The molecule has now been defined, but the *Reaction Editor* dialog does not automatically follow changes in the 3D Atomistic Document and needs to re-read its contents. This can be achieved by changing focus and returning to the original document.

Change focus to the [RuO2_surface_incomplete.std](#) study table document, then change focus back to the [CO@RuO2_110_cus.xsd](#) document.

In the *Reactions and structures* section of the Cantera Reaction Editor dialog, the **Name** has now changed to [CO@bridge](#) and the type is MS (for molecule on a surface). This means that Cantera correctly interprets the structure and actually recognizes that a species with the same chemistry is already present in the database, where it is called [CO@bridge](#). In this case, the Reaction Editor will not import and add the species to the reaction mechanism. As discussed above, this particular CO molecule is adsorbed on a cus site, so we need to add this information explicitly before we can import the species.

In the **Reactions and structures** section of the Cantera Reaction Editor dialog, change the **Name** to [CO@cus](#). Verify that the **Add** column has now changed to **Yes**. Click **Import**.

We now have all the gas and surface phase species required and we can once again try to import the reaction.

Ensure that **CO_{cus}+O_{bridge}.std** is in focus.

On the **Reactions and structures** section of the Cantera Reaction Editor dialog ensure that the reaction refers to a [CO@cus](#) species, change the **Name** accordingly if it does not.

Click **Import**.

A new reaction has been added to the Reactions tab. Observe how the reaction has been balanced automatically, by adding two surface unit cells to the product side. By default, the *Cantera Reaction Editor* only recognizes one single substrate species and applies that where necessary. However, the reaction we imported was purposefully chosen to contain both available surface sites. To make sure that Cantera will not change the surface topology, we will have to edit the reaction equation by hand to reflect the corrected product.

Select the **RuO₂_surface_incomplete.std** study table document and ensure that the **Reactions** tab is active. In the last row, change the equation to [CO@cus + O@bridge <=> bridge + cus + carbon_dioxide](#).

Finally, we need to make sure that there are no internal inconsistencies in the newly modified study table.

On the **Cantera Reaction Editor** dialog, click **Validate**. If validation is successful close the dialog.

If there are any error messages, go through the study table and the instructions above to address any issues and then make sure it validates successfully.

In the Project Explorer, rename the document **RuO₂_surface_incomplete.std** to **RuO₂_surface.std**.

Save and close all documents and save all files when prompted.

Note: This reaction was chosen specifically to demonstrate the import of a complex reaction. In practice, most reactions should be more straightforward.

3. Setting up the Cantera Equilibrium calculation for surfaces

The newly created **RuO₂_surface.std** study table can now be used to do simulations of surface reactions. Alternatively, if you have not completed sections 1 and 2, you can import the results and run the remainder of this tutorial directly.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Cantera\Surface Reactions** folder and import the **RuO₂_surface.std** study table document or open your own version.

The first calculation will find the equilibrium surface coverage for a RuO₂ surface in a CO and O₂ gas mixture.

Open the **Cantera Calculation** dialog.

We will use the Equilibrium task in this section.

Ensure that **Task** is set to **Equilibrium** and click **More...** to open the Cantera Equilibrium dialog.

Select the **Surface** radio button and close the dialog.

Selecting Surface indicates that you want to calculate the steady-state surface occupation of a reacting surface in a gas mixture, keeping temperature and pressure constant (for example, using the TP ensemble).

In the **Gas** section of the Cantera Calculation dialog, ensure that **Mole fraction** is selected.

Set **Temperature** to **550 K**.

From the **Species** dropdown list select **CO** and set the **Fraction** to **1**. In the second row, select **molecular_oxygen** and set the **Fraction** to **0.45**.

The *Surface* section of the Cantera Calculation dialog automatically detects which is most likely to be the empty site and assigns a coverage of 1. For the RuO₂ surface treated here, we have two distinct sites per surface unit cell so we need to enforce an initial surface coverage of half *bridge* and half *cus* sites.

In the **Surface** section, set **Temperature** to **550 K**.

Verify that the top row of the **Surface** table contains the species **bridge**, for the second row select **cus** from the **Species** dropdown list.

Set the **Coverage** of **cus** to **0.5**. Ensure that the **Coverage** for **bridge** is set automatically so that the total coverage is 1.

In cases where the dialog finds an incorrect default empty surface species, this can be resolved by specifying the correct set of sites with coverages adding up to unity. The automatically identified value will then be zero.

Next, run the Equilibrium calculation.

Select the **Job Control** tab and review the settings, select an appropriate **Gateway location** and **Queue**. Click **Run** to start the job.

A new folder, named **RuO₂_surface Cantera Equilibrium**, opens in the Project Explorer and a Cantera job is run by the server. Wait until the job completes and the results are downloaded before moving on to the next step.

A text document called **RuO₂_surface.txt** is opened when the job completes. This contains a notification that Python has started and that it completed successfully as well as summary reports on the thermodynamic properties of the initial and final states of the gas and surface. The **Equilibrium state** section reports the composition of the system at equilibrium, corresponding to the gas phase mixture after being in contact with the catalyst for a long time. For example:

	X	Y
CO	0.1	0.0660469
carbon_dioxide	0.9	0.933953
[+1 minor]	1.01029e-048	7.62276e-049

Where X is the mol fraction and Y is the mass fraction.

This indicates that almost all of the O₂ in the gas phase has been converted to CO₂ while 10% of CO remains.

Three other files were created in the RuO₂_surface Cantera Equilibrium directory, not including the calculation file, RuO₂_surface - Calculation and the input study table. The other files are RuO₂_surface.cti, RuO₂_surface.py, and a study table RuO₂_surface Results.std.

The RuO₂_surface.py file contains the Cantera Python script that is run to produce the data. This script can be modified before starting the job using the *Files...* button. We will now customize the script to run a loop over a range of pressures rather than performing a single point calculation.

Select **Window | Close All** from the menu bar.

Open the original **RuO₂_surface.std** study table document again.

Open the Cantera Calculation dialog, click **Files...** to open the Cantera Job Files dialog and click **Save Files**. This will create a new job folder and populate it with all the input files.

We can now amend the job by opening the RuO₂_surface.py file and modifying the code.

Open the file RuO₂_surface Cantera Equilibrium (2)\RuO₂_surface.py in the new job folder.

In the file you will see a section with pressure settings:

```
# Pressure settings
startPressureInPa = 100000
endPressureInPa = 100000
pressureStepInPa = 100000
```

By changing these settings you can modify the range of pressures that the calculation will run over and thereby generate an entire isotherm.

Set **endPressureInPa** to **100000 * 100** and save the file.

The section of the code should now read.

```
# Pressure settings
startPressureInPa = 100000
endPressureInPa = 100000 * 100
pressureStepInPa = 100000
```

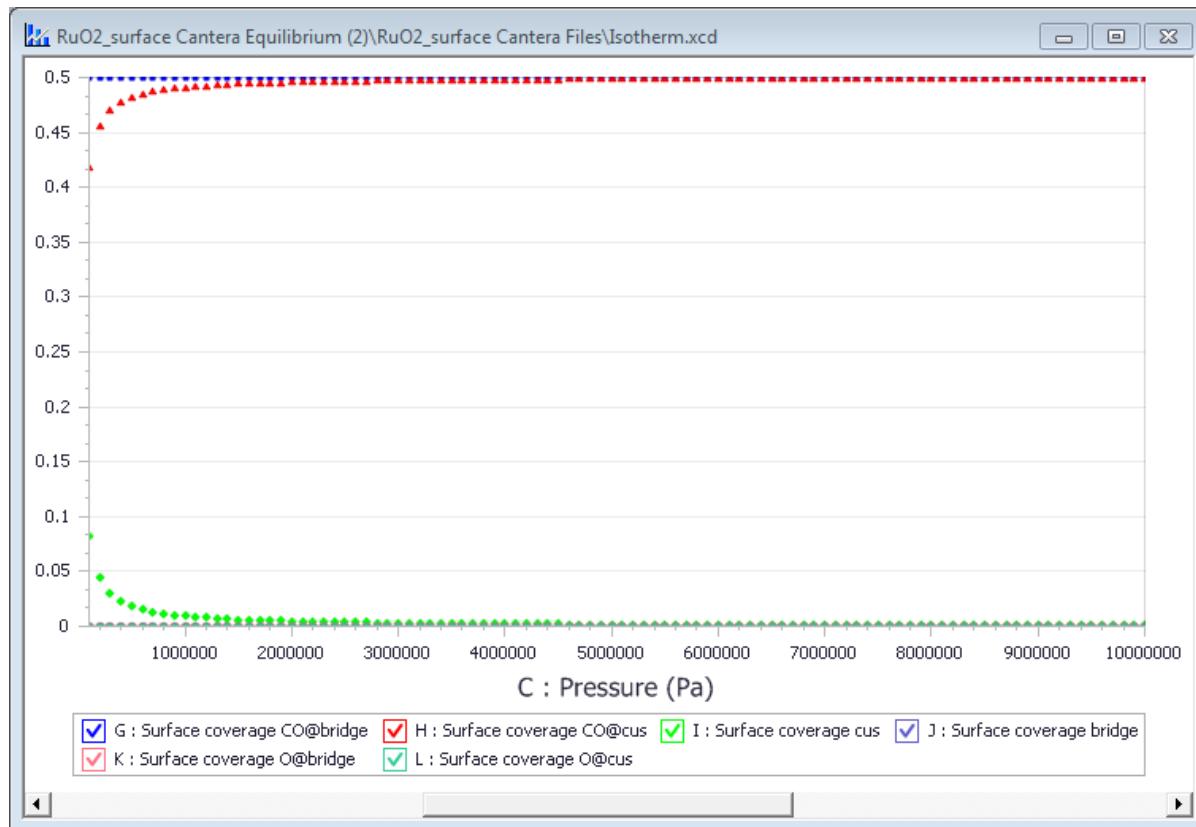
With the RuO₂_surface.py file in focus click **Run Files** on the Cantera Job Files dialog to start the modified job. If prompted to save files click **Yes**.

When the job completes an equivalent set of results files are returned.

The results will be stored in separate rows for each pressure in the output RuO₂_surface Results.std study table. The surface coverage and mass fraction columns are ordered according to the maximum value in each column.

Double-click on the file **RuO₂_surface Cantera Equilibrium (2)\RuO₂_surface Cantera Files\RuO₂_surface Results.std** in the **Project Explorer** to open it.

Press **SHIFT** and select columns **G** to **L**, then press **CTRL** and select column **C Pressure (Pa)**. Click the **Quick Plot** button . Change the name of the chart document to **Isotherm.xcd**.



This chart shows the site coverage at equilibrium for a range of gas pressures. The surface is almost entirely covered by carbon monoxide, only some *cus* sites are empty at low pressures. All of the *bridge* sites have CO molecules adsorbed. This plot allows a visual check for the reaction mechanism as the total number of *bridge* and *cus* sites (for example, empty and occupied sites) should add up to 0.5 for each type of site, giving a total coverage of 1.

Select **Window | Close All** from the menu bar, and save files if prompted.

4. Setting up the Cantera plug flow reactor calculation

A common use of catalytic surfaces is as the active medium in a plug flow reactor (PFR) or in a continuous tubular reactor (CTR). This type of reactor can be simulated as a series of short linked segment "plugs", each with a uniform gas phase and surface composition. It is assumed that the fluid in each segment reaches equilibrium and that there is no backflow. In Cantera we model this as a series of perfectly stirred tanks where each tank is allowed to reach steady state before it is used to setup the flow into the next segment.

Before you begin, return the Cantera settings to their default values.

Select **Tools | Settings Organizer** from the menu bar, select **Cantera** and click **Reset**. Close the dialog.

We will now setup a PFR filled with a RuO₂ catalytic surface as bed material.

Open the original RuO₂_surface . std study table document again.

Open the Cantera Calculation dialog and set the **Task** to **Plug Flow Reactor**, click **More...** to open the Cantera Plug Flow Reactor dialog.

Set the **Reactor length** to **0.1** m, the **Surface area per meter** to **5.0** and **Input mass flow rate** to **2.0e-7**. Close the dialog.

The units for the settings used to define the PFR have been chosen to give flexibility when defining different types of plug flow reactors. In this case we assume:

- A porous bed material with a porosity P :

$$P = \frac{V_G}{A} = 0.3$$

Where V_G is the gas volume per meter and A is the cross sectional area of the reactor.

- A catalytic area per volume C_{AV} (m²/m³):

$$C_{AV} = \frac{A_S P}{V_G(1-P)} = 214286$$

Here A_S is the catalytic surface area per meter.

With these material parameters the above settings will model a 10 cm long reactor with a cross section area of 3.3 cm². All that remains is to specify the input gas mixture and the surface. Since the surface will be run to steady state the initial condition is not important for the final result but a good initial choice could help in some applications.

In the **Gas** section, make sure that **Mole fraction** is selected. Set **Temperature** to **500** K.

Add **CO** and **molecular_oxygen** to the gas species list. Set the **Fraction** of **CO** to **1.0** and of **molecular_oxygen** to **0.45**.

In the **Surface** section, set **Temperature** to **500** K. Select **cus** from the **Species** dropdown list and set the **Coverage** to **0.5**.

We are now ready to run the calculation.

Select the **Job Control** tab and review the settings, select an appropriate **Gateway location** and **Queue**.

Click **Run** to start the job and close the dialog.

A text document called RuO₂_surface . txt opens when the job completes. This contains a notification that Python has started, that it completed successfully, and summary reports on the thermodynamic properties of the initial and final states of the gas and surface.

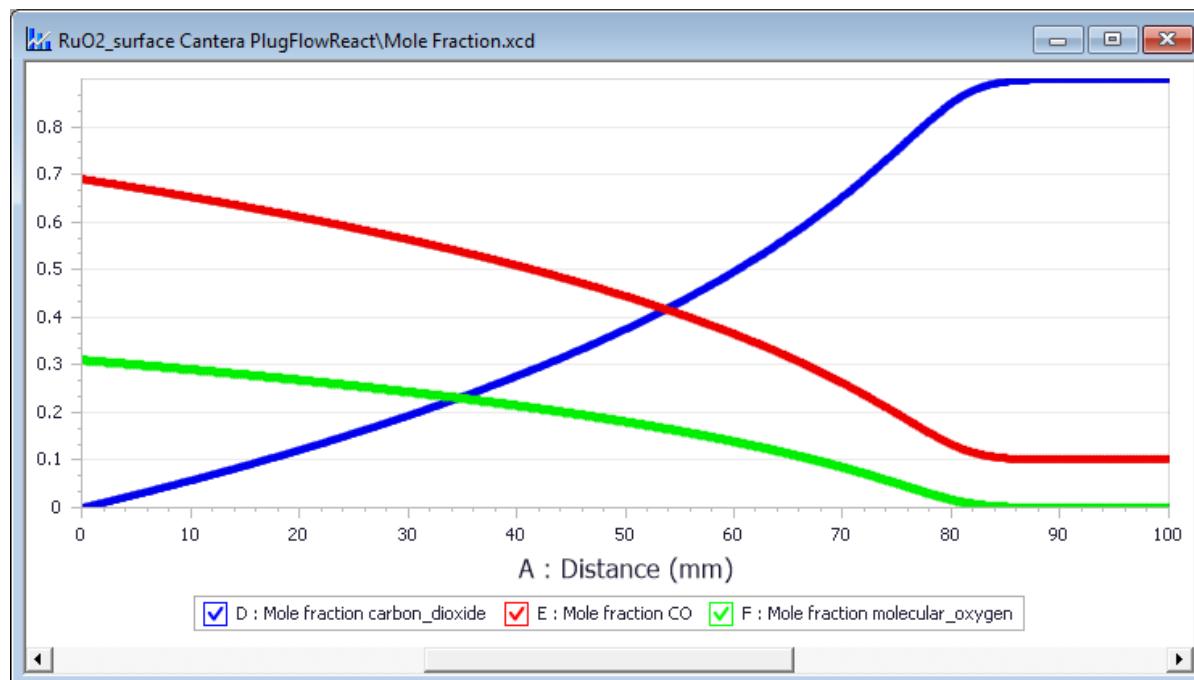
Three files were created in the RuO₂_surface_CanteraplugFlowReact directory in addition to the input documents. These are RuO₂_surface.cti, RuO₂_surface.py, and a study table RuO₂_surface_Results . std. The study table contains mole fractions and surface coverage for all species for each section in the PFR.

Double-click on **RuO₂_surface Cantera PlugFlowReact\RuO₂_surface Results.std** in the **Project Explorer** to open it.

Press **SHIFT** and select columns **D** to **F**, then press **CTRL** and select column **A Distance (mm)**. Click the **Quick Plot** button .

A chart document called **RuO₂_surface Results Scatter plot.xcd** has been created in the **RuO₂_surface Cantera PlugFlowReact** directory.

Change name of the chart document to **Mole Fraction.xcd**



This chart contains all the gas phase species as a function of distance along the reactor.

Not quite all the carbon monoxide has been oxidized into CO₂, as there was not enough O₂ available initially. To better understand the function of the catalyst, it is also important to study the coverages for different surface species.

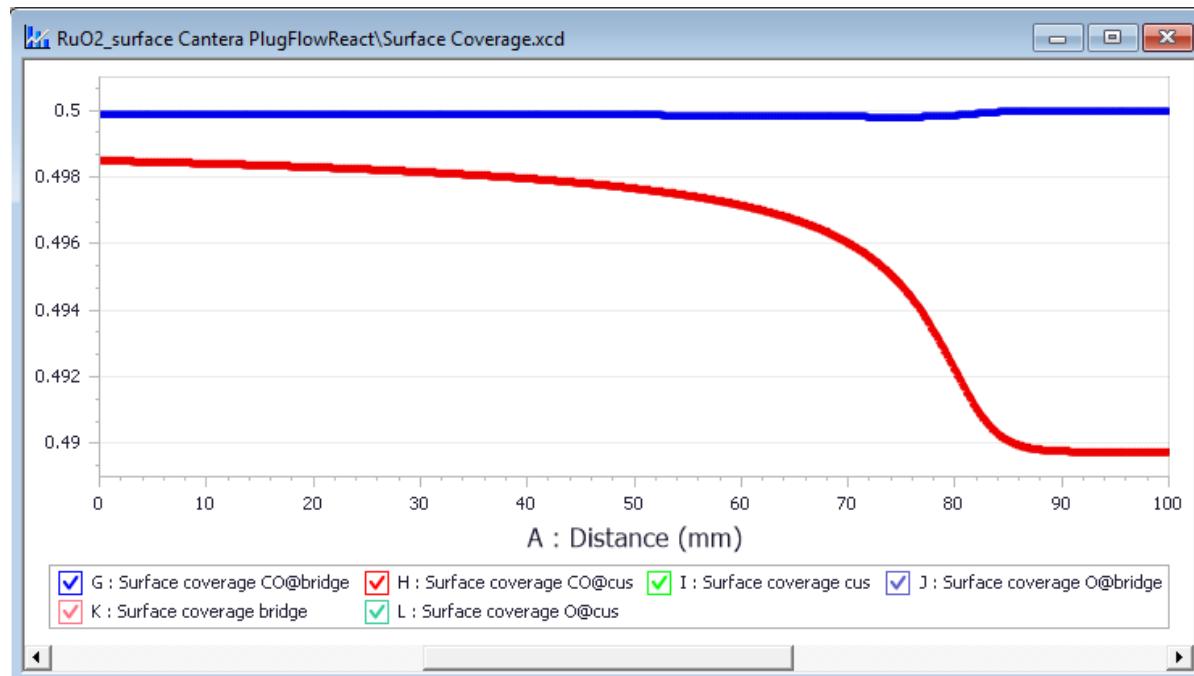
Tip: The *Plug Flow Reactor* task can depend significantly on the calculation tolerances and the steady state threshold used in Cantera. These are listed in the Python script at the top of the **Reactor Simulation** section. It is essential to make sure that the calculation is converged with respect to these numbers. Changing them appropriately can also aid the completion of the simulation.

Change focus to the **RuO₂_surface Results.std** study table and click on any cell to remove the existing selection.

Press **SHIFT** and select columns **G** to **L**, then press **CTRL** and select column **A Distance (mm)**. Click the **Quick Plot** button .

Change name of the chart document to **Surface Coverage.xcd**. If it is not already present, open the **Properties Explorer**. Set the **Filter** to **Y axis** and use the **Max / Min** values to focus on the area around **y=0.5**. Ensure that there are no single coverages that are greater than 0.5, which would indicate a problem with either the set up or the reaction mechanism.

This chart requires focusing the y-axis around the value 0.5.



This chart shows that most of the surface is "poisoned" by carbon monoxide, which suggests that the reaction is almost entirely driven by whatever small amounts of oxygen can adsorb on the surface. This phenomenon is common in catalytic converters in cars. Maximal catalytic activity is generally achieved when all the required species are present on the surface in substantial amounts and there are enough free surface sites to adsorb additional gases. Achieving this depends crucially on the exact operating conditions and catalyst dynamics. To optimize it, manufacturers often turn to dynamic processes such as changing the fuel to oxygen ratio on the fly when the catalyst needs to be cleared.

We should also inspect some of the Python code used to run this simulation.

Open the Python script **RuO₂_surface Cantera PlugFlowReact\RuO₂_surface.py** and scroll to the section titled **Reactor Simulation**.

This section consists of three subsections:

- In the first section, we initialize the data output for the basic temperature and pressure conditions, for the species concentrations, and for the surface coverages. The `title` array contains the list of study table titles for each column, while the `data_row` array contains the initial condition for the top row in the study table.
- Below the setup for the output, there is the main simulation loop. Again, the output is done in three sections, corresponding to temperature and pressure, gas phase concentrations, and surface coverages respectively. All of this output is done as a function of distance.
- Finally, once we are done with the simulation, we sort the output data in blocks by their largest values such that the largest gas phase concentrations are listed first, as are the largest coverages. Manipulating this section of the code before running the simulation might be useful in cases where there will be a lot of output.

By commenting out a section or adding custom code to all three parts of the output, we can print additional information about the reaction or manage larger data sets.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Reuter, K., Frenkel, D., Scheffler, M. "The steady-state of heterogeneous catalysis studied by first-principles statistical mechanics", *Phys. Rev. Lett.*, **93**, 116105 (2004).

Mechanism reduction using sensitivity analysis

Purpose: Introduces the use of Cantera sensitivity analysis for studying reaction mechanisms. The problem-specific reduction of a reaction mechanism to contain only the reactions essential for the final outcome is presented.

Modules: Materials Visualizer, Cantera

Time: 

Prerequisites: Continuous stirred-tank reactor, Visualizer Tutorial

Background

Reaction mechanisms in chemical kinetics can frequently contain hundreds of species and thousands of reactions. In many applications, only a small fraction of these species and reactions are relevant for a given situation. Performing calculations with unnecessary reactions will produce excessive data, and will be computationally inefficient. Sensitivity analysis provides a way to investigate specific situations and tell which reactions are most important. This allows you to better estimate the rate limiting step of a given reaction, and to reduce the mechanism to contain only the required information. It is typically undertaken to identify key reactions whose parameters should be optimized to improve accuracy and to remove irrelevant reactions to reduce the cost of large-scale fluid dynamics calculations.

Introduction

In this tutorial, you will learn how to use Cantera sensitivity analysis to perform a detailed investigation of the problem considered in the tutorial on the [Continuous stirred-tank reactor](#), and will generate a reduced reaction mechanism that has the same description of the chemistry as the full reaction.

This tutorial covers:

- [Getting started](#)
- [To set up the Cantera sensitivity analysis](#)
- [Analyze sensitivity data](#)
- [Detailed ignition analysis](#)
- [Reduce the reaction mechanism](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **sensitivity** as the project name, click the **OK** button.

The new project is created with *sensitivity* listed in the Project Explorer. In this tutorial you will be working with the hydrogen flame mechanism you already saw in the CSTR tutorial. You will begin by setting up the same initial conditions as for the adiabatic CSTR.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Cantera** folder, change the file type filter to **All Materials Studio Files**, and double-click on **MS_h2o2.std**.

The study table displayed contains all of the reactions we are going to work with for this tutorial, it will be used as input for Cantera.

2. To set up the Cantera sensitivity analysis

The data contained in **MS_h2o2.std** will be used as input to Cantera.

Click the **Cantera** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | Cantera | Calculation** from the menu bar to open the Cantera Calculation dialog.

Select **CSTR** from the **Task** dropdown list and ensure that **Mole fraction** is selected in the **Gas** section.

Select **H2** from the **Species** dropdown list and then in the next, newly created row, select **O2**.

Set the **Fraction of H2** to **2**, and the **Fraction of O2** to **1**.

Set the **Temperature** to **960 K** and change the **Pressure** to **101325 Pa**.

This sets up most of the basic reactor conditions. Next, you will set the sensitivity analysis and more specific CSTR options.

Click the **More...** button to open the Cantera CSTR dialog. Uncheck the **Isothermal** checkbox, set the output time window to between **From 0.0 s** and **To 50.0 s**, and set the **Time step** to **0.5 s**.

In the Sensitivity analysis section, check the **Mechanism reduction** checkbox. Select **H2** from the **Species** dropdown list, and then in the next, newly created, rows select **O2** and **H2O**.

Close the dialog.

We are now ready to run the same adiabatic calculation as in the [Continuous stirred-tank reactor](#) tutorial.

Select the **Job Control** tab and review the settings, select an appropriate **Gateway location** and **Queue**. Click **Run**.

When the calculation is complete, open the **MS_h2o2 Cantera CSTR\MS_h2o2 Results.std** study table.

This study table contains five sheets:

- *Results* stores the physical parameters of the gas as a function of time, such as pressure, temperature, enthalpy. It also contains the mass fraction for each species.
- *Mechanism reduction* contains the global sensitivity measure for each reaction in the mechanism, ordered by sensitivity value. We will use this information to eliminate reactions that are not essential later in this tutorial.
- *Sensitivity H₂* contains the sensitivity of the concentration of molecular hydrogen with respect to each reaction rate coefficient.
- *Sensitivity O₂* contains the sensitivity of the concentration of molecular oxygen with respect each reaction rate coefficient.
- *Sensitivity H₂O* contains the sensitivity of the concentration of water with respect to each reaction rate coefficient as a function of time.

All results on any given sheet are sorted by their largest absolute value.

3. Analyze sensitivity data

You will analyze the results from this calculation and then zoom in on the time window in which the reaction occurs.

Right-click on the **MS_h2o2 Cantera CSTR** folder in the Project Explorer and rename it to **coarse**. In the **coarse\MS_h2o2 Results.std** study table select the **Results** tab. Press **CTRL** and select Columns **A Time (s)** and **B Temperature (K)**, then click the **Quick Plot** button . Right-click on **MS_h2o2 Results Scatter plot.xcd** in the Project Explorer and rename it **temperature.xcd**.

Double-click on **MS_h2o2 Results.std** again, select column **M Mass fraction HO₂**, then hold down **SHIFT** and click to select all columns from **M Mass fraction HO₂** to **F Mass fraction O₂**. Press **CTRL** and select column **A Time (s)**. Click the **Quick Plot** button  and rename the chart to **fractions.xcd**.

So far, we have been following the exact same steps as in a previous tutorial. The system shows an explosive increase in temperature and pressure, and a near-instantaneous change in the mass fractions around 25.5s.

First, we will analyze the dominant reactions leading up to the explosion.

Click **More...** to open the Cantera CSTR dialog. Uncheck the **Isothermal** checkbox and set the output time window to between **From 0.0 s** and **To 25.0 s**. Ensure that the **MS_h2o2.std** study table is in focus and click **Run**.

Once the calculations has finished, plot and analyze the sensitivities for some of the most important species to identify the single-step reactions that are most responsible for this phenomenon.

Right-click on the **MS_h2o2 Cantera CSTR** folder in the Project Explorer and rename it to **pre-explosion**.

Double-click on **MS_h2o2 Results.std** study table and select the **Sensitivity H2O** tab. Press **SHIFT** and select columns **A Time (s)** to **E Sensitivity of H2O wrt rate H + H2O2 <=> H2 + HO2**. Click the **Quick**

Plot button  and rename the resulting chart **sensitivity_H2O.xcd**. Repeat this procedure for the first five columns of the **Sensitivity O2** and **Sensitivity H2** tabs on the results study table to generate the charts **sensitivity_O2.xcd** and **sensitivity_H2.xcd**.

Inspect the three sensitivity charts side by side.

The sensitivity of a species i with respect to a rate coefficient j is defined as:

$$S_i^j = \frac{\partial \ln c_i}{\partial \ln k_j} = \frac{k_j}{c_i} \frac{\partial c_i}{\partial k_j}$$

It measures the relative dependence of the concentration c_i of a species on the value of the rate coefficient k_j corresponding to a specific reaction. The logarithmic derivative makes sure that the influence of each reaction remains comparable, even if the size of either concentration or rate coefficient differs by many orders of magnitude. A sensitivity with a large magnitude corresponds to a very important reaction for a specific outcome.

With that in mind, display the charts you just generated and inspect the various lines. In all three cases, the same four reactions are mostly responsible for determining the concentration of water, molecular oxygen, and molecular hydrogen:

- $H + O_2 \leftrightarrow O + OH$
- $H + O_2 + M \leftrightarrow HO_2 + M$
- $H + 2 O_2 \leftrightarrow HO_2 + O_2$
- $H + H_2O_2 \leftrightarrow H_2 + HO_2$

The order might change, but all four reactions are present. Note that all of the reactions involve oxygen and hydrogen molecules, and none involve the formation of water. The most influential mechanisms on the final result is the O_2 dissociation.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. Detailed ignition analysis

In this section, we will focus on the actual moment of ignition and confirm in detail that the conclusion from the simple experiment in the last section remains valid. We will zoom into the exact same time window identified by the [Continuous stirred-tank reactor](#) tutorial to analyze the ignition point.

Double-click on **MS_h2o2.std** in the Project Explorer, open the **Cantera Calculation** dialog and the **Cantera CSTR** dialog.

Change the output time window to between **From 25.65969 s** and **To 25.65979 s**, and the **Time step to 1e-7 s**.

Click **Run** and close the dialogs.

This job should only take a few seconds to run. After it has been completed, you should plot some of the output data to get a better feel for the sensitivity.

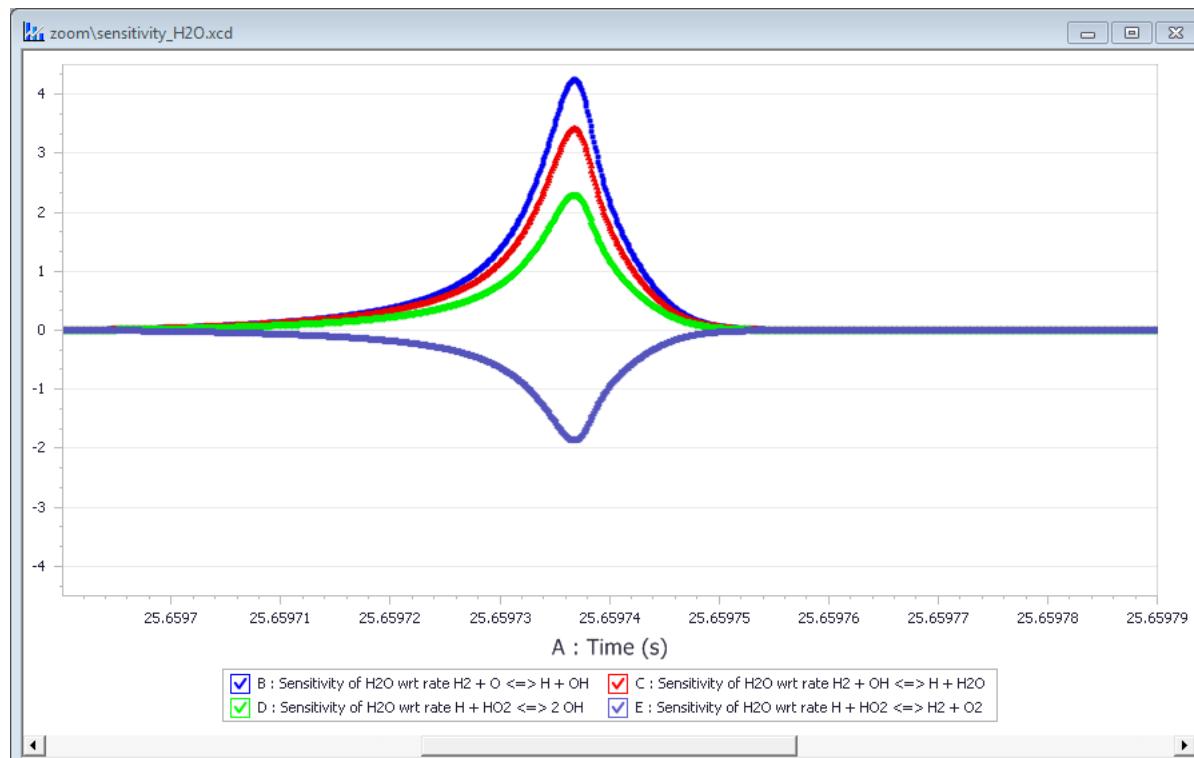
Rename the folder **MS_h2o2 Cantera CSTR to zoom**.

Open **zoom\MS_h2o2 Results.std** and select the **Sensitivity H2O** tab. Press **SHIFT** and select columns **A Time (s)** to **E Sensitivity of H2O wrt rate H + H2O2 <=> H2 + HO2**. Click the **Quick Plot** button  and rename the resulting chart **sensitivity_H2O.xcd**.

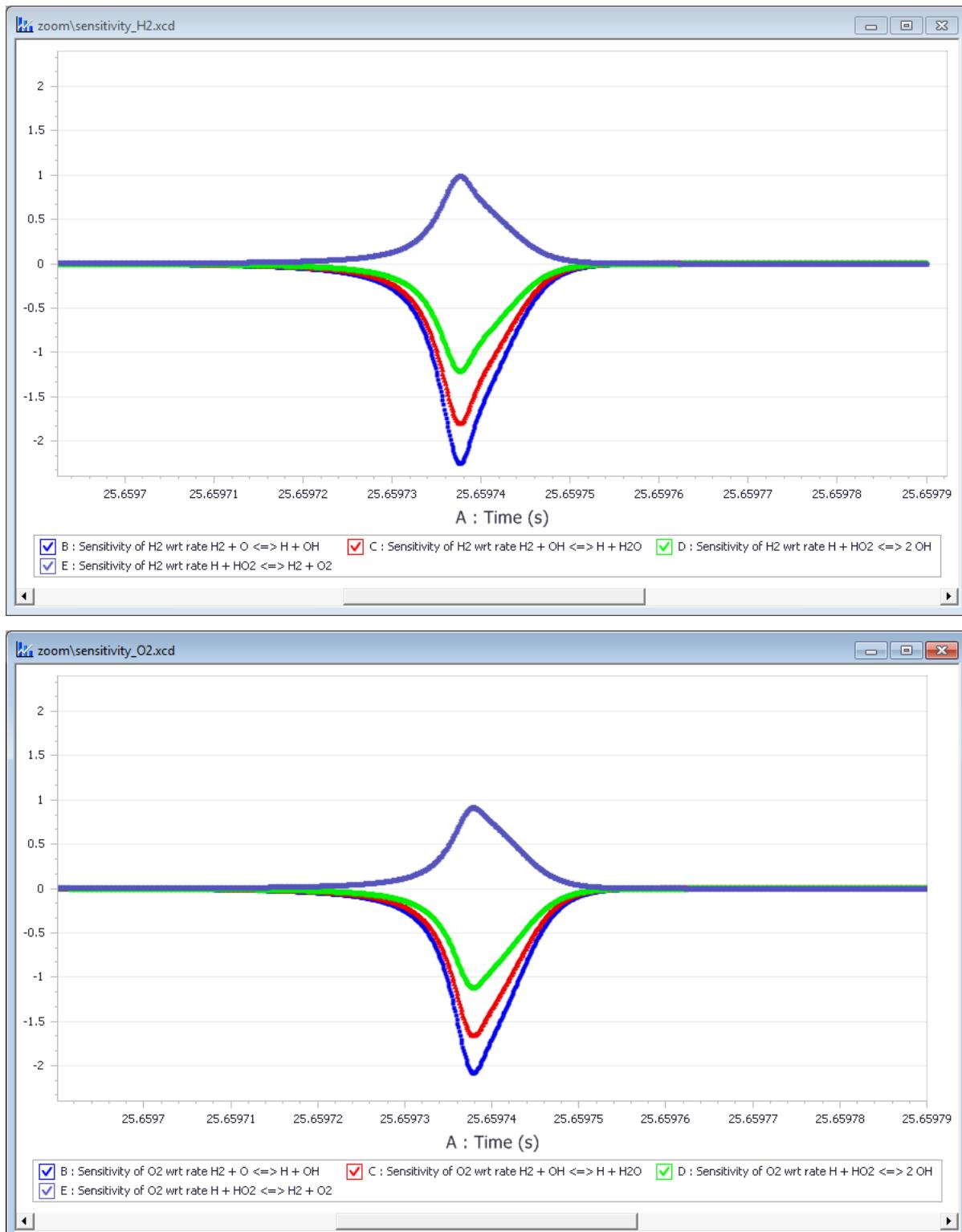
Repeat these steps for the tabs **Sensitivity H2** and **Sensitivity O2** to generate the charts **sensitivity_H2.xcd** and **sensitivity_O2.xcd**.

You should have generated charts similar to those below.

Note: These example charts have been scaled to compare the vertical axis. Use the Properties Explorer to change the *Max* and *Min* property values for the *Y Axis* so they are the same for all three charts.



Cantera: Mechanism reduction using sensitivity analysis



We can see that during a detailed analysis of the explosive reaction of the H₂ and O₂ gas mixture, the most prominent reactions have changed, compared to the pre-explosion run above. In the explosion, one of the prominent reactions now produces water. It is also apparent from the charts above that the sensitivity for the product species H₂O with respect to a given reaction has the opposite sign as the

sensitivity of either reactant H₂ or O₂ with respect to that same reaction. This makes sense intuitively, as the concentration rates of products and reactants are opposite in sign during the reaction.

In the sensitivity analysis, it is important to ensure that the relative order of the reactions has converged with respect to the time step. In particular, for rapid reactions like explosions.

So far, you have used a simple sensitivity measure to identify which reactions most contribute to a particular reactant's concentration and to track them through time. In the next section, you will formalize this process into a single measure to identify reactions which can be removed from the mechanism while still describing the full outcome.

5. Reduce the reaction mechanism

As you have probably noticed, the direct application of the sensitivity described above can generate enormous amounts of data and could require substantial visual interpretation. Instead of wading through large numbers of plots, we can also summarize the importance of a given reaction with a single measure B_j for each reaction step that averages all sensitivities over the duration of the entire process. This is computed by simply summing up the single sensitivities as:

$$B_j = \langle \sum_i \left(\frac{k_j}{c_i} \frac{\partial c_i}{\partial k_j} \right)^2 \rangle_t$$

Where the sum is taken over all species in the mechanism and the average is over time. The quantity in the outer brackets is computed for each point in time, then the average is taken over time steps. This quantity provides one number per reaction, which is listed on the *Mechanism reduction* sheet of the results study table. You will have to transfer the sensitivities from the results study table to a copy of the input study table in order to get a reduced mechanism.

Open the original **MS_h2o2.std** and select the **Reactions** tab, and rename it to **Reactions all**.

Materials Studio Cantera will interpret only the tab named *Reactions* and, on that tab, it will use only those columns which it recognizes. This allows us to add additional columns and tabs that contain, for example, the full original data set. We will now create different versions of the *Reactions* tab that contain a reduced mechanism.

On the **Reactions all** tab select column **D ID** and click the **Sort Ascending** button to sort the equations alphabetically. Insert a column to the right of **D ID**.

Change focus to the **zoom\MS_h2o2 Results.std** study table and select the **Mechanism reduction** tab. Sort by column **B ID** alphabetically, and copy the contents of column **C Global sensitivity**.

Paste into the newly created column of the **MS_h2o2.std** study table. This column will now be named **E Global sensitivity**.

Select column **E Global sensitivity** and click the **Sort Descending** button .

The list of reactions is now ordered by the importance of each single step, which allows us to reduce the mechanism. We will now use fewer reactions to re-run the simulation and see whether this reduced mechanism still gives a faithful representation of the original reaction.

Cantera: Mechanism reduction using sensitivity analysis

Select the top 23 rows on the **Reactions** all tab (corresponding to all reactions with a *Global sensitivity* greater than 10^{-5}). Click the **Filter** button  to generate a new sheet from this selection. Rename the new sheet **Reactions**.

IMPORTANT! When running Cantera on several reactions you must verify that all reactions marked "duplicate" occur in pairs. If a duplicate reaction is filtered out, you must remove the keyword before running Cantera.

Select the column **L Options** on the **Reactions** tab. Press  to bring all duplicate reactions to the top. **Delete** the word **duplicate** for all unpaired reactions.

When you run the same Cantera calculation now. Materials Studio will run the simulation based on the content of the new *Reactions* tab, which corresponds to the reduced reaction mechanism. To assess the quality of the reduced mechanism, you will re-run the initial combustion calculation and zoom in on the time window which the main reaction occurs.

Double-click on the **coarse\MS_h2o2 - Calculation** settings file to open the Cantera Calculation dialog with the same settings as you used in the first run. Ensure that the original **MS_h2o2.std** study table is in focus and click **Run**.

When the calculation is complete rename the output folder **reduced_coarse**. Open **reduced_coarse\MS_h2o2 Results.std** and create charts for the **H₂**, **O₂**, and **H₂O** sensitivities as well as the temperature as a function of time.

From the temperature curve, identify the point at which the step change happens in the reaction and use the time window controls on the **Cantera CSTR** dialog to zoom in on that particular region. You may require two or three separate runs before resolving it with a time step of 10^{-7} s.

When the calculation is complete rename the output folder **reduced_zoom**. Open **reduced_zoom\MS_h2o2 Results.std** and create charts for the **H₂**, **O₂**, and **H₂O** sensitivities.

You should find that the temperature range and final products are very close for the reduced mechanism, and that ignition time has only changed very little. This suggests that it is safe to use only 23 equations for the simulations done in this tutorial in a lot of situations.

Optionally, you may want to reduce the mechanism even further following the steps above, for example to restrict to only the top 15 or top 10 most important reaction steps. You should find that the temperature and final products remain identical, but that the ignition time changes by varying amounts for the different reaction sets. Depending on your final application, this may be acceptable and would be much quicker to calculate if you are dealing with long reactions.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Temperature programmed desorption

Purpose: Introduces the use of Cantera for temperature programmed desorption.

Modules: Materials Visualizer, Cantera

Time: 

Prerequisites: Continuous stirred-tank reactor

Background

Temperature programmed desorption (TPD) techniques, sometimes referred to as thermal desorption spectroscopy (TDS), are important methods for determining thermodynamic and kinetic parameters. The TPD method is often used to determine binding energy, and is one of the few experimental techniques that have direct access to molecule-surface interaction energies. A sample is placed in a continuously pumped ultra high vacuum (UHV) chamber. The chamber is evacuated through a mass spectrometer, such as a quadrupole mass spectrometer or a time-of-flight (TOF) mass spectrometer, where the mass of each species is measured as a function of temperature. The temperature of the sample surface is typically increased using a linear heating rate, typical heating rates are between 2 and 10 K/s. When the desorption rate of each species is plotted as a function of temperature it produces a desorption spectra with peaks where each species desorbs.

Introduction

In this tutorial, you will learn how to use Cantera to simulate temperature programmed desorption.

This tutorial covers:

- [Getting started](#)
- [Setting up and running the Cantera TPD calculation](#)
- [Analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **TPD** as the project name, click the **OK** button.

The new project is created with **TPD** listed in the Project Explorer. In this tutorial you will be working with a mechanism to simulate temperature programmed desorption of CO from a RuO₂ surface.

Import the initial surface study table.

Click the **Import** button  to open the **Import Document** dialog. Navigate to the **Examples\Cantera\Surface Reactions** folder and import the **RuO₂_surface.std** study table document.

Select the **Reference** sheet of the study table and double-click the **O2Ru_surface** cell in the **Structure** column.

A model of the ruthenium oxide surface is displayed.

On the RuO₂(110) surface, there are two distinct rows of non-equivalent ruthenium atoms on the top layer of the surface. Five-fold coordinated Ru atoms are located directly above an oxygen atom and bonded to four additional O atoms in the top layer; these are the adsorption positions for the *cus* site. Four-fold coordinated Ru atoms are bonded to two O atoms in the top layer and two more O atoms in the layer beneath; these are the bridge sites. There is one site of each type in each surface unit cell.

Close the O2Ru_surface document.

2. Setting up and running the Cantera TPD calculation

In this section you will set up and run three different TPD simulations, the analysis of the results will be done in the last section of this tutorial.

In the first simulation you will simulate the desorption from a surface covered in CO only.

With the **RuO₂_surface.std** study table in focus open the Cantera Calculation dialog.

You will use the TPD task to do the temperature programmed desorption simulation.

Ensure that **Task** is set to **TPD** and click **More...** to open the Cantera TPD dialog.

The dialog allows you to control the temperature ramps used in the simulation.

Set the **Temperature** range from **200 K** to **500 K** and close the dialog.

The atmosphere in the chamber should have a very low pressure.

Change the **Pressure** to **1.0e-7** and add **carbon_dioxide** to the **Species** list with a **Fraction of 1.00**.

The surface will be set up with only CO on both sites.

In the **Surface** list add **cus**, **CO@bridge**, and **CO@cus** species and set the **Coverage** for the **CO@bridge** and **CO@cus** to **0.50**.

Next, run the TPD calculation.

Select the **Job Control** tab and review the settings, select an appropriate **Gateway location** and **Queue**. Click **Run** to start the job.

A new folder, named **RuO₂_surface_Cantera_TPD**, opens in the Project Explorer and a Cantera job is run by the server. Wait until the job completes and the results are downloaded before moving on to the next step.

A text document called **RuO₂_surface.txt** is opened when the job completes. This contains a notification that Python has started and that it completed successfully as well as summary reports of the thermodynamic properties of the initial states of the gas and surface.

Three other files were created in the RuO₂_surface Cantera TPD directory, not including the calculation file, RuO₂_surface - Calculation and the input study table. These are RuO₂_surface.cti, RuO₂_surface.py, and a study table RuO₂_surface Results.std.

The RuO₂_surface.py file contains the Cantera Python script that was run to produce the data. This script can be modified before starting the job using the *Files...* button.

Change the name of the **RuO₂_surface** Cantera TPD folder to **TPD RuO₂_surface CO**.

Often the surface desorption barrier has a coverage dependence where the barrier decreases with increasing coverage. In the RuO₂_surface.std study table the reactions are not coverage dependent. However, it is possible to add a coverage dependence to a reaction.

Open the original **RuO₂_surface.std** file and select the **Reactions** sheet.

Add **coverage=[['CO@bridge', 0, 0, -5000],['CO@cus', 0, 0, -4000]]** to the **Extra parameters** column in the row with the **CO@bridge => CO + bridge** reaction equation and add **coverage=[['CO@bridge', 0, 0, -4000],['CO@cus', 0, 0, -5000]]** to **Extra parameters** in the row with the **CO@cus => CO + cus** reaction equation.

Now, run the TPD calculation again using the modified surface reactions.

Ensure that the original **RuO₂_surface.std** is the active document and click **Run** on the Cantera Calculation dialog to start the job.

Wait for the job to finish and then rename the job folder.

Change the name of the **RuO₂_surface** Cantera TPD folder to **TPD RuO₂_surface CO with CD**.

Finally you will simulate a surface set up where there is a combination of CO and oxygen.

Ensure that the original **RuO₂_surface.std** is the active document. In the **Surface** list of the Cantera Calculation dialog add **O@bridge** and **O@cus** species. Set the **Coverage** for the **CO@bridge** and **CO@cus** species to **0.30** and for the **O@bridge** and **O@cus** species to **0.20**.

Run the TPD calculation again.

Click **Run** to start the job and close the dialog.

Wait for the job to finish and then rename the job folder.

Change the name of the **RuO₂_surface** Cantera TPD folder to **TPD RuO₂_surface CO + O**.

3. Analyze the results

You will begin by looking at the data for the first calculation with only CO on the surface and no coverage dependence.

Open the **RuO₂_surface Results.std** study table in the **TPD RuO₂_surface CO** folder.

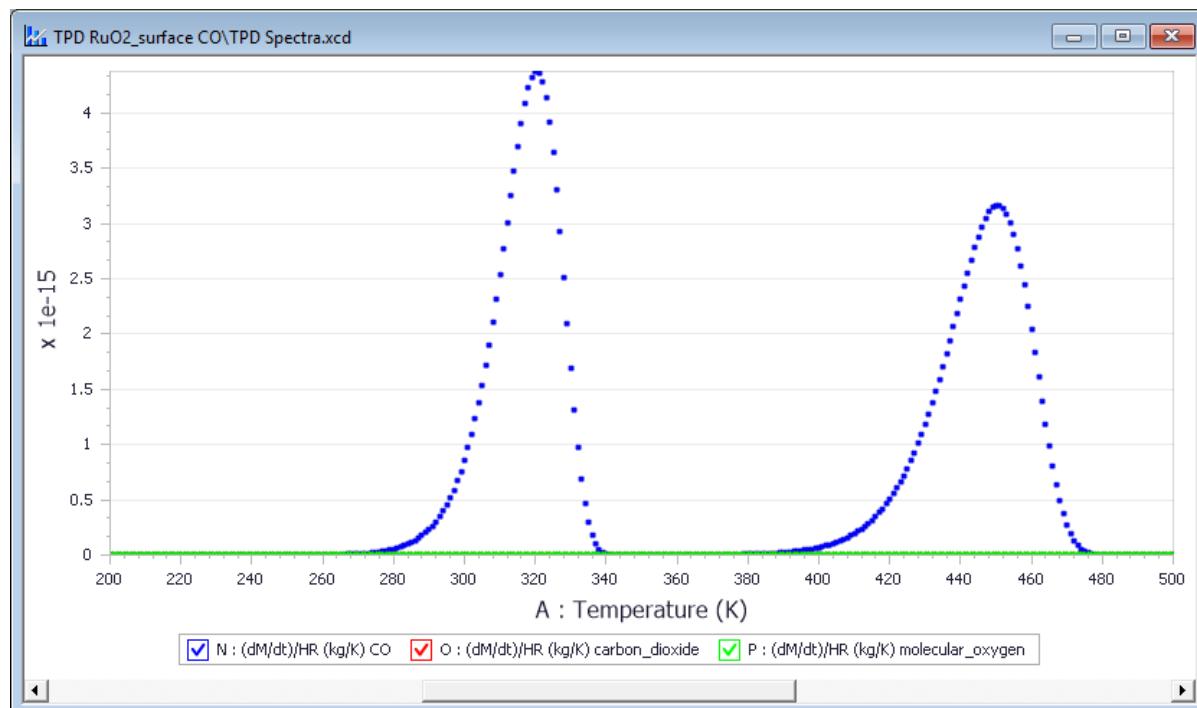
The study table contains the data from the first simulation. Each heating rate produces a data sheet named **HR X K/s**, which contains coverage, composition, and desorption rate data for each species as a function of temperature and time. The desorption rate is given as the species mass produced per second divided by the heating rate (HR):

[Cantera: Temperature programmed desorption](#)

$$\left(\frac{\frac{dM}{dt}}{HR} \right)$$

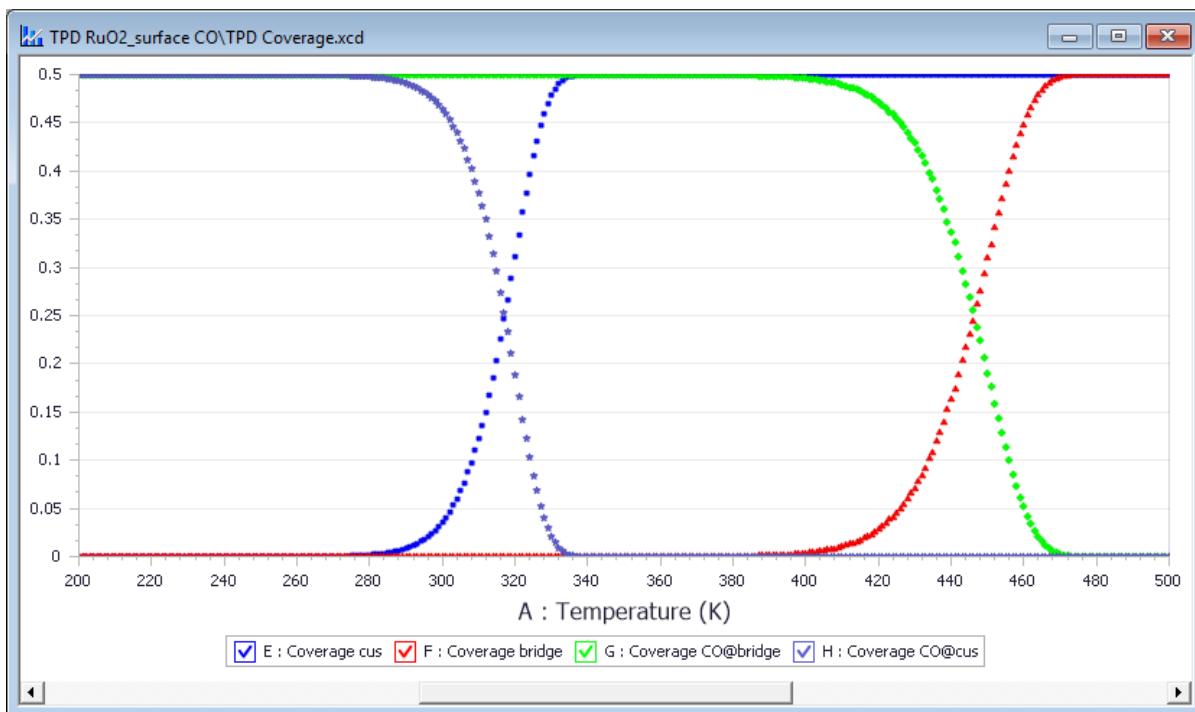
The peaks in the desorption rate spectra are detected and stored in a separate sheet called PeakData where you can track how the peaks are shifting as a function of heating rate. First you will create a chart with the thermal desorption spectra for each species. You can do this initial investigation for any of the temperature ramps, in this case you will use HR 6.

In the **HR 6 K/s** sheet, select columns **N** ($dM/dt)/HR$ (kg/K) **CO** to **P** ($dM/dt)/HR$ (kg/K) **molecular_oxygen** and column **A Temperature (K)** and click the **Quick Plot** button . Change the name of the chart document to **TPD Spectra.xcd**.



The two peaks in the chart belong to the CO desorption; one is the desorption from the bridge site and the other from the cus site. To find out which peak belongs to which site you should create a chart with the coverage as a function of time.

In the **HR 6 K/s** sheet select columns **E Coverage cus** to **H Coverage CO@cus** and column **A Temperature (K)** and click the **Quick Plot** button . Change the name of the chart document to **TPD Coverage.xcd**.



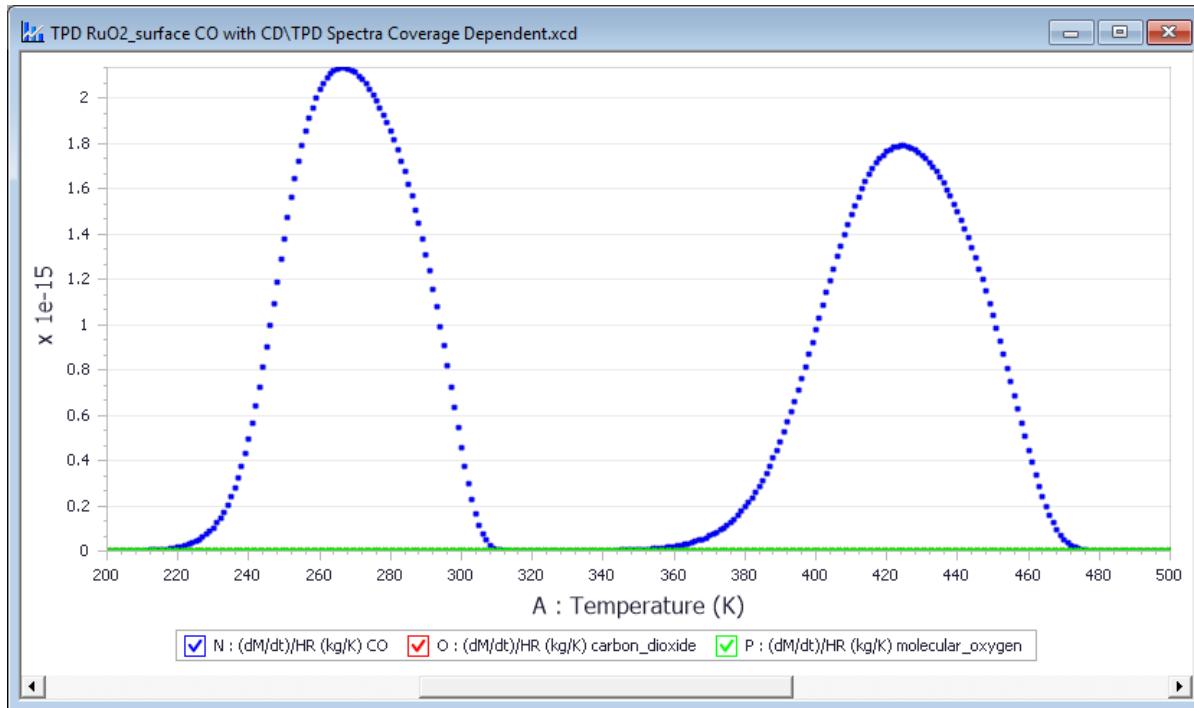
From the coverage chart you can determine that the low temperature peak at around 320 K belongs to the CO@cus site while the high temperature peak at around 450 K belongs to the CO@bridge site.

Note: Cus and bridge coverage is equivalent to vacant cus and bridge sites.

Now you will investigate how the TPD spectra change when the coverage dependence is introduced.

Open the **RuO₂_surface Results.std** study table in the **TPD RuO₂_surface CO with CD** folder. In the **HR 6 K/s** sheet select columns **N (dM/dt)/HR (kg/K) CO to P (dM/dt)/HR (kg/K) molecular_oxygen** and column **A Temperature (K)**. Click the **Quick Plot** button . Change the name of the chart document to **TPD Spectra Coverage Dependent.xcd**.

Cantera: Temperature programmed desorption

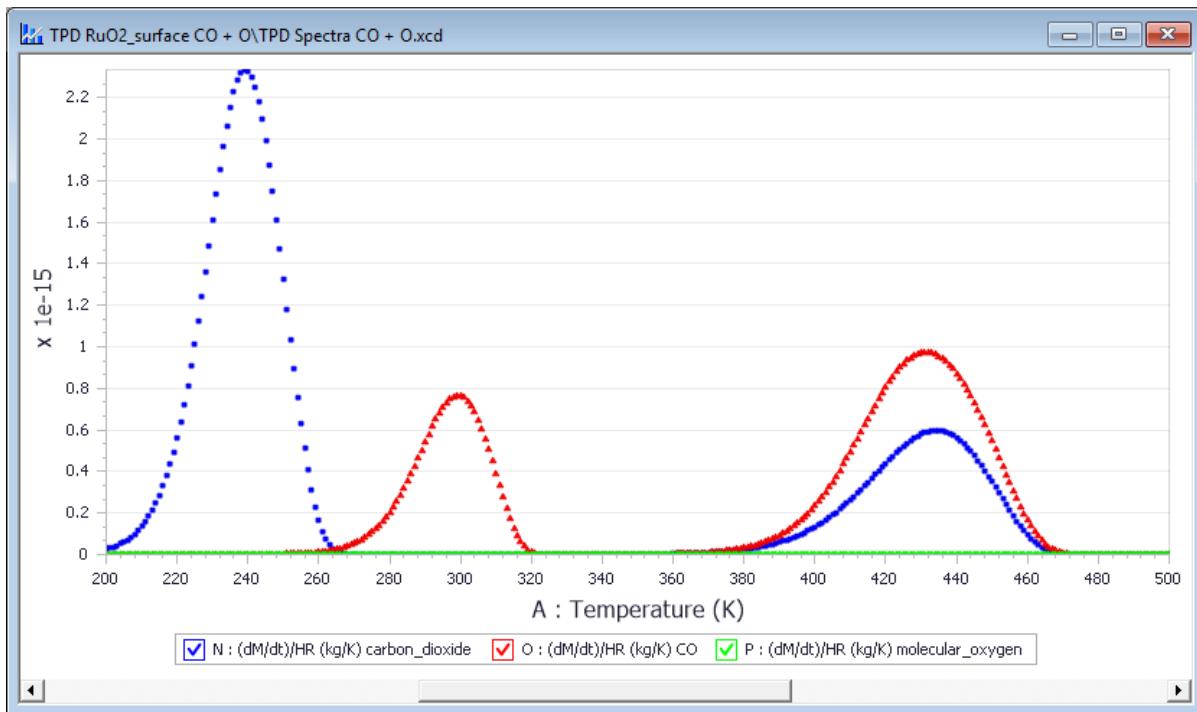


As expected both peaks have moved to lower temperatures since the activation barrier is lower at higher coverage. The width of each peak has also become broader.

Finally, you will investigate the result from the simulation where the surface was prepared with both CO and oxygen at the sites.

Open the **RuO₂_surface Results.std** study table in the **TPD RuO₂_surface CO + O** folder. In the **HR 6 K/s** sheet select columns **N (dM/dt)/HR (kg/K) carbon_dioxide** to **P (dM/dt)/HR (kg/K)**

molecular_oxygen and column **A Temperature (K)**. Click the **Quick Plot** button . Change the name of the chart document to **TPD Spectra CO + O.xcd**.

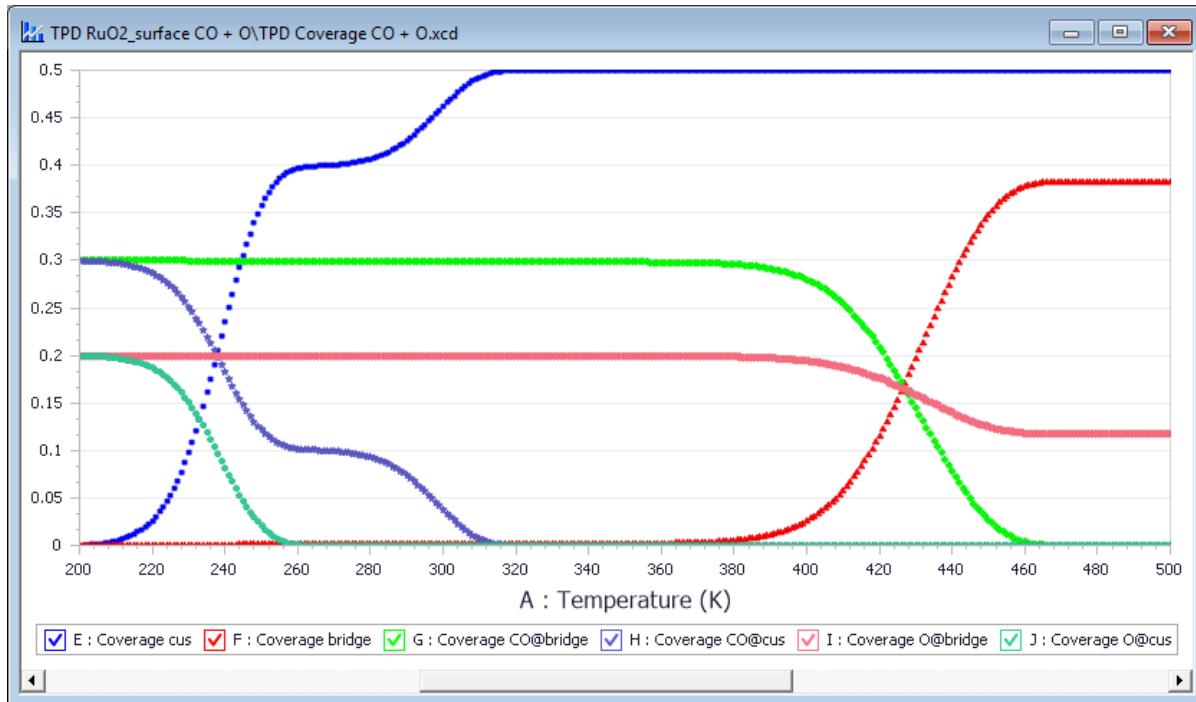


In this chart there are two extra peaks belonging to CO_2 . The CO_2 is the product of recombinative desorption where $\text{CO} + \text{O}$ react. The CO_2 will not bind to the surface and is instantly transferred in to the gas phase. To determine the origin of each peak it is helpful to produce a chart of the species coverage as a function of temperature.

In the **HR 6 K/s** sheet select columns **E Coverage cus to J Coverage O@cus** and column **A**

Temperature (K). Click the **Quick Plot** button . Change the name of the chart document to **TPD Coverage CO + O.xcd**.

Cantera: Temperature programmed desorption



This chart shows that the first CO₂ peak comes from CO and O at cus sites while the second CO₂ peak comes from bridge sites. Note that not all the oxygen at the bridge sites has been used up at 500 K, if you repeat this simulation with the temperature range extended to 1100 K you will find that the remaining oxygen desorbs at around 1000 K.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Chapter 5: CASTEP tutorials

The following tutorials illustrate how to utilize CASTEP's capabilities.

- [Predicting the lattice parameters of AlAs from first principles](#)
- [Adsorption of CO onto a Pd\(110\) Surface](#)
- [Calculating elastic constants for BN](#)
- [Predicting the thermodynamic properties of germanium](#)
- [Calculating phonon spectra for ferromagnetic Fe](#)
- [Assigning the \$^{17}\text{O}\$ NMR spectrum of L-alanine](#)
- [Charge density difference of CO on Pd\(110\)](#)
- [Simulating the STM profile of CO on Pd\(110\)](#)
- [Predicting the core level spectra of BN from first principles](#)

Predicting the lattice parameters of AlAs from first principles

Purpose: Introduces geometry optimization in CASTEP and the use of the volume visualization tools to display isosurfaces.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Recent developments in density functional theory (DFT) methods applicable to studies of large periodic systems have become essential in addressing problems in materials design and processing. The DFT tools can be used to guide and lead the design of new materials, allowing researchers to understand the underlying chemistry and physics of processes.

Introduction

This tutorial illustrates how CASTEP can be used to determine the lattice parameters and electronic structure of aluminum arsenide using quantum mechanical methods in Materials Studio. You will learn how to build a crystal structure and set up a CASTEP geometry optimization run, and then analyze the results.

This tutorial covers:

- [Getting started](#)
- [To build an AlAs crystal structure](#)
- [To set up and run the CASTEP calculation](#)
- [To analyze the results](#)
- [To compare the structure with experimental data](#)
 - Visualizing the charge density
 - Density of states and band structure

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **AlAs_lattice** as the project name, click the **OK** button.

The new project is created with *AlAs_lattice* listed in the Project Explorer. The next step is to create a document in which to generate the AlAs lattice.

In the Project Explorer, right-click on the root and select **New | 3D Atomistic Document** from the shortcut menu. Rename the new document **AlAs.xsd**.

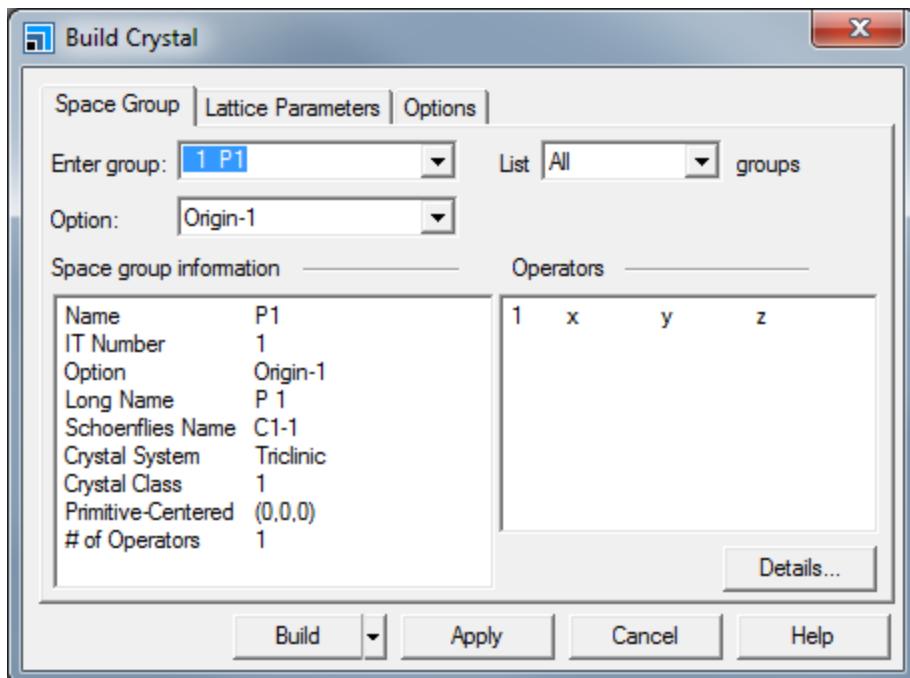
2. To build an AlAs crystal structure

To build a crystal structure, you need to know the space group, lattice parameters, and internal coordinates for the crystal you wish to construct. In the case of AlAs, the space group is F-43m, number 216. There are two atoms in the basis, Al and As with fractional coordinates of (0, 0, 0) and (0.25, 0.25, 0.25), respectively. The lattice parameter is 5.6622 Å.

The first step is to build the lattice.

Choose **Build | Crystals | Build Crystal...** from the menu bar.

This opens the Build Crystal dialog.



Build Crystal dialog, Space Group tab

Click in the **Enter group** box and type **216**, press **TAB**.

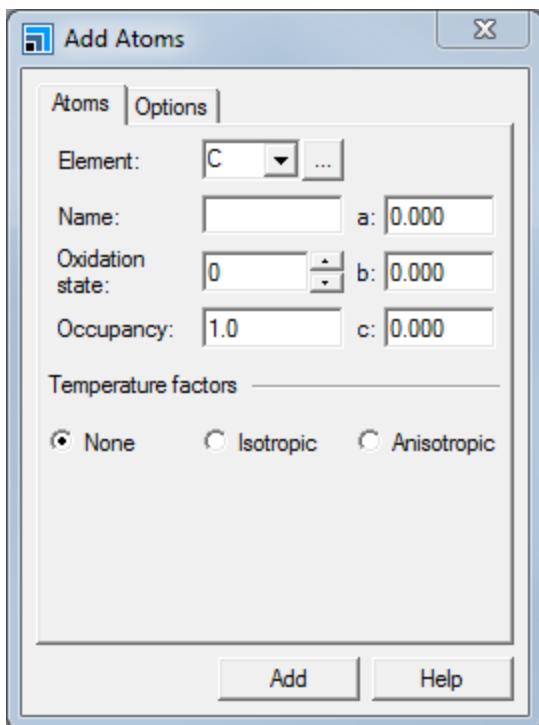
The *Space group information* box updates with the information for the F-43m space group.

Select the **Lattice Parameters** tab. Change the value of **a** from **10.00** to **5.6622**. Press **TAB** and click the **Build** button.

An empty 3D lattice is displayed in the 3D Viewer, now you can add the atoms.

Select **Build | Add Atoms** from the menu bar.

This opens the Add Atoms dialog.



Add Atoms dialog, Atoms tab

Using this dialog, you can add atoms at specific positions.

On the Add Atoms dialog, select the **Options** tab and ensure that the **Coordinate system** is set to **Fractional**. Select the **Atoms** tab, in the **Element** text box type **Al**. Click the **Add** button.

The aluminum atoms are added to the structure.

In the **Element** text box, type **As**. Enter **0.25** into the **a**, **b**, and **c** text boxes. Click the **Add** button and close the dialog.

The atoms are added and the symmetry operators are used to build the remaining atoms in the crystal structure. The atoms are also displayed in neighboring unit cells to illustrate the bond topology of the AlAs structure. You can remove these by rebuilding the crystal.

Choose **Build | Crystals | Rebuild Crystal...** from the menu bar to open the Rebuild Crystal dialog. Click the **Rebuild** button.

The extraneous atoms are removed and the crystal structure is displayed. You can change the display style to ball and stick.

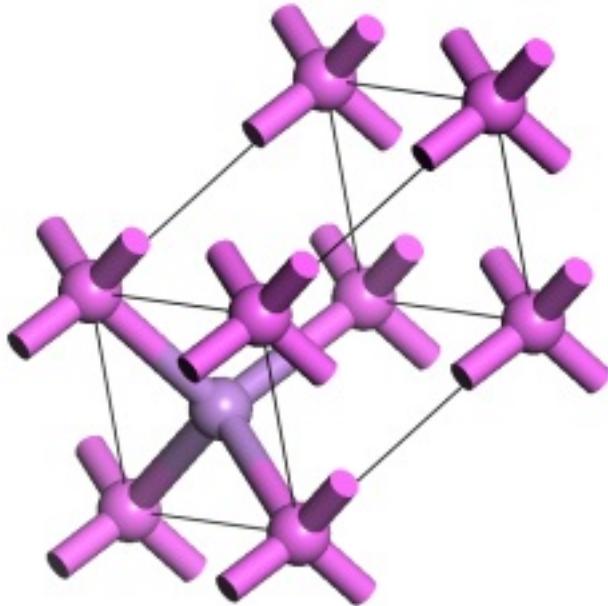
Right-click in the structure document and select **Display Style** from the shortcut menu. On the **Atom** tab, select the **Ball and stick** option and close the dialog.

The crystal structure in the 3D Viewer is the conventional unit cell, which shows the cubic symmetry of the lattice. CASTEP uses the full symmetry of the lattice if any exists. So the primitive lattice, containing 2 atoms per unit cell, can be used, as opposed to the conventional cell, which contains 8 atoms. The charge density, bond distances, and total energy per atom will all be the same no matter how the unit cell is defined, so by using fewer atoms in the unit cell the computation time will be decreased.

Note: When a spin-polarized calculation is performed on a magnetic system care should be taken if the charge density spin wave has a period which is a multiple of the primitive unit cell.

Choose **Build | Symmetry | Primitive Cell** from the menu bar.

The 3D Viewer displays the primitive cell.

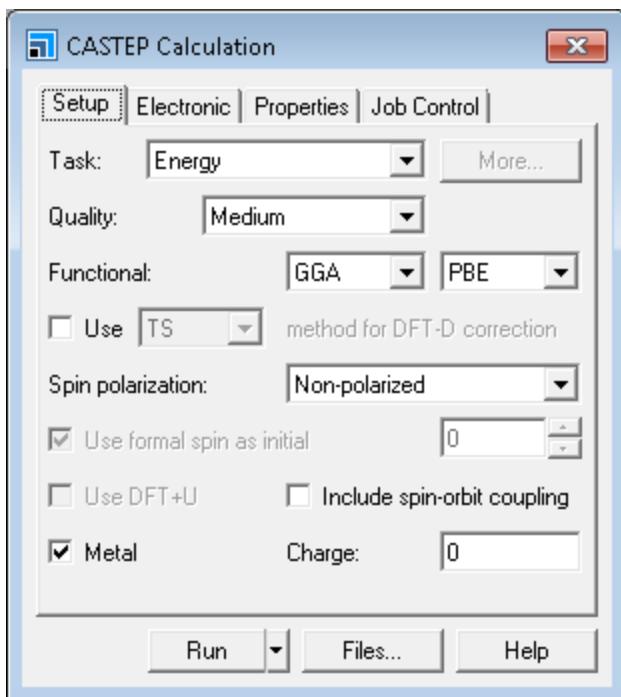


The primitive cell of AlAs

3. To set up and run the CASTEP calculation

Click the **CASTEP** button on the **Modules** toolbar and select **Calculation** or choose **Modules | CASTEP | Calculation** from the menu bar

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

You are going to optimize the geometry of the structure.

Change the **Task** to **Geometry Optimization** and the **Quality** to **Fine**.

The default setting for optimization is to optimize only the atomic coordinates. However, in this case, you want to optimize the lattice since the atomic coordinates in AlAs structure are fixed by symmetry.

Click the **More...** button for the **Task** to open the CASTEP Geometry Optimization dialog. Select **Full** from the **Cell optimization** dropdown list and close the dialog.

When you change the quality, the other parameters change to reflect this.

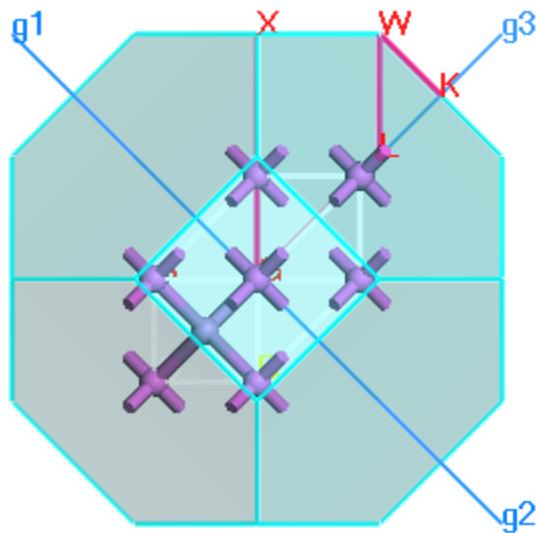
Select the **Properties** tab.

You can specify which properties you want to calculate from the *Properties* tab.

Check the **Band structure** and **Density of states** checkboxes.

With the **Band structure** option selected, click the **More...** button to open the CASTEP Band Structure Options dialog. Click the **Path...** button to open the Brillouin Zone Path dialog. Click the **Create** button and close both dialogs.

The reciprocal lattice and Brillouin zone paths and axes are displayed in the 3D viewer.



AlAs reciprocal lattice and Brillouin zone paths

You can also specify job control options such as live updates.

Select the **Job Control** tab. Click the **More...** button to open the CASTEP Job Control Options dialog. Change the **Update** interval to **5.0 s** and close the dialog.

If you are running the calculation on a remote server, you can specify this from the *Job Control* tab.

Click the **Run** button and close the CASTEP Calculation dialog.

After a few seconds, a new folder is displayed in the Project Explorer and this will contain all the results from the calculation. The Job Explorer is displayed, which contains information about the status of the job.

The Job Explorer displays the status of any currently active jobs that are associated with this project. It shows useful information such as the server and job identification number. You can also use this explorer to stop the job if you need to.

As the job progresses, four documents open which relay information on the job status. These documents include the crystal structure, showing updates of the model during optimization, a status document to relay information about the job setup parameters and run information, and charts of the total energy, and convergence in energy, forces, stress, and displacement as a function of the iteration number.

When the job finishes, the files are transferred back to the client and this can take some time due to the size of certain files.

4. To analyze the results

When the results documents are transferred, you should have several documents, among them:

- **AlAs.xsd** - the final optimized structure
- **AlAs.xtd** - a trajectory file containing the structure after each optimization step
- **AlAs.castep** - an output text document containing the optimization information
- **AlAs.param** - input information for the simulation

For each of the properties calculated, there are also **.param** and **.castep** documents.

In the AlAs structure, the forces are zero by symmetry, but the stresses depend on the lattice parameters. CASTEP thus attempts to minimize the total energy by finding the structure that corresponds to the zero stress. Therefore, to ensure that the calculation has completed properly, it is important to check that the stresses have converged.

Make **AlAs.castep** the active document and select **Edit | Find...** from the menu bar to open the Find dialog. Enter **completed successfully** in the text box and click the **Find Next** button. Scroll a few lines up.

You will see a table containing two rows, and the last column in each row should say **Yes**. This indicates that the calculation has succeeded.

5. To compare the structure with experimental data

You know that the lattice length should be 5.6622 Å from when you initially created the cell. You can compare your minimized lattice length with that of the initial experimental length. The experimental lattice length is based on a conventional cell and not a primitive one, so you should convert your cell.

Make the optimized **AlAs.xsd** the active document and select **Build | Symmetry | Conventional Cell** from the menu bar.

The conventional cell is displayed. There are several ways to view the lattice lengths, but the easiest is to open the Lattice Parameters dialog.

Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu.

The lattice vector should be approximately 5.731 Å, giving an error of about 1%. This is within the 1-2% typical error that is expected for pseudopotential plane-wave methods in comparison with experimental results. An over-estimation of the lattice parameters is typical of the GGA functional, use of LDA functionals may result in under-estimation.

Notes:

- More advanced exchange-correlation functionals such as PBESOL or WC are designed to produce more accurate crystal structures
- Convergence testing is always required to establish that the settings are sufficiently accurate. In this case you can repeat the calculations with a higher energy cutoff and with more accurate k-point sampling.

Before continuing, you should save the project and close all the windows.

Choose **File | Save Project** on the menu bar, then **Window | Close All**.

The charge density can be visualized using the CASTEP Analysis tool.

Click the **CASTEP** button  on the **Modules** toolbar and select **Analysis** or choose **Modules | CASTEP | Analysis** from the menu bar to display the CASTEP Analysis dialog.

Choose the **Electron density** option.

A message is displayed reporting that no results file is available, so you need to specify a results file.

In the Project Explorer, double-click on **AlAs.castep**.

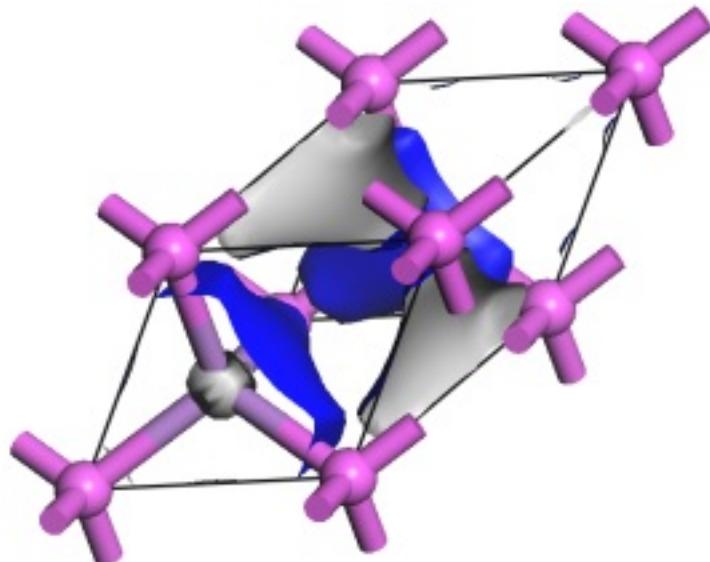
This will associate the results document with the analysis dialog but you also need to designate a 3D Atomistic document in which to display the isosurface.

In the Project Explorer, double-click on the optimized **AlAs.xsd**. Choose **Build | Symmetry | Primitive Cell** from the menu bar.

The *Import* button on the CASTEP Analysis dialog is now active.

Click the **Import** button.

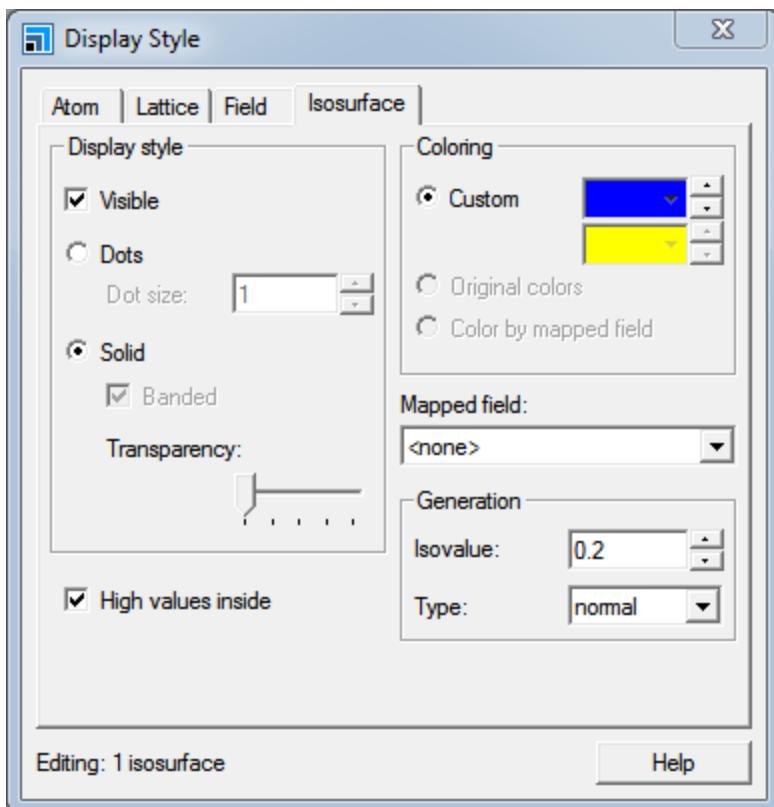
The isosurface is overlaid onto the structure.



Electron density isosurface of AlAs

You can change the isosurface settings using the Display Style dialog.

Open the **Display Style** dialog and select the **Isosurface** tab.



Display Style dialog, Isosurface tab

You can change various settings here.

In the **Isovalue** text box, type **0.1** and press **TAB**.

Note how the isosurface changes.

Move the **Transparency** slider bar to the right.

As you move the *Transparency* slider bar, the surface becomes more transparent.

Hold down the right mouse button and move the mouse to rotate the model.

As the model rotates, the isosurface reverts to a dot display to increase the speed of rotation. If you have a fast machine, you can disable this feature by unchecking the *Fast render on move* checkbox on the *Graphics* tab of the Display Options dialog.

You can toggle display of the isosurface at any time by checking or unchecking the *Visible* checkbox on the *Isosurface* tab of the Display Style dialog.

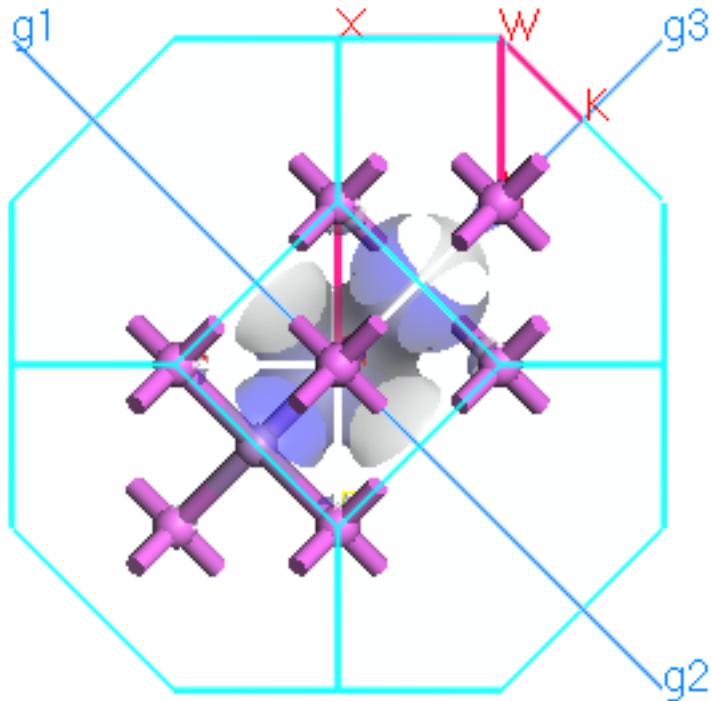
You can display the Brillouin zone path for the reciprocal lattice, see the Brillouin zone theory topic for further information.

Select **Tools | Brillouin Zone Path** from the menu bar to open the Brillouin Zone Path dialog. Click the **Create** button and close the dialog.

The Brillouin zone and k-paths display can be manipulated using the Display Style dialog.

Select the **Reciprocal** tab and move the **Transparency** slider all the way to the right. Set the **Scale** to **33** and change the **Path Line width** to **5.00**. Close the dialog.

Rotate the structure to view the high-symmetry points and the standard Brillouin zone path for this lattice type.



Brillouin zone paths and isosurface of AlAs

The CASTEP Analysis tool can be used to display density of states, DOS, and band structure information. Band structure charts show the dependence of electronic energies on k-vector along high symmetry directions in the Brillouin zone. These charts provide a useful tool for qualitative analysis of the electronic structure of the material - for example, it is easy to identify narrow bands of d and f states as opposed to nearly free electron-like bands that correspond to s and p electrons.

DOS and PDOS charts give a quick qualitative picture of the electronic structure of the material, and sometimes they can be directly related to experimental spectroscopic results.

The main CASTEP output file, `AlAs.castep`, contains limited band structure and DOS information, but more detailed information is contained in the `AlAs_BandStr.castep` and `AlAs_DOS.castep` documents, respectively.

On the CASTEP Analysis dialog select the **Band structure** option.

From this dialog, you can choose to display both the band structure and density of states information on the same chart document and control the DOS chart quality.

Note: You can also display them in separate chart documents by analyzing the band structure and density of states separately.

CASTEP: Predicting the lattice parameters of AlAs from first principles

Check the **Show DOS** checkbox and click the **More...** button to open the CASTEP DOS Analysis Options dialog. Set the **Integration method** to **Interpolation** and the **Accuracy level** to **Fine**. Click the **OK** button.

On the CASTEP Analysis dialog, click the **View** button.

A chart document is generated containing the band structure and density of states charts.

Note: You can export any chart document as a comma-separated variable file which can then be read in any spreadsheet package, for example, Excel.

You can also use CASTEP to calculate many other properties, such as reflectivity and dielectric functions.

This is the end of the tutorial.

Adsorption of CO onto a Pd(110) surface

Purpose: Introduces the use of CASTEP for calculating the adsorption energy of a gas onto a metal surface.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

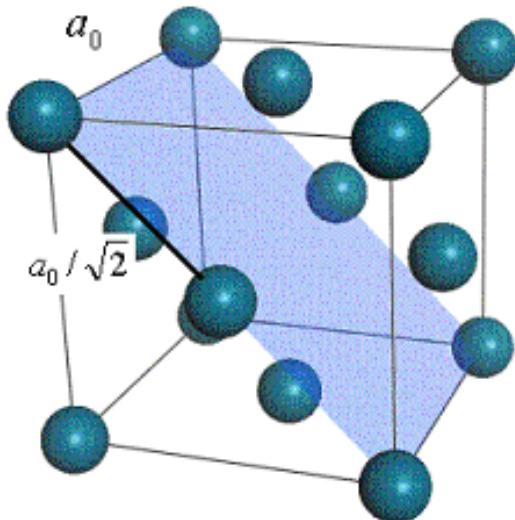
Background

In this tutorial you will examine the adsorption of CO on Pd(110). The Pd surface plays a crucial role in a variety of catalytic reactions. Understanding how molecules interact with such surfaces is one of the first steps to understanding catalytic reactions. In this context, DFT simulations can contribute to this understanding by addressing the following questions:

- Where does the molecule want to adsorb?
- How many molecules will stick to the surface?
- What is the adsorption energy?
- What does the structure look like?
- What are the mechanisms of adsorption?

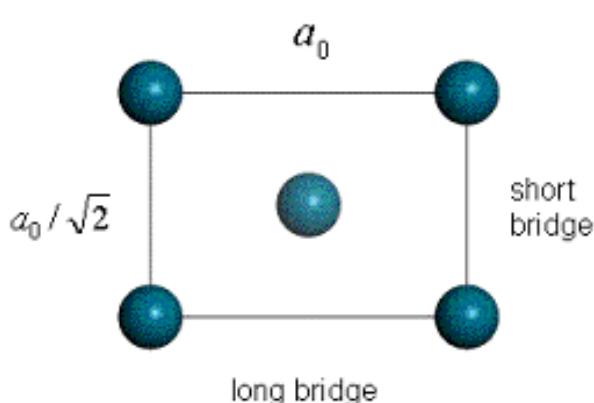
You will focus on one adsorption site, the short bridge site, as it is known to be energetically preferred at fixed coverage. At 1 ML coverage the CO molecules repel each other preventing them from aligning exactly perpendicular to the surface. You will calculate the energy contribution of this tilting to the chemisorption energy by considering a (1 × 1) and (2 × 1) surface unit cell.

Pd bulk



Pd(110) surface

Top view



Pd bulk and a top view on the Pd(110) surface. The (110) cleave plane is highlighted in blue. a_0 is the bulk lattice constant, also known as the lattice parameter.

Introduction

In this tutorial, you will use CASTEP to optimize and calculate the total energies of several different systems. Once you have determined these energies, you will be able to calculate the chemisorption energy for CO on Pd(110).

This tutorial covers:

- [Getting started](#)
- [To optimize bulk Pd](#)
- [To build and optimize CO](#)
- [To build the Pd\(110\) surface](#)
- [To relax the Pd\(110\) surface](#)
- [To add CO to the 1 × 1 Pd\(110\) surface and optimize the structure](#)
- [To set up and optimize the 2 × 1 Pd\(110\) surface](#)
- [To analyze the energies](#)
- [To analyze the density of states \(DOS\)](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CO_on_Pd** as the project name, click the **OK** button.

The new project is created with *CO_on_Pd* listed in the Project Explorer.

This tutorial consists of five distinct calculations. To make it easier to manage your project, you should begin by preparing five subfolders in your project.

Right-click on the root icon in the Project Explorer and select **New | Folder**, repeat this four more times. Rename the folders **Pd bulk**, **Pd(110)**, **CO molecule**, **(1x1) CO on Pd(110)** and **(2x1) CO on Pd(110)**.

2. To optimize bulk Pd

The crystal structure of Pd is included in the structure library provided with Materials Studio.

In the Project Explorer, right-click on the **Pd bulk** folder and select **Import...** to open the Import Document dialog. Navigate to **Structures/metals/pure-metals** and import **Pd.xsd**.

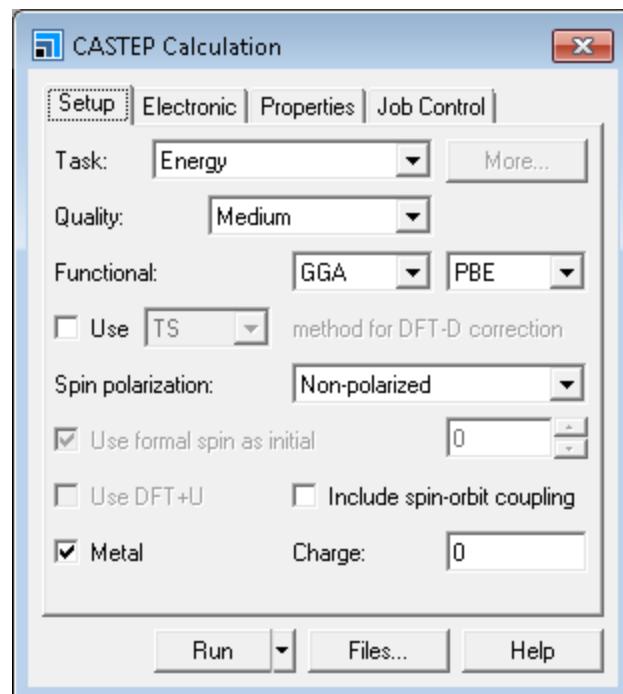
The bulk Pd structure is displayed. You can change the display style to ball and stick.

Right-click in the **Pd.xsd** 3D Viewer and select **Display Style** to open the Display Style dialog. On the **Atom** tab, select **Ball and stick** and close the dialog.

Now optimize the geometry of the bulk Pd using CASTEP.

Click the **CASTEP** button  on the **Modules** toolbar then select **Calculation** or select **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

Cell optimization of crystals requires more accurate calculations than those performed with default settings.

CASTEP: Adsorption of CO onto a Pd(110) surface

Change the **Quality** from Medium to **Fine**.

To maintain consistency across the calculations that you are going to perform, you should make some changes on the Electronic tab.

Select the **Electronic** tab and click the **More...** button to open the CASTEP Electronic Options dialog. On the **Basis** tab check the **Use custom energy cutoff** checkbox and make sure that the field value is **570.0 eV**. This ensures that all calculations in the tutorial use the same energy cut-off.

The default values for geometry optimization do not include optimization of the cell.

Change the **Task** from Energy to **Geometry Optimization**. Click the **More...** button to open the CASTEP Geometry Optimization dialog. Select **Full** from the **Cell optimization** dropdown list and close the dialog.

Click the **Run** button. A message dialog about conversion to the primitive cell is displayed. Click the **Yes** button.

The job is submitted and starts to run. You should proceed to the [next section](#) and build the CO molecule but return here when the calculation is complete to display the Lattice Parameters.

When the job has finished, you must convert the primitive cell result back to a conventional cell representation in order to proceed with building the Pd(110) surface in step 4.

In the Project Explorer, open **Pd.xsd** located in the **Pd CASTEP GeomOpt** folder. Select **Build | Symmetry | Conventional Cell** from the menu bar.

You should now save your project files.

Select **File | Save Project**, then **Window | Close All** from the menu bar. In the Project Explorer, re-open the optimized **Pd.xsd**.

Right-click in the 3D Viewer and select **Lattice Parameters**.

This opens the Lattice Parameters dialog. The value of a should be approximately 3.962 Å, compared with the experimental value of 3.89 Å.

Close the **Lattice Parameters** dialog and **Pd.xsd**.

3. To build and optimize CO

CASTEP will only work with periodic systems. To optimize the geometry of the CO molecule, you must put it into a crystal lattice.

In the Project Explorer, right-click on the **CO molecule** folder and select **New | 3D Atomistic Document**. Rename the new document **CO.xsd**.

An empty 3D Viewer is displayed. You will use the Build Crystal tool to create an empty cell and then add the CO molecules to it.

Select **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog. Choose the **Lattice Parameters** tab and change each cell **Length a, b, and c** to **8.00**. Click the **Build** button.

An empty cell is displayed in the 3D Viewer.

Select **Build | Add Atoms** from the menu bar to open the Add Atoms dialog.

The C-O bond length in the CO molecule has been determined experimentally as 1.1283 Å. By adding the atoms using Cartesian coordinates you can create your CO molecule with exactly this bond length.

Select the **Options** tab and ensure that the **Coordinate system** is set to **Cartesian**. On the **Atoms** tab click the **Add** button.

A carbon atom is added at the origin of the cell.

Change the **Element** to **O**, leave the **x** and **y** values as **0.000**. Change the **z** value to **1.1283**. Click the **Add** button and close the dialog.

You are now ready to optimize your CO molecule.

Open the **CASTEP Calculation** dialog.

The settings from the previous calculation have been retained. However, you do not need to optimize the cell for this calculation.

Open the **CASTEP Geometry Optimization** dialog. Select **None** from the **Cell optimization** dropdown list and close the dialog.

On the **Properties** tab of the CASTEP Calculation dialog check the **Density of states** checkbox. Change the **k-point set** to **Gamma** and check the **Calculate PDOS** checkbox. Click the **Run** button.

When asked about converting to higher symmetry, click the **No** button to proceed with the current symmetry.

The calculation starts. You can move onto [building the Pd\(110\) surface](#) as you will analyze the energy at the end of the tutorial.

4. To build the Pd(110) surface

This section of the tutorial uses the optimized Pd structure from the [Pd bulk](#) part of the tutorial.

Select **File | Save Project**, then **Window | Close All** from the menu bar. Open **Pd.xsd** in the **Pd bulk/Pd CASTEP GeomOpt** folder.

Creating the surface is a two step process. The first step is to cleave the surface and the second is to create a slab containing the surface and a region of vacuum.

Select **Build | Surfaces | Cleave Surface** from the menu bar to open the Cleave Surface dialog. Change the **Cleave plane (h k l)** from **-1 0 0** to **1 1 0** and press **TAB**. Increase the **Fractional Thickness** to **1.5**. Click the **Cleave** button and close the dialog.

A new 3D Viewer is opened containing the 2D periodic surface. However, CASTEP requires a 3D periodic system as input, this is obtained using the Vacuum Slab tool.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. Change the **Vacuum thickness** from **10.00** to **8.00** and click the **Build** button.

CASTEP: Adsorption of CO onto a Pd(110) surface

The structure changes from 2D to 3D periodic and a vacuum is added above the atoms. Before continuing, you must reorient the lattice.

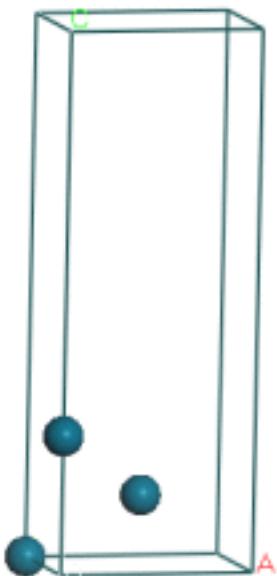
Open the **Lattice Parameters** dialog and select the **Advanced** tab, click the **Re-orient to standard** button. Close the dialog.

You should also change the lattice display style and rotate the structure so that the z-axis is vertical on the screen.

Open the **Display Style** dialog and select the **Lattice** tab. In the **Display style** section, change the **Style** from Default to **Original**. Close the dialog.

Press the **UP** arrow key twice.

The 3D view shown below is displayed:



The Pd atom with the largest z-coordinate will be called "the uppermost Pd layer".

Later in this tutorial, you will need to know the bulk interlayer spacing d_0 . You can calculate this using the atom coordinates.

Select **View | Explorers | Properties Explorer** from the menu bar. Select the Pd atom with **FractionalXYZ x = 0.5** and **y = 0.5**. Note the **z** value of this atom from the **XYZ** property.

The z value should be 1.401 Å and this is the interlayer spacing. This z value refers to the Z coordinate from the (Cartesian) XYZ property and not FractionalXYZ.

Note: For an fcc(110) system, d_0 can be calculated as:

$$d_0 = \frac{a_0}{\sqrt{8}}$$

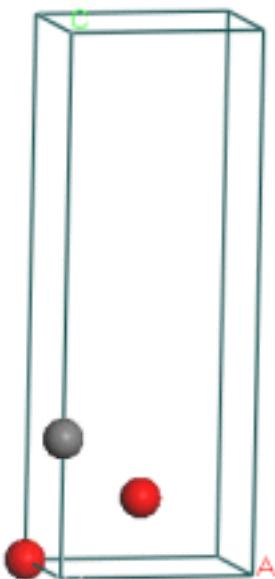
Before you relax the surface, you must constrain the Pd atoms in the bulk as you only need to relax the surface.

Hold down **SHIFT** and select all the Pd atoms except the uppermost Pd layer. Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. Check the **Fix fractional position** checkbox and close the dialog.

The bulk atoms have been constrained. You can see the constrained atoms by changing their display color.

In the 3D Viewer, click anywhere to deselect the atoms. Open the **Display Style** dialog and select the **Atom** tab. Change the **Color by** option to **Constraint**.

This 3D view is now displayed:



Change the **Color by** option back to **Element** and close the dialog.

This structure is needed for the Pd(110) surface relaxation and also as a starting model for (1x1) CO on Pd(110) optimization.

Select **File | Save As...** from the menu bar. Navigate to the **Pd(110)** folder and click the **Save** button.

Hold down **CTRL** and drag the document into the **(1x1) CO on Pd(110)** folder. Rename the document **(1x1) CO on Pd(110)**.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

5. To relax the Pd(110) surface

Now you are ready to optimize the Pd(110) surface.

From the Project Explorer, open **Pd (1 1 0).xsd** in the **Pd(110)** folder. Open the **CASTEP Calculation** dialog and then the **CASTEP Geometry Optimization** dialog. Ensure that **Cell optimization** is set to **None** and close the dialog.

You should also calculate the density of states for the system.

CASTEP: Adsorption of CO onto a Pd(110) surface

Select the **Properties** tab on the CASTEP Calculation dialog. Check the **Density of states** and **Calculate PDOS** checkboxes and change the **k-point set** to **Fine**.

You are ready to run the calculation.

Click the **Run** button and close the CASTEP Calculation dialog.

When asked about converting to higher symmetry, click the **No** button to proceed with the current symmetry.

The calculation will take some time to run and so you will perform the analysis at the end. You should move on and construct the next set of surfaces.

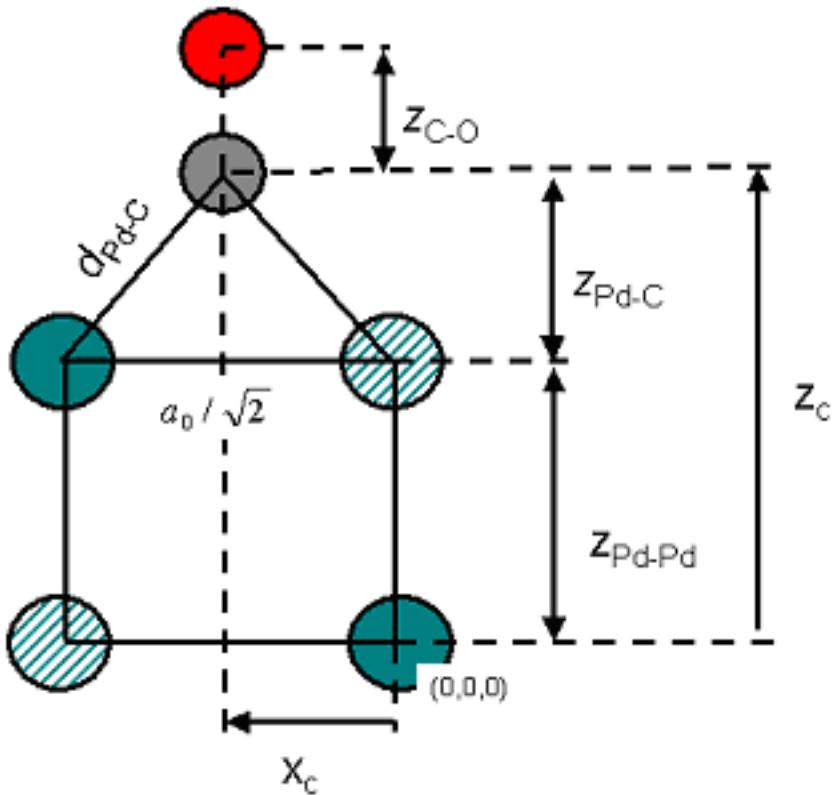
Select **File | Save Project** then **Window | Close All** from the menu bar.

6. To add CO to the 1×1 Pd(110) surface and optimize the structure

Now you are going to work with the structure in the (1×1) Co on Pd(110) folder.

In the Project Explorer, open **(1x1) CO on Pd(110).xsd** in the **(1x1) CO on Pd(110)** folder.

Now add the CO molecule above the short bridge position. You will make use of the fact that for CO on Pd(110), bond lengths have been experimentally determined.



Geometry of CO on Pd(110) in the yz-plane. Hatched atoms are not displayed in Lattice: Original display mode.

The first step is to add the carbon atom. The Pd-C bond length (denoted above as d_{Pd-C}) should be 1.93 Å. When you use the Add Atom tool you can enter either Cartesian or fractional coordinates but in this case you will use fractional coordinates, x_C , y_C , and z_C . x_C and y_C are simple as $y_C = 0.5$ and $x_C = 0$.

However, determination of z_C is slightly more difficult. You will construct it from the two distances z_{Pd-C} and z_{Pd-Pd} .

z_{Pd-Pd} is simply the lattice parameter a_0 divided by $\sqrt{2}$ (it should be 2.80 Å).

z_{Pd-C} is obtained from the formula:

$$z_{Pd-C} = \sqrt{d_{Pd-C}^2 - \frac{1}{8}a_0^2}$$

It should be 1.33 Å.

Add z_{Pd-C} and z_{Pd-Pd} to obtain z_C (it should be 4.13 Å). Now convert this distance into a fractional length. You do this using the Lattice parameters.

Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu. Note the value of **c**.

To calculate the fractional z coordinate, you divide z_C by the c lattice parameter (you should obtain 0.382).

Open the **Add Atoms** dialog and choose the **Options** tab. Check that the **Coordinate system** is **Fractional**. On the **Atoms** tab change the **Element** to **C**, change **a** to **0.0**, **b** to **0.5**, and **c** to **0.382**. Click the **Add** button.

If you want to confirm that you have set up the model correctly, use the Measure/Change tool.

Click the **Measure/Change** arrow  on the toolbar and select **Distance** from the dropdown list.
Click on the Pd-C bond.

The next step is to add the oxygen atom.

On the **Add Atoms** dialog, change the **Element** to **O**.

Experimentally, the C-O bond length has been determined as 1.15 Å. In fractional coordinates this is 0.107, adding this value to the fractional z-coordinate of carbon (0.382), the z-coordinate of oxygen is 0.489.

Change the value of **c** to **0.489** and click the **Add** button. Close the dialog.

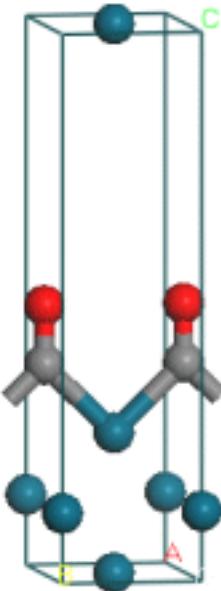
The calculations for the Pd surface model were carried out using P1 symmetry. However, the system has a higher symmetry, even after the addition of the CO molecule. You can find and impose symmetry, using the Find Symmetry tool, to speed up further calculations.

Click the **Find Symmetry** button  on the **Symmetry** toolbar to open the Find Symmetry dialog.
Click the **Find Symmetry** button then the **Impose Symmetry** button.

The symmetry is PMM2.

Open the **Display Style** dialog and select the **Lattice** tab. Change the **Style** to **Default**. On the **Atom** tab, select the **Ball and stick** display style and close the dialog.

The structure should look similar to this:



Before you optimize the geometry of the structure, you should save it in the (2x1) CO on Pd(110) folder.

Select **File | Save** from the menu bar to save the 1x1 system. Then also select **File | Save As...** from the menu bar, navigate to the **(2x1) CO on Pd(110)** folder and save the document as **(2x1) CO on Pd (110).xsd**.

You are now ready to optimize the structure.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

In the Project Explorer, open **(1x1)CO on Pd(110).xsd** in the **(1x1)CO on Pd(110)** folder.

Open the **CASTEP Calculation** dialog.

The parameters from the previous calculation should have been retained.

Click the **Run** button and close the dialog.

Once again, you can move onto building the final structure while the calculation progresses.

7. Setting up and optimizing the 2 × 1 Pd(110) surface

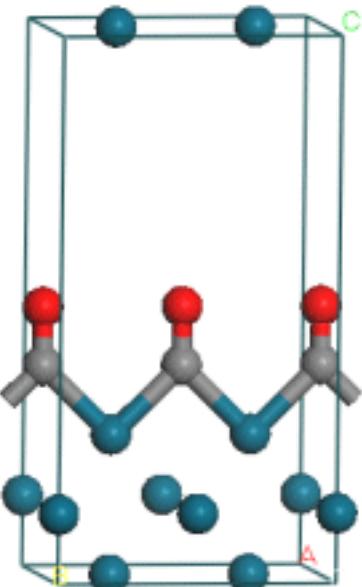
The first step is to open the 3D Atomistic document in the (2 × 1) CO on Pd(110) folder.

In the Project Explorer, open **(2x1) CO on Pd(110).xsd** in the **(2x1) CO on Pd(110)** folder.

This is currently a 1 × 1 cell so you need to use the Supercell tool to change it to a 2 × 1 cell.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase **B** to **2** and click the **Create Supercell** button and close the dialog.

The structure should look like this:



(2 × 1) Cell of CO on Pd(110)

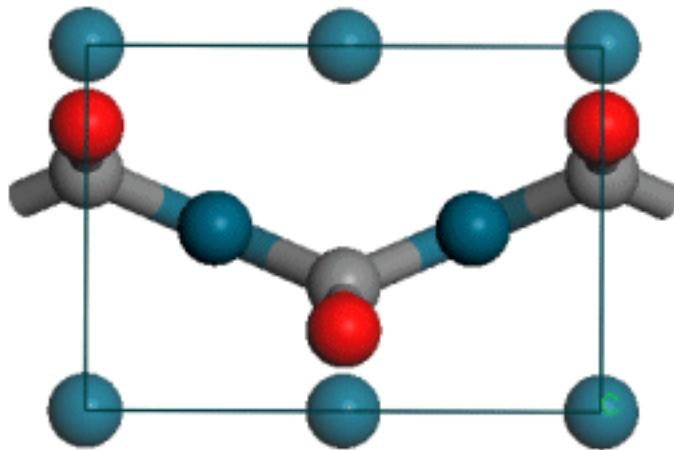
Now tilt the CO molecules with respect to each other. To simplify this operation, identify the CO molecule at $y = 0.5$ as molecule A and the one at $y = 0.0$ as molecule B.

Select the **carbon** atom of molecule B. In the Properties Explorer, open the **XYZ** property and subtract **0.6** from the **X** field. Repeat this for the **oxygen** atom of molecule B but subtract **1.2** from the **X** field.

Now repeat this for molecule A.

Select the **carbon** atom of molecule A. In the Properties Explorer, open the **XYZ** property and add **0.6** to the **X** field. Repeat this for the **oxygen** atom of molecule A but add **1.2** to the **X** field.

The view down the z-axis of the molecule should look like this:



However, you will notice that the Pd-C and C-O bond lengths have changed from their original values.

Select the **carbon** atom in molecule A and use the Properties Explorer to change the **Z** field of the **FractionalXYZ** property to **0.369**. Repeat this for molecule B.

CASTEP: Adsorption of CO onto a Pd(110) surface

This corrects the Pd-C bond length. You can use the Measure/Change tool to correct the C-O bond length.

Click the **Measure/Change** button  on the **Sketch** toolbar and select **Distance** from the dropdown list. Click on the **C-O** bond for molecule A.

Choose the 3D Viewer **Selection Mode** tool  on the **3D Viewer** toolbar and select the monitor. In the Properties Explorer, change the **Filter** to **Distance**.

Change the **Distance** property to **1.15 Å**. Repeat this for molecule B.

Now recalculate the symmetry of the system.

Open the **Find Symmetry** dialog and click the **Find Symmetry** button then the **Impose Symmetry** button.

The symmetry is PMA2. The view of the unit cell changes from 3 CO molecules on the Pd surface to only 2. You are now ready to optimize the geometry of your system.

Open the **CASTEP Calculation** dialog and click **Run**.

The calculation starts. When the calculation finishes, you will need to extract the total energy of the system as detailed in the next section. You can move onto the next section to extract the energies from the previous calculations.

8. To analyze the energies

In this section you are going to calculate the chemisorption energy ΔE_{chem} . This is defined as:

$$\Delta E_{chem} = 0.5E_{(2\times1)CO \text{ on } Pd(110)} - E_{Pd(110)} - E_{CO \text{ molecule}}$$

Allowing the CO atoms to tilt against each other, hence reducing the self repulsion of the CO molecules, should result in a gain in energy. The repulsion energy can be calculated from:

$$\Delta E_{rep} = 0.5E_{(2\times1)CO \text{ on } Pd(110)} - E_{(1\times1)CO \text{ on } Pd(110)}$$

To calculate these properties, you need to extract the total energies from CASTEP text output documents for each simulation.

In the Project Explorer, open **CO.castep** in the **CO molecule/CO CASTEP GeomOpt** folder. Press **CTRL + F** and search for **Final Enthalpy**. Note down the value that appears in that line. Repeat the procedure to find the total energies of the other systems and so complete the table.

Simulation	Total Energy (eV)
CO molecule	
Pd(110)	
(1×1)CO on Pd(110)	
(2×1)CO on Pd(110)	

Once you have the energies, simply use the above equations to calculate ΔE_{chem} and ΔE_{rep} . These should have values of approximately -1.79 eV and -0.06 eV, respectively.

9. To analyze the density of states (DOS)

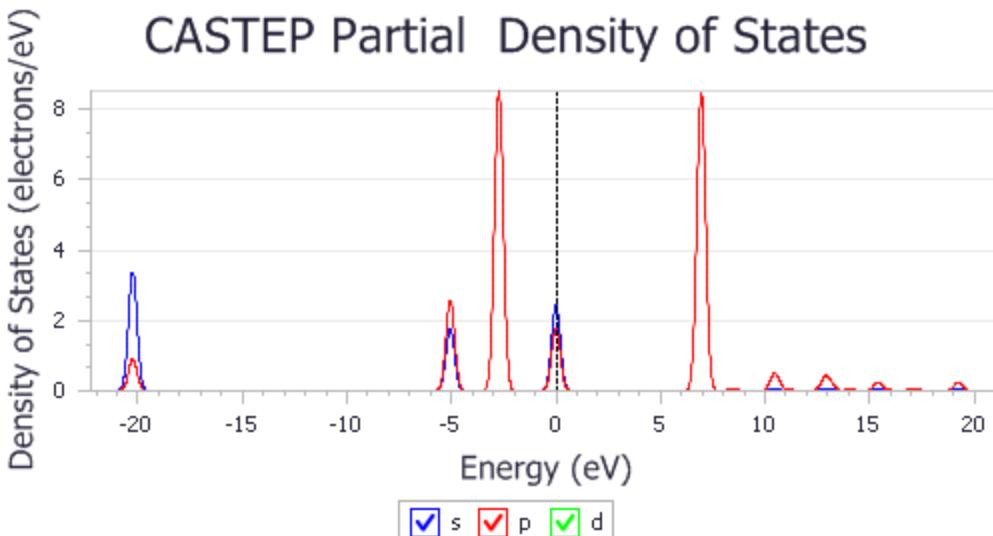
Next, you will examine the changes in the density of states (DOS). This will allow you to obtain an insight into the bonding mechanism of CO on Pd(110). To do this, you need to display the density of states of the isolated CO molecule and of (2x1) CO on Pd(110).

In the Project Explorer, open **CO.xsd** in the **CO molecule/CO CASTEP GeomOpt** folder.

Click the **CASTEP** button  on the **Modules** toolbar, then select **Analysis** to open the CASTEP Analysis dialog.

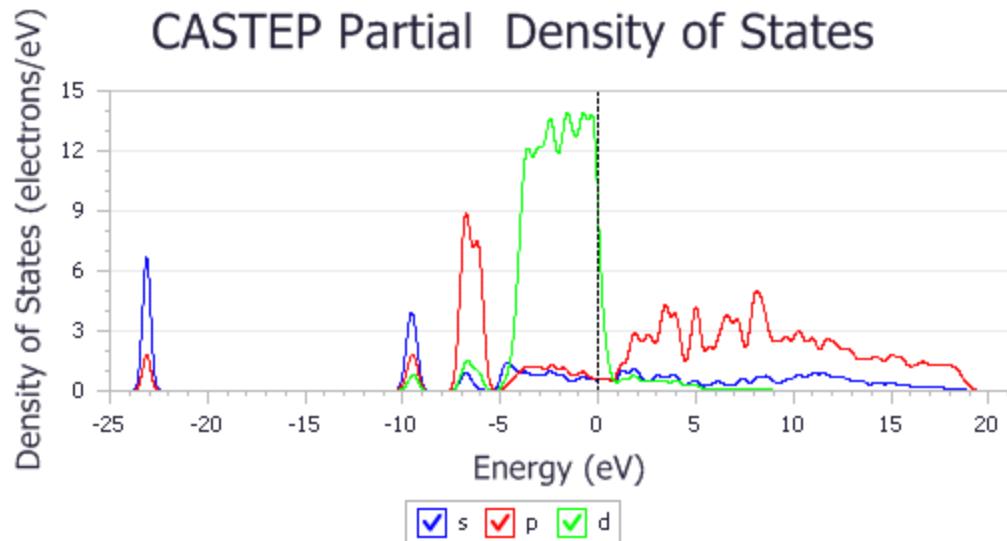
Select the **Density of states**. Click the **Partial** radio button and uncheck the **f** and **Sum** checkboxes. Click the **View** button.

A chart document is displayed showing the PDOS for the CO molecule.



PDOS of CO molecule

Repeat the above for **(2x1) CO on Pd(110).xsd**.



PDOS of (2x1) CO on Pd(110)

It is clear that the electronic states of the isolated CO molecule at approximately -20, -5, and -2.5 eV are considerably lowered in energy as the CO binds to the surface.

Note: The default pseudopotential for Pd, `Pd_2017R2.otfg`, treats 4s and 4p semicore states as valence. This results in sharp peaks in the calculated DOS at about -84 and -49 eV. The chart above excludes those states; this can be achieved by using Properties Explorer to change the maximum and minimum values along X and Y axes.

As an independent exercise you can analyze PDOS further by investigating contributions to the PDOS of the adsorbate complex that arise from the C and O atoms.

Hold down **SHIFT** and select all C and O atoms in the **(2x1) CO on Pd(110).xsd** document. Generate partial DOS as described above - the chart shows the effect of hybridization with Pd states which manifests itself as broadening of the energy levels and their general shift towards lower energies.

There are a number of additional experiments that can be carried out as an independent exercise, for example:

- Investigate the accuracy of the results by checking convergence with respect to calculation parameters:
 1. Repeat the chemisorption calculation with a significantly higher value for the vacuum thickness (for example, 15 Å instead of 8 Å).
 2. Repeat the chemisorption calculation with a more accurate k-point sampling; on the *CASTEP Electronic Options* dialog, *k-points* tab, use a *Separation* of 0.03 1/Å to produce a denser k-point grid. This step can be repeated with few more values until the chemisorption energy is converged to the desired accuracy.
 3. Similar to the previous step, repeat the calculations by increasing the energy cutoff on the *CASTEP Electronic Options* dialog, *Basis* tab; check *Use custom energy cutoff* to enable this step.

- The number of substrate layers can affect the result substantially; you can repeat this tutorial with more Pd layers by using a higher value for the *Fractional Thickness* when generating the surface.
- Surface calculations in a slab geometry often benefit from application of a dipole correction, especially when there is a pronounced dipole moment - as in the CO molecule.

CASTEP allows you to apply such a correction by selecting a *Self-consistent* option for the *Apply dipole correction* on the *CASTEP Electronic Options* dialog, *SCF* tab. Repeat calculations with this setting to check whether it affects the energetics of CO adsorption.

Tip: It is recommended to use the *All Bands/EDFT* option for the *Electronic minimizer* setting in this tutorial (on the *SCF* tab of the *CASTEP Electronic Options* dialog). The default *Density Mixing* option exhibits convergence problems for the elongated thin cells that are used in these calculations.

You could additionally examine electrostatic potential by using the *Potentials* selection on the *CASTEP Analysis* dialog. A chart of the average profile of the electrostatic potential will be created when the *Import* button is clicked.

Tip: There is a difference between the charts generated for calculations with and without a dipole correction applied.

Note: Vacuum width has to be greater than 8 Å in order to generate the chart of electrostatic potential, so this last exercise can be performed only by increasing the vacuum thickness.

This is the end of the tutorial.

Calculating elastic constants for BN

Purpose: Illustrates the use of CASTEP to calculate elastic constants.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: [Predicting the lattice parameters of AlAs from first principles](#)

Background

Recent developments in density functional theory (DFT) methods applicable to studies of large periodic systems have become essential in addressing problems in materials design and processing. The DFT tools can be used to guide and lead the design of new materials, allowing researchers to understand the underlying chemistry and physics of processes.

Introduction

In this tutorial, you will learn how to use CASTEP to calculate elastic constants and other mechanical properties. In the first part you will optimize the structure of cubic BN and then you will calculate its elastic constants.

This tutorial covers:

- [Getting started](#)
- [To optimize the structure of cubic BN](#)
- [To calculate the elastic constants of BN](#)
- [Description of the elastic constants file](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

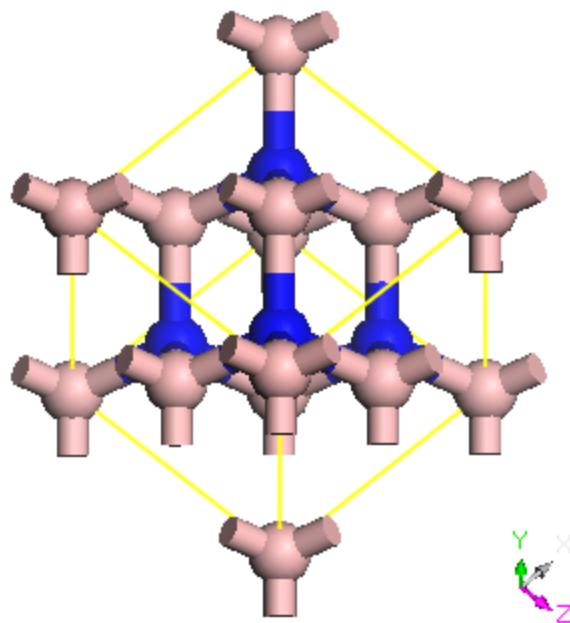
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **BN_elastic** as the project name, click the **OK** button.

The new project is created with *BN_elastic* listed in the Project Explorer. The next step is to import the BN structure.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to the folder **Structures/semiconductors/** and select **BN.xsd**. Click the **Open** button.

The crystal structure of BN is displayed.



Structure of BN cubic

This is the conventional representation of the BN structure. In order to reduce the computation time, you should convert to the primitive representation.

Select **Build | Symmetry | Primitive Cell** from the menu bar.

2. To optimize the structure of BN cubic

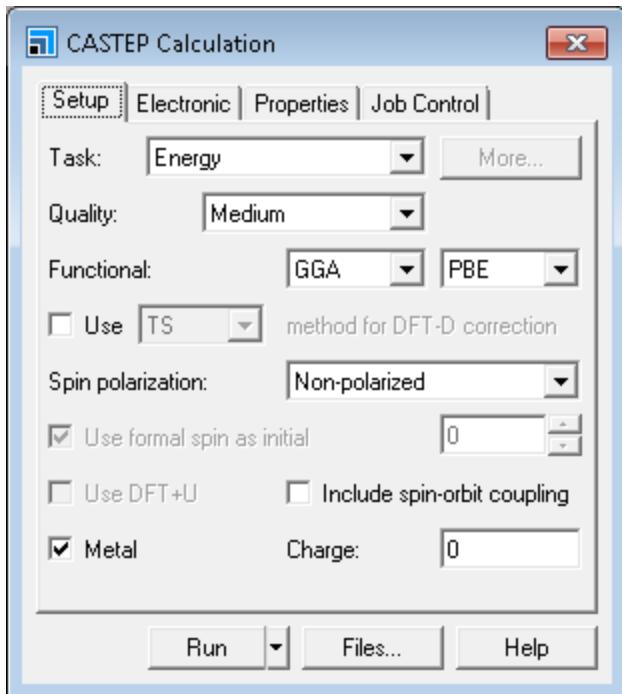
It is not necessary to perform geometry optimization before calculating elastic constants, so you can generate C_{ij} data for experimentally observed structures. However, more consistent results are obtained if you perform full geometry optimization, including cell optimization, and then calculate the elastic constants for the structure corresponding to the theoretical ground state.

The accuracy of the elastic constants, especially of the shear constants, depends strongly on the quality of the SCF calculation and, in particular, on the quality of the Brillouin zone sampling and the degree of convergence of wavefunctions. Therefore, you should use the **Fine** setting for SCF tolerance and k-point sampling and a **Fine** derived FFT grid.

Now you will set up the geometry optimization.

Click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

On the **Setup** tab, set the **Task** to **Geometry Optimization**, the **Quality** to **Fine**, and the **Functional** to **GGA** and **PBESOL**.

Click the **More...** button to open the CASTEP Geometry Optimization dialog. Select **Full** from the **Cell optimization** dropdown list and close the dialog.

Choose the **Job Control** tab on the CASTEP Calculation dialog and select the **Gateway** on which you wish to run the CASTEP job.

Click the **Run** button.

After optimization, the structure should have cell parameters of about $a = b = c = 2.553 \text{ \AA}$ which corresponds to 3.610 \AA lattice parameter for the conventional unit cell (experimental value is 3.615 \AA).

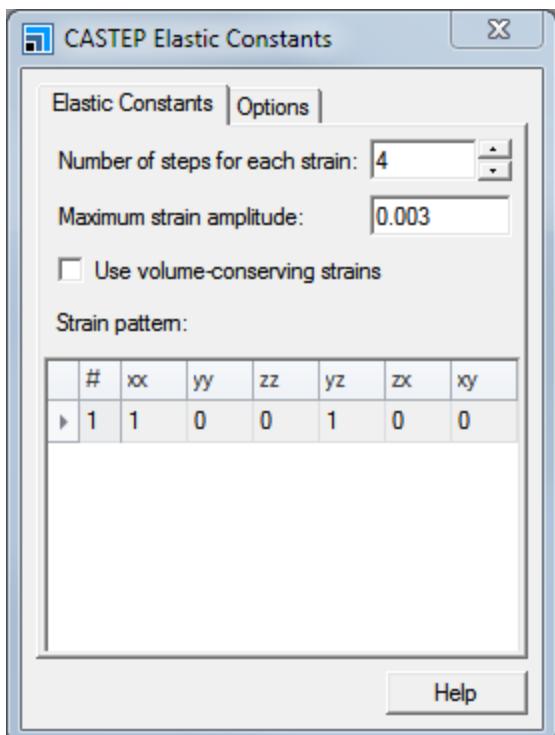
Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu.

The lattice parameters are shown. Now you can go on to calculate the elastic constants of the optimized structure.

3. To calculate the elastic constants of BN

Select the **Setup** tab on the CASTEP Calculation dialog. Select **Elastic Constants** from the **Task** dropdown list and click the **More...** button.

This opens the CASTEP Elastic Constants dialog.



CASTEP Elastic Constants dialog, Elastic Constants tab

Increase the **Number of steps for each strain** from 4 to 6 and close the dialog. Ensure that **BN CASTEP GeomOpt/BN.xsd** is the active document and click the **Run** button on the CASTEP Calculation dialog.

Note: If BN CASTEP GeomOpt/BN.xsd is made active before the CASTEP Elastic Constants dialog is opened, the *Strain pattern* grid on this dialog will contain values.

CASTEP results for the **Elastic Constants** task are returned as a set of .castep output files. Each of them represents a geometry optimization run with a fixed cell, for a given strain pattern and strain amplitude. The naming convention for these files is:

seedname_cij_m_n

where *m* is the current strain pattern and *n* is the current strain amplitude for the given pattern.

CASTEP can use these results to analyze the calculated stress tensors for each of these runs and generate a file with information about elastic properties.

Click the **CASTEP** button  on the **Modules** toolbar and select **Analysis** from the dropdown list or choose **Modules | CASTEP | Analysis** from the menu bar.

Select the **Elastic constants** option. The results file from the **Elastic Constants** job for BN should be displayed automatically in the **Results file** selector. Click the **Calculate** button.

A new text document, **BN Elastic Constants.txt**, is created in the results folder.

The information in this document includes a summary of the input strains and calculated stresses, results of linear fitting for each strain pattern (including quality of the fit), the correspondence between

calculated stresses and elastic constants for a given symmetry, a table of elastic constants (C_{ij}) and elastic compliances (S_{ij}). The derived properties, such as bulk modulus and its inverse, compressibility, Young modulus, and Poisson ratios for three directions, and the Lamé constants that are needed for modeling the material as an isotropic medium, are also reported in this document.

4. Description of the elastic constants file

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.

Only one strain pattern is required for this lattice type. There is a summary of calculated stresses as extracted from the respective .castep files:

```
=====
Elastic constants from Materials Studio: CASTEP
=====

Summary of the calculated stresses
*****
```

Strain pattern: 1

```
=====
```

Current amplitude: 1
Transformed stress tensor (GPa) :
-8.185512 -0.000000 -0.000000
-0.000000 -10.013060 1.374720
-0.000000 1.374720 -10.013060

Current amplitude: 2
Transformed stress tensor (GPa) :
-9.116397 -0.000000 -0.000000
-0.000000 -10.216359 0.838757
-0.000000 0.838757 -10.216359

Current amplitude: 3
Transformed stress tensor (GPa) :
-10.048265 -0.000000 -0.000000
-0.000000 -10.416350 0.292454
-0.000000 0.292454 -10.416350

Current amplitude: 4
Transformed stress tensor (GPa) :
-10.989498 -0.000000 -0.000000
-0.000000 -10.613108 -0.258026
-0.000000 -0.258026 -10.613108

Current amplitude: 5
Transformed stress tensor (GPa) :
-11.916355 -0.000000 -0.000000
-0.000000 -10.807650 -0.799337
-0.000000 -0.799337 -10.807650

Current amplitude: 6
Transformed stress tensor (GPa) :
-12.830064 -0.000000 -0.000000
-0.000000 -10.994485 -1.332785
-0.000000 -1.332785 -10.994485

All the information about the connection between components of the stress, strain, and elastic constants tensors is provided. At this stage, each elastic constant is represented by a single compact

index rather than by a pair of ij indices. The correspondence between the compact notation and the conventional indexing is provided later in the file:

Stress corresponds to elastic coefficients (compact notation):
 1 7 7 4 0 0

as induced by the strain components:
 1 1 1 4 0 0

A linear fit of the stress-strain relationship for each component of the stress is given in the following format:

Stress index	cij index	value of stress	value of strain
1	1	-8.185512	-0.003000
1	1	-9.116397	-0.001800
1	1	-10.048265	-0.000600
1	1	-10.989498	0.000600
1	1	-11.916355	0.001800
1	1	-12.830064	0.003000
C (gradient) :	775.330167		
Error on C :	1.606541		
Correlation coeff:	0.999991		
Stress intercept :	-10.514348		
2	7	-10.013060	-0.003000
2	7	-10.216359	-0.001800
2	7	-10.416350	-0.000600
2	7	-10.613108	0.000600
2	7	-10.807650	0.001800
2	7	-10.994485	0.003000
C (gradient) :	163.756095		
Error on C :	1.145946		
Correlation coeff:	0.999902		
Stress intercept :	-10.510169		
3	7	-10.013060	-0.003000
3	7	-10.216359	-0.001800
3	7	-10.416350	-0.000600
3	7	-10.613108	0.000600
3	7	-10.807650	0.001800
3	7	-10.994485	0.003000
C (gradient) :	163.756095		
Error on C :	1.145946		
Correlation coeff:	0.999902		
Stress intercept :	-10.510169		
4	4	1.374720	-0.003000
4	4	0.838757	-0.001800
4	4	0.292454	-0.000600
4	4	-0.258026	0.000600
4	4	-0.799337	0.001800
4	4	-1.332785	0.003000
C (gradient) :	452.435405		
Error on C :	1.053660		
Correlation coeff:	0.999989		
Stress intercept :	0.019297		

The gradient provides the value of the elastic constant (or a linear combination of elastic constants); the quality of the fit, indicated by the correlation coefficient, provides the statistical uncertainty of that

CASTEP: Calculating elastic constants for BN

value. The stress intercept value is not used in further analysis, it is simply an indication of how far the converged ground state was from the initial structure.

The results for all the strain patterns are then summarized:

```
=====
Summary of elastic constants
=====
```

id	i	j	Cij (GPa)
1	1	1	775.33017 +/- 1.607
4	4	4	452.43540 +/- 1.054
7	1	2	163.75610 +/- 0.810

The errors are only provided when more than two values for the strain amplitude are used, since there is no statistical uncertainty associated with fitting a straight line to only two points.

Elastic constants are then presented in a conventional 6×6 tensor form, followed by a similar 6×6 representation of the compliances:

```
=====
Elastic Stiffness Constants Cij (GPa)
=====
```

775.33017	163.75610	163.75610	0.00000	0.00000	0.00000
163.75610	775.33017	163.75610	0.00000	0.00000	0.00000
163.75610	163.75610	775.33017	0.00000	0.00000	0.00000
0.00000	0.00000	0.00000	452.43540	0.00000	0.00000
0.00000	0.00000	0.00000	0.00000	452.43540	0.00000
0.00000	0.00000	0.00000	0.00000	0.00000	452.43540

```
=====
Elastic Compliance Constants Sij (1/GPa)
=====
```

0.0013923	-0.0002428	-0.0002428	0.0000000	0.0000000	0.0000000
-0.0002428	0.0013923	-0.0002428	0.0000000	0.0000000	0.0000000
-0.0002428	-0.0002428	0.0013923	0.0000000	0.0000000	0.0000000
0.0000000	0.0000000	0.0000000	0.0022103	0.0000000	0.0000000
0.0000000	0.0000000	0.0000000	0.0000000	0.0022103	0.0000000
0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0022103

The final part of the file contains the derived properties:

Bulk modulus = 367.61412 +/- 0.761 (GPa)

Compressibility = 0.00272 (1/GPa)

Elastic Debye temperature = 1888.24550 K

Averaged sound velocity = 11448.15958 (m/s)

Axis	Young Modulus (GPa)	Poisson Ratios
X	718.21921	Exy= 0.1744 Exz= 0.1744
Y	718.21921	Eyx= 0.1744 Eyz= 0.1744
Z	718.21921	Ezx= 0.1744 Ezy= 0.1744

```
=====
Elastic constants for polycrystalline material (GPa)
=====
```

Bulk modulus : Voigt Reuss Hill
367.61412 367.61412 367.61412

Shear modulus (Lame Mu)	:	393.77606	379.61381	386.69494
Lame Lambda	:	105.09675	114.53824	109.81750
Young modulus	:	870.50830	847.21734	858.91818
Poisson ratio	:	0.10533	0.11589	0.11059
Hardness (Tian 2012)	:	68.41824	63.94740	66.16553
Fracture toughness (MPa m ^{0.5})	:	5.11167	5.01890	5.06550
Universal anisotropy index:		0.18653		
Kube AL anisotropy index :		0.08029		

The values reported above are roughly within 10% of experimentally measured values ($B=396 \text{ GPa}$, $C_{11}=820 \text{ GPa}$, $C_{12}=190 \text{ GPa}$, $C_{44}=457 \text{ GPa}$) which is typical for DFT calculations.

Calculated elastic properties of crystals are significantly more sensitive to the accuracy of the electronic structure calculation than, for example, calculated lattice parameters and atomic coordinates. It is always necessary to check the convergence of the calculated properties with respect to the following parameters:

- density of k-points (most important)
- energy cutoff
- augmentation density scaling factor - in the case of ultrasoft pseudopotentials, either generated on the fly or tabulated ones
- force convergence tolerance in optimization of distorted structures

An additional consideration in elastic properties calculations is the choice of exchange-correlation functional. Modern functionals that are designed to reproduce solid state properties more accurately than traditional LDA or PBE functionals are PBESOL and Wu-Cohen; these are recommended for calculating elastic coefficients of solids.

This is the end of the tutorial.

Predicting the thermodynamic properties of germanium

Purpose: Introduces the use of CASTEP for calculating linear response and thermodynamic properties.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: [Predicting the lattice parameters of AlAs from first principles](#)

Background

Linear response, or density functional perturbation theory (DFPT), is one of the most popular methods of ab initio calculation of lattice dynamics. However, potential applications of the method extend beyond the study of vibrational properties. Linear response provides an analytical way of computing the second derivative of the total energy with respect to a given perturbation. Depending on the nature of this perturbation, a number of properties can be calculated. A perturbation in ionic positions gives the dynamical matrix and phonons; in magnetic field - NMR response; in unit cell vectors - elastic constants; in an electric field - dielectric response, and so on. The basic theory of phonons, or lattice vibrations, in crystals is well understood and has been described in detail in several textbooks. The importance of the phonon interpretation of lattice dynamics is illustrated by the large number of physical properties that can be understood in terms of phonons: infrared, Raman, and neutron scattering spectra; specific heat, thermal expansion, and heat conduction; electron-phonon interaction and thus resistivity and superconductivity, and so on. Density Functional Theory (DFT) methods can be used to predict such properties and CASTEP provides this functionality.

Note: DFPT phonon calculations using ultrasoft pseudopotentials are not yet supported. Nevertheless phonon spectra and related properties can be calculated with those settings in the framework of the finite difference technique.

Introduction

In this tutorial, you will learn how to use CASTEP to perform a linear response calculation in order to calculate phonon dispersion and density of states as well as predict thermodynamic properties such as enthalpy and free energy.

This tutorial covers:

- [Getting started](#)
- [To optimize the structure of the germanium cell](#)
- [To calculate phonon dispersion and density of states \(DOS\)](#)
- [To display phonon dispersion and density of states](#)
- [To display thermodynamic properties](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Ge_phonon** as the project name, click the **OK** button.

The new project is created with *Ge_phonon* listed in the Project Explorer.

Begin by importing the Ge structure, which is included in the structure library provided with Materials Studio.

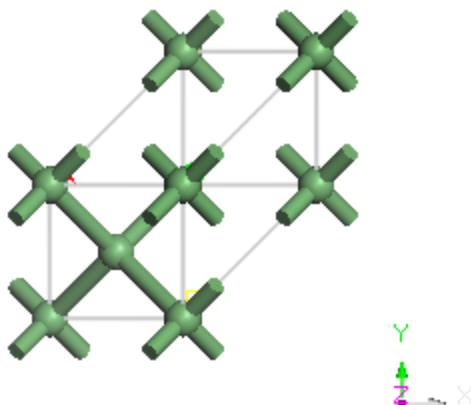
Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Structures/metals/pure-metals** and select **Ge.xsd**.

2. To optimize the structure of the germanium cell

It is often possible to get significant speedup by converting the structure to a primitive cell.

Select **Build | Symmetry | Primitive Cell** from the menu bar.

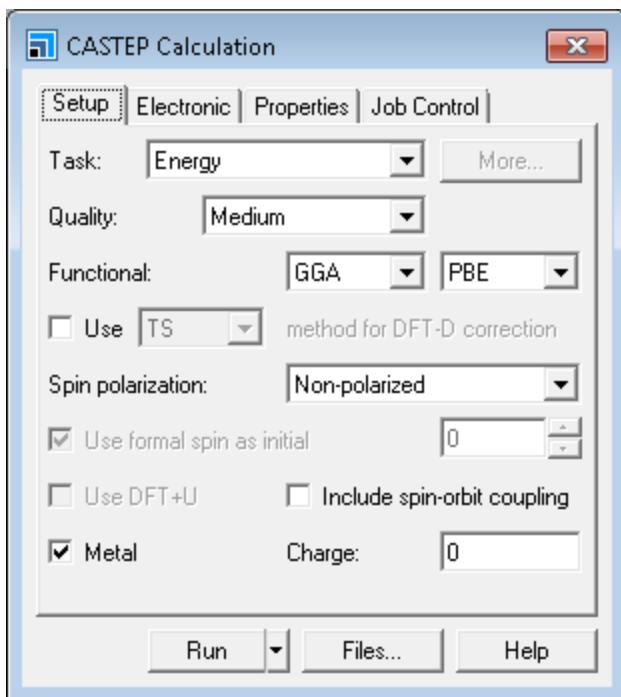
The primitive germanium cell is displayed.



Now optimize the geometry of the Ge structure using CASTEP.

Click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

The default values for geometry optimization do not include optimization of the cell.

On the **Setup** tab change the **Task** from Energy to **Geometry Optimization** and the **Functional** to **LDA**. Uncheck the **Metal** checkbox as Ge is a semiconductor. Change **Quality** to **Ultra-fine**, which is a recommended setting for calculating vibrational properties of materials.

Click the **More...** button to open the CASTEP Geometry Optimization dialog, select **Full** from the **Cell optimization** dropdown list and close the dialog.

Select the **Electronic** tab of the CASTEP Calculation dialog and set **Pseudopotentials to Norm conserving** (linear response calculations of phonon properties are available only for norm-conserving potentials).

On the **Job Control** tab select the location for the job to run in the **Gateway location** dropdown list, and set the **Runtime optimization** to **Speed**.

Click the **Run** button to start the job.

The job is submitted and starts to run. It should take a few minutes, depending on the speed of your computer. The results are placed in a new folder called `Ge_CASTEP_GeomOpt`.

3. To calculate phonon dispersion and phonon density of states (DOS)

DFPT gives an opportunity to accurately calculate phonon frequencies at any given point in reciprocal space. However, a calculation for each q-point can be expensive. An alternative approach may be used for calculations that require phonon frequencies for large numbers of q-points, for example, for phonon DOS and thermodynamic properties. This alternative scheme takes advantage of the relatively short range of effective ion-ion interactions in crystals. Interpolation can be used to reduce computation time

without loss of accuracy. The accurate DFPT calculations are performed only at a small number of q-vectors, and then a cheap interpolation procedure is used to obtain frequencies at other q-points of interest. One advantage of using an interpolation scheme instead of the exact calculation is that thermodynamic properties at low temperatures depend strongly on the number of points in the phonon DOS grid. Using the interpolation approach, this number can be increased at no computational cost.

In order to calculate the phonon dispersion and phonon density of states you must perform a single point energy calculation, after selecting the appropriate properties from the *Properties* tab on the *CASTEP Calculation* dialog.

Ensure that **Ge.xsd** in the **Ge CASTEP GeomOpt** folder is the active document.

On the **Setup** tab of the CASTEP Calculation dialog set the **Task to Energy**.

On the **Properties** tab choose **Phonons** and request Density of states and Dispersion by selecting the **Both** option.

Click the **More...** button, to display the CASTEP Phonon Properties Setup dialog. Ensure the **Method** is **Linear response** and the **Use interpolation** checkbox is checked. Ensure that **q-vector grid spacing for interpolation** is **0.05** 1/Å, and the **Quality for Dispersion** and **Density of states** is set to **Fine**. Close the dialog.

Click the **Run** button and close the CASTEP Calculation dialog.

The job is submitted and starts to run. This is a more time-consuming job and could take about 10 minutes on a multi-core computer. A new folder, called **Ge CASTEP Energy**, is created in the **Ge CASTEP GeomOpt** folder. When the energy calculation is finished two new results files are placed in this folder, **Ge_PhonDisp.castep** and **Ge_Phondos.castep**.

4. To display phonon dispersion and density of states

Phonon dispersion curves show how phonon energy depends on the q-vector, along high symmetry directions in the Brillouin zone. This information can be obtained experimentally from neutron scattering experiments on single crystals. Such experimental data are available for only a small number of materials, so theoretical dispersion curves are useful for establishing the validity of a modeling approach to demonstrate the predictive power of ab initio calculations. In certain circumstances it is possible to measure the density of states (DOS) rather than the phonon dispersion. Furthermore, the electron-phonon interaction function, which is directly related to the phonon DOS can be measured directly in the tunneling experiments. It is therefore important to be able to calculate phonon DOS from first principles. Materials Studio can produce phonon dispersion and DOS charts from any **.phonon** CASTEP output file. These files are hidden in the Project Explorer but a **.phonon** file is generated with every **.castep** file that has a PhonDisp or PhonDOS suffix.

Tip: When evaluating phonon DOS, use only the results of phonon calculations on the Monkhorst-Pack grid.

Now use the results of the previous calculation to create a phonon dispersion chart.

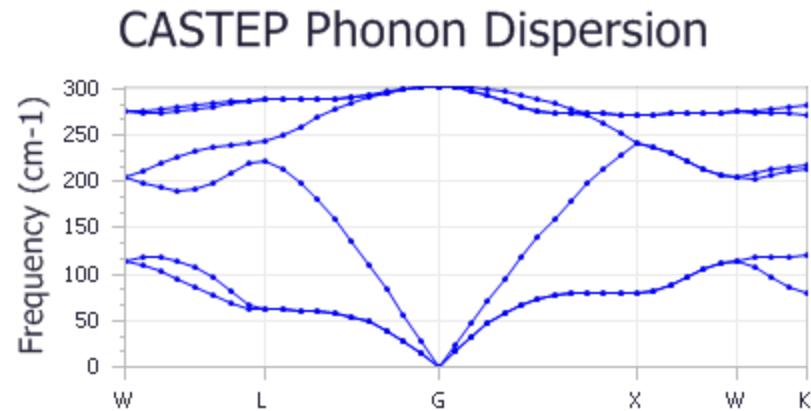
CASTEP: Predicting the thermodynamic properties of germanium

Select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog. Choose **Phonon dispersion** from the list of properties. Ensure that the **Results file** selector displays **Ge_PhonDisp.castep**.

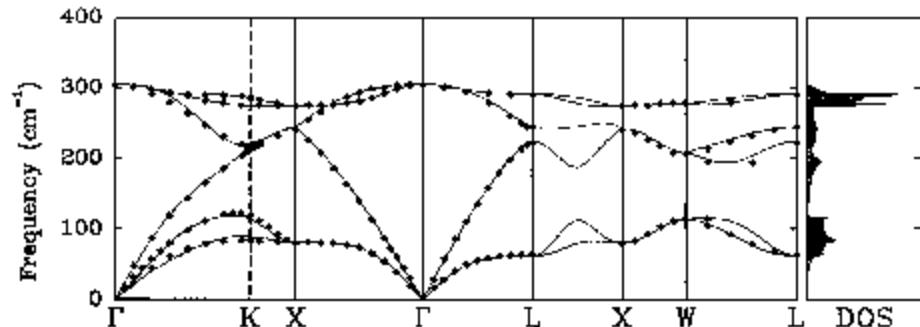
Select **cm-1** from the **Units** dropdown list and **Line** from the **Graph style** dropdown list.

Click the **View** button.

A new chart document, **Ge Phonon Dispersion.xcd**, is created in the results folder. It should look something like the chart shown below:



The experimental phonon dispersion is shown below:



The predicted frequencies are available in the **Ge_PhonDisp.castep** file.

Double-click on **Ge_PhonDisp.castep** in the Project Explorer. Press **CTRL + F** and search for **Vibrational Frequencies**.

The following portion of the results file is displayed:

```
=====
+                               vibrational Frequencies
+ -----
+ 
+ Performing frequency calculation at  40 wavevectors (q-pts)
+ -----
+ 
+ q-pt=    1 (  0.500000  0.250000  0.750000)      0.0487804878
+ -----
```

```

+ Acoustic sum rule correction < 0.002528 cm-1 applied +
+ N      Frequency irrep. +
+          (cm-1) +
+
+   1    114.828225  a +
+   2    114.828225  a +
+   3    204.776057  b +
+   4    204.776057  b +
+   5    274.984105  a +
+   6    274.984105  a +
+
+ ..... +
+ Character table from group theory analysis of eigenvectors +
+ Point Group = 32, Oh +
+
+ Rep Mul | E 2 2 m -4 +
+ |-----+
+ a     2 | 2 0 0 0 -1 +
+ b     1 | 2 0 0 0 1 +
+ -----+
+
....
```

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.

The frequencies for every q-point and for every branch (Longitudinal Optical or Acoustical (LO/LA), Transverse Optical or Acoustical (TO/TA)) are given in cm^{-1} , as well as the positions of the q-points, in the reciprocal space. The high symmetry points Γ , L and X are at reciprocal space positions (0 0 0), (0.5 0.5 0.5) and (0.5 0.5 0.5) respectively.

The predicted and experimental frequencies in cm^{-1} are:

	Predicted	Experimental
Γ_{TO}	302	304
Γ_{LO}	302	304
Γ_{TA}	0	0
Γ_{LA}	0	0
L _{TA}	62	63
L _{LA}	223	222
L _{TO}	243	245
L _{LO}	288	290
X _{TA}	80	80
X _{LA}	241	241
X _{TO}	272	276

Overall, the accuracy of the calculation is acceptable. Better agreement with the experimental results may be obtained by running the calculation with a better SCF k-point grid.

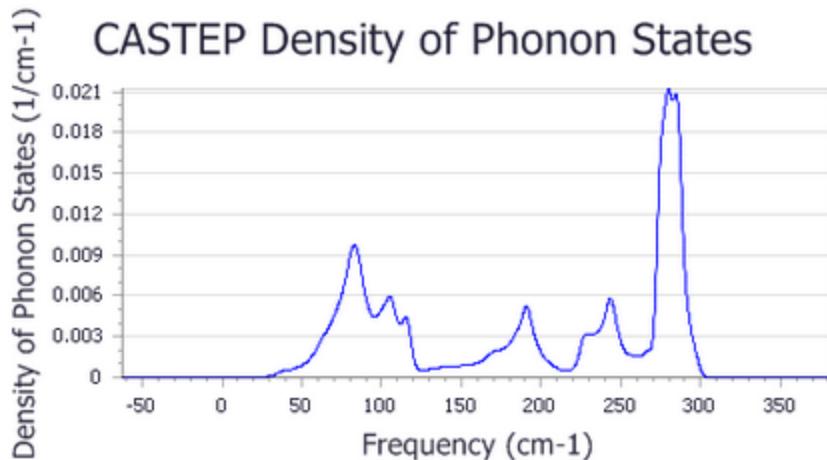
Now create a phonon DOS chart.

On the CASTEP Analysis dialog select **Phonon density of states** from the list of properties. Make **Ge.xsd** the active document and ensure that the **Results file** selector displays **Ge_PhonDOS.castep**.

Set **Display DOS** to **Full**. Click the **More...** button to open the CASTEP Phonon DOS Analysis Options dialog. Select **Interpolation** from the **Integration method** dropdown list and set the **Accuracy level** to **Fine**. Click the **OK** button and on the CASTEP Analysis dialog click the **View** button to create the DOS chart.

Interpolation scheme was chosen to get the best representation of DOS; an alternative setting, smearing, produces DOS with too few fine details.

A new chart document, **Ge Phonon DOS.xcd**, is created. It should look something like the chart shown below:



5. To display thermodynamic properties

Phonon calculations in CASTEP can be used to evaluate the temperature dependence of the enthalpy, entropy, free energy, and lattice heat capacity of a crystal in a quasi-harmonic approximation. These results can be compared with experimental data (for example heat capacity measurements) or used to predict phase stability of different structural modifications or phase transitions.

All energy-related properties are plotted on one graph, and the calculated value of the zero-point energy is included. The heat capacity is plotted separately on the right.

Note: The entropy is present as a TS product to allow comparison with the enthalpy.

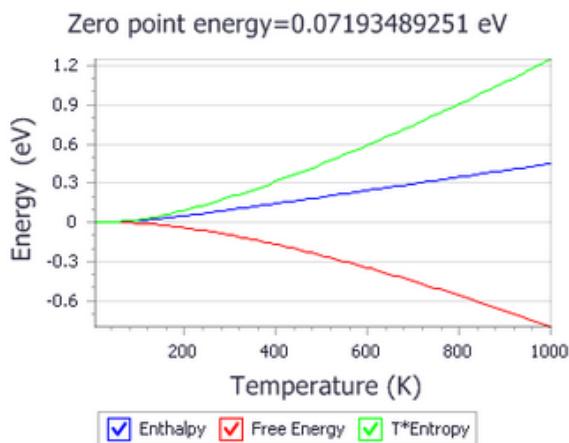
Now use the results of the phonon calculation to create a thermodynamic properties chart.

On the **CASTEP Analysis** dialog choose **Thermodynamic properties** from the list of properties. Make **Ge.xsd** the active document and ensure that the **Results file** selector displays **Ge_PhonDOS.castep**.

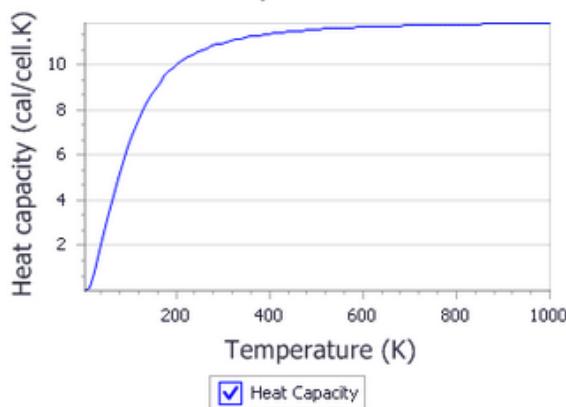
Check the **Plot Debye temperature** checkbox and click the **View** button.

Two new chart documents, **Ge Thermodynamic Properties.xcd** and **Ge Debye Temperature.xcd**, are created in the results folder:

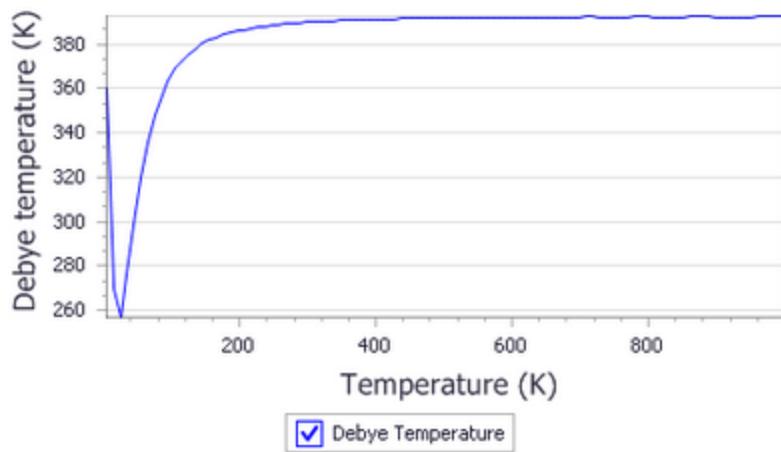
CASTEP Thermodynamic Properties



CASTEP Thermodynamic Properties



CASTEP Thermodynamic Properties



Experimental results without anharmonicity ([Flubacher et al., 1959](#)) show that the Debye temperature at the high temperature limit is 395(3) K. The simulated Debye temperature is 392 K, in excellent agreement with the experimental value.

Overall, the experimental plot is qualitatively very similar to the one generated by CASTEP. There is a dip at about 25 K, with the lowest value of Debye temperature of the order of 255 K, exactly as predicted by CASTEP results. The exact shape of the curve at very low temperatures is not accurate with the calculation settings used in this tutorial. A better sampling of low-frequency acoustic modes is required, and this can be achieved by using a finer Monkhorst-Pack grid in the phonon density of states calculation.

6. To display atomic displacement parameters

Atomic displacement parameters, also known as temperature factors, can be estimated from phonon calculations and displayed in the visualizer as ellipsoids.

CASTEP: Predicting the thermodynamic properties of germanium

On the **CASTEP Analysis** dialog choose **Thermodynamic properties** from the list of properties. Make **Ge.xsd** the active document and ensure that the **Results file** selector displays **Ge_PhonDOS.castep**.

Click **Assign temperature factors to structure** button.

This action adds information about anisotropic temperature factors to each atom. The values can be examined using Properties Explorer. The value of the B factor produced in this tutorial, 0.545 \AA^2 , is in excellent agreement with experimental reports (between 0.52 and 0.55 \AA^2).

In order to visualize temperature factors as ellipsoids, open the **Temperature Factor** tab of the **Display Style** dialog and click **Add**. Ellipsoids are added to the display, but they might be obscured by the reciprocal space objects. You can hide reciprocal space objects by clearing the **Display reciprocal lattice** checkbox on the **Reciprocal** tab of the **Display Style** dialog.

This is the end of the tutorial.

References

Flubacher, P.; Leadbetter, A. J.; Morrison, J. A. "The heat capacity of pure silicon and germanium and properties of their vibrational frequency spectra", *Phil. Mag.*, **4**, 273-294 (1959).

Calculating phonon spectra for ferromagnetic iron

Purpose: Introduces the use of CASTEP for calculating phonon spectra using the finite difference formalism.

Modules: Materials Visualizer, CASTEP

Time:  

Prerequisites: [Predicting the lattice parameters of AlAs from first principles](#), [Predicting the thermodynamic properties of germanium](#)

Background

Phonons are an important concept in solid state physics, which provides access to a wide range of important properties such as specific heat, thermal expansion, heat conduction, electron-phonon interactions, resistivity, and superconductivity. Density Functional Theory (DFT) methods are able to predict such properties, and CASTEP provides the necessary functionality. There are two main approaches in lattice dynamics calculations: density functional perturbation theory (DFPT) and the finite displacement method. The first is generally faster and more accurate, but its implementation is problematic and is subject to a set of restrictions. Currently, DFPT in CASTEP can only be used for norm-conserving pseudopotentials. So phonon calculations with efficient ultrasoft pseudopotentials can only be carried out by using the finite displacement algorithm.

Introduction

In this tutorial, you will learn how to use CASTEP to perform a finite displacement calculation to obtain the phonon dispersion and density of states for a magnetic metal.

This tutorial covers:

- [Getting started](#)
- [To optimize the structure of the iron cell](#)
- [To calculate phonon dispersion and density of states \(DOS\)](#)
- [To display phonon dispersion and density of states](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Fe_phonon** as the project name, click the **OK** button.

The new project is created with *Fe_phonon* listed in the Project Explorer.

Begin by importing the Fe structure, which is included in the structure library provided with Materials Studio.

CASTEP: Calculating phonon spectra for ferromagnetic iron

Select **File | Import...** from the menu bar to open the Import File dialog. Navigate to **Structures/metals/pure-metals** and select **Fe.xsd**. Click the **Open** button.

It is often possible to decrease the calculation time by converting the structure to a primitive cell.

Select **Build | Symmetry | Primitive Cell** from the menu bar.

The primitive cell of iron is displayed.

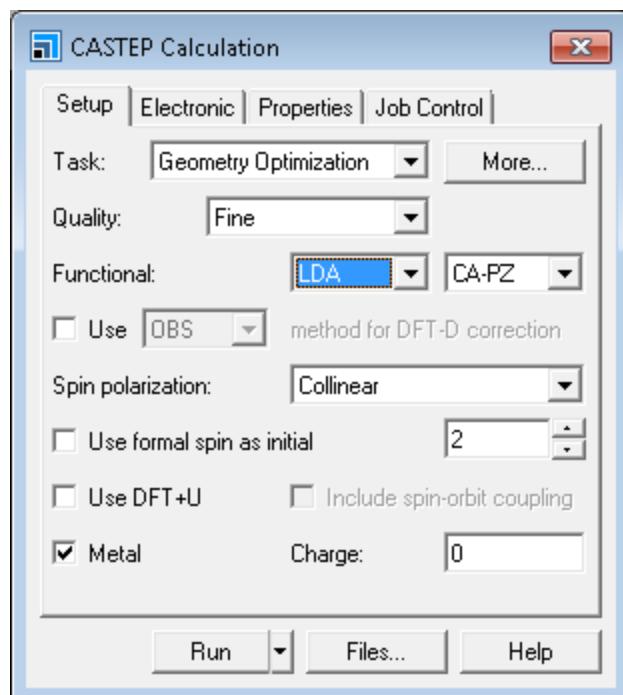
2. Optimizing the structure of iron

Now optimize the geometry of the Fe structure using CASTEP.

Click the **CASTEP** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.

On the **Setup** tab, change the **Task** from Energy to **Geometry Optimization**, set the **Quality** to **Fine**, and the **Functional** to **LDA**. Set the **Spin polarization** to **Collinear** and uncheck the **Use formal spin as initial** checkbox. Set the **Initial spin** value to **2**.



CASTEP Calculation dialog, Setup tab

The default values for geometry optimization do not include optimization of the cell.

Click the **More...** button to open the CASTEP Geometry Optimization dialog, select **Full** from the **Cell optimization** dropdown list and close the dialog.

On the **Electronic** tab select **OTFG ultrasoft** from the **Pseudopotentials** dropdown list.

On the **Job Control** tab, select the **Gateway location** for the job.

Click the **More...** button to open the CASTEP Job Control Options dialog, **uncheck** all of the options in the **Live updates** section, and close the dialog.

Click the **Run** button to start the job.

Note: If you are running this calculation on a cluster with a large amount of RAM (for example more than 10 GB in total) you should use *Speed* for the *Runtime optimization*.

When the job has completed the results are placed in a new folder called **Fe CASTEP GeomOpt**.

3. To calculate phonon dispersion and phonon density of states (DOS)

In order to calculate the phonon dispersion and phonon density of states you have to perform a single point energy calculation, with the appropriate properties selected for calculation.

Ensure that **Fe.xsd** in the **Fe CASTEP GeomOpt** folder is the active document.

On the **Setup** tab on the CASTEP Calculation dialog, set the **Task to Energy**.

On the **Properties** tab, check the **Phonons** checkbox and request both density of states and dispersion by selecting the **Both** radio button. Uncheck the **Calculate LO-TO splitting** checkbox and choose **Finite displacement** from the **Method** dropdown list.

The finite displacement scheme has been designed for use with metallic and spin-polarized systems (as well as for calculations that make use of efficient ultrasoft potentials). This is ideal for calculating phonon properties for ferromagnetic iron.

Click the **More...** button to open the CASTEP Phonon Properties Setup dialog. Ensure that the **Method** is **Finite displacement**. Choose **One large supercell** from the **Use** dropdown list. Set the **Supercell defined by cutoff radius** to **3.5 Å**. Set the **Quality** for both **Dispersion** and **Density of states** to **Fine** and close the dialog.

Note: The cutoff radius chosen is a crucial parameter for a finite displacement calculation. The accuracy is higher when a larger cutoff radius is used, as longer range interactions are taken into account. The computational time, however, grows very rapidly with the increase of this value. For practical reasons, in this tutorial, a small value is chosen for this parameter. The convergence of the phonon frequencies as a function of the cutoff radius should be investigated when performing meaningful calculations.

On the **Job Control** tab select a **Gateway** for the calculation.

Click the **More...** button to open the CASTEP Job Control Options dialog and check all of the **Live updates** options and close the dialog.

Click the **Run** button and close the CASTEP Calculation dialog.

The job is submitted and starts to run. A new folder, named **Fe CASTEP Energy**, is created in the **Fe CASTEP GeomOpt** folder. When the energy calculation is finished the new results files are placed in this folder, including **Fe_PhonDisp.castep** and **Fe_PhonDOS.castep**.

If you decide not to wait for the job to finish, you can access pre-computed version of these files as follows.

Use the Windows File Explorer to navigate to the **share\Examples\Projects\CASTEP** directory, from the top level of your Materials Studio installation. Double-click on the file **Fe_phonons.stp**.

Tip: For Windows users who are not administrators, you should copy the *Fe_phonons.stp* project and associated *Fe_phonons_Files* folder to a location where you have write permissions. Then open the new copy of the *Fe_phonons.stp* project.

4. To display phonon dispersion and density of states

Phonon dispersion curves show how phonon energy depends on the q-vector, along high symmetry directions in the Brillouin zone. This information can be obtained experimentally from neutron scattering experiments on single crystals. Such experimental data are available for only a small number of materials, so theoretical dispersion curves are useful both for establishing the validity of a modeling approach and to demonstrate the predictive power of ab initio calculations. In certain circumstances it is possible to measure the density of states (DOS) rather than the phonon dispersion. Furthermore, the electron-phonon interaction function, which is directly related to the phonon DOS, can be measured directly in the tunneling experiments. It is therefore important to be able to calculate phonon DOS from first principles.

Materials Studio can produce phonon dispersion and DOS charts from any **.phonon** CASTEP output file. This file is generated with every CASTEP job that includes a calculation of Phonon Dispersion or Phonon DOS. The **.phonon** file is hidden, so you will not see it in the Project Explorer.

Tip: When evaluating phonon DOS, use only the results of phonon calculations on the Monkhorst-Pack grid.

Now use the results of the previous calculation to create a phonon dispersion chart.

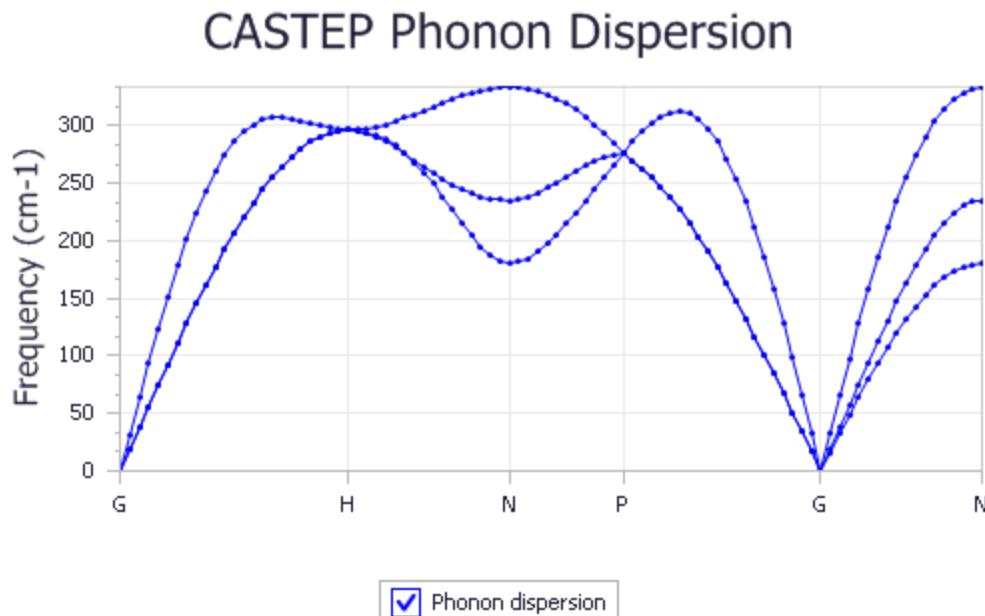
Ensure that **Fe CASTEP GeomOp/Fe CASTEP Energy/Fe.xsd** is the active document.

Select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog. Select **Phonon dispersion** from the list of properties. Ensure that the **Results file** is **Fe_PhonDisp.castep**.

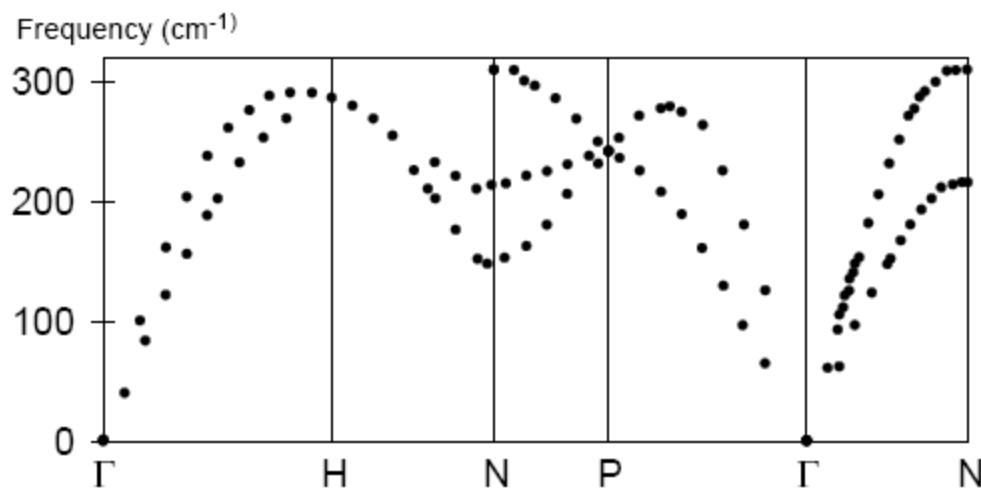
Select **cm-1** from the **Units** dropdown list and **Line** from the **Graph style** dropdown list.

Click the **View** button.

A new chart document, Fe Phonon Dispersion.xcd, is created in the results folder. It should be similar to the chart shown below:



The experimental phonon dispersion ([Minkiewicz et al., 1967](#)) is shown below:



Overall, the accuracy of the calculation is qualitatively acceptable, better agreement with the experimental results will be obtained by running the calculation with a larger cutoff radius.

Now create a phonon DOS chart.

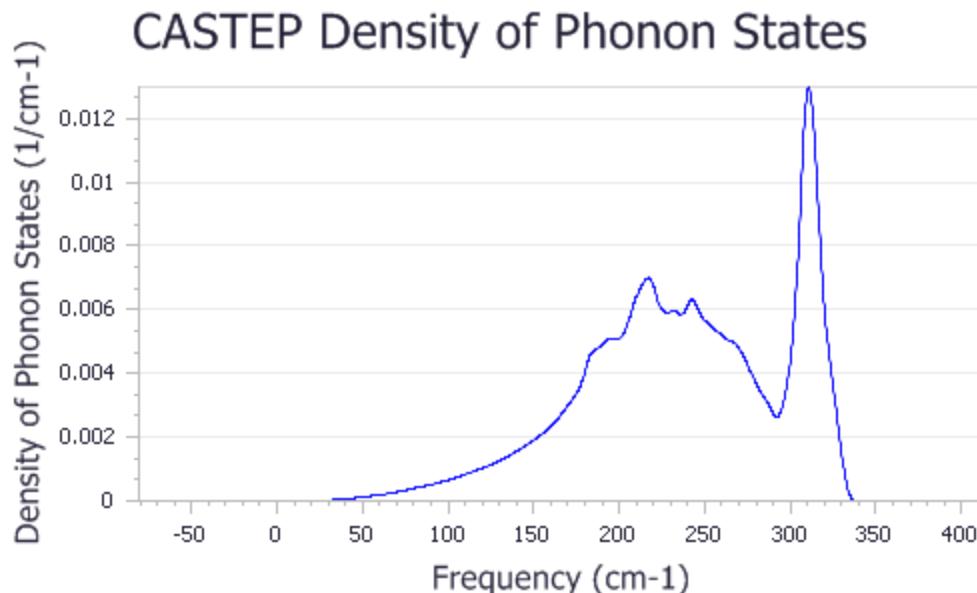
CASTEP: Calculating phonon spectra for ferromagnetic iron

Make **Fe.xsd** the active document and select **Phonon density of states** from the list of properties on the CASTEP Analysis dialog. Ensure that the **Results file** is **Fe_PhonDOS.castep**.

Set **Display DOS** to **Full**. Click the **More...** button to open the CASTEP Phonon DOS Analysis Options dialog. Select **Interpolation** as the **Integration method** and **Fine** as the **Accuracy level**. Click the **OK** button.

On the CASTEP Analysis dialog click the **View** button.

A new chart document, **Fe Phonon DOS .xcd**, is created. It should look similar to the chart shown below:



Phonon calculations in CASTEP can be used to evaluate the temperature dependence of the enthalpy, entropy, free energy, and lattice heat capacity of a crystal in a quasi-harmonic approximation. These results can be compared with experimental data (for example, heat capacity measurements) and used to predict phase stability of different structural modifications or phase transitions.

More details can be found in the [Predicting the thermodynamic properties of germanium](#) tutorial.

This is the end of the tutorial.

References

Minkiewicz, V. J.; Shirane, G.; Nathans, R. "Phonon Dispersion Relation for Iron ", *Phys. Rev.*, **162**, 528-531 (1967).

Assigning the ^{17}O NMR spectrum of L-alanine

Purpose: Introduces the capabilities of NMR CASTEP and the use of the visualization tools for displaying isotropic shielding values.

Modules: Materials Visualizer, CASTEP, NMR CASTEP

Time: 

Prerequisites: [Predicting the lattice parameters of AlAs from first principles](#)

Background

NMR CASTEP predicts the NMR chemical shielding of molecules and solid-state materials from first principles. Based on density functional theory (DFT), NMR CASTEP provides a way to predict key magnetic resonance properties, NMR chemical shielding and electric field gradient (EFG) tensors, with unprecedented accuracy. The method can be applied to compute the NMR shifts of molecules, solids, interfaces, and surfaces for a wide range of materials classes including organic molecules, ceramics and semiconductors. First-principles calculations allow researchers to investigate the nature and origin of the magnetic resonance properties of a system without the need for any empirical parameters.

NMR is often used as an analytical tool to aid in structure prediction. The relative complexity of solid-state structures makes this a challenging task. Often, even though the general features of the crystal structure are understood, a detailed analysis of the geometry proves elusive. Using NMR CASTEP it is possible to simulate the NMR spectrum for a series of related structures until a match is discovered between the computed and experimental results. In this way, theory complements experiment, with both contributing to the determination of the structure.

Note: NMR in CASTEP is part of the separately licensed module NMR CASTEP. NMR calculations can only be performed if you have purchased this module.

Introduction

In this tutorial, you will use NMR CASTEP to assign the observed ^{17}O chemical shifts to the two unique atoms in crystalline L-alanine. You will learn how to run an NMR CASTEP calculation, display the results in the Materials Visualizer, and to interpret the results.

L-Alanine is one of the smaller amino acids. The unit cell contains 4 molecules for a total of 48 atoms. There are 2 distinct oxygen sites. This tutorial will use the computed NMR chemical isotropic shielding values to tell them apart. Experiment can also distinguish between the two oxygens, but only with a very sophisticated solid-state NMR apparatus.

This tutorial covers:

- [Getting started](#)
- [To run an NMR CASTEP calculation](#)
- [To analyze the results](#)
- [To compare the results with experimental data](#)

CASTEP: Assigning the 17-O NMR spectrum of L-alanine

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

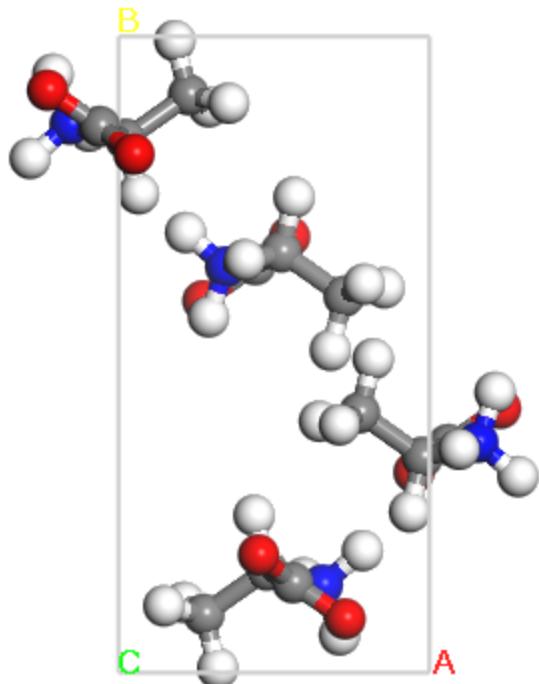
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **NMR_alanine** as the project name, click the **OK** button.

The new project is created with *NMR_alanine* listed in the Project Explorer. The next step is to import the structure.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Examples\Documents\3D Model** and select the **L_alanine.xsd** file, click the **Open** button.

The **L_alanine** document is displayed.



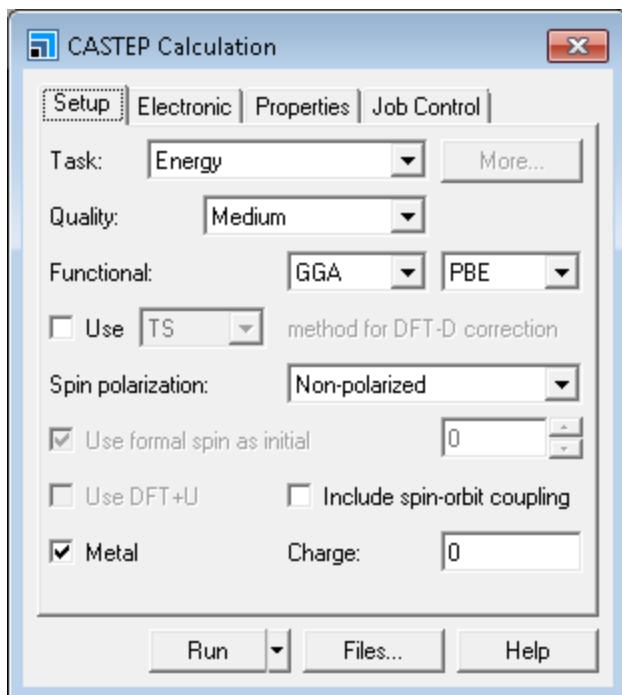
Crystal structure of L-alanine

2. To run an NMR CASTEP calculation

Begin by opening the crystal structure for L-alanine. This is a neutron diffraction crystal structure ([Lehmann et al., 1972](#)). You could also build this crystal structure from scratch and optimize it with CASTEP. Using experimental crystal structures, however, yields results comparable with the DFT-optimized geometry and saves computation time.

Click the **CASTEP** button on the **Modules** toolbar and choose **Calculation** or select **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

You are going to run an energy calculation on the structure and request a calculation of the NMR chemical shielding tensor.

Ensure that the **Task** is set to **Energy** and the **Functional** is **GGA PBE**. Change the **Quality** to **Ultra-fine**. Uncheck the **Metal** checkbox (chemical shielding cannot be calculated for metallic systems).

Note: As a rule, the computed NMR results are sensitive to the *Quality* of the calculation. In order to obtain results that are comparable with experiment, you should use the **Ultra-fine** *Quality* setting. These calculations will take longer than **Fine** or **Medium** calculations, but the results are considerably more reliable.

On the **Electronic** tab select **OTFG ultrasoft** from the **Pseudopotentials** dropdown list.

On the fly (OTFG) pseudopotentials are required to compute the magnetic shielding properties. If you choose a different type of pseudopotential, the NMR calculation cannot be performed.

Now specify the properties you want to calculate from the *Properties* tab.

On the **Properties** tab check the **NMR** checkbox and ensure that the **Shielding** and **EFG** checkboxes are checked.

This will compute both the NMR chemical shielding and the value of the electric field gradient at the nuclei. If you are running the calculation on a remote server, you can specify the server using the *Job Control* tab.

On the **Job Control** tab choose an appropriate server from the **Gateway** dropdown list.

Click the **Run** button and close the dialog.

CASTEP: Assigning the ^{17}O NMR spectrum of L-alanine

Depending on the speed of the computer you are using the NMR calculation will take a few minutes to complete. Alternatively, rather than running the calculation yourself, you can open the pre-computed results in the **Examples** folder as described below.

While the calculation is running several things will happen in the Materials Studio interface. After a few seconds, a new folder is displayed in the Project Explorer and this will contain all the results when the calculation is complete. The Job Explorer is displayed, which contains information about the status of the job. The Job Explorer displays the status of any currently active jobs that are associated with this project. It shows useful information such as the server and job identification number. You can also use this explorer to stop the job if you need to.

As the job progresses, four documents open which relay information on the job status. These documents include the crystal structure, a status document to relay information about the job setup parameters and run information, and charts of the total energy and its convergence as a function of the iteration number.

When the job finishes, the files are transferred back to the client and this can take some time due to the size of certain files.

3. To analyze the results

When the results are transferred, you should have several documents, among them:

- `lAlanine.xsd` - the crystal structure
- `lAlanine.castep` - an output file from the CASTEP energy calculation
- `lAlanine_NMR.castep` - an output file from the NMR CASTEP calculation
- `lAlanine.param` - input information
- `lAlanine.castep_bin` and `lAlanine_NMR.castep_bin` - binary files containing a summary of the results. Although not visible in the Explorer, these hidden files are required for the analysis

If you chose to run the NMR calculation, you should find these files in folder called `lAlanine CASTEP Energy` once the calculation completes.

If you decide not to wait for the job to finish, you can access a pre-computed version of these files as follows.

Use the Windows File Explorer to navigate to the `\share\Examples\Projects\CASTEP` directory, from the top level of your Materials Studio installation. Double-click on the file `lAlanine.stp`.

Tip: For Windows users who are not administrators, you should copy the `lAlanine.stp` project and associated `lAlanine Files` folder to a location where you have write permissions. Then open the new copy of the `lAlanine.stp` project.

Whether you choose to wait for the long calculation to finish or you decide to open the pre-computed results, the tutorial is the same from this point. If you ran the `lAlanine` calculations using the **Medium Quality** setting to save time, the steps are still the same, but your numerical results will differ from the ones discussed here. First, examine the data in the NMR output file.

In the Project Explorer, open `lAlanine CASTEP Energy/lAlanine_NMR.castep` and locate the line that reads **Chemical Shielding and Electric Field Gradient Tensors**.

This is located about 100 lines up from the end of the file. The output data will look something like this (for clarity, the results for H, C, and N have been removed):

Chemical Shielding and Electric Field Gradient Tensors						
Nucleus Species	Ion	Shielding tensor		EFG Tensor		
		Iso(ppm)	Aniso(ppm)	Asym	Cq(MHz)	Eta
O	1	-27.61	419.12	0.49	8.304E+00	0.26
O	2	-9.52	307.31	0.66	6.773E+00	0.65
O	3	-27.61	419.12	0.49	8.304E+00	0.26
O	4	-9.52	307.31	0.66	6.773E+00	0.65
O	5	-27.61	419.12	0.49	8.304E+00	0.26
O	6	-9.52	307.31	0.66	6.773E+00	0.65
O	7	-27.61	419.12	0.49	8.304E+00	0.26
O	8	-9.52	307.31	0.66	6.773E+00	0.65

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.

The magnetic shielding data are displayed for each element that used an OTFG pseudopotential. In the case of L-alanine, this includes the elements, H, C, N, and O. In this tutorial, you will focus on the ^{17}O results.

The first column of the results simply indicates the element symbol. The second column, called *Ion*, is the relative order of a particular atom in the input file. The subsequent columns are defined as follows:

- Iso (ppm) - the isotropic chemical shielding in ppm. This is defined as $\sigma_{\text{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, where σ refers to the chemical shielding tensor in the principal axis frame, that is after diagonalization. This is an *absolute* value of the isotropic chemical shielding, not relative to a standard.
- Aniso (ppm) - the anisotropy defined as $\Delta = \sigma_{zz} - \sigma_{\text{iso}}$.
- Asym - the asymmetry parameter defined as $\eta = (\sigma_{xx} - \sigma_{yy})/\Delta$.
- Cq (MHz) - the quadrupolar coupling constant, $C_Q = eQV_{zz}/h$, where V_{zz} is the largest component of the diagonalized EFG tensor, Q is the nuclear quadrupole moment, and h is the Planck constant.
- Eta - the quadrupolar asymmetry parameter, $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$.

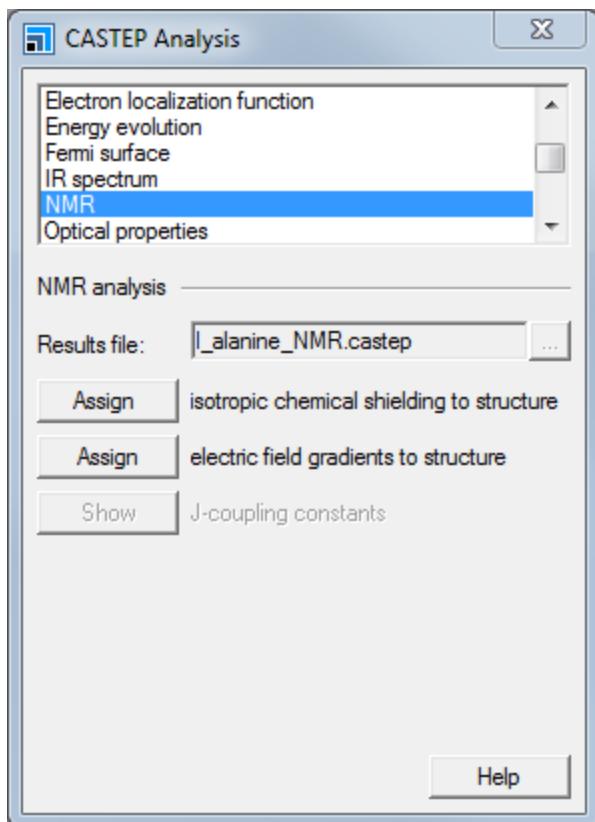
Scroll down to the results for oxygen. Notice that although there are 8 individual oxygen atoms in the unit cell, there are only 2 distinct results. This is because there are only 2 symmetry-unique oxygen atoms in the cell. Now you will use the Materials Visualizer and the experimental data to determine which NMR signal corresponds to which atom.

Open **I_alanine CASTEP Energy/I_alanine.xsd**.

Click the **CASTEP** button  on the **Modules** toolbar, then choose **Analysis** or select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog.

Choose the **NMR** option and click the **Assign isotropic chemical shielding to structure** button.

CASTEP: Assigning the 17-O NMR spectrum of L-alanine



CASTEP Analysis dialog, NMR selection

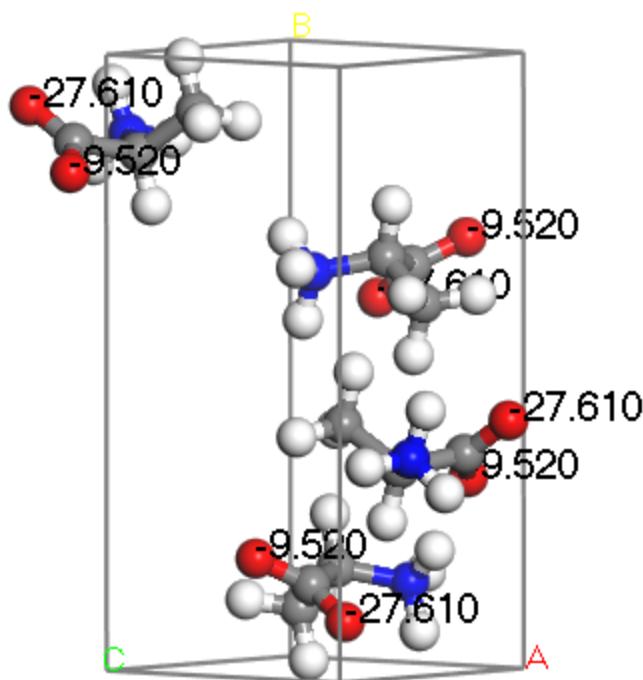
The isotropic chemical shielding values have been loaded into the structure. Now you will display the shielding values for the oxygen atoms.

Hold down **ALT** and double-click on any of the oxygen atoms.

This selects all the oxygen atoms in the system.

Right-click in lAlanine.xsd and select Label from the shortcut menu to open the Label dialog. From the Properties select NMRShielding and click the Apply button.

The NMR isotropic shielding values are displayed for the oxygen atoms.



L-Alanine with ^{17}O isotropic chemical shielding displayed

You can use a similar process to import the electric field gradient data. Atoms can be labeled using either the quadrupolar coupling or the asymmetry parameter.

4. To compare the structure with experimental data

The experimental results for the ^{17}O magnetic resonance data may be found in [Pike et al., \(2004\)](#). In general, the EFG values and asymmetry parameters can be compared directly with experiment. The isotropic chemical shifts require some analysis because the program reports *absolute* chemical shielding whereas most experimentalists are concerned with shifts relative to a known standard. This difference can be dealt with in two ways:

1. In most cases, such as in this example, the primary interest is in comparative shifts, which shift is lowest and which is highest, so there is no need to convert the shielding to the same relative standard used by the experiment. The relative positions are all that is needed in order to assign the shifts to atoms unambiguously. This is easy to do because the relative positions of the peaks do not change when shifted with respect to a standard.
2. When dealing with several related systems, it is necessary to determine a value empirically such that you can convert the shielding to a relative shift. Rather than calculate the chemical shielding of the reference compound explicitly, the reference is obtained by comparing it to a system that is experimentally well-characterized and is similar to the systems being investigated. For example, [Yates et al. \(2004\)](#) investigated ^{17}O shifts for glutamic acid polymorphs. The reference that was chosen was the one which provided the best match between computed and observed values for D-glutamic acid-HCl. The same value was applied to *all* of the polymorphs.

So, why not compute the value of the standard? Typical standards are liquids like water and tetramethylsilane (TMS). A simple calculation on an isolated molecule is quite easy to do, but yields a result very different from the experimental value. On the other hand, computing a value for the liquid state is a complex task, involving the creation of an accurate model of the liquid and subsequent evaluation of the NMR chemical shielding averaged over time and molecular orientation. The results obtained by comparing to one known experimental system provides a more rapid approach, and in addition, provides an immediate coherence check on the results.

CASTEP: Assigning the ^{17}O NMR spectrum of L-alanine

The table below summarizes the computed and observed results.

Quantity	Theory	Experiment
$\sigma_{\text{iso}} \text{ O1 (ppm)}$	-27.61	
$\delta_{\text{iso}} \text{ O1 (ppm)}$		284
$\sigma_{\text{iso}} \text{ O2 (ppm)}$	-9.52	
$\delta_{\text{iso}} \text{ O2 (ppm)}$		260.5
$ \delta \text{ O1} - \delta \text{ O2} $	18.09	23.5
$C_Q \text{ O1 (MHz)}$	8.30	7.86
$C_Q \text{ O2 (MHz)}$	6.77	6.53
$\eta_Q \text{ O1}$	0.26	0.28
$\eta_Q \text{ O2}$	0.65	0.70

Notice that the values of C_Q and η_Q are in close enough agreement to experiment to provide an unambiguous assignment of the spectrum. Notice also that the spacing between the ^{17}O peaks is comparable: 18.09 ppm versus 23.5 ppm. The *larger* experimentally observed shift corresponds to the *smaller* (more negative) computed value of the shielding. This is because of the way the experimentally observed shifts are computed with respect to the standard:

$$\delta_{\text{iso}} = \sigma_{\text{reference}} - \sigma_{\text{observed}}$$

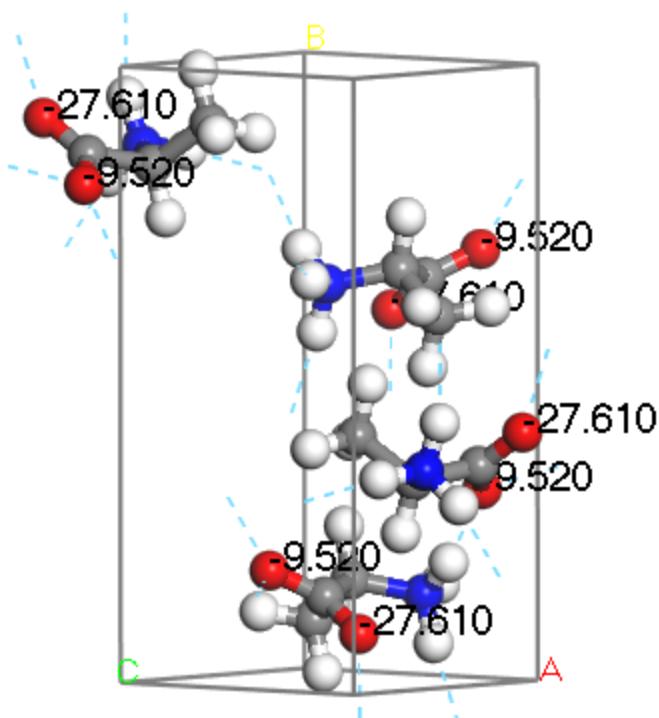
Assume a reference value of 267.3 ppm and convert each computed σ_{iso} into a δ_{iso} . How well do the computed and observed shifts match?

You can see how hydrogen bonding in the crystal affects the chemical shifts.

Label the oxygen atoms by the NMR chemical shifts as you did at the end of [section 3](#).

Select **Build | Hydrogen Bonds** from the menu bar to open the Hydrogen Bond Calculation dialog, click the **Calculate** button.

Hydrogen bonds are displayed as dashed lines.



L-Alanine with hydrogen bonds displayed

Notice that one oxygen is hydrogen bonded to 2 hydrogen atoms associated with the amine group, whereas the other is bonded only to one. The oxygen bonded to 2 hydrogen atoms is nominally the hydroxyl oxygen while the other is the carbonyl oxygen. Based on the computed results and the visualization you can see that the carbonyl oxygen is the one with the observed shift of 284 ppm and the hydroxyl oxygen has the observed shift of 260.5 ppm.

This is the end of the tutorial.

References

- Lehmann, M. S.; Koetzle, T. F.; Hamilton, W. C. *J. Am. Chem. Soc.*, **94**, 2657 (1972).
- Pike, K. J., et al. *J. Phys. Chem. B*, **108**, 9256 (2004).
- Yates, J. R., et al. *J. Phys. Chem A*, **108**, 6032 (2004).

Charge density difference of CO on Pd(110)

Purpose: Demonstrates the use of CASTEP for calculating the charge density difference that occurs when a molecule adsorbs on a surface.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: [Adsorption of CO onto a Pd\(110\) surface](#)

Background

In this tutorial you will investigate how the bonding of the CO molecule affects the electron distribution relative to the isolated CO molecule and the unperturbed Pd(110) surface. The charge density difference can be computed in two different ways. The first option is to compute the charge density with respect to fragments. This is useful for describing the formation of large systems in terms of smaller ones. This method illustrates how the charge density changes during a chemical reaction or on binding of a molecule to a surface. In the case of CO on Pd(110) the electron density difference can be expressed as:

$$\Delta\rho = \rho_{\text{CO@Pd}(110)} - (\rho_{\text{CO}} + \rho_{\text{Pd}(110)})$$

where $\rho_{\text{CO@Pd}(110)}$ is the electron density of the total CO + Pd(110) system, and ρ_{CO} and $\rho_{\text{Pd}(110)}$ are the unperturbed electron densities of the sorbate and substrate, respectively.

The other option is to compute the density difference with respect to atoms:

$$\Delta\rho = \rho_{\text{CO@Pd}(110)} - \sum (\rho_i)$$

where the subscript i runs over all atoms. This option shows the changes in the electron distribution due to the formation of all the bonds. It is useful for illustrating how chemical bonds are formed across the whole system by delocalization of atomic charge density.

The display of the density difference can contribute to an understanding of adsorption processes. Where does the molecule want to adsorb? Why does the molecule adsorb there? What bonding mechanisms contribute to the stabilization of the molecule at this site?

You will focus on one adsorption site: the short bridge site you studied in the tutorial [Adsorption of CO onto a Pd\(110\) surface](#).

Introduction

In this tutorial, you will use CASTEP to compute the charge density difference of CO on Pd(110) in two different ways. You will use the optimized geometry of CO on Pd, as determined [previously](#). Once you have completed the calculations you will use the Materials Visualizer to display the density differences as 3D fields and 2D slices.

This tutorial covers:

- [Getting started](#)
- [To define fragments](#)
- [To run the calculation](#)
- [To display the fragment density difference](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by opening the Materials Studio project that you created for the tutorial [Adsorption of CO onto a Pd\(110\) surface](#). If you have not performed this tutorial or if you did not save the project files, you must do so before proceeding.

Open the file **(1x1) CO on Pd(110).xsd** in the folder **(1x1) CO on Pd(110)\(1x1) CO on Pd (1 1 0) CASTEP GeomOpt**.

2. To define fragments

To compute the fragment density difference you must first define the fragments. You will do this using the *Edit Sets* option. Begin by creating a set containing the carbon and oxygen atoms.

Select **Edit | Edit Sets** from the menu bar to open the **Edit Sets** dialog.

Click on the **carbon** atom to select it. Hold down **SHIFT** and click on the **oxygen** atom.

On the **Edit Sets** dialog, click the **New...** button to open the **Define New Set** dialog. Enter the name **CO DensityDifference**, click the **OK** button and close the dialog.

Tip: In order for CASTEP to recognize the set as a fragment for charge density difference calculations, the name must contain the text string *DensityDifference*.

Notice that in the model **(1x1) CO on Pd (1 1 0) .xsd** the CO molecule is now highlighted and labeled using the name you gave the set. You do not have to define the Pd surface as set since CASTEP automatically assumes that the remaining atoms are to be subtracted when computing the electron density difference.

Atoms belonging to a Set are displayed with a mesh around them. The Set is also labeled.

Tip: To remove the label *CO DensityDifference*, select it with the mouse and press **DELETE**.

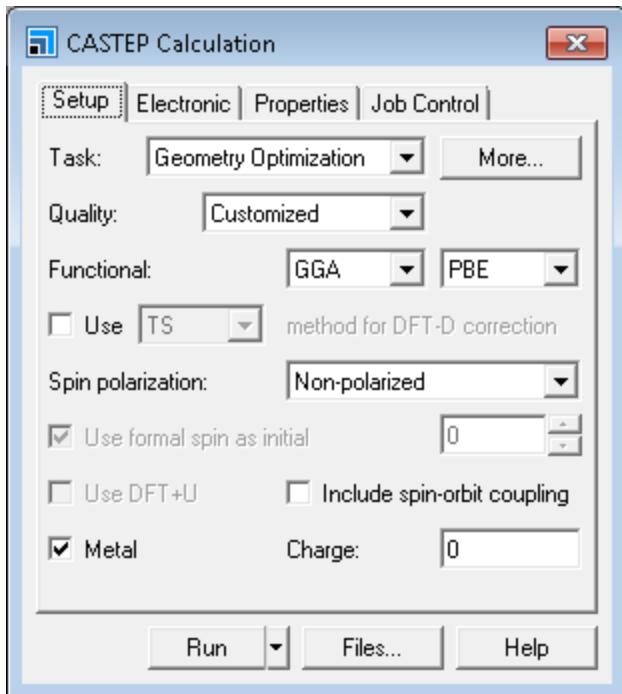
Finally, before you can start the calculation, you must reset the symmetry of the structure to **P1**.

Select **Build | Symmetry | Make P1** from the menu bar.

3. To run the calculation

Double-click on the **(1x1) CO on Pd(110) Calculation** file in the **(1x1) CO on Pd(110)\(1x1) CO on Pd (1 1 0) CASTEP GeomOpt** folder.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

Since you have already run a geometry optimization on the system, you only need to perform a single point energy calculation in order to obtain the density differences.

Change the **Task** to **Energy**.

On the **Properties** tab select the **Electron density difference** and select the **Both atomic densities and sets of atoms** radio button. Ensure that you uncheck any other properties.

Click the **Run** button.

The job is submitted and begins to run. You should wait for it to complete before proceeding to the [next section](#).

When the job has finished, you should save the project.

Select **File | Save Project** from the menu bar.

4. To display the fragment density difference

When the calculation finishes, you can display the charge density difference. Begin by closing all the open windows.

Select **Window | Close All** from the menu bar.

Now open the output structure for the job you just ran.

Open the document **(1x1) CO on Pd (1 1 0).xsd** in the folder **(1x1) CO on Pd (1 1 0) CASTEP Energy**.

Click the **CASTEP** button  on the **Modules** toolbar and select **Analysis**.

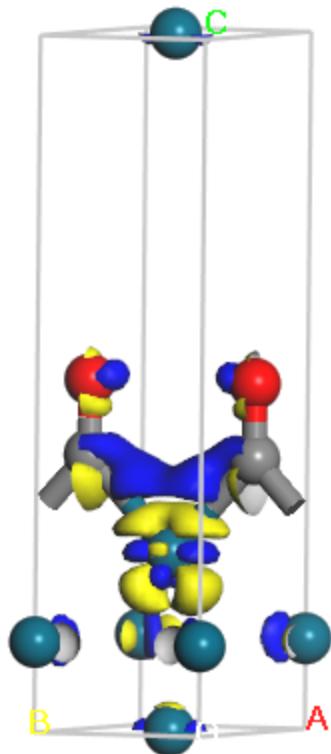
Select the **Electron density difference** option, check the **View isosurface on import** checkbox and uncheck the **Use atomic densities** checkbox. Click the **Import** button.

Tip: When you select *Use atomic densities* the density difference is computed with respect to atoms. When it is unchecked, the difference is computed with respect to fragments.

This displays an isosurface of the difference density at a value of about 0.1 electrons / Å³. Now you should create a more chemically useful isosurface.

Right-click on the document and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Isosurface** tab set the **Isovalue** to **0.05** and select **+/-** from the **Type** dropdown list.

This procedure displays two isosurfaces together. One is at a value of 0.05 and is colored blue, the other is at -0.05 and is colored yellow. The blue areas show where the electron density has been enriched with respect to the fragments. Conversely, the yellow areas show where the density has been depleted.



Charge density difference for CO Pd (110)

You can gain further insight into the changes in bonding by displaying the density difference as a 2D slice. You can do this using the *Volume Visualization* toolbar.

Select one of the isosurfaces and press **DELETE**.

CASTEP: Charge density difference of CO on Pd(110)

Tip: The visibility of isosurfaces and slices can also be controlled, without deleting, using the Volumetric Selection dialog.

Select **View | Toolbars | Volume Visualization** from the menu bar.

Now use the *Create Slices* tool to create a 2D slice from the data.

Click the **Create Slices** arrow  tool and select **Parallel to B & C Axis** from the dropdown list.

Click on the 2D slice to select it, hold down the **SHIFT** and **ALT** keys and the **right mouse button** to move the slice so that it cuts through the CO molecule.

You now have a 2D slice showing the density difference through the CO molecule. Next you will adjust the data range of the slice and change the color scheme to differentiate more easily between regions of electron depletion and electron enrichment.

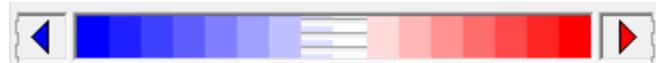
Select the slice. Click the **Color Maps** button  on the **Volume Visualization** toolbar to open the Color Maps dialog.

Change the **Spectrum** to **Blue-White-Red**, set **From** to **-0.2** and **To** to **0.2**, and set the value of **Bands** to **16**.

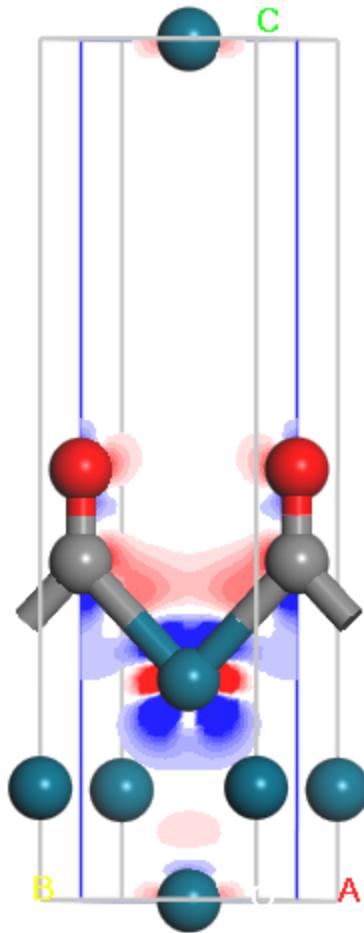
Each of the 16 colors represents a specific range of the charge density. In this plot a loss of electrons is indicated in blue, while electron enrichment is indicated in red. White indicates regions with very little change in the electron density. You can see the red and blue areas more clearly if you hide the white areas.

Click on the two colors in the center of the **selector** on the Color Maps dialog.

The **selector** should now look like this:



The final image should resemble the one shown here:



2D charge density difference for CO Pd (110)

Based on this, which atoms have lost electron density? Can you tell which orbitals lost electrons? Which orbitals on which atoms gained electrons? Does this match your expectations for carbon-metal bonding?

If you are interested you could repeat this section of the tutorial using the atomic density difference rather than the fragment density difference. Simply make sure that you check *Use atomic densities* when you import the density difference.

This is the end of the tutorial.

Simulating the STM profile of CO on Pd(110)

Purpose: Demonstrates the use of CASTEP for simulating the transmission microscope (STM) profile of a system.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: [Adsorption of CO onto a Pd\(110\) surface](#)

Background

The scanning transmission microscope (STM) provides an image of a material, but it can also be used to provide quantitative information at the atomic scale. The ability to simulate the STM image therefore provides a way to compare computed results with experiment.

CASTEP models the STM profile by representing it as an isosurface of the electron density generated only by states at a certain energy away from the Fermi level. The distance from the Fermi level corresponds to the applied bias in STM experiments: positive bias corresponds to empty (conduction) states and negative bias to occupied (valence) states. This approach neglects the actual geometry of the STM tip.

STM profile visualization makes sense only for models that represent surfaces in the slab supercell geometry. In addition, information about charge density at a distance from the surface is likely to be inaccurate as a result of DFT failing to reproduce the asymptotics of the wavefunction decay into a vacuum.

Introduction

In this tutorial, you will use CASTEP to simulate the STM profile of a CO molecule adsorbed onto a Pd (110) surface. The aim of the tutorial is to check whether STM is likely to confirm that the 2x1 structure found in the tutorial "Adsorption of CO onto a Pd(110) surface" is more stable or whether there will be little difference observed between the 1x1 and 2x1 systems. You will make use of results obtained [previously](#) for this system.

This tutorial covers:

- [Getting started](#)
- [To run the calculation](#)
- [To create an STM isosurface](#)
- [To add extra information to the STM isosurface](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by opening the Materials Studio project that you created for the tutorial [Adsorption of CO onto a Pd\(110\) surface](#). If you have not performed this tutorial or if you did not save the project files, you must do so before proceeding.

Select **File | Open Project...** from the menu bar to open the Open Project dialog. Navigate to the **CO_on_Pd.stp** project and click the **Open** button.

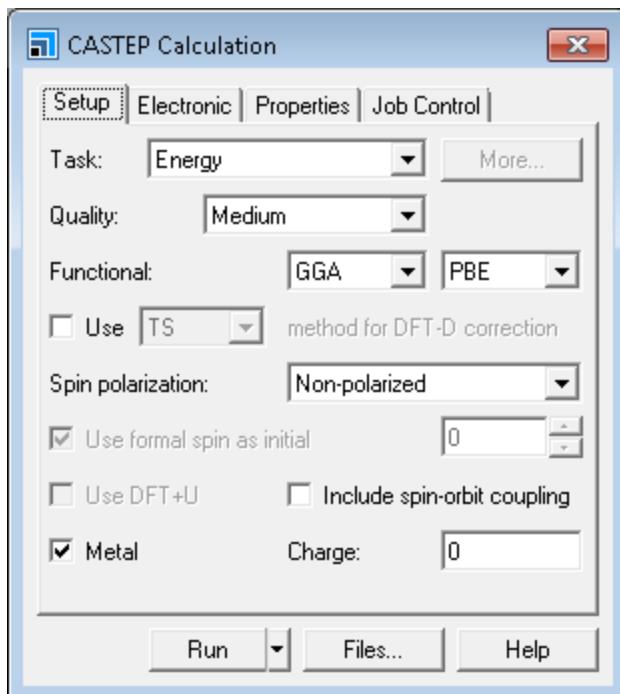
You will use the Pd(1 1 0) surface with CO adsorbed for this calculation.

Open the file **(1x1) CO on Pd(110).xsd** in the **(1x1) CO on Pd(110)\(1x1) CO on Pd (110) CASTEP GeomOpt** folder.

2. To run the calculation

Click the **CASTEP** button  on the **Modules** toolbar then select **Calculation** or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

Since you have already run a geometry optimization on the system, you only need to perform a single point energy calculation in order to obtain the orbitals.

Change the **Task** to **Energy**.

On the **Properties** tab check the **Orbitals** checkbox and ensure that you **uncheck** any other properties.

On the **Electronic** tab click the **More...** button to open the CASTEP Electronic Options dialog. On the **k-points** tab ensure that the **Custom grid parameters** radio button is selected and that the **Grid parameters** fields are set as **a** to **3**, **b** to **4** and **c** to **1**.

Click the **Run** button.

CASTEP: Simulating the STM profile of CO on Pd(110)

The job is submitted and begins to run.

Repeat the same procedure for the optimized 2x1 structure in **(2x1) CO on Pd(110).xsd** located in the **(2x1) CO on Pd(110)** folder, making sure that the k-points Grid parameters are set as **a** to **2**, **b** to **3** and **c** to **1**.

Click the **Run** button on the CASTEP Calculation dialog and close both dialogs.

When the job has finished, you should save the project.

Select **File | Save Project** from the menu bar.

3. To create an STM isosurface

When the calculation finishes, you can display the charge density difference. Begin by closing all the open windows.

Select **Window | Close All** from the menu bar.

Now open the output structure for the (1x1) and (2x1) calculations side by side.

Open **(1x1) CO on Pd (110).xsd** in the **(1x1) CO on Pd (110) CASTEP Energy** folder. Also open **(2x1) CO on Pd(110).xsd** in the **(2x1) CO on Pd (110) CASTEP Energy** folder. Select **Window | Tile Vertically** from the menu bar.

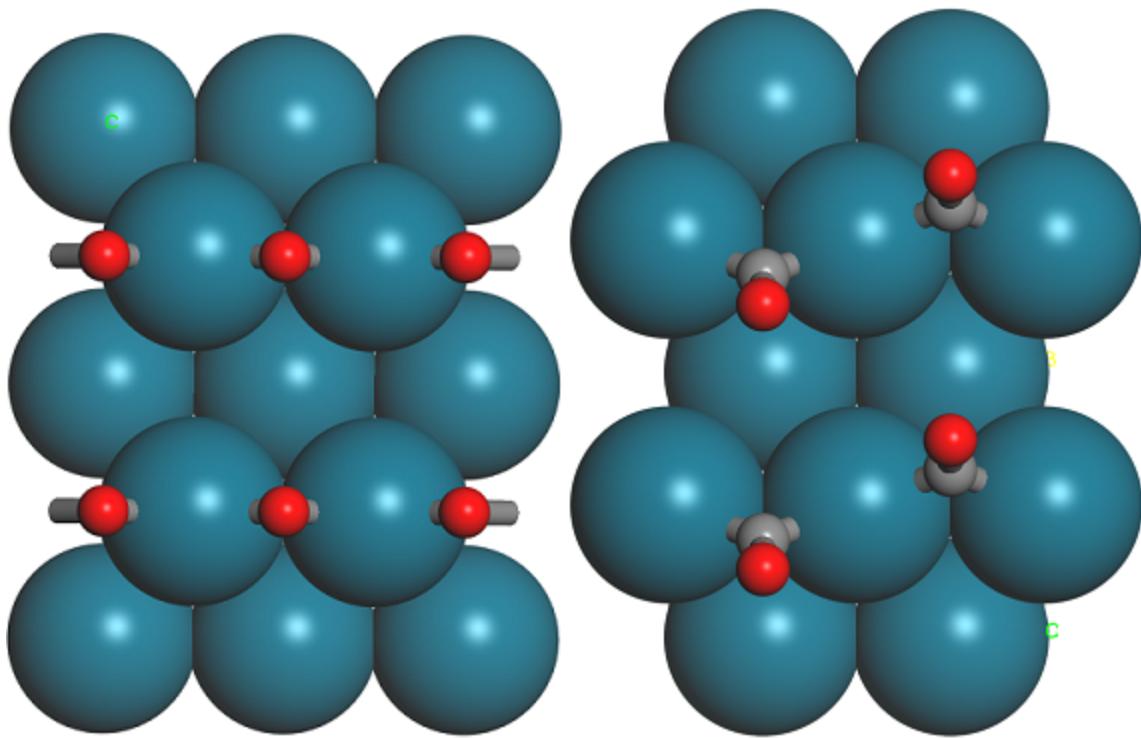
Make **(1x1) CO on Pd (110).xsd** the active document and open the **Display Style** dialog. On the **Lattice** tab set the **Max.** value of the range in the **A** direction to **2.00**, in the **B** direction to **2.00**, and in the **C** direction to **0.90**. Select the **(2x1) CO on Pd(110).xsd** document and change the **Max.** ranges to **2.00** in the **B** direction and **0.90** in the **C** direction.

To better differentiate between surface and adsorbate, you may want to change the Atom display style of all Pd atoms.

For each document, select one atom of each Pd layer. On the **Atom** tab of the **Display Style** dialog, select the **CPK** radio button and change the **CPK scale** to **0.9**. Close the Display Style dialog.

Orient both structures such that the (110) surface rows are facing the same way.

The models should look similar to the images below.



1 × 1 and 1 × 2 supercells of CO on Pd(110)

Take a note of the z-coordinate of the oxygen atoms in either case, they should be approximately 5.4 and 5.3 Å.

4. To add extra information to the STM isosurface

Now you will import the volumetric information into the two structure documents.

Click the **CASTEP** button on the toolbar, then select **Analysis** from the dropdown list to open the CASTEP Analysis dialog. Select **STM profile** from the list.

Open **(1x1) CO on Pd (110).castep** and ensure this is listed as the **Results file**. Set the value of **STM bias** to **1.0** and uncheck the **View isosurface on import** checkbox. Make **(1x1) CO on Pd (110).xsd** the active document and click the **Import** button.

Repeat this for the **(2x1) CO on Pd (110).castep** output document and the **(2x1) CO on Pd (110).xsd** structure. Close the CASTEP Analysis dialog.

The next step will be to create simulated images to model STM experiments in the *constant height mode* for our two structures. This can be achieved by displaying slices through our simulated STM volumetric information.

On the **Volume Visualization** toolbar, click arrow for the **Slice** button and select **Parallel to A & B axis**. Repeat for the other document.

This procedure creates a volume slice that will become our STM images. Scanning tunneling microscopy is usually done well above the actual atoms in any experiment and relies on tunneling. To mimic this setup in our simulation, we have to set our slice relatively high above the oxygen atoms, but also well

CASTEP: Simulating the STM profile of CO on Pd(110)

away from the bottom periodic images of the Pd atoms. A value of 1.0 Å above the O atoms is a good compromise, as long as we remember to compare like with like and set the same value for both simulations.

Select the **Slice**. In the **Properties Explorer**, double-click on the **Slice Position** property and change the **Z** value to **6.4**. Repeat for the other document.

Note: For high-quality STM simulations in research problems, you will have to go at least 3 Å higher above the highest atom and use an accordingly large unit cell height. To achieve a reasonable resolution of your simulations, you may have to significantly increase the plane wave cut

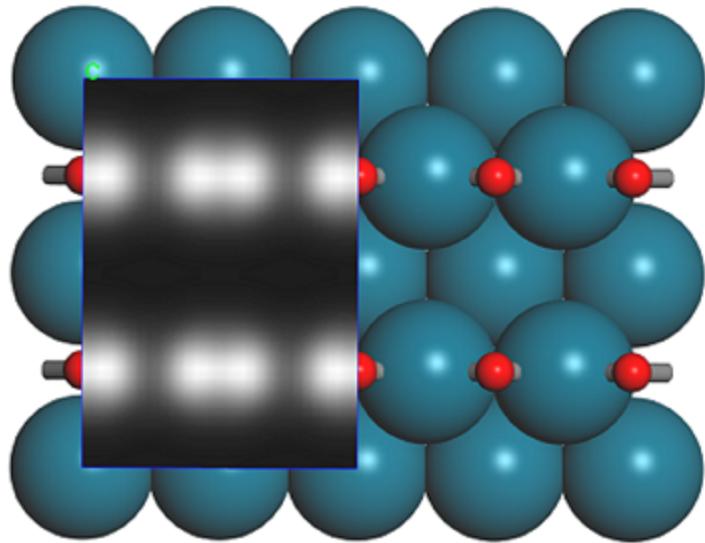
We now have to adjust the color scale to show the relevant information.

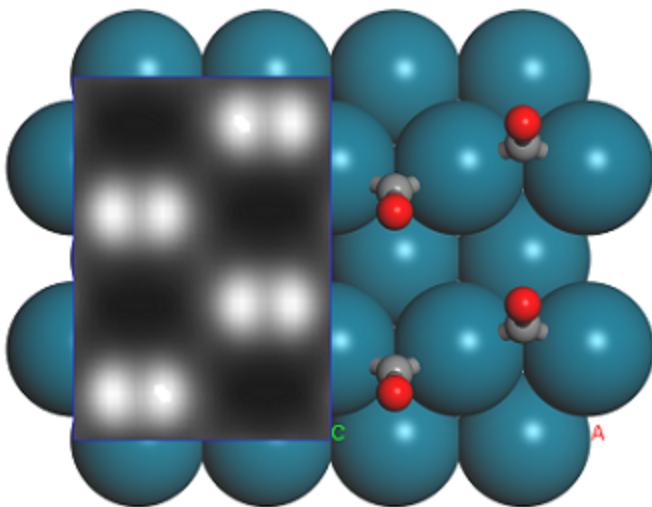
Select the **Slice** and click the **Color Maps** button . Use the **right-arrow**  buttons to set the **From** and **To** values to the **SliceMappedMin** and **SliceMappedMax** values shown in the Properties Explorer respectively. Change the **Spectrum** to **Black-White** and set **Bands** to **128**.

Repeat this for the other document and close the Color Maps dialog.

Note: In complex simulations, an estimate of the relative brightness for different adsorbates may be obtained if the color scales are identical. However, this only works if all the settings in all calculations are absolutely identical.

You may want to change the representation such that a part of the periodic surface is not covered by the slices. Your final results should look similar to this:





1×1 and 1×2 Supercells of CO on Pd(110) with simulated STM profile. The calculated volume slice on the left side of each image corresponds to the predicted STM contrast, while the extended supercell shows the location of the atoms underneath the STM image.

According to this simulation, it should be very easy to distinguish between the 1×1 and 2×1 structures of CO adsorbed on Pd(110) in an STM simulation. The shape of the STM image suggests that the contrast is mainly due to the π -orbitals of the CO molecule, which are aligned in the 1×1 supercell, but offset in the 2×1 structure. The volume slice is constructed from the density due only to orbitals corresponding to the bias, that is, those about 1 eV above the Fermi level. The color corresponds to the total density of states, with the white regions corresponding to the highest DOS.

This is the end of the tutorial.

Predicting the core level spectra of BN from first principles

Purpose: Introduces the core level spectroscopy feature in CASTEP.

Modules: Materials Visualizer, CASTEP

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Density functional theory provides a robust and reliable framework for calculations of core-level spectra. This technique has been applied to numerous systems with good results (Gao et al., [2008](#)). DFT as a method is somewhat limited, and recent developments in core-level spectroscopy calculations using the Bethe-Salpeter equation or time-dependent DFT (or a combination of the two) provide more rigorous approaches for a core level spectrum calculation. In these methods many-body effects, such as the broadening of spectra due to electron-hole lifetime, can be taken into account. While good agreement with experimental results has been achieved, this necessarily comes with a much greater computational burden in comparison to standard ground state DFT calculations.

A systematic observation of core hole effects and a quantitative estimation of the core hole strength in materials can assist in the simulation and interpretation of core level spectra. Applying empirical rules, a core-level spectrum is not likely to be heavily influenced by core-hole effects, so information on the ground electronic structure of a material can be inferred directly from the experimental spectrum. In this case, traditional ground state calculations should predict the main features of experimental results and allow interpretation of the spectrum. If this is not the case, inclusion of the influence of the core hole is essential in the theoretical simulation. Analysis of experimental results should take into account that near-edge fine structure includes influences in the core excitation processes beyond the ground state electronic structure.

For a more general discussion of the core level spectroscopy and details of its implementation see [S.-P. Gao et al., 2008](#) and references.

Introduction

CASTEP can calculate spectroscopic properties of solids that are due to electronic transitions from a core level of an ion to the conduction band (X-ray absorption) and from the valence band to a core level (X-ray emission). This can be used to describe a wide variety of experimental results connected to such processes. Core holes can be created by X-ray or electron incident radiation.

The core level is localized, so core level spectroscopy provides a detailed element-specific picture of the local electronic structure around a given atomic site. There is no contribution from the other atoms in the system, so the electronic states for a specific atom can be investigated.

In the case of anisotropic systems angular-dependent experiments enable the separation of states with different symmetries for the involved orbitals. An important consequence is that symmetry states which result solely from chemical bonding can be studied. For further information see the core level spectroscopy theory topic.

This tutorial illustrates how CASTEP can be used to determine the core level spectra of a material in Materials Studio using quantum mechanical methods. You will learn how to build a crystal structure and

set up a CASTEP energy calculation, followed by core-hole spectroscopy calculations and then analyze the results.

This tutorial covers:

- [Getting started](#)
- [To set up and run a CASTEP calculation](#)
- [To set up the core holes](#)
- [To set up and run a CASTEP calculation with core holes](#)
- [To analyze the results](#)
- [To compare the results with experimental data](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **BN** as the project name, click the **OK** button.

The new project is created with *BN* listed in the Project Explorer. Now you will import the BN structure for your calculation.

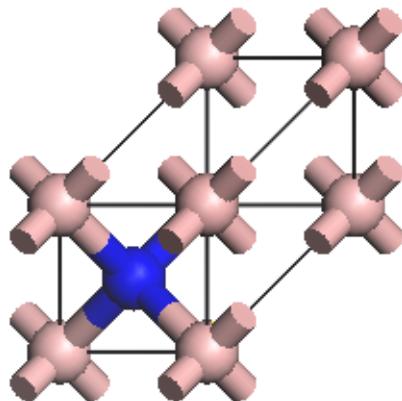
Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to the folder **Structures/semiconductors/** and select **BN.xsd**. Click the **Open** button.

The crystal structure in the 3D Viewer is the conventional unit cell containing 8 atoms, which shows the cubic symmetry of the lattice. CASTEP uses the full symmetry of the lattice if any exists, so the primitive lattice, containing 2 atoms per unit cell, can be used. The charge density, bond distances, and total energy per atom will be the same no matter how the unit cell is defined, so by using fewer atoms in the unit cell, the computation time is decreased.

Note: The only time that care is needed is when a spin-polarized calculation is performed on a magnetic system, where the charge density spin wave has a period which is a multiple of the primitive unit cell.

Choose **Build | Symmetry | Primitive Cell** from the menu bar.

The 3D Viewer displays the primitive cell.

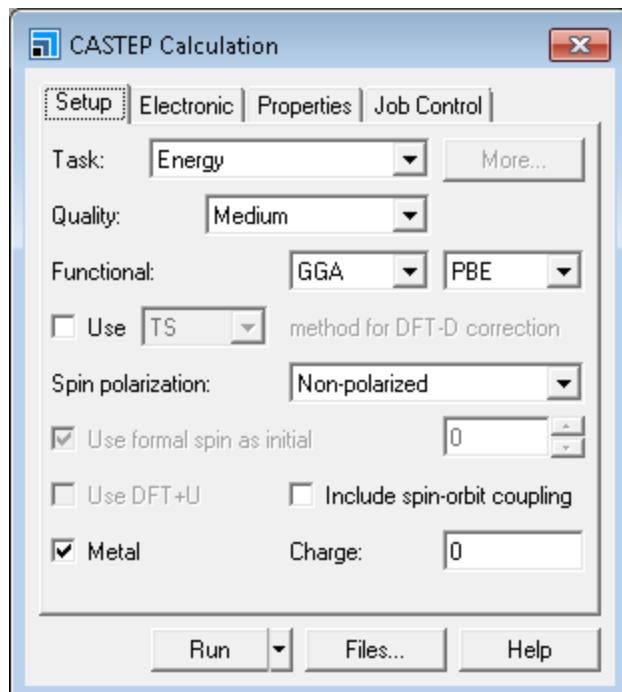


BN primitive cell

2. To set up and run a CASTEP calculation

Click the **CASTEP** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

On the **Setup** tab of the CASTEP Calculation dialog, ensure the **Task** is set to **Energy** and the **Quality** is set to **Medium**.

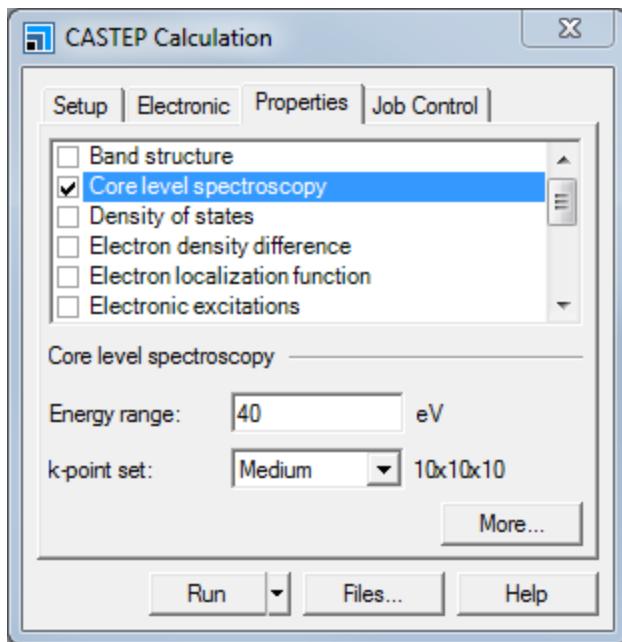
If you change the quality, the other parameters change to reflect this. Next, you will specify the electronic options for the calculation.

On the **Electronic** tab, select **OTFG ultrasoft** from the **Pseudopotentials** dropdown list.

On the fly (OTFG) pseudopotentials are required to compute the core level spectra. If you choose a different type of pseudopotential, the core level spectroscopy calculation cannot be performed.

Next, you will specify which properties you want to calculate.

On the **Properties** tab, check the **Core level spectroscopy** checkbox and set the **Energy range** to **40 eV**.



CASTEP Calculation dialog, Properties tab

An energy range of 40 eV for the core level spectroscopy will allow access to energies up to 40 eV above the Fermi level.

On the **Job Control** tab click the **More...** button to open the CASTEP Job Control Options dialog. Change the **Update interval** to **30.0 s** and close the dialog.

If you wish to run the calculation on a remote server, you can specify this on the Job Control tab.

Click the **Run** button and close the dialog.

After a few seconds, a new folder is displayed in the Project Explorer and this will contain all the results from the calculation. The Job Explorer is displayed, which contains information about the status of the job.

When the job finishes, the files are transferred back to the client and this can take some time due to the size of certain files. When the results are transferred, you should have several documents, among them:

- BN.xsd - the crystal structure
- BN.castep - an output file from the CASTEP energy calculation
- BN_EELS.castep - an output file from the CASTEP core level spectroscopy calculation
- BN.param and BN_EELS.param - input information, saving the input files before proceeding with the calculation creates these files and gives you the opportunity to edit them

You will find these files in the Project Explorer in a folder called BN CASTEP Energy once the calculation completes.

3. To set up the core holes

To simulate core hole effects you should create a supercell of sufficiently large size, so that artificial interactions between periodic images of the atoms containing core holes are reduced. However, large supercells are very computationally expensive, so a supercell of 32 atoms (6 Å) is used to strike a balance in this tutorial.

Note: For investigative experiments, where greater computational resources are available, larger supercells should be used in order to obtain more accurate results.

Now you will construct a supercell from the primitive cell by redefining the extent of the lattice.

Make **BN.xsd** in the project root the active document.

Select **Build | Symmetry | Redefine Lattice** from the menu bar to open the Redefine Lattice dialog. Enter **-3 1 1** for **A**, **-1 -1 3** for **B**, and **1 1 1** for **C**. Click the **Redefine** button and close the dialog.

Select **File| Save As...** from the menu bar and save the 3D Atomistic document as **BN_N_hole.xsd**. Repeat this to save the document as **BN_B_hole.xsd**.

Choose **Window | Close All** from the menu bar, then double-click on **BN_N_hole.xsd** in the Project Explorer.

You will create a core hole on a nitrogen atom and ensure that the symmetry is properly imposed.

Select any **N** atom in the supercell.

Select **Modify | Electronic Configuration** from the menu bar to open the Electronic Configuration dialog. On the **Core Hole** tab select **1s** from the **Shell** dropdown list and close the dialog.

Choose **Build | Symmetry | Find Symmetry...** from the menu bar to open the Find Symmetry dialog. On the **Options** tab check the **CoreShellWithHole** from the list of properties. On the **Find** tab click the **Find Symmetry** button, then the **Impose Symmetry** button. Close the dialog.

Now you should create a core hole on a boron atom and ensure that the symmetry is properly specified.

Repeat these steps for **BN_B_hole.xsd**.

Select **File | Save Project** from the menu bar.

4. To set up and run a CASTEP calculation with core holes

You will repeat the previous CASTEP energy calculation determining the core level spectra, but this time taking account of the B and N core holes.

Make **BN_N_hole.xsd** the active document.

Open the **CASTEP Calculation** dialog, on the **Electronic** tab check the **Use core hole** checkbox.

Click the **Run** button, click the **Yes** button to convert to a primitive cell and close the CASTEP Calculation dialog.

When the job finishes, the files are transferred back to the client.

Make **BN_B_hole.xsd** the active document and click the **Run** button on the CASTEP Calculation dialog again.

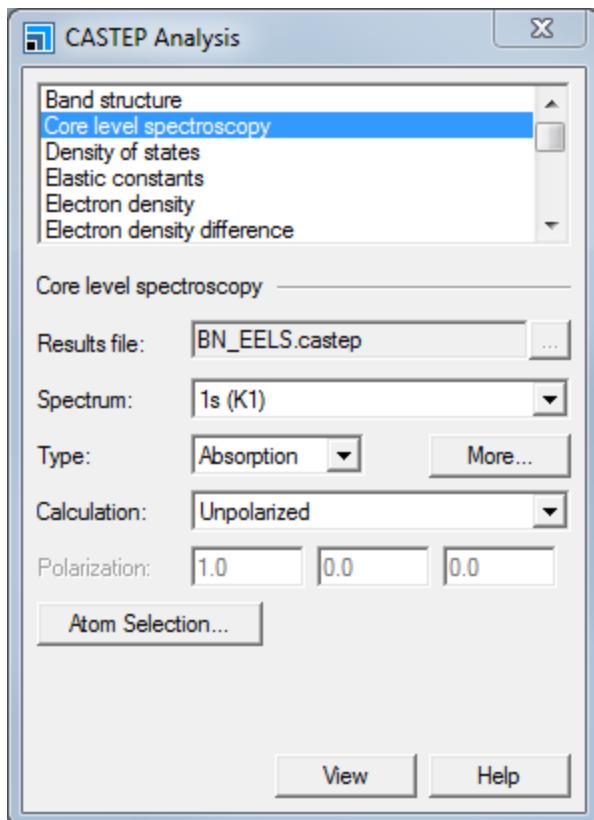
Choose **File | Save Project** from the menu bar, followed by **Window | Close All**.

5. To analyze the results

Now you can analyze and visualize the results of the CASTEP calculation.

Make **BN CASTEP Energy/BN.xsd** the active document and select the **N** atom.

Choose **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog.



CASTEP Analysis dialog, Core level spectroscopy selection

Select **Core level spectroscopy** and ensure that **BN_EELS.castep** is the specified **Results file**. Select **1s (K1)** from the **Spectrum** dropdown list and choose **Absorption** for the **Type**. Click the **More...** button to open the CASTEP EELS Analysis Options dialog. Set the **Instrumental smearing** to **0.8 eV** and close the dialog.

The **1s[K1]** spectrum corresponds to the core level spectrum for a core electron in the **1s** orbital. An absorption spectrum simulates the required energy absorbed during the creation of the core hole; an emission spectrum would reflect the energy of an X-ray photon emitted during relaxation of the core hole back to the ground state. The smearing applied by CASTEP is a Gaussian broadening of the calculated results. The value used in this tutorial is selected to correspond to the resolution of the

CASTEP: Predicting the core level spectra of BN from first principles

experimental spectra (Jaouen et al., [1995](#)). For a cubic system, such as BN, both polarized and unpolarized incident radiation will produce the same core level spectrum.

Click the **View** button.

A new core level spectrum for nitrogen in BN is displayed in a chart viewer. Now create the equivalent spectrum for boron.

Select any **B** atom in **BN CASTEP Energy/BN.xsd** and, on the CASTEP Analysis dialog, click the **View** button.

The core level spectrum for boron in BN is displayed. The B and N core level spectra taking into account a 1s core hole can also be created. To ensure that the core hole is used you need to select the correct atom.

Make **BN_N_hole CASTEP Energy/BN_N_hole.xsd** the active document.

Click the **Atom Selection...** button on the CASTEP Analysis dialog to open the Atom Selection dialog. Choose **Contains Core Hole** from the **Select by Property** dropdown list and click the **Select** button.

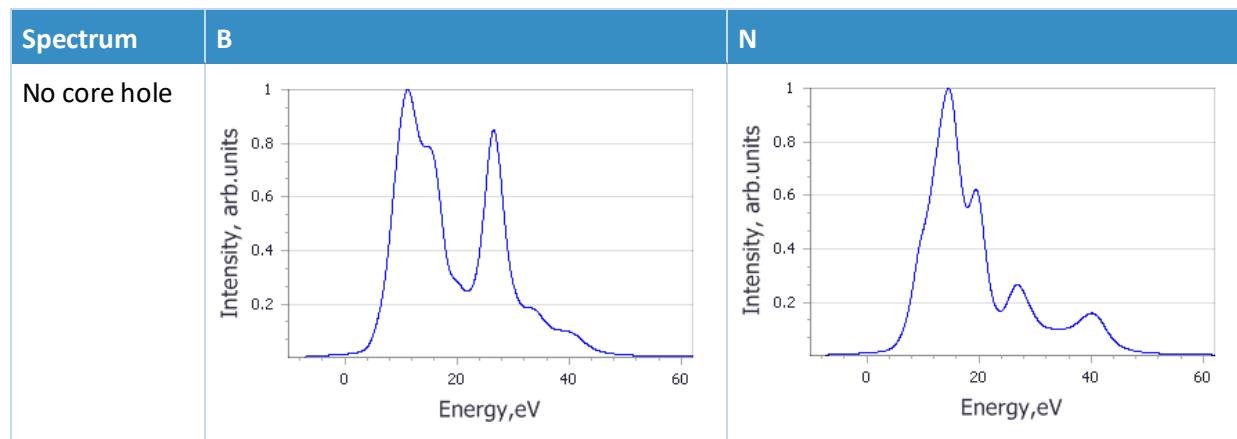
You can now view the core level spectrum for the nitrogen atom with the 1s core hole.

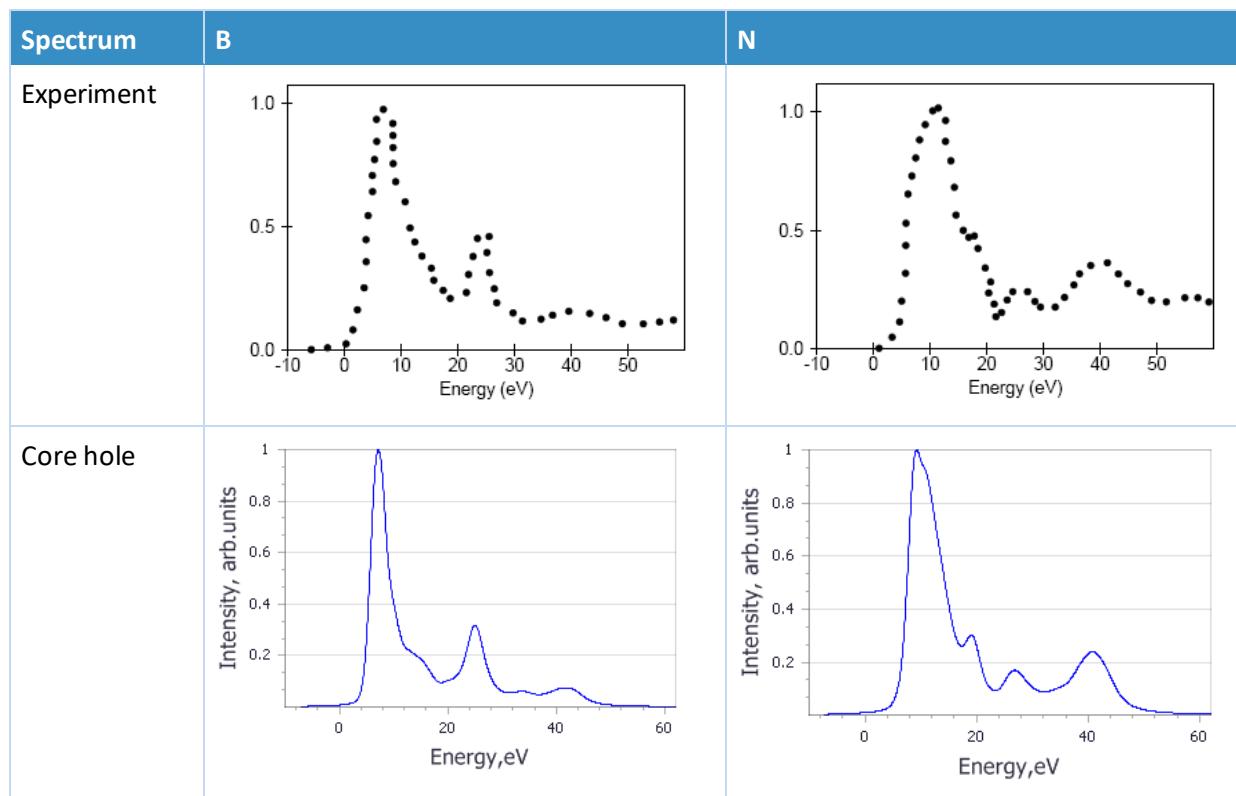
On the CASTEP Analysis dialog, click the **View** button.

Repeat the core hole atom selection and CASTEP analysis for **BN_B_hole CASTEP Energy/BN_B_hole.xsd**.

6. To compare the results with experimental data

Analysis of the core level spectroscopy properties of BN with and without consideration of a core hole effects has provided you with four spectra, which can be compared with experimentally collected data (Jaouen et al., [1995](#)).





This is the end of the tutorial.

References

Gao, S-P.; Pickard, C.J.; Payne, M.C.; Zhu, J.; Yuan, J. "Theory of core-hole effects in 1s core-level spectroscopy of the first-row elements", *Phys. Rev. B*, **77**, 115122 (2008).

Jaouen et al., *Microsc. Microanal. Microstruct.*, **6**, 127 (1995)

Chapter 6: CCDC tutorials

The following tutorials illustrate how to utilize CCDC's capabilities.

- [Using the CSD together with Materials Studio](#)
- [Crystal identification using CCDC and experimental powder diffraction](#)
- [Analyzing hydrogen bonds in potential polymorphs of hydantoin](#)

Using the CSD together with Materials Studio

Purpose: Illustrates the use of Materials Studio in conjunction with the CSD.

Modules: Materials Visualizer, Polymorph, VAMP, Forceite, COMPASS

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial

Introduction

The Cambridge Structural Database (CSD) is a repository of small molecule crystal structures. It is the principal product of the Cambridge Crystallographic Data Centre (CCDC; <https://www.ccdc.cam.ac.uk/>). The CSD records bibliographic, chemical, and crystallographic information for organic molecules and metal-organic compounds.

This tutorial illustrates how to use information from the CSD to add value to results from Materials Studio calculations. This tutorial predicts polymorphs of a small molecule compound and compares them to known crystal structures of this compound registered in the CSD.

Notes:

- This tutorial requires a license for the CSD.
- The results described in this tutorial were obtained using CCDC v.5.31, 2010 Release. If you have a different version of CCDC, you might observe numerically different results.

This tutorial covers:

- [Getting started](#)
- [To sketch and optimize the structure](#)
- [To predict polymorphs and identify known experimental structures](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

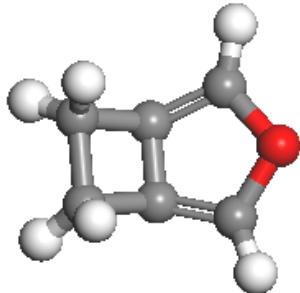
Open the **New Project** dialog and enter **CSD** as the project name, click **OK**.

This creates a new project with *CSD* listed in the Project Explorer.

2. To sketch and optimize the structure

This tutorial uses Polymorph to generate a list of potential polymorphs of 3-oxabicyclo(3.2.0)hepta-1,4-diene (OHD) in the P 21/c space-group. After generating this list, you can verify that one of the low energy packing arrangements indeed corresponds to an experimentally known crystal structure.

In the Project Explorer, right-click **CSD** and select **New | 3D Atomistic Document**. Change the name of the new structure document to **OHD-mol**. Use the Sketch tools to sketch an OHD molecule shown below.



Molecular structure of OHD

Next, optimize the molecule using VAMP.

Select **Modules | VAMP | Calculation** from the menu bar to open the VAMP Calculation dialog. On the **Setup** tab, change the **Task** to **Geometry Optimization**. Click **Run** and close the dialog.

When the calculation has finished, save the project and close all windows.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To predict polymorphs and identify known experimental structures

Next, set up the Polymorph prediction calculation.

In the Project explorer, open **OHD-mol VAMP GeomOpt/OHD-mol.xsd**. Select **Modules | Polymorph | Calculation** from the menu bar to open the Polymorph Calculation dialog. On the **Setup** tab, click **Assign** to make the OHD molecule a motion group.

Confirm that the **Task** is **Prediction** and click **More...** to open the Polymorph Prediction dialog. Select both the **Clustering** checkboxes and close the dialog.

This includes pre-clustering steps in the prediction sequence both before and after the geometry optimization stage. Clustering before the geometry optimization requires fewer minimizations afterward, so the calculation takes less time.

On the **Energy** tab of the Polymorph Calculation dialog, change the **Forcefield** to **COMPASSIII**. On the **Space Groups** tab, clear all space groups except for **P21/C**. Click **Run** and close the dialog.

While the calculation is running, you can query the CSD against the OHD-mol structure you sketched earlier. First, close all windows.

Select **File | Save Project** from the menu bar followed by **Window | Close All**.

Open the **OHD-mol.xsd** document you created earlier.

In the Project Explorer, double-click the **OHD-mol.xsd** document in the root of the project.

Select **Build | Bonds** and select **Convert representation to Kekule**. Click **Calculate** and close the dialog.

Select **Modules | CCDC | ConQuest Search** from the menu bar to open the ConQuest Search dialog.

On the **Setup** tab, change the **Task** to **Substructure search** and click **Search** and close the dialog.

This returns the results in a study table named **OHD-mol.std**. The search retrieves two structures, one in the **Pbca** and one in the **P 21/c** space group. Now extract the **P 21/c** structure from the study table and optimize this structure using the same forcefield as used in the polymorph prediction sequence. This is useful to account for slight deviations between experimental and predicted lattice and structural parameters.

In the **OHD-mol.std** study table, in the **Structures** column double-click the entry in the row that corresponds to the **P 21/c** space group.

This opens a 3D representation of the structure in a *Detail View*. To save the structure, copy and paste it into a new 3D Atomistic document.

Ensure that **OHD-mol Detail View** is the active document, press **CTRL+ C**. In the Project Explorer, right-click the project root and select **New | 3D Atomistic Document**, then press **CTRL + V**. Select **File | Save As...** from the menu bar to open the Save As dialog. Type **OHD P21c** as the filename and click **Save**.

Now use Forcite to optimize this structure.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog. On the **Setup** tab, change the **Task** to **Geometry Optimization** and click **More...** to open the Forcite Geometry Optimization dialog. Select the **Optimize cell** checkbox and close the dialog.

On the **Energy** tab, change the **Forcefield** to **COMPASSIII**. Verify the selection of **Ewald** for both **Electrostatic** and **van der Waals** in the **Summation method** section. Click **Run** and close the dialog.

Once the Polymorph calculation finishes, collect the results of the run into a study table using the analysis tool of Polymorph.

In the Project Explorer, navigate to **OHD-mol VAMP GeomOpt/OHD-mol PMP Predict**. Select **Modules | Polymorph | Analysis** from the menu bar. Select **OHD-mol P21-C.xtd** on the Insert Polymorph Results File dialog and click **Open**.

This creates a study table called **Polymorph Analysis.std**, containing the polymorphs.

Select column A containing the structures and click **Models**  on the **QSAR Models** toolbar. Select **Crystal Similarity Measure** from the **Models** dialog and double-click this model to open the Model Editor - Crystal Similarity Measure dialog.

On the **Inputs** tab, click the cell for **Value** in the **Reference crystal** row, select **OHD P21c Forcite GeomOpt/OHD P21c.xsd** from the dropdown list. Click **Save** and close the dialog.

On the **Models** dialog make sure that **Crystal similarity** remains selected, click **Run** and close the dialog.

When the calculation has finished, this adds a new column labeled *Crystal Similarity Measure* to the study table. Within a range of 0.2–0.3 kcal/mol from the lowest energy structure proposed by the Polymorph prediction sequence, you can find the equivalent structures with a similarity of about 0.1.

Tip: If there is no structure within 0.3 kcal/mol of the lowest energy with a similarity of 0.1, rerun the Polymorph prediction steps. Polymorph prediction is a random process, so you might have to run the prediction sequence more than once to ensure identification of all potential crystal structures.

Sort the results according to the crystal similarity measure, to confirm that there are no other structures even closer to the experimental structure.

In the study table, select the column labeled **Crystal Similarity Measure**. Click **Sort Ascending**  on the **Study Table Viewer** toolbar.

The second lowest energy structure has by far the lowest crystal similarity score. You can verify that the predicted structure is equivalent to the experimental structure by generating simulated powder X-ray diffraction patterns using the Reflex module or visually inspecting the packing motifs and each cell volume.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Crystal identification using CCDC and experimental powder diffraction

Purpose: Illustrates the use of Materials Studio in conjunction with the CSD.

Modules: Materials Visualizer, Reflex, QSAR

Time:  

Prerequisites: Sketching simple molecules Visualizer Tutorial

Introduction

The Cambridge Structural Database (CSD) is a repository of small molecule crystal structures. It is the principal product of the Cambridge Crystallographic Data Centre (CCDC; <https://www.ccdc.cam.ac.uk/>). The CSD records bibliographic, chemical, and crystallographic information for organic molecules and metal-organic compounds.

This tutorial illustrates how information from the CSD can be used to add value to results from Materials Studio calculations. An experimental powder X-ray spectrum is compared to automatically generated spectra from compounds registered in the CSD that contain the chemical name of the experimental structure.

Note: This tutorial requires a license for the CSD.

Note: The results described in this tutorial were obtained using CSD Portfolio v.5.31, 2010 Release. If you have a different version of CSD Portfolio you may observe numerically different results.

This tutorial covers:

- [Getting started](#)
- [To search the ConQuest database](#)
- [To compare an experimental powder X-Ray diffraction pattern to structures available in the CSD](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **crystal_ID** as the project name, click the **OK** button.

The new project is created with **crystal_ID** listed in the Project Explorer.

2. To search the ConQuest database

In this section you will compare an experimental powder X-ray diffraction (PXRD) pattern to structures registered in the CSD using an automatic powder comparison algorithm based on the Reflex module. This allows you to check whether a compound crystallized in a lab corresponds to a known crystalline lattice.

First you will load the experimental spectrum.

Click on the **crystal_ID** project root in the Project Explorer. Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Examples/Reflex/Experimental Data**, select **Chart Files** from the file types dropdown list for the **File name**. Choose **indigo_1.3cam** and click the **Open** button.

The experimental spectrum of a crystalline form of the indigo pigment is loaded. The automatic powder comparison tool is unable to fit background functions. Therefore you will have to subtract a fitted background. You will also have to estimate the full width at half maximum (FWHM) of the peaks as this is later needed as an input.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. On the **Pattern Preparation** tab, change the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document is created, called **indigo_1 (Background Removed).xcd**. Zoom in to the first peak at 10.5 and determine the FWHM which is roughly 0.4.

Now you will query the CSD.

Select **Modules | CCDC | ConQuest Search** from the menu bar to open the ConQuest Search dialog.

On the **Setup** tab, change the **Task** to **Chemical name search** and enter **indigo** as the **Chemical name**. Click the **Search** button and close the dialog.

When the search finishes, a study table named **indigo.std** is returned containing the search results.

3. To compare an experimental powder X-Ray diffraction pattern to structures available in the CSD

You will now use the automatic powder comparison model to find the closest match between the experimental PXRD and the structures in the CSD.

Ensure that **indigo.std** is the active document, select the column labeled **Structures**. Click the **Models** button  on the **QSAR Models** toolbar. Double-click the row for **Figure of merit (Powder Comparison)** to edit the input to this model.

On the Model Editor - Powder Comparison dialog select the **Inputs** tab and change the **Value** column for **Experimental data** to **indigo_1 (Background Removed).xcd**. Change **Max 2-Theta** to **80** and **Profile FWHM U** and **Profile FWHM V** to **0**. Set **Profile FWHM W** to **0.16**.

Note: The square-root of the profile parameter W describes the FWHM independent from 2-Theta, while U and V describe its variation across the 2-Theta range.

Change **Profile NA** and **Profile NB** to **0**. Click the **Save** button and close this dialog. Click the **Run** button and close the Models dialog.

When the calculation has finished, three columns are added to the study table, one of them containing R_{wp} factors. You will sort the entries in the study table according to R_{wp} to determine the most likely match between the experimental PXRD and the entries in the CSD.

Ensure that **indigo.std** is the active document, select the column labeled **Rwp (Powder Comparison)** and click the **Sort Ascending** button  on the **Study Table Viewer** toolbar.

The structure with the lowest R_{wp} (which should be around 32) has the CSD Refcode "INDIGO02". To confirm that this structure actually corresponds to the experimental powder X-ray diffraction pattern you will carry out a full Pawley refinement.

Double-click the icon for **INDIGO02** in the **Structure** column of **indigo.std** to open the Detail View. Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog. On the **Setup** tab change **2-Theta Max** to **80** in the **Range** section.

On the **Exp. Data** tab select the row with **indigo_1.xcd** in the **Document** column and **1** in the **Pattern** column.

On the **Pattern** tab check all boxes in the **Refine** column. On the **Lattice** tab check all boxes in the **Refine** section. On the **Display** tab check the **Display simulation/experiment difference** checkbox and click the **Refine** button. When the refinement process completes **close** the dialog.

The resulting R_{wp} should be between 9 and 12. You can further lower the R_{wp} by including asymmetry corrections and/or crystalline size effects. But for the purpose of identifying that the experimental structure is indeed the previously registered form, the current R_{wp} value ensures this finding.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Analyzing hydrogen bonds in potential polymorphs of Hydantoin

Purpose: Illustrates how to categorize Polymorph results based on hydrogen bond motifs.

Modules: Materials Visualizer, CCDC, Polymorph (optional), DMol³ (optional)

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Polymorphism in crystals of organic molecules poses challenges, as well as opportunities, in solidification applications, pharmaceutical development, and the fine and specialty chemicals industries. Depending on the molecular arrangement, properties such as solubility, bioavailability, and stability can be drastically influenced. One way to characterize and categorize differences in packing is by analyzing the hydrogen bond topologies, or motifs. Figure 1 gives a schematic overview of some of the common types of hydrogen bond motifs.

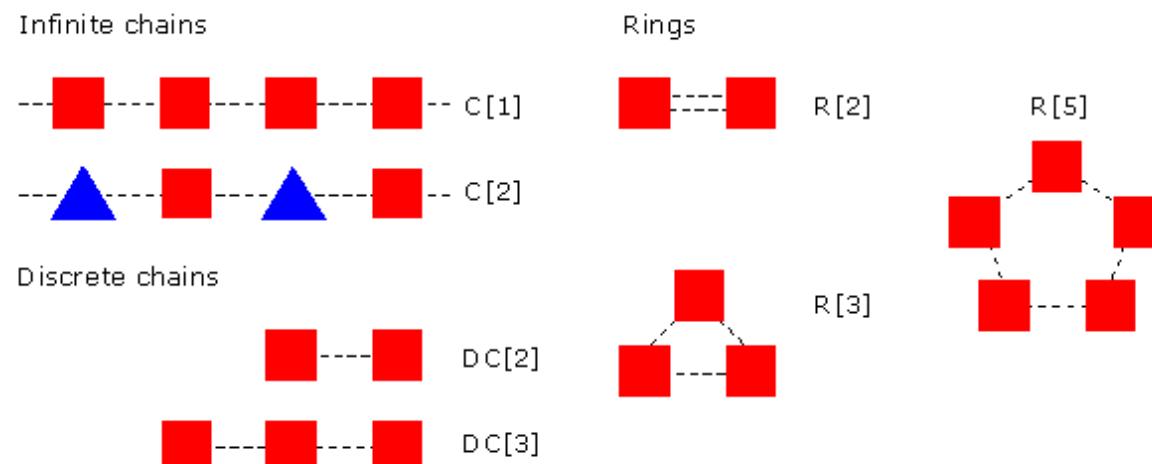


Figure 1. Schematic representation of some common hydrogen bond motifs

Motifs are annotated in Materials Studio as **nM[s]**, where **M** labels the motif type, **n** is the number of motifs of type **M**, and **s** is the size of the motif of type **M**. CCDC distinguishes the following motif types, **M**:

- **R** = ring
- **C** = infinite chain
- **DC** = discrete chain
- **S** = intramolecular contact
- **M** = intermolecular contact

This tutorial discusses the basic steps needed to generate motif information from Polymorph calculations. First, the molecule is characterized in terms of functional groups that represent key features of the molecular architecture. Next, hydrogen bond donors and acceptors are assigned within

these functional groups. When the molecule has been prepared for analysis, the CCDC module queries the CSD for compounds containing the defined functional groups. The resulting matches are analyzed in terms of their motif information. Finally, a scoring step analyzes the results of a Polymorph calculation and compares the motif information of each suggested polymorph against the results of the CSD query.

Note: Motif makes use of CCDC's CSD ([Allen et al., 2002](#)) and Mercury ([Macrae et al., 2006](#)) functionality. These tools are directly available from the CCDC.

Introduction

Hydantoin was one of the molecules used in the third CCDC blind test for polymorph prediction ([Day et al., 2005](#)). When Polymorph is used to predict the packing of hydantoin, the experimentally observed crystal structure is predicted along with two additional structures with lower lattice energies. In this tutorial you will use the CCDC Motif Search to generate a statistical measure of how close the predicted hydrogen bond motifs are to the known structure.

This tutorial covers:

- [Getting started](#)
- [To sketch the molecular structure of hydantoin](#)
- [To prepare the structure and define functional groups and donor/acceptor sites](#)
- [To query the CSD for related structures](#)
- [To assign motif information to Polymorph output and score the top ranked Polymorph structures](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

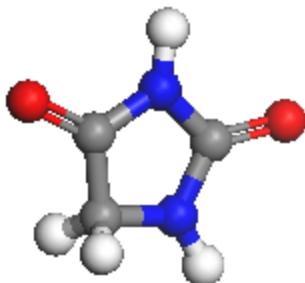
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **hydantoin** as the project name, click the **OK** button.

The new project is created with *hydantoin* listed in the Project Explorer.

2. To sketch the molecular structure of hydantoin

In the Project Explorer, right-click on the project root and select **New | 3D Atomistic Document**. Change the name of the new structure document to **hydantoin-mol**. Use the Sketch tools to sketch a hydantoin molecule (shown below) and clean the structure by clicking the **Clean** button .

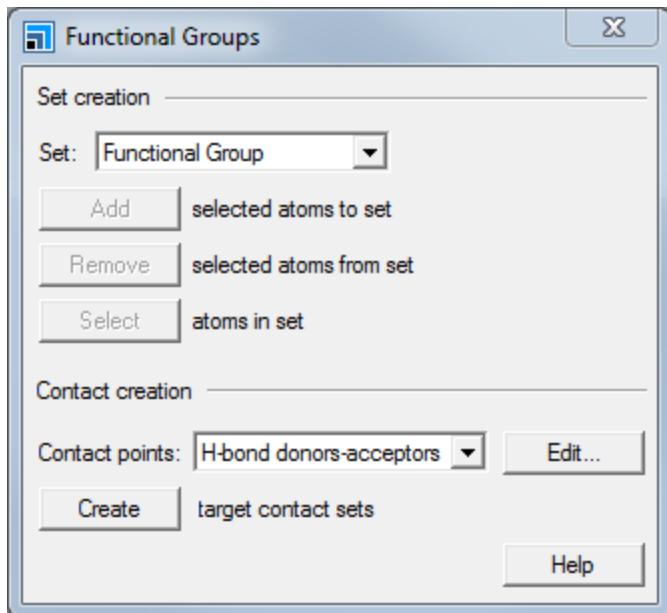


Molecular structure of hydantoin

3. To prepare the structure and define functional groups and donor/acceptor sites

In this section you will use the *Functional Groups* dialog to define functional groups and donor/acceptor sites. Functional groups are essential to define what constitutes a similar structure when querying the CSD.

Select **Modules** | **CCDC** | **Functional Groups** from the menu bar or click the  button on the **Modules** toolbar and select **Functional Groups** to open the Functional Groups dialog.

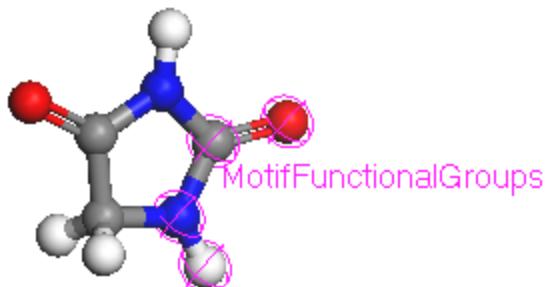


Functional Groups dialog

The hydantoin molecule contains two equivalent donor and acceptor sites. To run a meaningful CCDC Motif Search you should select a functional group that contains both the donor (nitrogen) and the acceptor (oxygen) sites. The smallest functional group that fulfills this requirement is O=C-N, however the O=C-NH-C fragment captures more of the molecular topology. You could also select the entire molecule as a functional group. The type of functional group you define will control what results are retrieved from the CSD and depends on the intended application of the search. For the purpose of this tutorial you will try to retrieve as many relevant structures as possible to maximize the statistical relevance of the scoring function to rank Polymorph results.

Select an **O=C-NH** fragment in **hydantoin-mol.xsd**. On the **Functional Groups** dialog, make sure that **Functional Group** is selected as the **Set**. Click the **Add selected atoms to set** button and click anywhere in the 3D Viewer to deselect everything.

Your hydantoin molecule should look like the one below:



Functional groups in hydantoin

Next, you will define the donor and acceptor sites.

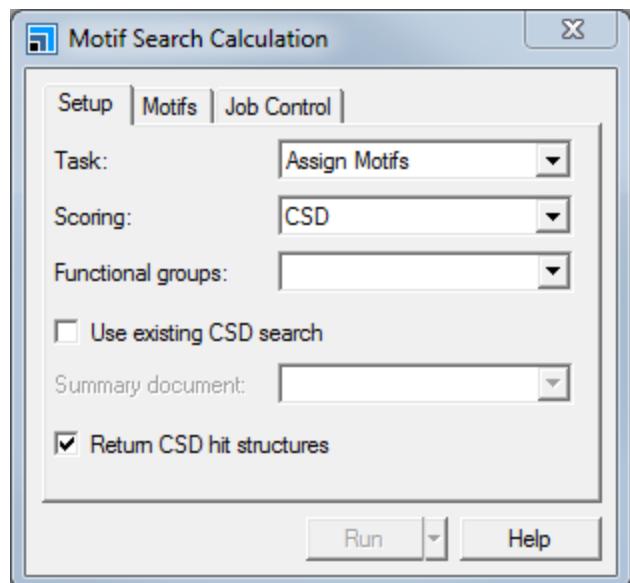
On the **Functional Groups** dialog change the **Set to Acceptors**. Select the **oxygen** atom in your defined functional group and click the **Add selected atoms to set** button.

Change the **Set to Donors**, select the **nitrogen** atom in your functional group and click the **Add selected atoms to set** button. Close the dialog.

4. To query the CSD for related structures

In this section you will query the CSD for structures containing the defined functional groups and extract the connectivity information between the acceptor and donor sites.

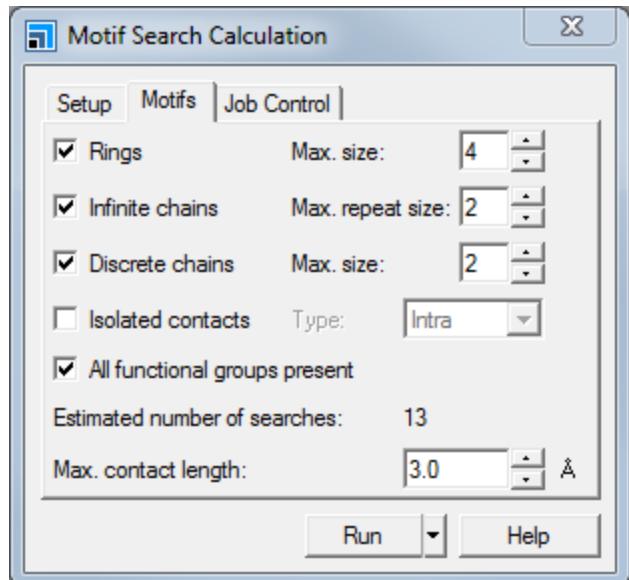
Select **Modules | CCDC | Motif Search** from the menu bar to open the **Motif Search Calculation** dialog.



Motif Search Calculation dialog, Setup tab

On **Setup** tab change the **Task** to **CSD Search** and make sure that the **Return CSD hit structures** checkbox is checked.

On the **Motifs** tab check the **Rings**, **Infinite chains**, **Discrete chains**, and **All functional groups present** checkboxes. Set the **Max. size** for **Rings** to **4** and the **Max. repeat size** for **Infinite chains** and **Max. size** for **Discrete chains** both to **2**. Set the **Max. contact length** to **3.0 Å**.



Motif Search Calculation dialog, Motifs tab

On the **Job Control** tab select an appropriate server from the **Gateway location** dropdown list. Click the **Run** button.

When the query has finished, results will be automatically downloaded from the server and stored in a folder named *hydantoin-mol Motif Search*. The matching structures together with their motif formulae are collected in a study table document. A summary document *hydantoin-mol Summary.txt* is also created. In the next section you will use this summary document as an input to the scoring task when comparing the Polymorph predicted structures to the CSD hit structures.

5. To assign motif information to Polymorph output and score the top ranked Polymorph structures

Since you will not run a polymorph prediction sequence in this tutorial you will import results from a previous prediction sequence into this project. If you would like to try to predict the packing arrangements yourself, it is suggested that you perform a DMol³ GGA-PBE optimization of hydantoin to determine the ESP charges and then to run Polymorph using these charges together with the Dreiding force-field. For more details on how to run polymorph prediction sequences please refer to the Polymorph tutorials section.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to **Examples/StudyTables**, choose **All Files** file types dropdown list for the **File name**, and select **M8_all_Polymorph.std**. Click the **Open** button.

Next, you will set the input parameters to assign and score the predicted packing arrangements. Note that to run the assignment/scoring the study table document containing the predicted structures has to be in focus and the document containing the fragment/contact point information needs to be selected in the interface.

On the **Motif Search Calculation** dialog, change the **Task** to **Assign Motifs** and select **CSD** from the **Scoring** dropdown list. Select **hydantoin-mol.xsd** from the **Functional groups** dropdown list. Check the **Use existing CSD search** checkbox and select the **hydantoin-mol Summary.txt** file from the **Summary document** dropdown list.

On the **Motifs** tab make sure that the settings are the same as in the previous section. Click the **Run** button and close the dialog.

Once the calculation finishes, results are returned. The main results document is the study table called **M8_all_Polymorph.std** in the **M8_all_Polymorph Motif Assign** folder. It lists the original structures along with their motif formulas. The first two structures share the same motif formula, **R[3] C[1] C[2]** and have the lowest energies calculated by Polymorph. The motif formula of the third and fourth structures is **R[2]**. Inspecting the *Matching score* and *Averaged score* indicates that the motif of the third and fourth structures is significantly more representative of previously known structures that contain the same fragment. Note that the third structure is the experimentally known structure.

	A	B	C	E	J	K	L	M	N	O	P
	Structures	Space group name	Space group number		Cell volume	Motif Formula	Rings	Chains	Matching score	Averaged score	Scoring
1	M8Dreding P 21/c P21-C - 1		14	418.51500000	R[3] C[1] C[2]		1	2	4.284323e-004	0.01998233	
2	M8Dreding P 21/c P21-C - 2		14	417.31400000	R[3] C[1] C[2]		1	2	4.284323e-004	0.01998233	
3	M8Dreding P 21/c P21-C - 3		14	414.80000000	R[2]		1	0	0.01688413	0.04687583	
4	M8Dreding C 2/c C2-C - 1		15	833.59600000	R[2]		1	0	0.01688413	0.04687583	
5	M8Dreding P 21 21 21 P212121 -		19	426.56400000	R[3] C[1] C[2]		1	2	4.284323e-004	0.01998233	
6	M8Dreding C 2/c C2-C - 1		15	844.52500000	R[2] C[1]		1	1	0.00218111	0.05781841	

Results from scoring the top 6 Polymorph predicted structures using Motif Search

Note: The values in the study table may differ depending on your version of CSD System Software.

Double-click in the **Structure** cells for the third and fourth structures, with the **R[2]** motif formula.

A new 3D Viewer opens, containing the Polymorph predicted unit cells for the structure, the assigned hydrogen bonding motifs are displayed as pink dashed lines.

The scoring values obtained from the CCDC Motif search calculation indicate that the third and fourth structures are candidates for further investigation and should not be discounted because there are other structures with lower energies. For example, X-ray powder diffraction patterns could be simulated and compared with experimental patterns using the Reflex module.

This is the end of this tutorial.

References:

F. H. Allen, *Acta Cryst. B*, **58**, 380 (2002)

[**CCDC: Analyzing hydrogen bonds in potential polymorphs of hydantoin**](#)

C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, **39**, 453 (2006).

G. M. Day, W. D. S. Motherwell, H. L. Ammon, S. X. M. Boerrigter, R. G. Della Valle, E. Venuti, A. Dzyabchenko, J. D. Dunitz, B. Schweizer, B. P. van Eijck, P. Erk, J. C. Facelli, V. E. Bazterra, M. B. Ferraro, D.W. M. Hofmann, F. J. J. Leusen, C. Liang, C. C. Pantelides, P. G. Karamertzanis, S. L. Price, T. C. Lewis, H. Nowell, A. Torrisi, H. A. Scheraga, Y. A. Arnautova, M. U. Schmidt and P. Verwer, *Acta Crys. B*, **61**, 511 (2005).

Chapter 7: Conformers tutorials

The following tutorial illustrates how to utilize Conformers' capabilities.

Using Conformers to probe geometry-energy relationships

Purpose: Introduces the Conformers module for searching low energy conformations and probing conformation-property relationships.

Modules: Materials Visualizer, Conformers, COMPASS

Time: 

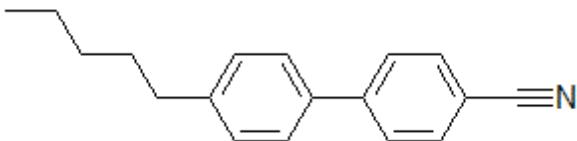
Prerequisites: Sketching simple molecules Visualizer Tutorial

Introduction

The potential energy surface of a given molecule becomes increasingly complex as the number of atoms in the molecule increases. Although modern geometry optimization methods are stable enough to find low energy conformers, they may not necessarily find the global energy minimum of a structure. For example, you might know the lowest energy conformation for a chain. But, when you attach this to a ring, you need to find the lowest energy conformation of the chain relative to the ring. The Conformers module allows you to change a set of defined torsions either systematically, randomly, or with temperature jumps, while keeping the rest of the molecule unchanged. Using the previous example, this allows you to specify a chain as all-trans while varying the connecting torsion to a ring.

By using systematic searches around particular torsion angles Conformers allows you to build up a picture of the energy barriers to rotation for a torsion angle. This is coupled with the ability to predict properties such as dipole moments for the molecule. Thus Conformers provides a suite of tools to systematically study the effects of conformation on key properties.

This simple example examines the change in the energy barrier as you rotate the interannular torsion in the biphenyl moiety of a liquid crystal molecule, 5CB, with varying substituents on the ring. The analysis tools help you to study the dependency of the dipole moment on the conformation and energy.



5CB - a simple liquid crystal molecule

This tutorial covers:

- [Getting started](#)
- [To perform a systematic conformational analysis for 5CB](#)
- [To substitute fluorines on the rings and the effect on the energy barrier](#)
- [To analyze the effect of conformation on the dipole moment](#)

Conformers: Using Conformers to probe geometry-energy relationships

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **5CB** as the project name, click the **OK** button.

The new project is created with **5CB** listed in the Project Explorer.

The first step is to load in a pre-defined structure, the liquid crystalline molecule **5CB**.

Click the **Import** button  on the toolbar and navigate to **Examples\Documents\3D Model**. Double-click on **5CB.xsd**.

2. To perform a systematic conformational analysis for 5CB

Once you have imported the molecule, you need to define the torsions that you want to vary. You can do this by either adding torsions to the molecule or using the Torsions functionality of the Conformers tool. Initially, use the Torsions functionality.

Click **Conformers**  on the **Modules** toolbar and select **Calculation** from the list.

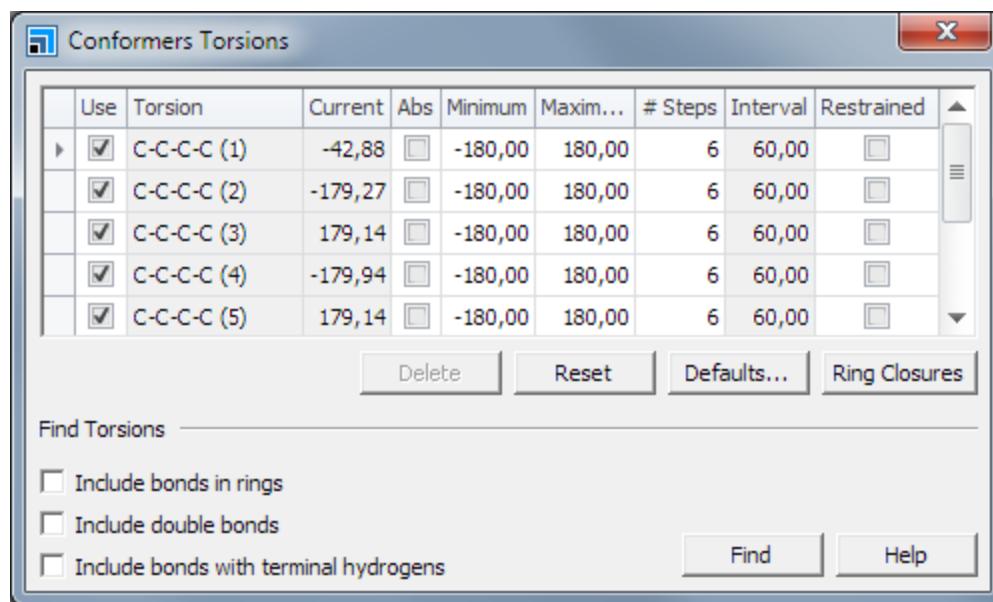
This opens the Conformers Calculation dialog.

Click **Torsions...** to open the Conformers Torsions dialog.

This displays all the rotatable torsions in the molecule. You can choose to include bonds in rings, double bonds, and bonds with terminal hydrogen atoms.

Move the open dialog boxes so that you can see **5CB**. Click **Find**.

The Conformers Torsions dialog lists all the rotatable torsions.



Conformers Torsions dialog

You can select the torsions you want to rotate by checking Use. The Absolute column allows you to select either absolute or relative values for the torsion angles. You can also edit the minimum and maximum angles, the number of steps, and whether to restrain the angle.

Click the left row heading cell for a torsion to select the entire row.

Selecting **Use** also selects the corresponding torsion in the molecule. For this calculation, vary the torsion between the two benzene rings, which has a current value of -42.88.

Click the row heading cell for the topmost row. Scroll to the bottom, hold down SHIFT, and click the row heading cell for the bottommost row. This selects all the torsions. Clear selection of **Use** for any torsion; this clears **Use** for all the rows.

Click the row heading cell for **C-C-C-C(1)** and select **Use**.

Note: If you want to study the conformations of rings, you need to break a bond using the Ring Closures tool.

As you are doing a systematic search, the number of conformers depend on the number of steps you define.

Change the **# Steps** value to **72**.

The Interval changes to 5.00, indicating that this configuration performs an energy calculation every 5 degree. On the Conformers Calculation dialog, the Estimated conformers updates to 72.

Close the **Conformers Torsions** dialog.

As this is a classical simulations calculation, you need to specify the forcefield and charges to use in the simulation.

On the **Conformers Calculation** dialog, select the **Energy** tab.

For this simulation, use the COMPASSIII forcefield and the charges assigned by this forcefield.

Ensure that the **Forcefield** is **COMPASSIII** and that the **Charges** are **Forcefield assigned**.

You can also use filtering to remove conformers before Conformers returns them from the server.

Select the **Filters** tab.

Conformers allows you to filter by Energy difference, RMS difference for coordinates or torsions, and radial distribution function. Filters are very useful if you are sampling thousands of conformers and you want to eliminate similar conformers to produce a diverse conformer set.

As you are running a very quick calculation with a small number of conformers, you can do this without filtering.

Click **Run** and close the dialog.

When the calculation is complete, the *Job Completed* dialog displays. A new folder, entitled 5CB Conformers Calculation, opens in the Project Explorer and contains the results files.

Tip: You can generate to either the study table, trajectory, or both. If you are generating many thousands of conformers, use a trajectory document.

Conformers: Using Conformers to probe geometry-energy relationships

There are several files returned:

5CB.xsd is the input structure updated with the results from the calculation.

5CB - Calculation is the saved settings for the calculation.

5CB_Energies.xcd is the live update of the conformer energies.

5CB_reference.xsd is the structure that contains the sets, atoms, and torsions that you can use in an extended search.

5CB_RMS_Deviation.xcd is a plot of the RMS deviation of the Cartesian coordinates.

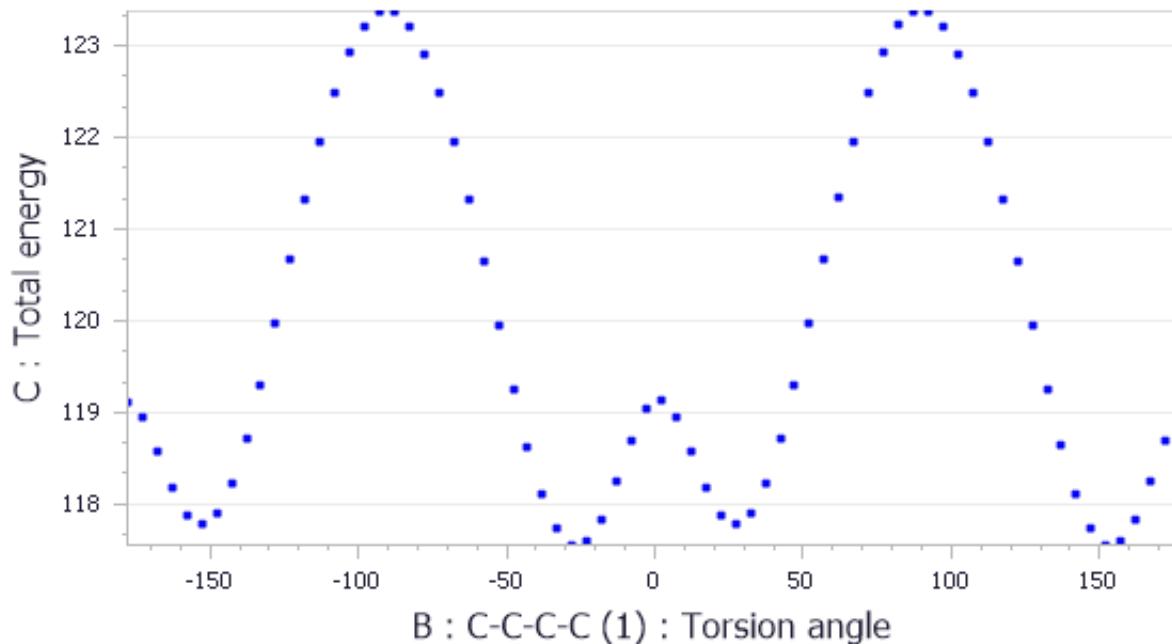
5CB.std is the study table containing the results of the calculation.

5CB.txt and Status.txt are text files containing information about the calculation.

Focus on the study table for your initial analysis.

Make **5CB.std** the active document. Select columns **B** and **C** and click **Quick Plot** .

The plot shows two main peaks indicating larger barriers to rotation and, in the valleys, two other energy minima.



On the chart document **5CB Scatter plot.xcd**, select several points around the energy peak near 0 degree. Change focus to the **5CB.std**.

The high energy conformers are highlighted in the study table. You can extract these to a collection document to overlay them.

Right-click in one of the selected cells in column A and choose **Extract To Collection**.

In the new collection document **Extracted From 5CB.xod**, you can see that the high energy conformers had high steric hindrance. When you review the chart, you can see that the potential energy surface goes through a higher maximum as well.

On the chart document **5CB Scatter plot.xcd**, select a few points at one of the higher maxima. On the study table **5CB.std**, extract the selected structures to a new collection document, named **Extracted From 5CB(2).xod**.

The structures near this energy maximum place the rings perpendicular to each other. This shows that the rings prefer to sit slightly off-plane to each other but not to flip completely.

3. To substitute fluorines on the rings and the effect on the energy barrier

You can begin to substitute some halogens for hydrogens on the biphenyl ring system to see the effect this has on the energy barrier to rotation.

Import **5CBF.xsd** and **5CB2F.xsd**.

5CBF.xsd contains the **5CB** structure with an added fluorine on one of the benzene rings. **5CB2F** contains fluorine on both benzene rings. Initially, work with **5CBF.xsd**.

Make **5CBF.xsd** the active document.

Previously you used the Torsions tool to find all the rotatable torsions, this can be very useful if you are sampling many torsions using Boltzmann jump or random sampling. However, if you want to rotate only one torsion, you can define it using the geometry monitors.

Click the **Measure/Change** arrow  on the **Sketch** toolbar and select **Torsion** from the list. Click the bond connecting the two phenyl rings.

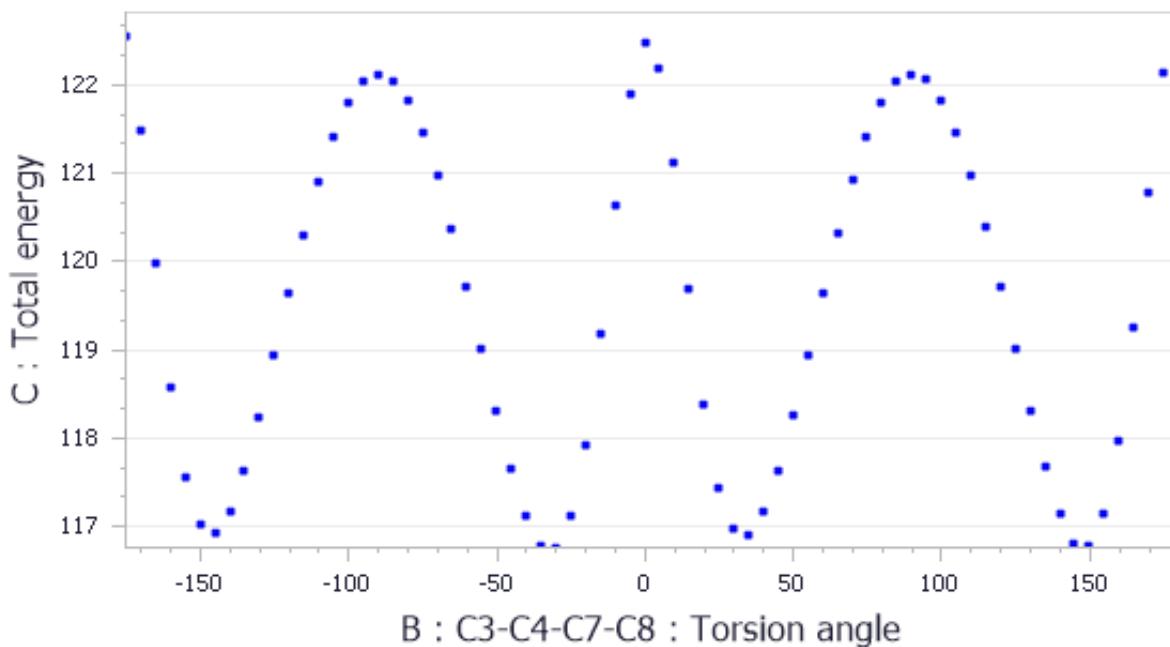
A torsion monitor is added to the structure. Now you can select this from the Conformers Calculation, Torsions dialog.

Open the **Conformers Calculation** dialog and click **Torsions...** on the Search tab.

Ensure that *Use* is already selected. Increase the number of steps and run the calculation.

Change the **# Steps** to **72**. Close the **Conformers Torsions** dialog and click **Run**.

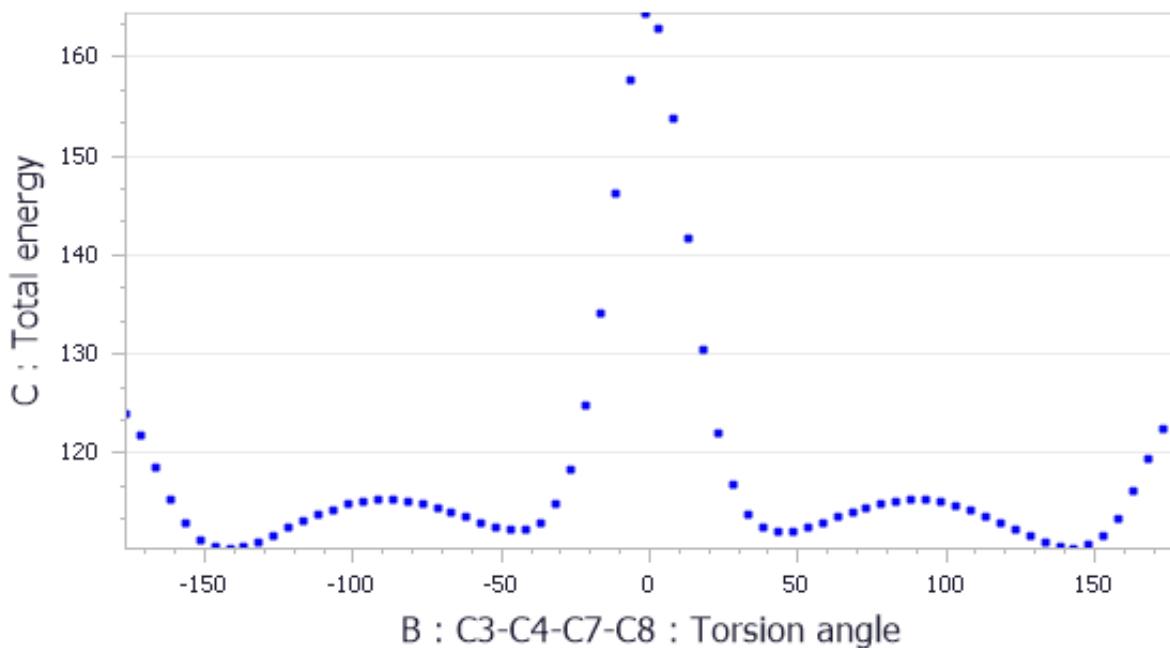
When the calculation is complete, click **OK** on the Job Completed dialog. In the study table, **5CBF.std**, plot the **Torsion angle** (column B) against the **Total energy** (column C).



5CBF Scatter plot.xcd

The addition of the fluorine increases the energy barrier to rotation about the cis-conformation by about a factor four due to the increased steric interactions.

Repeat the above calculation for **5CB2F.xsd** and plot the **Torsion angle** against the **Total energy**.



5CB2F Scatter plot.xcd

Adding in the second fluorine further increases the energy barrier to rotation about the cis-conformation by another factor 10.

4. To analyze the effect of conformation on the dipole moment

You can use the Conformers analysis tool to perform clustering and calculate different properties. For this tutorial, you can calculate the change in the dipole moment for 5CB2F and plot it against the energy.

Make sure that the study table **5CB2F.std** is in focus. Select the structures column, **A**. Click

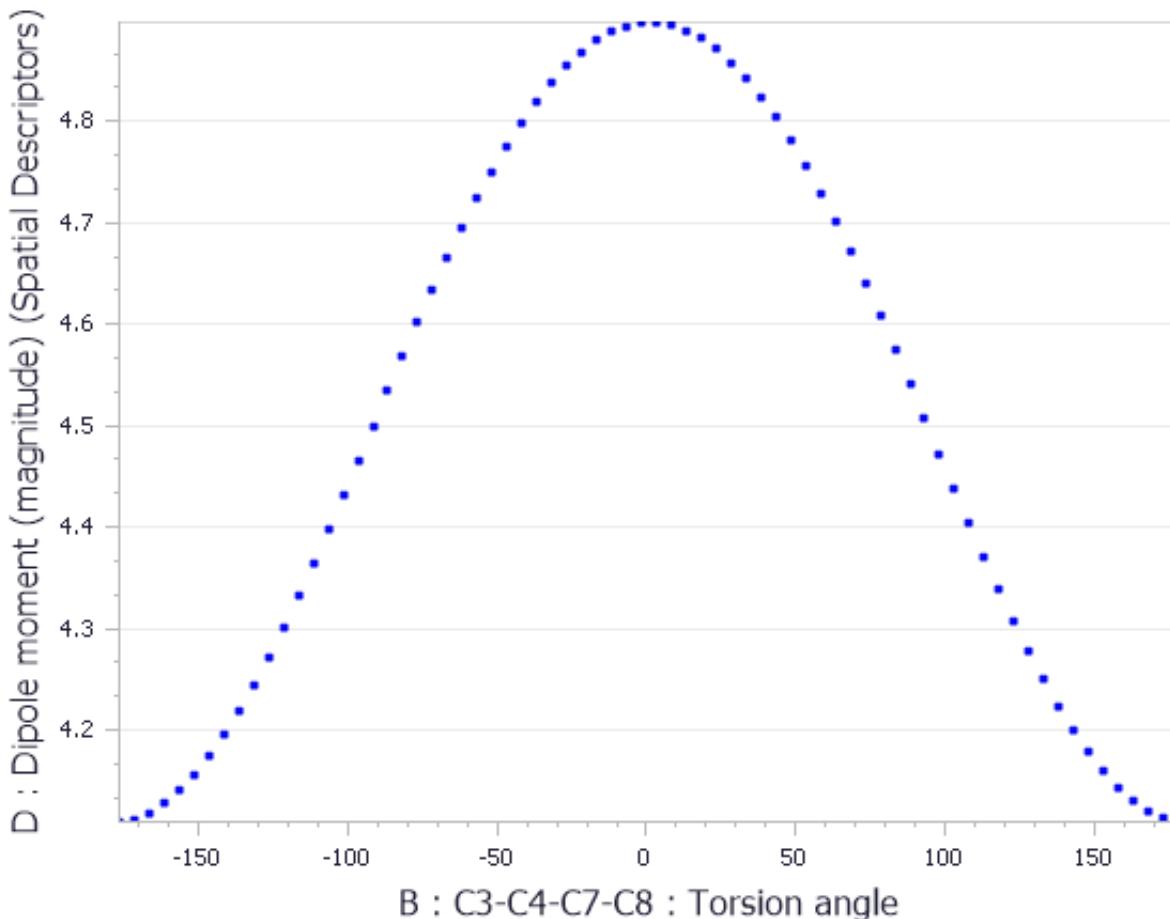
Conformers  on the **Modules** toolbar and select **Analysis** to open the Conformers Analysis dialog.

The Dipole moment analysis functionality uses the current charges on the atoms to calculate the dipole moment for the system.

Select **Dipole moment** and click **Analyze**.

A job run and when it completes, adds a new column to the study table.

Plot the **Torsion angle** against the **Dipole moment**.



5CB2F Scatter plot (2).xcd

Conformers: Using Conformers to probe geometry-energy relationships

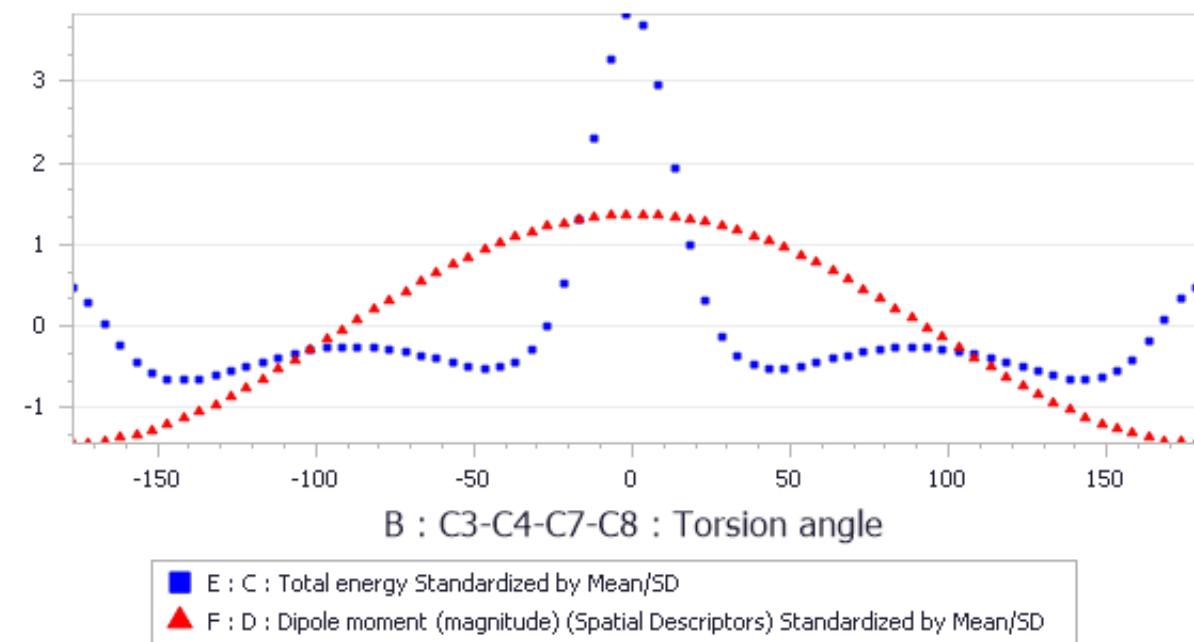
You can see that the dipole moment reaches a maximum at about 0 degree. This makes sense as at 0 degree, the fluorines are aligned.

To compare the change in dipole moment with the energy of the conformer, you need to scale the energies and dipoles so that you can plot them on the same chart. You can use the Standardize data tool to automate this.

In the study table **5CB2F.std**, select columns **C** and **D**. From the menu bar, select **Statistics | Initial Analysis | Standardize Data...** to open the Standardize Data dialog and click **OK**.

The study table has two new columns added, *Total energy Standardized by Mean/SD* and *Dipole moment (magnitude)*.

Select columns **B**, **E**, and **F** by pressing **CTRL** and clicking each column heading, then click **Quick Plot**



5CB2F Scatter plot (3).xcd

You can now see that the maximum dipole moment is at the energy maximum. Again, this makes sense as the fluorine atoms are coincident and hence the steric hindrance is very high.

This is the end of the tutorial.

Chapter 8: DFTB+ tutorials

The following tutorials illustrate how to utilize DFTB+'s capabilities.

- [Geometry optimization of a carbon nanotube](#)
- [Creating parameters for DFTB+](#)
- [Simulating electron transport with DFTB+](#)
- [Calculating the Minimum Energy Path of a molecular switch](#)

Geometry optimization of a carbon nanotube

Purpose: To introduce basic DFTB+ calculations of structural and electronic properties

Modules: Materials Visualizer, DFTB+

Time: 

Prerequisites: None

Background

DFTB+ is a semi-empirical tight binding method based on a two-centered approach to density functional theory (DFT). The use of a tight binding approach makes it faster than ordinary DFT methods but it also makes it dependent on parameter sets known as Slater-Koster libraries. Libraries are provided for standard organic molecules and semi-conductors.

Interactions with carbon nanotubes (CNT) are typically handled better by quantum mechanics techniques than by classical forcefield-based approaches. However, the system size limitations imposed by using quantum mechanics techniques narrows the range of applications that can be handled. DFTB+ represents a good compromise between classical and quantum simulation techniques for studying carbon nanotubes, giving the accuracy and electronic information of the quantum calculation but applying it to system sizes outside the reach of standard quantum techniques.

Introduction

In this tutorial you will use the DFTB+ module to do a geometry optimization for a carbon nanotube and calculate its band structure.

This tutorial covers:

- [Getting started](#)
- [Initial preparation](#)
- [To set up a Geometry optimization job:](#)
- [To select properties](#)
- [To control the job settings and run the job](#)
- [To analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DFTB CNT** as the project name, click the **OK** button.

The new project is created with DFTB CNT listed in the Project Explorer.

2. Initial preparation

The first step is to use the nanostructure building tools to create a 10×10 carbon nanotube.

Select **Build | Build Nanostructure | Single-Wall Nanotube** from the menu bar to open the Build Single-Wall Nanotube dialog. Set **N** and **M** to **10** and click the **Build** button. Close the **Build Single-Wall Nanotube** dialog.

To avoid interactions between periodic images of the CNT you should increase the lattice parameters perpendicular to the CNT.

Select **Build | Symmetry | Lattice Parameters** from the menu bar to open the Lattice Parameters dialog. On the **Advanced** tab, uncheck the **Keep fractional coordinates fixed during changes to the lattice** checkbox. On the **Parameters** tab, set the lengths **a** and **b** to **30** and close the dialog.

You will perform a geometry optimization of the CNT, including optimization of the cell lengths. To keep the periodic lattice lengths that you have just set, you should constrain these axes.

Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. On the **Lattice** tab, check the **a**, **b**, **α** , **β** , and **y** checkboxes and close the dialog.

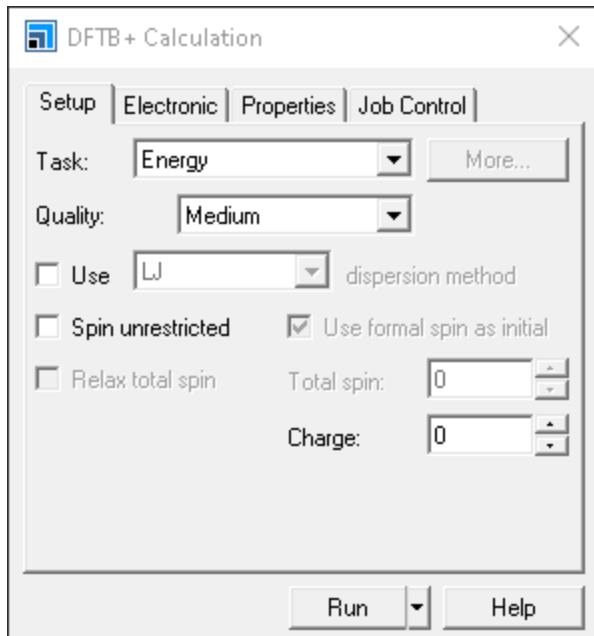
When you perform the calculation, the **a** and **b** cell lengths will remain fixed.

3. To set up the DFTB+ job

You are now ready to begin setting up the DFTB+ job.

Click the **DFTB+**  button on the **Modules** toolbar and select **Calculation** or choose **Modules | DFTB+ | Calculation** from the menu bar.

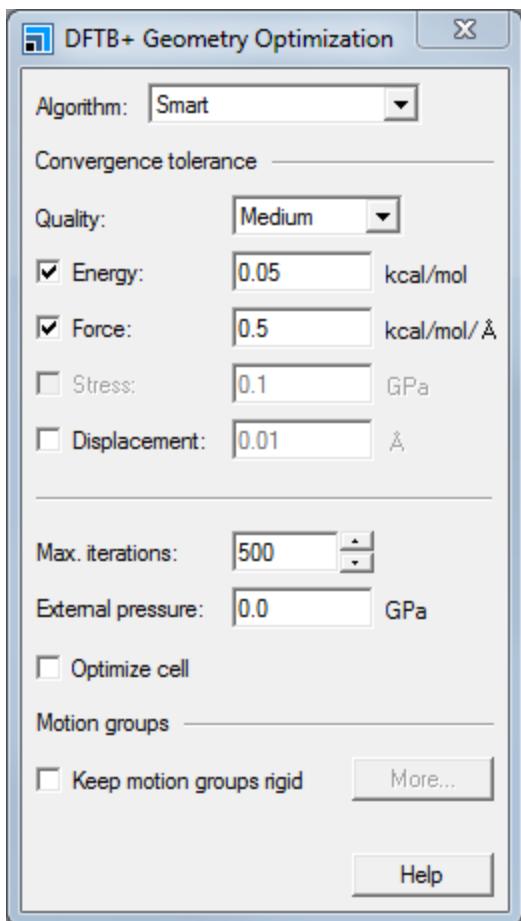
This opens the DFTB+ Calculation dialog.



DFTB+ Calculation dialog, Setup tab

Select **Geometry Optimization** from the **Task** to dropdown list.

Click the **More...** button to open the DFTB+ Geometry Optimization dialog.



DFTB+ Geometry Optimization dialog

You will use the optimize cell option to relax the lattice parameters. As you have constrained the a and b lattice lengths, the *Optimize cell* option will only optimize the c lattice length.

Check the **Optimize cell** checkbox and close the dialog.

In order to run a DFTB+ job a valid Slater-Koster library must be selected. DFTB+ requires interactions between all available elements in the target structure to be defined in the library. A quick overview for each library can be displayed by clicking the **View** button. In this tutorial you will use the **CHNO** library.

On the **Electronic** tab of the DFTB+ Calculation dialog, select the **CHNO** library from the **Slater-Koster library** dropdown list.

Note: If you want to use DFTB+ with a structure that contains atom interactions that are not supported in any of the available parameter sets, you can use the DFTB+ Parameterization task for creating your own parameters. This uses DMol³ to perform the DFT calculations. For more information, see the [Creating parameters for DFTB+](#) tutorial.

4. To select properties

As well as performing a geometry optimization, you can also select from a range of properties that will be calculated on the optimized structure. For this tutorial, you will calculate the band structure of the CNT.

On the **Properties** tab, check the **Band structure** checkbox in the list of properties and set the **k-point set to Fine**.

Since you are calculating the band structure for a 1D object, you should create the Brillouin zone paths and only keep the one corresponding to the direction of the nanotube.

Click the **Path...** button to open the Brillouin Zone path dialog, click the **Create** button and then delete all Brillouin zone paths except the **Z to G** path.

Note: If you generate a trajectory using the Dynamics task, you can use Forcite Trajectory Analysis to perform further analysis.

5. To control the job settings and run the job

You can use the commands on the *Job Control* tab on the DFTB+ Calculation dialog to control the calculation.

You can choose the gateway location where you will run your calculation and set various options such as the job description. You can also specify live update settings and job completion options.

You are now ready to run your DFTB+ Geometry optimization job.

Click the **Run** button and close the dialog.

A text document named **Status . txt** is displayed, reporting the status of the calculation. This document is updated regularly until the calculation is complete, it can be a useful aid to indicate the progress of your calculation.

6. To analyze the results

When the calculation is complete, the results are returned to the **SWNT DFTB+ GeomOpt** folder in the Project Explorer.

In the **SWNT DFTB+ GeomOpt** folder, double-click on **SWNT.txt**.

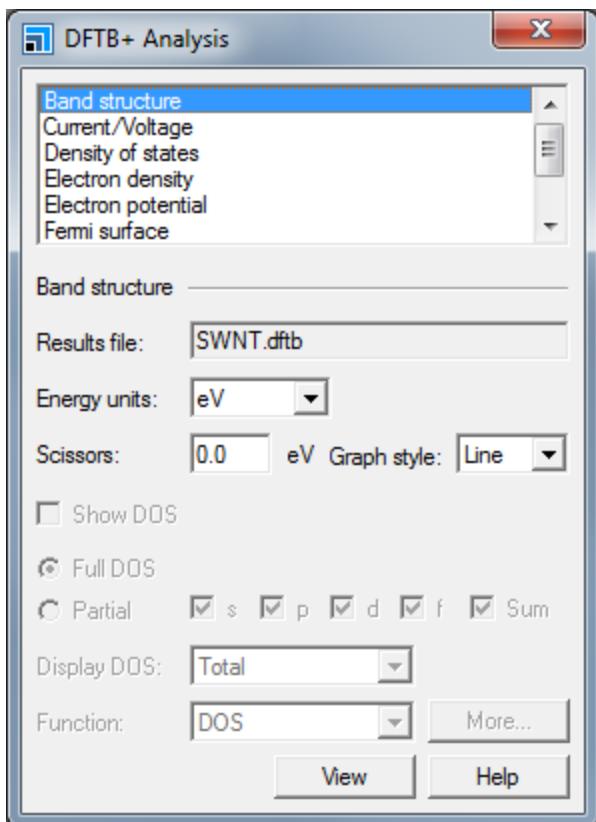
The **SWNT . txt** document contains an overview of the job and the result. The **SWNT . dftb** file contains the output from the last single point energy DFTB+ calculation. This file can contain helpful information if there are issues with a calculation.

Change focus to the optimized **SWNT.xsd**.

To visualize the band structure, you need to analyze the output documents.

Click the **DFTB+ ** button on the **Modules** toolbar and select **Analysis** or choose **Modules | DFTB+ | Analysis** from the menu bar.

This opens the DFTB+ Analysis dialog.



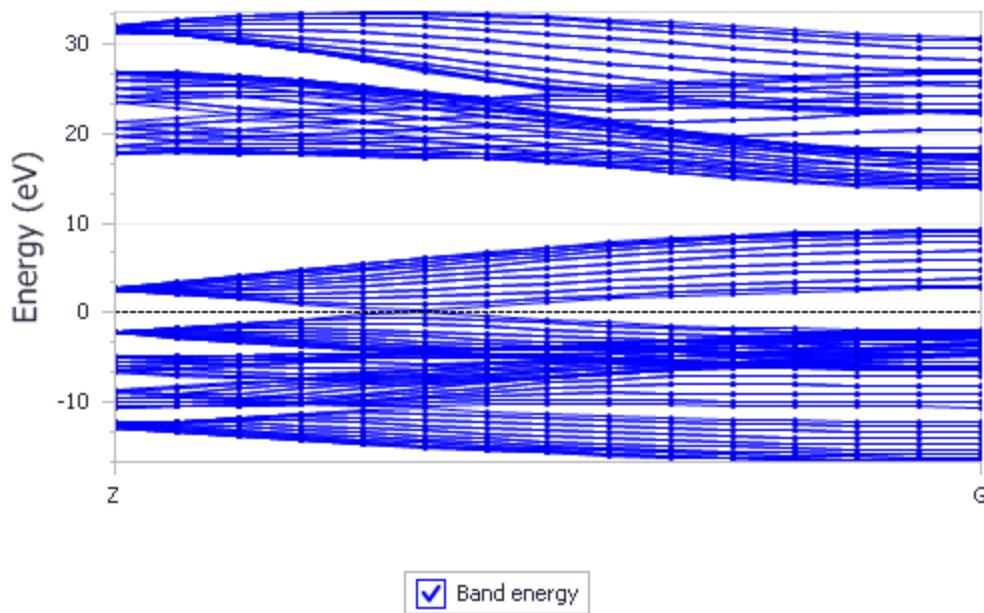
DFTB+ Analysis dialog

Select **Band structure** and click the **View** button.

This generates and displays a chart showing the band structure for the CNT, note the characteristic band crossing at the Fermi level.

DFTB+ Band Structure

Band gap is 0.270 eV



Band energy

DFTB+ Analysis view, Band structures

This is the end of the tutorial.

Creating parameters for DFTB+

Purpose: To introduce the use of the DFTB+ parameterization tool for the creation of DFTB+ parameter libraries.

Modules: Materials Visualizer, DMol³, DFTB+, CASTEP

Time: 

Prerequisites: Sketching molecules Visualizer Tutorial

Background

DFTB+ requires atomic parameters for the interaction between atoms. A number of parameter sets are available in Materials Studio. If you want to use DFTB+ with a structure that contains atom interactions that are not supported in any of the available parameter sets, Materials Studio supplies a tool for creating your own parameters.

The parameters created by the DFTB+ parameterization tool are in a Slater-Koster Library file (.skflib) and contain the following:

- README.txt file with information about the parameters
- Slater-Koster files (.skf) for the element pairs in question, containing:
 - Electronic parameters
 - Short range potential
 - Hubbard terms
- Spin constants for the elements
- Wave plot data for each element
- An skf.aux file containing extra settings

Introduction

In this tutorial, you use the DFTB+ parameterization tool to create a carbon and hydrogen parameter set.

This tutorial covers:

- [Getting started](#)
- [To find electronic settings for elements](#)
- [To prepare for short range fitting](#)
- [To prepare the DFTB+ parameterization:](#)
 - Defining conformation systems
 - Defining electronic settings
 - Defining settings for the fitting
- [To control the job settings and run the job](#)
- [To evaluate the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CHparameters** as the project name, click **OK**.

The new project is created with CHparameters listed in the Project Explorer.

Note: You cannot run the DFTB+ Parameterization scripd tools used in this tutorial on a server whose gateway uses the secure authentication level. For more information, see [Gateway Security Overview](#).

2. To find electronic settings for elements

Before creating the DFTB+ parameters, you need to determine what electronic settings to use for each element. You can do this using the *DFTB+ Generate Electronic Parameters* and *DFTB+ Electronic Evaluation* scripts. The first script generates the Slater-Koster libraries with different electronic settings. The second script can then evaluate how well the libraries reproduce the electronic structure for different structures. Here, you only evaluate the settings for carbon. You can prepare the hydrogen settings in the same manner. For the sake of time, this tutorial provides a reasonable value for hydrogen.

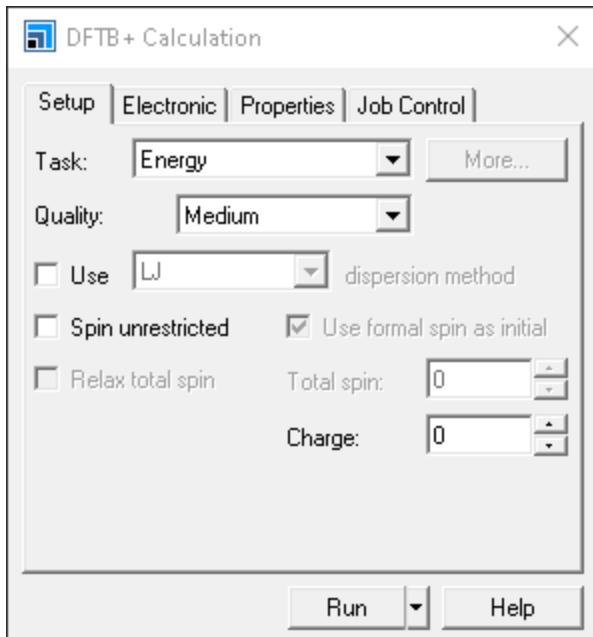
As the input you need a dummy Slater-Koster library for carbon.

In the Project Explorer, create a folder named **Electronic**. In this folder, create a new **3D Atomistic Document** and name it **C-C.xsd**. Using the sketching tool, create a diatomic carbon molecule.

Click **DFTB+**  on the **Modules** toolbar and select **Calculation** or choose **Modules | DFTB+ | Calculation** from the menu bar.

This opens the DFTB+ Calculation dialog.

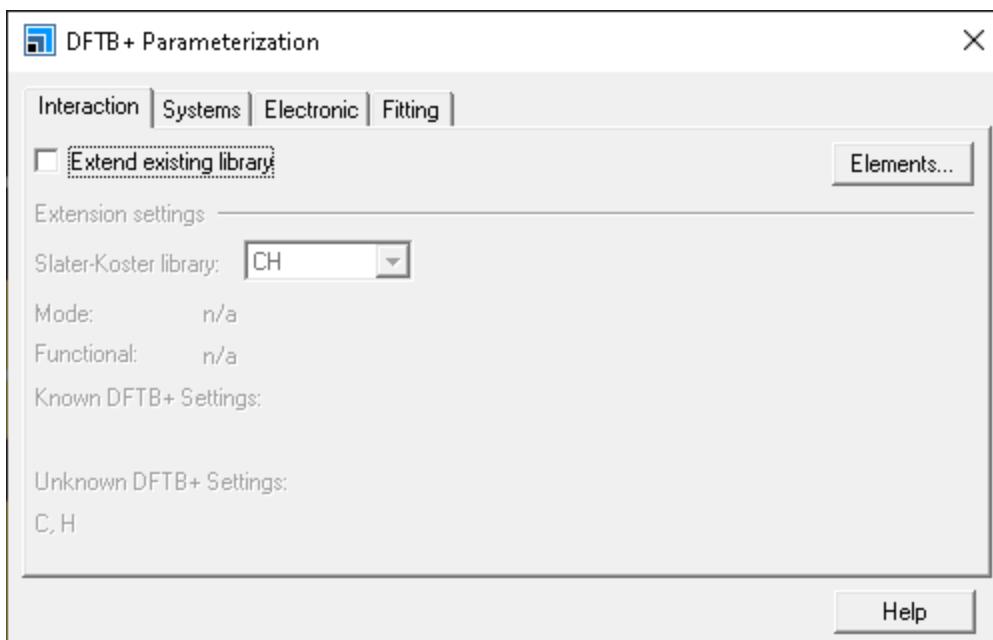
DFTB+: Creating parameters for DFTB+



DFTB+ Calculation dialog, Setup tab

For the **Task**, select **Parameterization**. Change the **Quality** from Medium to **Fine**.

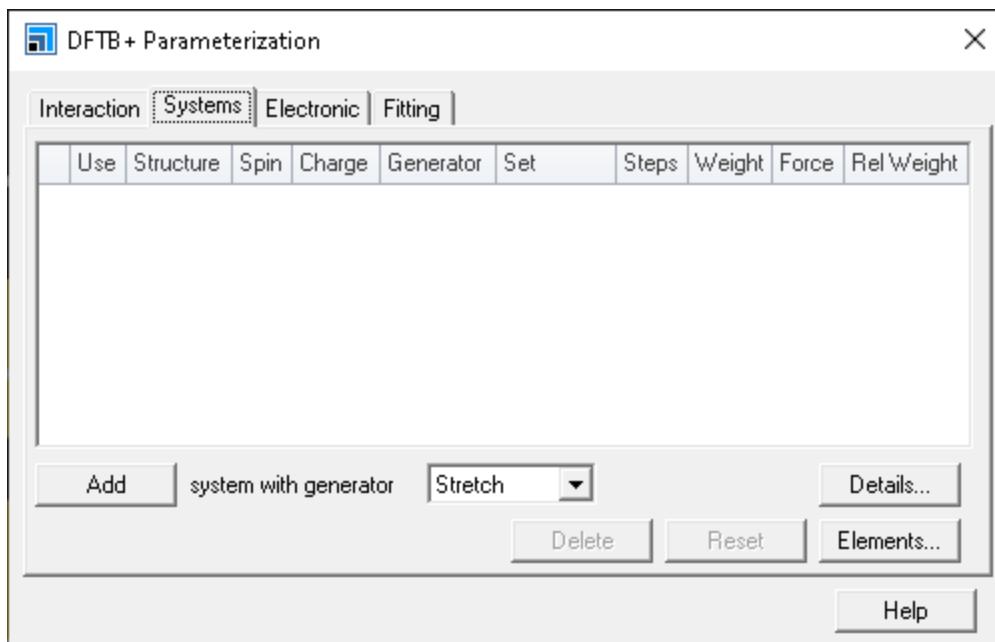
Click **More...** to open the DFTB+ Parameterization dialog.



DFTB+ Parameterization dialog

The DFTB+ Parameterization dialog facilitates the preparation of a parameterization.

Select the **Systems** tab to prepare the C-C conformation paths required for the short range potential fitting.



Select an atom and bond in the **C-C.xsd** document and click **Add**.

This creates a configuration path that stretches the C-C bond in the molecule. This is all that you require to create a dummy Slater-Koster library. The quality of the short range potential is not important since this tutorial does not use this library for anything involving forces or total energies.

On the Electronic tab, for the **Functional** select **GGA PBE**.

On the DFTB+ Calculation dialog, click **Run** and close the dialog.

When the parameterization task finishes, the library loads. The folder also contains a **.elec** file with the electronic settings used in the parameterization.

Using the **.skflib** and **.elec** files as templates, you can now create the Slater-Koster files with different electronic settings. In a real-world investigation, you would do this in two stages: first creating a large but coarse grid, then when you have identified the values of interest, creating a second, finer grid. In this tutorial, you use the fine grid.

Open the **C.skflib** file. From the menu bar, select **Tools | Materials Studio Scripts | Quantum Mechanics | DFTB+ Parameterization | DFTB+ Generate Electronic Parameters** to open the DFTB+ Generate Electronic Parameters dialog. For **MinRadius1** specify **2.2**, for **MaxRadius1** specify **2.8**, and for **MaxRadiusStep1** specify **0.05**, click **OK**.

The tool generates the **.skflib** files where the Radius1 and Power settings vary. It does not use the Radius2 setting when working in the Potential mode. When the calculation has finished the results folder **C DFTB+ Generate Electronic Parameters** includes **SkfLib.zip**, which contains all the **.skflib** files created. The tool uses this zip file evaluate the electronic settings using the band structure for different crystal structures.

Create a new folder called **Band structure** and copy the **SkfLib.zip** file into this folder. Ensure selection of the **Band structure** folder, open the Import Document dialog, navigate to **Structures\ceramics**, and select the **diamond.xsd** and **graphite.xsd** structures. Click **Open**.

Ensure that **diamond.xsd** is the active document and select **Build | Symmetry | Primitive Cell**.

Open the Import Document dialog, navigate to **Structures\metals\pure-metals** and select the **Al.xsd** structure. Click **Open**.

Select **Build | Symmetry | Primitive Cell**. Select all the atoms and modify the element type to **C**. Change the lattice parameter to **2.0 Å**. Rename the document to **C_fcc.xsd**.

To ensure you have a realistic geometry for the evaluation structures, run a geometry optimization on each structure. Here, we are using a shape conserving optimization with CASTEP to ensure that the structure does not converge to a lower energy structure.

Click **CASTEP**  on the **Modules** toolbar and select **Calculation** or choose **Modules | CASTEP | Calculation** from the menu bar. For **Quality** select **Ultra-fine** and for **Functional** select **GGA PBE**. For the **Task** select **Geometry Optimization** and click **More...** to open the CASTEP Geometry Optimization dialog. For the **Cell optimization**, select **Fixed Shape**. On the Options tab, for the **Algorithm** select **TPSD**, and close the dialog.

Run this geometry optimization with the same settings for all the input structures.

Make **diamond.xsd** the active document and click **Run** on the CASTEP Calculation dialog.

Repeat this for **graphite.xsd** and **C_fcc.xsd**. Close the CASTEP Calculation dialog.

Once the calculations have finished, you need to gather the optimized structures together in the same folder so they are available for the evaluation script.

Delete the original structures and replace each of them with the geometry optimized structure.

Make **diamond.xsd** the active document and select **Tools | Materials Studio Scripts | Script Job...** from the menu bar to open the Script Job Control dialog. Choose a server gateway, queue (if appropriate), and the number of cores on which to run the band structure calculations. Close the Script Job Control dialog.

From the menu bar, select **Tools | Materials Studio Scripts | Quantum Mechanics | DFTB+ Parameterization | DFTB+ Electronic Evaluation** to open the DFTB+ Electronic Evaluation dialog. For the **UpperLimit** specify **4.0 eV** and click **OK**.

This starts the script job, performing band structure calculations for all structures in the same folder as the active document, with DMol³ and DFTB+. The script compares the band structures in the specified energy window and returns the results in a study table. For each structure, the study table contains:

- The mean absolute error (MAE) for the band structure comparison.
- A band structure document showing the DFTB+ and DMol³ band structures in the same chart.

The far right-hand column contains the mean of the MAE for all structures. To find the setting that gives the best band structure fit, sort the *mean(MAE)* column.

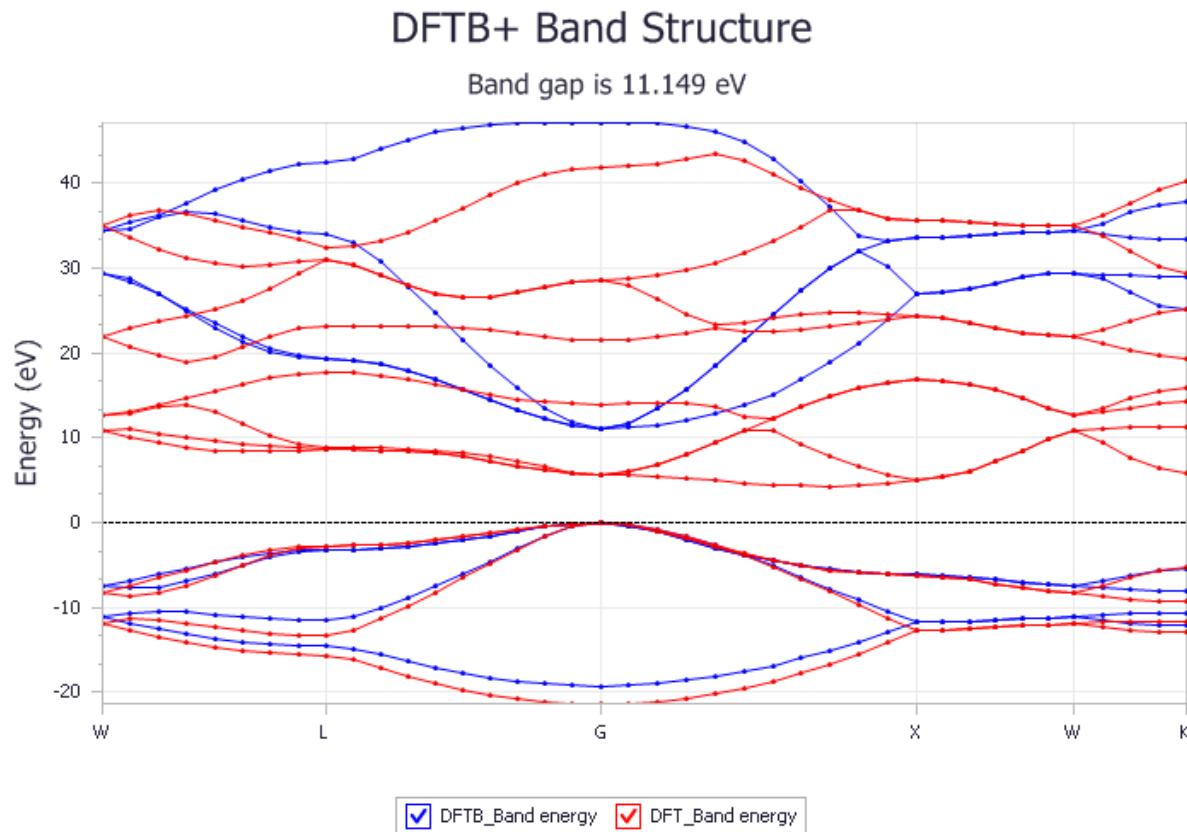
Open the output **BandStructures.std** study table, select the column **K mean(MAE)**, and sort it in ascending order by clicking **Sort Ascending** .

	A	B	C	D	E	F	G	H	I	J	K
	Source	N	Radius1	Radius2	BS(C_fcc)	MAE (eV)	BS(diamond)	MAE (eV)	BS(graphite)	MAE (eV)	mean(MAE)
1	DMol3(GGA(PBE)					0		0		0	0
2	C_2.55_4.skflib	4	2.55	N/A	 Band	0.32037475	 diamond Band	0.69349477	 graphite Band	0.56979270	0.52788741
3	C_2.6_4.skflib	4	2.6	N/A	 Band	0.34839783	 diamond Band	0.66863748	 graphite Band	0.57930306	0.53211279
4	C_2.5_4.skflib	4	2.5	N/A	 Band	0.31943737	 diamond Band	0.72165744	 graphite Band	0.56183483	0.53430988
5	C_2.65_4.skflib	4	2.65	N/A	 Band	0.37700360	 diamond Band	0.64929309	 graphite Band	0.59125487	0.53918385

From the first row of the DFTB+ library evaluations, we see that $\text{Radius1} = 2.55$ and $N = 4$ gives the best fit to all the evaluated structures. Sorting the rows according to the MAE for each single structure shows that the Radius1 value varies slightly. The best fit for graphite has a value of 2.45 and for diamond, a value of 2.8.

In the study table, double-click the document in the first row for the **G BS(diamond)** column.

This opens a chart document showing the DFTB+ and DMol³ band structures in the same chart, with the energy shifted to have the same Fermi energy. The valence bands are well described, while the band gap is too large for the DFTB+ results, because you used the minimal basis set here.



Before you start the fitting, save the project, and then close all the windows.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

3. To prepare for short range fitting

When you have determined what electronic settings to use, you are ready to perform a complete parameterization, including the fitting of the short range potentials. The first step is to decide which systems to use for the short range fitting. In this project, you try to create a parameter set that works well for most hydrocarbons. To achieve this, you need to fit against the different types of bonds that these systems can contain.

You use the following systems:

- hydrogen-hydrogen bonds
 - hydrogen molecule
- carbon-carbon bonds
 - ethane, single bond
 - ethene, double bond
 - benzene, hybrid bond
- carbon-hydrogen bonds
 - methane

You can import ethane, methane, and benzene from Materials Studio's collection of structures.

In the Project Explorer, create a folder named **Short range**.

Open the Import Document dialog, navigate to **Structures\organics**, and select the **ethane.xsd**, **methane.xsd**, and **benzene.xsd** structure files. Click **Open**.

Create the hydrogen and ethene molecule using the sketching tools.

In two new 3D Atomistic documents, create an H-H and an $\text{H}_2\text{C}=\text{CH}_2$ molecule and rename the documents **H2.xsd** and **ethene.xsd**.

You now have all the molecules required to prepare the parameterization. However, before you start using them you need to perform a geometry optimization on each molecule using DMol³. This ensures that the unperturbed molecule has the optimized structure that the parameterization aims to reproduce.

Click **DMol3**  on the **Modules** toolbar and select **Calculation** or choose **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.

For the **Task** select **Geometry optimization**, the **Quality** to **Fine**, the **Functional** to **GGA PBE**. On the Electronic tab, for the **Basis file** specify **4.4**.

Ensure that **ethene.xsd** is the active document and click **Run**.

Run this geometry optimization with the same settings for all the input structures.

Make **H2.xsd** the active document and click **Run** on the DMol3 Calculation dialog.

Repeat this for **ethane.xsd**, **methane.xsd**, and **benzene.xsd**.

When the jobs are all complete, copy the optimized structures into a new folder, and then clean the workspace.

In the **Short range** folder create a subfolder named **Structures**, copy the optimized structures into this folder.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

4. To prepare the DFTB+ parameterization

You are now ready to begin preparing the parameterization job.

Open the **DFTB+ Calculation** dialog, ensure that the **Task** is **Parameterization**, and that the **Quality** is **Fine**.

Click **More...** to open the DFTB+ Parameterization dialog.

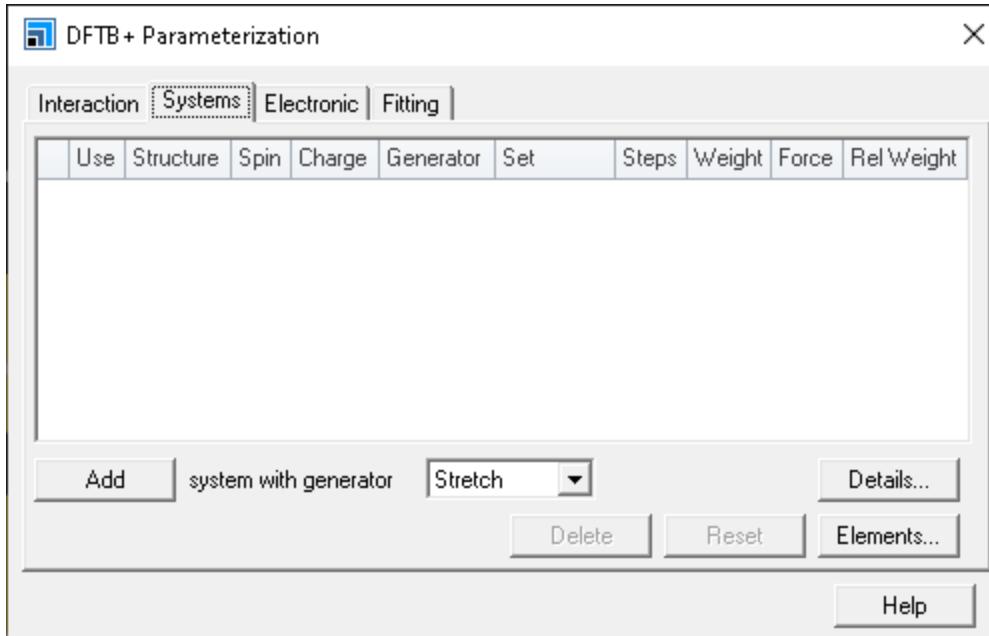
The DFTB+ Parameterization dialog facilitates the preparation of a parameterization. You can use the **Systems** tab to prepare the system conformation paths to use for the fitting. As you previously used this

DFTB+: Creating parameters for DFTB+

task to create the dummy Slater-Koster library for carbon, the systems grid still contains a C-C structure. You do not need this in the full parameterization, so remove it.

On the **Systems** tab, select the row with the **C-C** structure and click **Delete**.

This leaves you with an empty systems grid.



There are four different conformation generators:

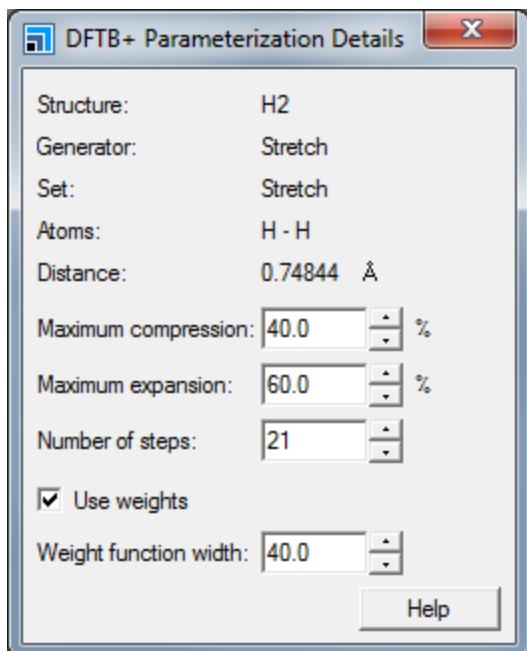
- Stretch - moves a selected set of atoms along a selected direction.
- Perturb - randomly moves an atom around its original position.
- Scale - uniformly scales the size of the system.
- Trajectory - uses the conformations contained in a trajectory file.

For more details about generators, see the Systems tab - DFTB+ Parameterization dialog.

Make **Short range\Structures\H2.xsd** the active document and select the bond and one of the hydrogen atoms. On the **Systems** tab, select **Stretch** as the generator and click **Add**.

This creates a stretch definition for the hydrogen molecule, where the selected atom moves along the direction of the bond. You can review details of the generated path of conformations on the DFTB+ Parameterization Details dialog.

Click **Details...** to open the DFTB+ Parameterization Details dialog.



DFTB+ Parameterization Details dialog

The DFTB+ Parameterization Details dialog contains detailed information about the selected path. For a stretch generator, you can select the *Maximum compression*, the *Maximum expansion*, the *Number of steps* to generate, and the *Weight function width*. Since the minimum fitting distance is about 0.65 Å, reduce the *Maximum compression*.

For the **Maximum compression**, specify **20 %** and for the **Number of steps**, specify **81**.

Next, work on the C-H interaction using the methane molecule. First create a stretch path that covers the range of interest for the C-H bond.

Make **Short range\Structures\methane.xsd** the active document and select one of the hydrogen atoms and its bond. On the **Systems** tab, select **Stretch** as the generator, click **Add**. Select the new methane row, on the **DFTB+ Parameterization Details** dialog, for the **Number of steps**, specify **61** and close the dialog.

To improve the fitting quality around the equilibrium position, add a small stretch to the hydrogen atom and a sharp weight function.

With **Short range\Structures\methane.xsd** the active document, select another hydrogen atom and its bond. Add a **Stretch** generator, and select the new row. On the DFTB+ Parameterization Details dialog change **Maximum compression** to **15 %**, **Maximum expansion** to **15 %** and the **Weight function width** to **7.5**. For the **Number of steps**, specify **41**.

Creating the paths for the H-H and the C-H interactions is simple because these paths only have single bonds. Setting up the paths for the C-C interaction is more complicated as there is overlap between potentials of different bond orders. Try to solve this problem by preparing paths with sharp weight functions, such that when there is an overlap, the bond closest to its equilibrium dominates. Start with the longest bond as it needs to cover the tail of the short range potential.

Make **Short range\Structures\ethane.xsd** the active document, create a distance measurement between the two carbon atoms, and select it.

Select **Stretch** as generator and click **Add**, select the new row. On the DFTB+ Parameterization Details dialog, change the **Maximum compression** to **10 %**, **Maximum expansion** to **70 %**, and the **Number of steps** to **81**.

Create a second stretch path for the same selection, and click **OK** for the warning. Change the **Maximum compression** to **15 %**, **Maximum expansion** to **15 %** and the **Weight function width** to **7.5**. For the **Number of steps**, specify **41**.

For the ethene molecule, you try to cover the core section of the potential.

Make **Short range\Structures\ethene.xsd** the active document, create a distance measurement between the two carbon atoms, and select it.

Create a stretch path for the distance measure. For the **Maximum compression** specify **30 %**, for the **Maximum expansion** specify **10 %**, and for the **Number of steps** specify **61**.

Create a second stretch path for ethene. For the **Maximum compression** specify **15 %**, for the **Maximum expansion** specify **15 %**, for the **Weight function width** specify **7.5**, and for the **Number of steps** specify **41**.

Now that you have ensured that there is coverage for the tail and core section, you can add the benzene molecule with sharp weight functions only. Ensure that the maximum perturbation is long enough to reach the neighboring bond type, with the width of the weight function about half the maximum perturbation.

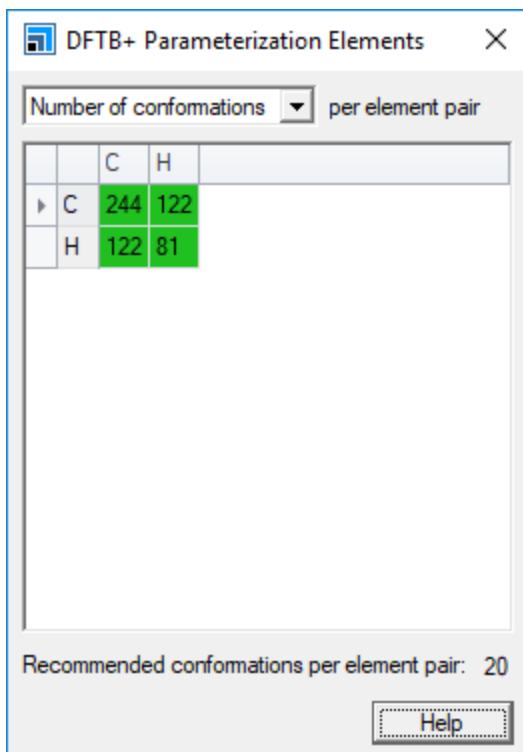
Make **Short range\Structures\benzene.xsd** the active document. Select a carbon atom and select **Perturb** from the generator list and click **Add** to create a perturb path for it. For the **Number of shells** specify **10**, for the **Maximum perturbation** specify **15 %**, and for the **Weight function width** specify **7.5**.

For a perturb generator, you can choose the *Maximum perturbation*, the *Number of shells* to generate, and the *Weight function width*. Each shell has four positions with a fixed radius.

You have now created paths that cover all the important bonds for a hydrocarbon system.

To ensure that you have enough coverage on all element pairs, click **Elements...** on the Systems tab of the DFTB+ Parameterization dialog.

This opens the DFTB+ Parameterization Elements dialog.



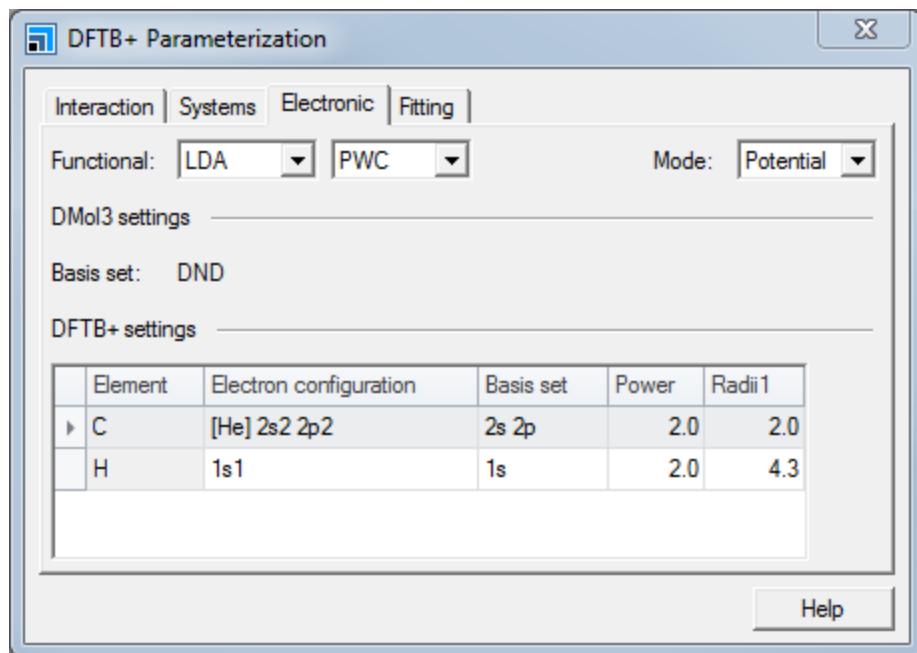
DFTB+ Parameterization Elements dialog

The DFTB+ Parameterization Elements dialog provides an overview of how many conformations are created for each element pair. If the number of conformations for a pair is considered sufficient, the cell is green. You can change the view to show percentage contribution per element pair, useful when your parameterization uses different weights for different paths.

Close the DFTB+ Parameterization Details and DFTB+ Parameterization Elements dialogs.

You are now ready to configure the electronic settings for the parameterization.

Select the Electronic tab of the DFTB+ Parameterization dialog.



DFTB+ Parameterization dialog, Electronic tab

The same functional used for the creation of the electronic parameters in the Slater-Koster files, is also used by DMol³ when calculating the total energy and forces for your path conformations. The *Quality* setting determines the basis set used by DMol³.

For the **Functional**, select **GGA PBE**.

The *Mode* determines how DFTB+ determines the electronic parameters in the Slater-Koster files. The **Potential** mode uses the potential of each single atom to create the pair potential. In the **Density** mode, DFTB+ adds the electron densities of each atom and uses them to determine the potential for each pair. The choice of *Mode* affects the settings for the elements. The **Potential** mode has one compression radius, while the **Density** mode has two compression radii for each element. The compression radii compress the wavefunction and the electron density so that they avoid areas far away from the nucleus. In literature reports the **Potential** mode is commonly used for band structures and the **Density** mode is often used for bio-molecules and energetic calculations. For more details about the two modes, see the DFTB+ theory section.

In this case, use the **Potential** mode.

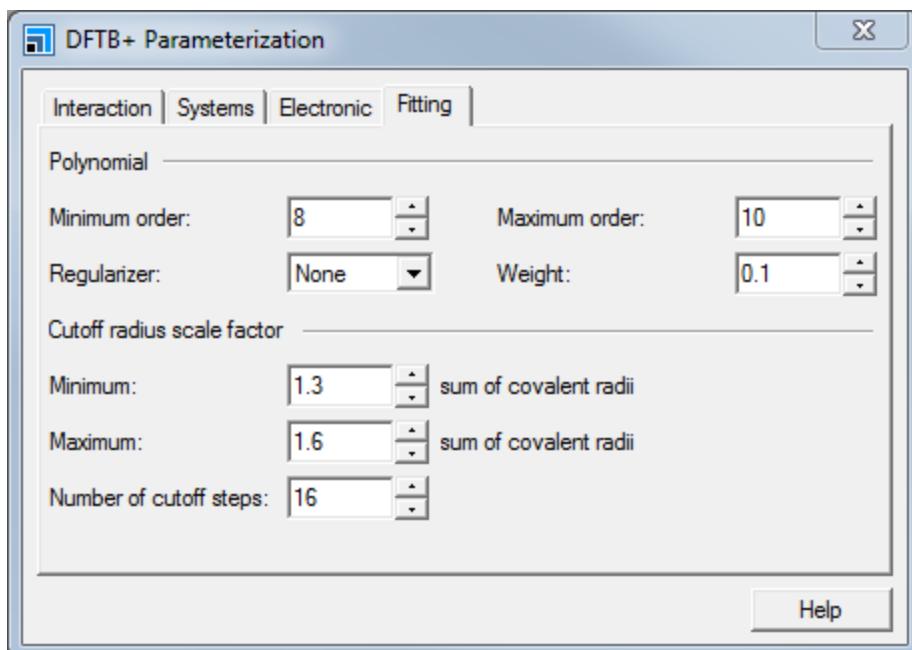
Ensure that the **Mode is Potential**.

Now you need to specify the DFTB+ settings for each atom. The default settings give a good starting point, but you can change them to improve the electronic properties of the target systems. You can use the *Electron configuration* and the *Basis set* to improve the electronic properties. Often the conduction band and LUMO depend on excited orbitals, for example in silicon a 3s3p basis set provides good valence bands but poor conduction bands. You can alleviate this by changing the basis set to 3s3p3d where the excited d-orbital interacts with the conduction bands. The settings for the compression radius not only affect electronic properties but also how good geometry agreement you can get. Unfortunately, sometimes the settings that give good electronic agreement are not the same as those that result in the best geometry, so you might require a compromise. Here, use the carbon settings found in the earlier section. For hydrogen, use a known good value.

For carbon, for **Power** specify **4** and for **Radii1** specify **2.55**. For hydrogen, for **Radii1** specify **2.8**.

Now modify the settings used for the fitting of the short ranged potential.

Select the **Fitting** tab.



DFTB+ Parameterization, Fitting tab

The fitting uses a polynomial basis set where each term in the polynomial has a cut-off radius:

Eq. 1

$$f_v(r) = \begin{cases} (r - r_0)^v & \text{if } r < r_0 \\ 0 & \text{otherwise} \end{cases}$$

Short range potentials are generated for a defined set of cutoff factors. For each cutoff factor, DFTB+ performs fittings using different maximum polynomial orders. The tool returns the best fit for each cutoff factor.

In the Polynomial section, for **Minimum order** specify **10** and for **Maximum order** specify **12**.

The cutoff factor is typically around 1.5 times the bond length. If the cutoff factor extends too far, for example into second neighbor atoms, it can have an adverse impact on the transferability of the parameters.

Close the **DFTB+ Parameterization** dialog.

Before you start the parameterization, save the project, and then close all the windows.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

5. To control the job settings and run the job

Before launching the job, save these settings.

Select the **CHparameters** item in the Project Explorer.

Click **DFTB+ ▾** on the **Modules** toolbar and select **Save Settings...**, enter **CH No Forces** as the name, and click **OK**.

You can use the commands on the *Job Control* tab on the DFTB+ Calculation dialog to control the calculation.

Select the **Job Control** tab on the DFTB+ Calculation dialog.

You can choose the gateway location where you run your calculation and choose various options such as the job description. You can also specify live update settings and what happens when the job completes.

Uncheck the **Automatic** checkbox and enter **CH No Forces** as the **Job description**.

You are now ready to run your DFTB+ parameterization.

Click **Run** and close the dialog.

A text document named **Status . txt** displays, containing the status of the calculation. This document updates regularly until the calculation is complete. It provides a useful aid to indicate the progress of your calculation.

The **CH No Forces** job only uses the total energies to fit the short range potential. This ensures good energy accuracy for the fitting but does not necessarily result in very good geometries. You can improve the accuracy of the fitting by fitting toward both energies and forces. You can modify the relative weight between energy and forces for each path.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

Tip: The location of the job folder depends on the current selection in the Project Explorer. If there is no selection, the job appears under the project folder.

Double-click on **CH No Forces - Calculation** in the Project Explorer to open the saved settings. Open the **DFTB+ Parameterization** dialog and, on the **Systems** tab, select all the **Force** checkboxes, and for the **Rel weight** values specify **5**.

To get a good fit for the C-C bond, increase the weight on that path.

For the **Weight** for the **Stretch5**, specify **4.0**. Close the DFTB+ Parameterization dialog.

On the **Job Control** tab of the DFTB+ Calculation dialog, specify the **Job description** as **CH With Forces**. Save these new settings as **CH With Forces** and click **Run** on the DFTB+ Calculation dialog.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

6. To evaluate the results

When the calculations are complete, the results for the jobs return to the **CH No Forces DFTB+ Parameterization** and **CH With Forces DFTB+ Parameterization** folders in the Project Explorer.

In the **CH With Forces DFTB+ Parameterization** folder, double-click **CH With Forces.txt**.

```
#####
## CALCULATING ELECTRONIC PARAMETERS ##
#####
Mode : Potential

Computing spin constants for C
Computing spin constants for H
Begin Pair C H
    Computing orbital energies for C
    Hubbard terms:      C=(0.39919 0.36460 0.00000)
    Computing electronic parameters for C-C
    Computing orbital energies for H
    Hubbard terms:      H=(0.41963 0.00000 0.00000)
    Computing electronic parameters for H-H
    Computing electronic parameters for C-H
    Creating .coef and .skf files.
End Pair
Assembling waveplot data in CH_With_Forces.hsd
Electronic parameter creation finished
```

```
#####
## CALCULATING REPULSIVE PARAMETERS ##
#####
DFT code : DMol3
    Basis          : DNP
    Functional     : PBE
    Integration grid : fine
Fitting basis : cutoffpoly
    Lowest degree   : 3
    Highest degree  : From 10 to 12
Regularizer : None

Fit    Cutoff Polynomial      Total error      Regularization penalty
factor  degree        (Ha^2)           (Ha^2)
-----
1      1.300   12            7.577e-01       0.000e+00
2      1.320   11            7.187e-01       0.000e+00
3      1.340   12            6.533e-01       0.000e+00
4      1.360   11            6.239e-01       0.000e+00
5      1.380   11            5.776e-01       0.000e+00
6      1.400   11            5.366e-01       0.000e+00
7      1.420   11            4.943e-01       0.000e+00
8      1.440   11            4.582e-01       0.000e+00
9      1.460   11            4.224e-01       0.000e+00
10     1.480   11            3.900e-01       0.000e+00
11     1.500   11            3.593e-01       0.000e+00
12     1.520   11            3.289e-01       0.000e+00
13     1.540   11            3.020e-01       0.000e+00
14     1.560   11            2.778e-01       0.000e+00
15     1.580   11            2.547e-01       0.000e+00
16     1.600   11            2.338e-01       0.000e+00
```

DFTB+: Creating parameters for DFTB+

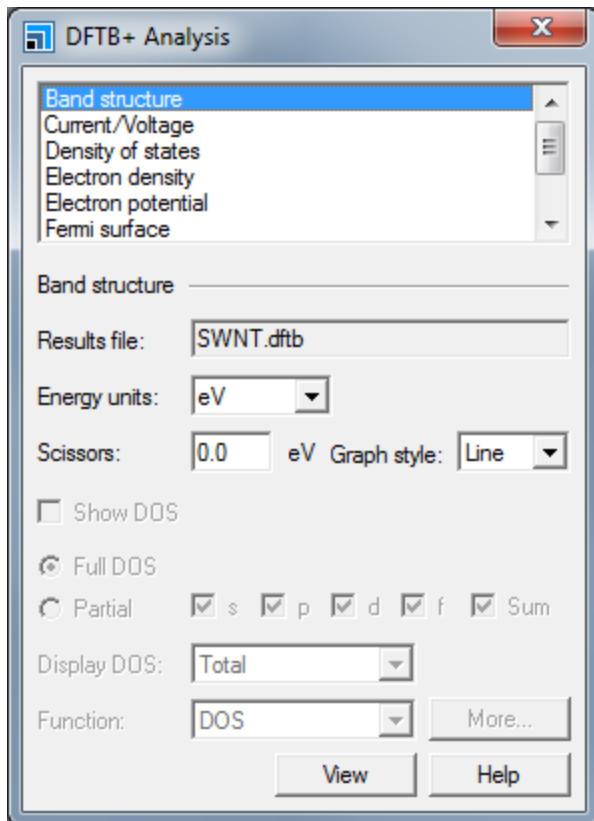
```
Repulsive parameter creation finished  
Returned parameterization found in Fit16
```

The CH With Forces.txt document contains the job output (there could be slight numerical differences compared to the sample output above). At the bottom of the document, find a table with fitting results for the different cut-off factors used. The total error is the accumulated squared fitting error in Hartree for all conformations. The fit with the lowest error is not necessarily going to give the best results when tested. The error measurement is for the total error, while you want good accuracy around the equilibrium points. So it is worthwhile to validate more than one of the returned parameter sets. The fitting with the lowest total error returns in the job folder, while the [Alternatives](#) subfolder contains a collection of all fittings.

To visualize the parameters, you need to analyze the .skflib output documents.

Click **DFTB+**  on the **Modules** toolbar and select **Analysis** or choose **Modules | DFTB+ | Analysis** from the menu bar.

This opens the DFTB+ Analysis dialog.

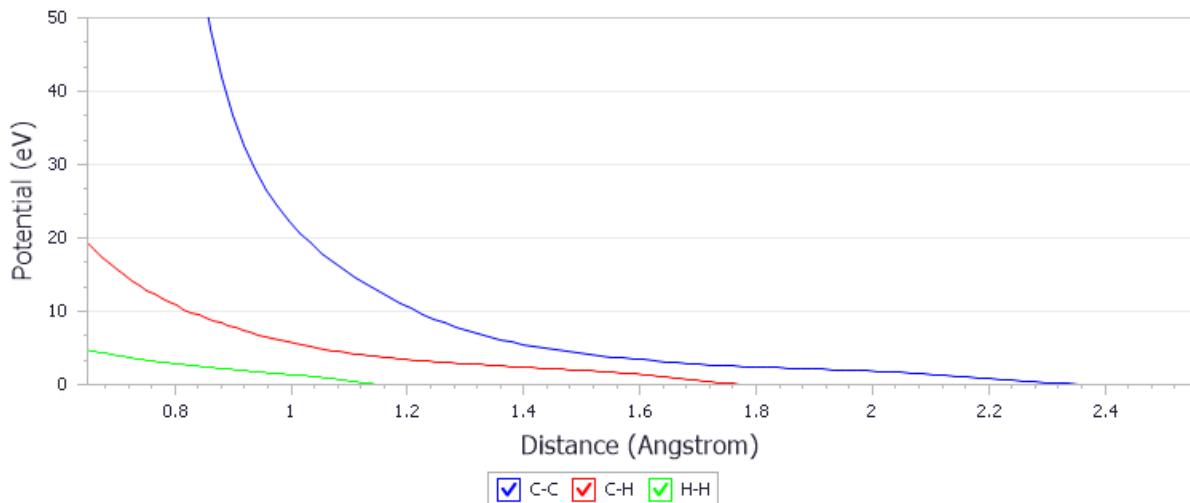


DFTB+ Analysis dialog

Select **Slater-Koster parameters** and ensure the CH With Forces.skflib file is the active document and displayed as the **Results file**. Select the **View Hamiltonian matrix elements** and the **View overlap matrix elements** checkboxes. Click **View**.

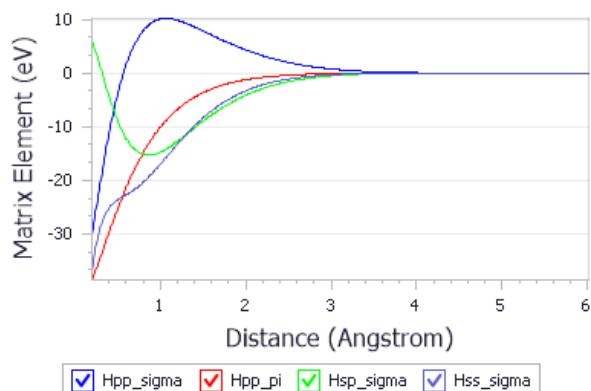
This opens two charts, one showing the short range potentials, and one showing the Hamiltonian and overlap matrix elements.

DFTB+ Short range potential

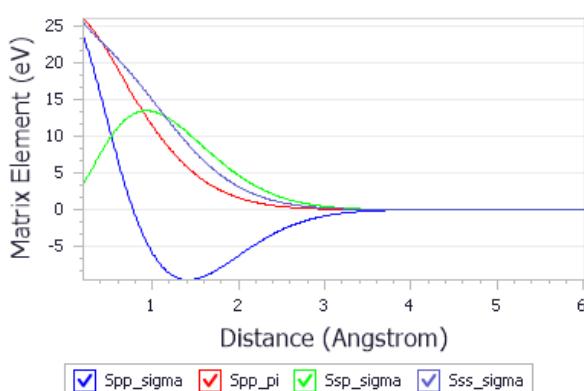


DFTB+ Analysis view, Short range potential

DFTB+ Hamiltonian Matrix Elements - C-C



Overlap Matrix Elements - C-C



DFTB+ Analysis view, Slater-Koster Parameters

The short range potential chart is important, any oscillations in the tail indicate that there is not enough data to fit against in this region. If the curve oscillates around zero you are likely better off with a shorter cut-off radius, otherwise you need to extend the conformation path responsible for the data in that region.

Zoom in at the tail of the curves and investigate whether there are any oscillations.

Generate the same analysis charts for the other job and compare the results.

To evaluate your parameterization, you perform a geometry optimization on hydrocarbon structures using both DFTB+ and DMol³ and compare the results. Since a parameter evaluation is likely to be repeated many times, it is good practice to script the test. For this tutorial, a Materials Studio script is supplied which compares geometry optimization results between DMol³ and DFTB+.

Select the CHparameters root in the Project Explorer and create a new folder named **Validation**.

Copy the optimized **H2.xsd**, **methane.xsd**, **ethane.xsd**, **ethene.xsd**, and **benzene.xsd** structures into the **Validation** folder.

Copy the **CH No Forces.skflib** file from the **CH No Forces DFTB+ Parameterization** folder to the **Validation** folder.

The DFTB+ Final Evaluation Perl script performs geometry optimization on all 3D Atomistic documents in the folder and compare any distance and angle measurements in the files. The results return in an **output.txt** file with detailed data for each structure and a statistical analysis of the results.

Create a distance measurement for each bond type and an angle measurement for each angle type in each of the structures in the Validation folder.

Ensure that one of the **.xsd** documents in the **Validation** folder is the active document.

From the menu bar, select **Tools | Materials Studio Scripts | Quantum Mechanics | DFTB+ Parameterization | DFTB+ Final Evaluation** to open the DFTB+ Final Evaluation dialog. Specify the **Slater_Koster_Name** as **CH No Forces.skflib** and click **OK**.

The calculations take a few minutes. Also run the validation for the parameterization with forces.

Delete the **CH No Forces.skflib** file from the **Validation** folder.

Copy the **CH With Forces.skflib** file to the **Validation** folder.

From the menu bar, select **Tools | Materials Studio Scripts | Quantum Mechanics | DFTB+ Parameterization | DFTB+ Final Evaluation** to open the DFTB+ Final Evaluation dialog. Specify the **Slater_Koster_Name** as **CH With Forces.skflib** and click **OK**.

The evaluation script generates an **output.txt** file containing the comparisons between each of the geometry monitor lengths or angles after optimization with DFTB+ and DMol³. For example, the validation of the **CH With Forces.skflib** library gives:

DFTB+ Settings:

Quality	:	Fine
UseSmearing	:	Yes
Smearing	:	0.002
SmearingFunction	:	Fermi
SKFLibrary	:	CH With Forces.skflib
Optimizecell	:	Yes
MaximumSCCIterations	:	100
WriteLevel	:	Silent

DMol3 Settings:

Quality	:	Fine
TheoryLevel	:	GGA
NonLocalFunctional	:	PBE
BasisFile	:	4.4
UseSmearing	:	Yes
Smearing	:	0.002

```
MaximumSCFCycles      : 100
OptimizeCell          : Yes

H2
--
DMol3 H1-H2 = 0.74844
DFTB+ H1-H2 = 0.75390
Diff  H1-H2 = 0.00546
=====

benzene
-----
DMol3 H9-C3 = 1.09090  C4-C5 = 1.39829
DFTB+ H9-C3 = 1.09740  C4-C5 = 1.41618
Diff  H9-C3 = 0.00650  C4-C5 = 0.01789

DMol3 H12-C7-C6 = 120.00000  C4-C5-C6 = 120.00000
DFTB+ H12-C7-C6 = 119.99954  C4-C5-C6 = 120.00100
Diff  H12-C7-C6 = -0.00046  C4-C5-C6 = 0.00100
=====

ethane
-----
DMol3 C1-C2 = 1.52854  H3-C1 = 1.10061
DFTB+ C1-C2 = 1.55031  H3-C1 = 1.10915
Diff  C1-C2 = 0.02177  H3-C1 = 0.00853

DMol3 H4-C1-H3 = 107.37930  C2-C1-H5 = 111.48988
DFTB+ H4-C1-H3 = 107.76310  C2-C1-H5 = 111.12885
Diff  H4-C1-H3 = 0.38380   C2-C1-H5 = -0.36103
=====

ethene
-----
DMol3 C1-C2 = 1.33526  H4-C1 = 1.09150
DFTB+ C1-C2 = 1.33716  H4-C1 = 1.09942
Diff  C1-C2 = 0.00190  H4-C1 = 0.00792

DMol3 H3-C1-C2 = 121.65091  H4-C1-H3 = 116.69818
DFTB+ H3-C1-C2 = 122.41706  H4-C1-H3 = 115.16937
Diff  H3-C1-C2 = 0.76615   H4-C1-H3 = -1.52881
=====

methane
-----
DMol3 H5-C2 = 1.09753
DFTB+ H5-C2 = 1.10547
Diff  H5-C2 = 0.00794

DMol3 H5-C2-H4 = 109.47122
DFTB+ H5-C2-H4 = 109.47139
Diff  H5-C2-H4 = 0.00017
=====
```

Bond Error Statistics:

H-H = 5.46422e-03

C-C = 1.38548e-02

H-C = 7.72175e-03

=====

Total Average = 9.73947e-03

Angle Error Statistics:

CCC = 1.00252e-03

HCH = 6.37593e-01

CCH = 3.61033e-01

HCC = 3.83305e-01

=====

Total Average = 4.34489e-01

Your results vary as the conformations for the perturb paths are randomly generated. An error for a bond distance around 0.02 Å is acceptable.

If you compare the evaluation data between the parameterizations you can find that, as expected, the CH With Forces gives the best results. While CH No Forces parameterization is much less accurate.

You can improve the accuracy for bond types that give poor results by adding more data or, if the number of steps is already high, by increasing the weight for the corresponding path. It is also possible that data from neighboring bond types disturb the fitting, in this case a decrease in the conformation width and the weight function width could counteract the problem.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

This is the end of the tutorial.

Suggested further studies:

- Compare the carbon nanotube band structures between DMol³ and the DFTB+ generated parameters. The band structure is independent of the short range potential, so the CH No Forces and CH With Forces parameterizations give the same result.
- Expand the evaluation set, locate, and try to correct poorly performing structures. Sometimes poor performance results from missing physics and cannot be corrected.
- Extend the library with a third element using the *Extend existing library* checkbox on the *Interactions* tab.

Simulating electron transport with DFTB+

Purpose: To introduce DFTB+ calculations on transport devices

Modules: Materials Visualizer, DFTB+

Time: 

Prerequisites: Building transport devices for electron transport calculations Visualizer Tutorial, Sketching a porphyrin, Working with isosurfaces and slices, Geometry optimization of a carbon nanotube

Background

DFTB+ is a semi-empirical tight binding method based on a two-centered approach to density functional theory (DFT). The use of a tight binding approach makes it faster than ordinary DFT methods but it also makes it dependent on parameter sets known as Slater-Koster libraries. Libraries are provided for standard organic molecules and semi-conductors.

The Electron Transport task in DFTB+ applies the non-equilibrium Green's function (NEGF) formalism to model electron transport between two or more electrodes. The Electron Transport task allows you to calculate properties such as transmission function and current voltage characteristics as well as potential charge density distributions.

Introduction

In this tutorial you will use the DFTB+ module to calculate transport properties for graphene nano ribbons.

This tutorial covers:

- [Getting started](#)
- [Initial preparation](#)
- [To set up the electron transport job](#)
- [To analyze the transmission](#)
- [To analyze the electron potential](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DFTB Transport** as the project name, click the **OK** button.

The new project is created with DFTB Transport listed in the Project Explorer.

2. Initial preparation

The first step is to import a graphene unit cell.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Examples\Documents\3D Model\Graphene.xsd**, then click the **Open** button.

From the graphene unit cell you will create a zig-zag graphene nanoribbon.

Select **Build | Symmetry | Supercell** to open the Supercell dialog. Set **B** to **6** and click the **Create Supercell** button. Close the dialog.

Delete the top-most hexagon and cap the edges with hydrogen atoms by clicking the **Adjust Hydrogen** button.



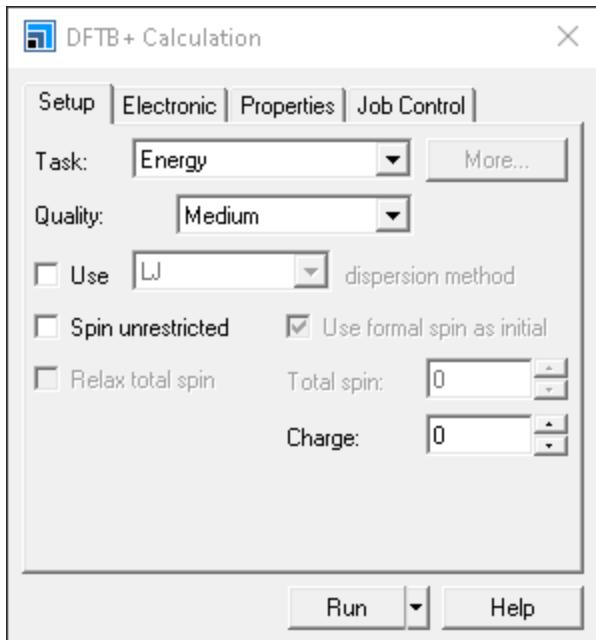
Graphene nanoribbon unit cell

Increase the lattice constants to avoid interaction between periodic copies.

Right-click in the document and select **Lattice Parameters**. On the **Advanced** tab uncheck the **Keep fractional coordinates fixed during changes to the lattice** checkbox. On the **Parameters** tab, set **b** to **80 Å** and **c** to **50 Å**. Close the dialog.

Optimize the geometry of the nano ribbon using the DFTB+ Geometry optimization task.

Click the **DFTB+ ▾** button on the **Modules** toolbar and select **Calculation** or choose **Modules | DFTB+ | Calculation** from the menu bar.



DFTB+ Calculation dialog, Setup tab

Change the **Task** from Energy to **Geometry Optimization**. Click the **More...** button to open the Geometry Optimization dialog, check the **Optimize cell** checkbox and close the dialog.

Ensure the **Quality** is set to **Medium**.

On the **Electronic** tab set the **Slater-Koster library** to **mio**.

To improve the SCC convergence it is good to use a non-zero temperature for the calculation.

Check the **Use smearing** checkbox and set the **Smearing** to **0.001 Ha**. Click **More...** to open the DFTB+ Electronic Options dialog, for the **Distribution function** select **Fermi**, and close the dialog.

Start the geometry optimization calculation.

Click the **Run** button and close the dialog.

A folder is created, **Graphene DFTB+ GeomOpt**, which will contain the optimized structure when the calculation is complete.

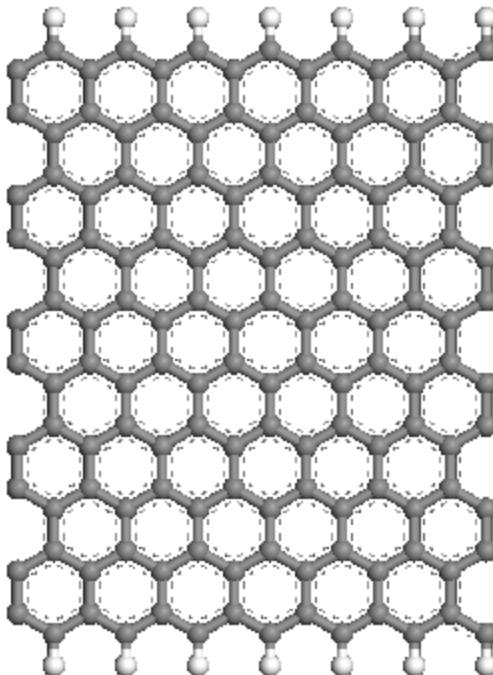
You will now use the optimized nanoribbon to create an ideal nanoribbon and a nanoribbon containing a quantum dot for transport.

Use copy and paste to create two copies of the optimized **Graphene.xsd** document in the top level of the project. Rename them **GrapheneWireIdeal.xsd** and **GrapheneWireQD.xsd**.

Ensure that **GrapheneWireIdeal.xsd** is the active document. Open the **Supercell** dialog and set **A** to **7**. Click the **Create Supercell** button.

Open the **Display Style** dialog, on the **Lattice** tab change the **Style** to **Original**.

Select **Build | Symmetry | Nonperiodic Superstructure** from the menu bar. Ensure the contact ends are straight, and if not, remove atoms until they are aligned as shown in this image.



Nanoribbon

The structure is now ready to have electrodes added to it.

Select **Build | Build Transport Device | Build Electrode** to open the Build Electrode dialog. Set **Electrode direction** to **-X** and click the **Build** button. Then set **Electrode direction** to **+X** and click the **Build** button again.

Use the optimized nano ribbon to create a nanoribbon with a central quantum dot.

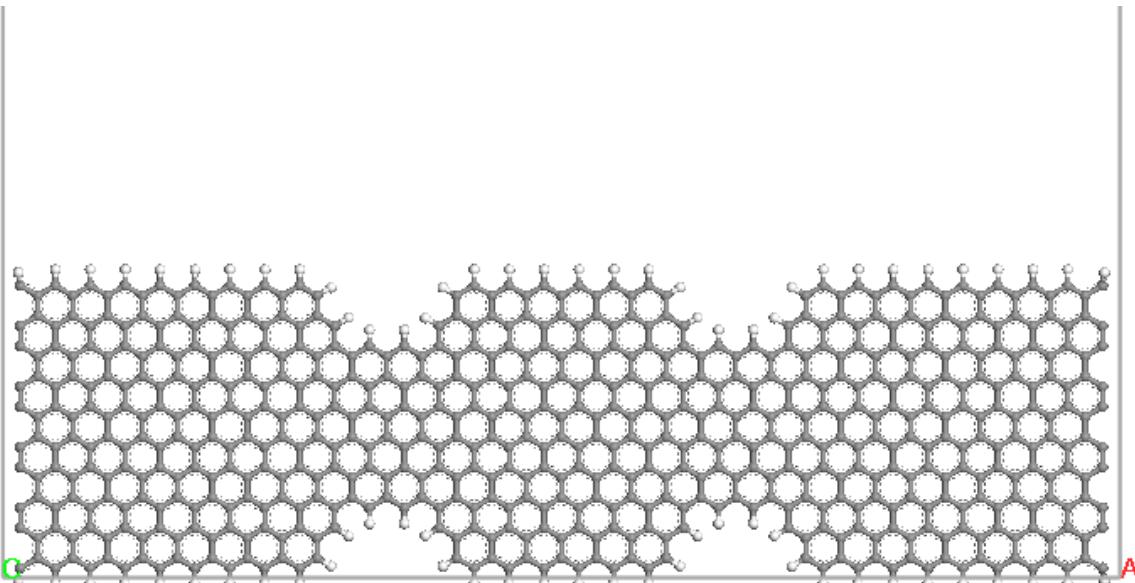
Make **GrapheneWireQD.xsd** the active document. On the **Supercell** dialog set **A** to **32** and click the **Create Supercell** button. Close the dialog.

Change the display style for the lattice to **Original** and close the Display Style dialog.

Remove atoms and cap the edges with hydrogen atoms using the **Adjust Hydrogen** tool to create the nanoribbon in the image below. Do not adjust the hydrogens for the terminal carbon atoms at the limits of the unit cell.

Tips:

- There are 18 carbons (9 hydrogens) on the left edges before the first defects and 18 carbons (9 hydrogens) on the right after the second defects.
- The central sections have 13 carbons (6 hydrogens) along the edge.
- You may need to remove some carbon atoms along the left side to obtain a structure matching the image below.



Nanoribbon with quantum dot

Tip: If you wish to geometry optimize the new structure it can be done now. Remember to constrain enough atoms on both sides of the central structure to ensure the Build Electrode tool can detect the periodicity of the contacts.

Once you are happy with the structure remove the periodicity and add electrodes to the end of the device.

Select **Build | Symmetry | Nonperiodic Superstructure** from the menu bar. Ensure the contact ends are straight, and if not, remove atoms until they are straight.

On the **Build Electrode** dialog, set **Electrode direction** to **-X** and click the **Build** button. Then set **Electrode direction** to **+X** and click the **Build** button again. Close the Build Electrode dialog.

Tip: If the **Build** button on the Build Electrode dialog is disabled, this means that the structure's periodicity is not sufficient. To improve the organization of the structure, click the **Clean** button (you may need to do this more than once before the **Build** button becomes enabled).

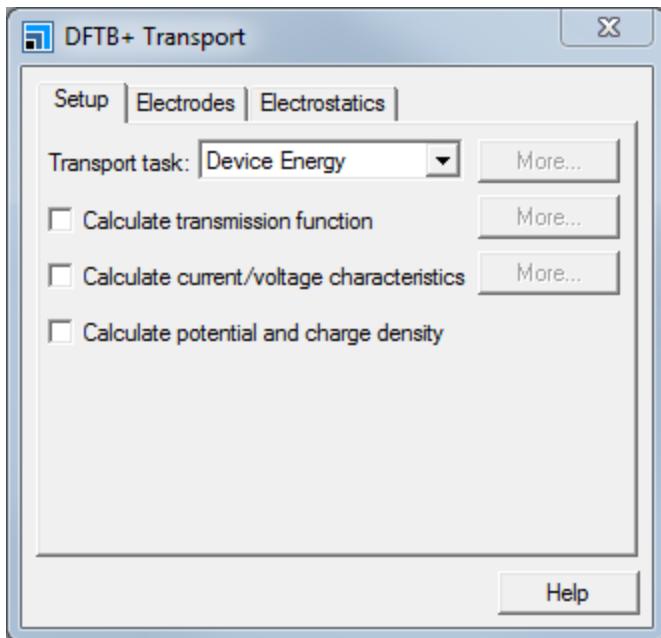
3. To set up the electron transport job

You now have two device structures ready for use with the DFTB+ Electron transport task.

Begin by setting up a calculation of the transmission for the ideal nanoribbon.

Make **GrapheneWire1deal.xsd** the active document.

Open the **DFTB+ Calculation** dialog, on the **Setup** tab select **Electron Transport** from the **Task** dropdown list. Click the **More...** button to open the DFTB+ Electron transport dialog.

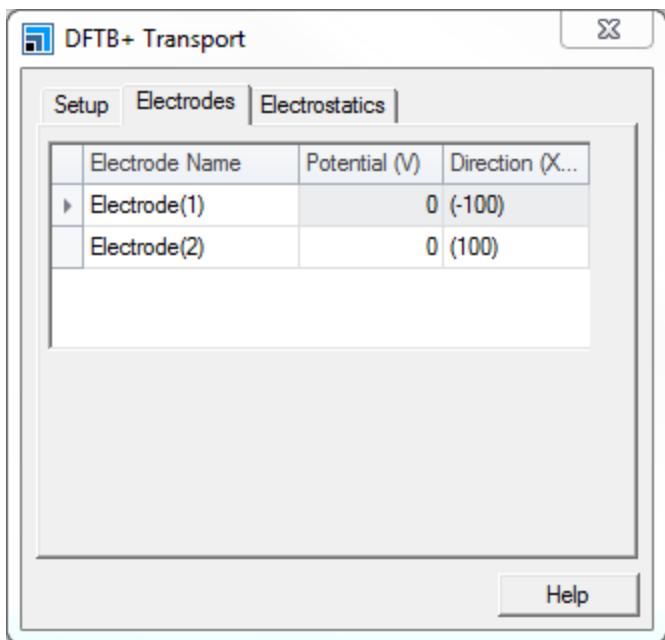


The DFTB+ Electron transport dialog contains settings specific to the Electron transport task.

Check the **Calculate transmission function** and **Calculate potential and charge density** checkboxes.

The job will now calculate the transmission functions between the electrodes and return data for electron potential and charge density.

Select the **Electrodes** tab.



The Electrodes tab shows information about and allows you to modify settings for the electrodes. Change the name of the electrodes.

Change the name of **Electrode(1)** to **source** and **Electrode(2)** to **drain**. Close the DFTB+ Transport dialog.

The names of the electrode objects are also modified in the 3D Atomistic document.

Note: If you use the Properties Explorer to change the name of electrodes, the electrode will use any settings related to *new name*. If no settings exist the default settings will be applied. When the name is changed on the DFTB+ Transport dialog the current settings will be used with the new name.

As part of the calculation each electrode will be modeled as a semiperiodic structure in order to calculate charge, potential and Fermi level. You need to set the k-point settings to be used for the calculation. For 2D periodic devices you also need to set the k-points perpendicular to the device. Employing the **Separation** setting allows you to specify a custom value of 0.02, this provides better sampling than the **Fine Quality** option.

Systems with open boundary conditions often have problems with convergence for the self consistent convergence. To improve the convergence reduce the mixing parameter for the charge mixing.

On the **Electronic** tab of the DFTB+ Calculation dialog click the **More...** button to open the DFTB+ Electronic Options dialog.

On the **SCC** tab set the **Max. SCC cycles** to **500** and the **Mixing amplitude** to **0.05**.

On the **k-points** tab select the **Separation** radio button and set a value of **0.02** 1/Å. Close the dialog.

You are now ready to start the transport job.

Click the **Run** button.

A text document named **Status .txt** is displayed, reporting the status of the calculation. This document is updated regularly until the calculation is complete, it can be a useful aid to indicate the progress of your calculation.

You will now set up a calculation for the nano ribbon with the central quantum dot.

First change the name of the electrodes to source and drain.

Make **GrapheneWireQD.xsd** the active document. Open the **DFTB+ Transport** dialog, on the **Electrodes** tab change the name of **Electrode(1)** to **source** and **Electrode(2)** to **drain**.

Since we expect the transmission spectra of this device to be more complex you should increase the number of steps for the transmission function.

On the **Setup** tab of the DFTB+ Transport dialog, click the **More...** button for **Calculate transmission function** and set the number of **Steps** to **401**. Close both dialogs.

You are now ready to launch the job.

Click the **Run** button and close the dialog.

4. To analyze the transmission function

When the calculations are complete the results are returned in the **GraphenewireIdeal DFTB+ Transport** and **GraphenewireQD DFTB+ Transport** folders in the Project Explorer.

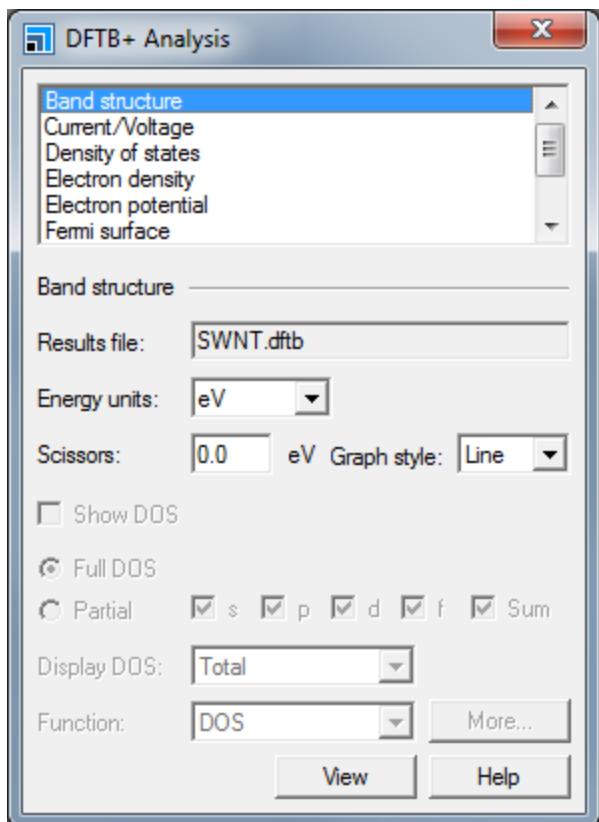
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

In the **GrapheneWireIdeal DFTB+ Transport** folder double-click on **GrapheneWireIdeal.xsd**

You will now analyze the results using the DFTB+ Analysis module.

Click the **DFTB+ ** button on the **Modules** toolbar and select **Analysis** or choose **Modules | DFTB+ | Analysis** from the menu bar.

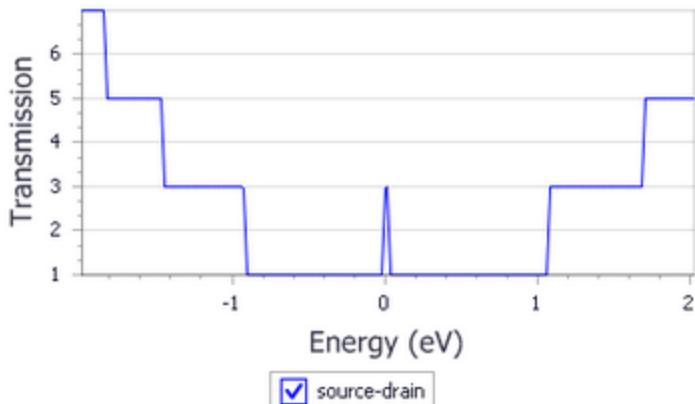
This opens the DFTB+ Analysis dialog.



Select **Transmission** from the list and click the **View** button.

A plot of the transmission function is shown.

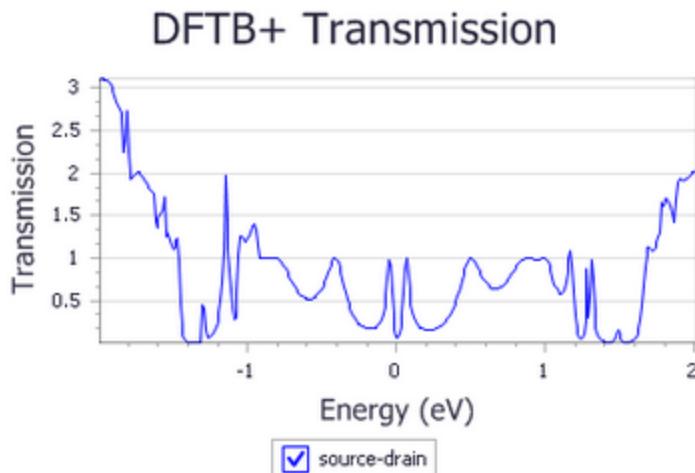
DFTB+ Transmission



The transmission for an ideal wire will have a step like structure where the transmission value is equal to the number of available bands in the band structure for the wire. The energies of the transmission function are plotted relative to the lowest chemical potential of the electrodes. Notice that zig-zag nanoribbons have a characteristic peak at the Fermi level.

In the **GrapheneWireQD DFTB+ Transport** folder double-click on **GrapheneWireQD.xsd** and click the **View** button on the **DFTB+ Analysis** dialog.

This shows the transmission function for the nanoribbon with a quantum dot.



Note: If your Transmission chart has two graphs plotted (one for drain-source and the other for source-drain) this indicates that your electrodes are not symmetric. In this case the graphs correspond to transmission in each direction, a single graph indicates that transmission is identical in both directions.

The quantum dot causes electrons to scatter and creates a more complicated transmission function.

5. To analyze the electron potential

Further insight into the electron transport properties of the structure can be gained.

Select **Electron potential** from the list and uncheck the **View isosurface on import** checkbox.

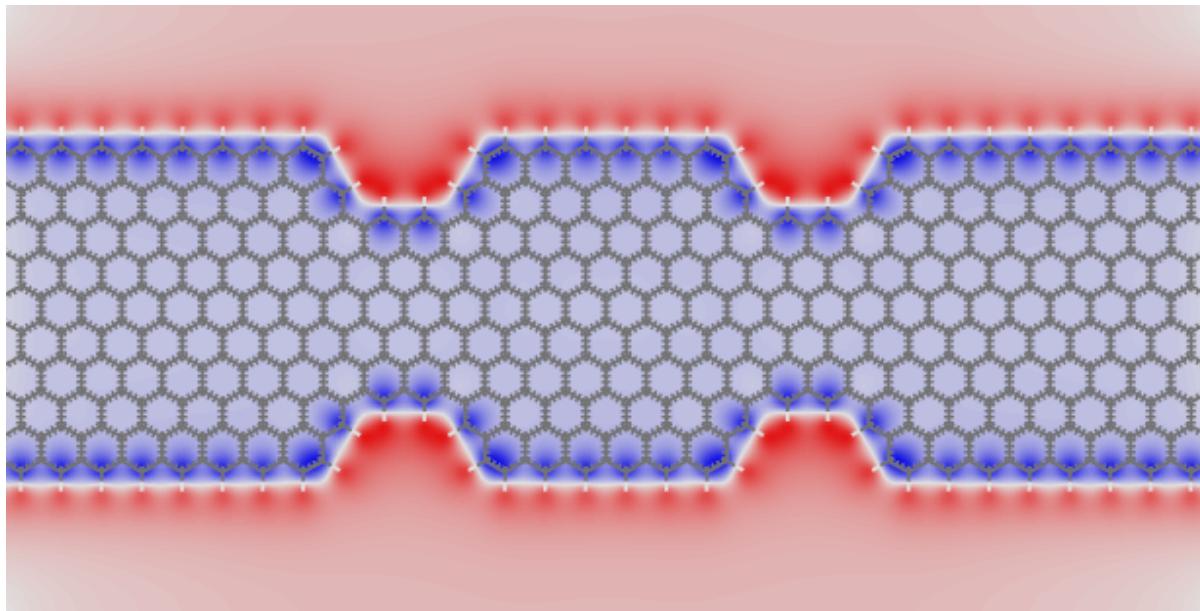
Make **GrapheneWireQD.xsd** the active document and click the **Import** button.

This imports the electron potential field to the document.

Click the arrow for the **Create Slices** button  on the toolbar and select **Parallel to A & B axis**.

Click the **Color Maps** button  to open the Color Maps dialog, change the range to **-0.85** and **0.85** and set the **Spectrum to Blue-White-Red**.

This creates a slice along the X and Y plane of the structure where blue is negative potential and red is positive potential.



The hydrogen atoms have a large positive potential while the carbon atoms have a large negative potential at the surface and a potential close to zero in the central region.

This is the end of the tutorial.

Calculating the Minimum Energy Path of a molecular switch

Purpose: Introduces the use of FlexTS together with DMol³ and DFTB+ to compute and refine a multi-step reaction pathway.

Modules: Materials Visualizer, DMol³, DFTB+, FlexTS, optionally Pipeline Pilot Connector

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial, Sketching a porphyrin Visualizer Tutorial

Background

The modeling of chemical reactions requires an efficient way to identify and validate chemical transition states; a universal problem in theoretical chemistry. Chemical reaction pathways frequently have multiple steps, requiring the correct identification of intermediate states for the simulation of reaction pathways.

Introduction

This tutorial introduces you to the main working modes of the FlexTS module, using a hierarchical method to investigate the tautomerization barriers of the molecular switch naphthalocyanine ([Liljeroth, Repp, Meyer, 2007](#)). You start by exploring the entire reaction pathway using the DFTB+ module in Materials Studio, which shows two separate equivalent steps in the tautomerization reaction. Then you use the DMol³ module to accurately determine the transition state for one of the barriers, which fully determines the energy landscape of the entire switch.

This tutorial covers:

- [Getting started](#)
- [To prepare the molecular structures for the calculation](#)
- [To calculate the reaction pathway using DFTB+ and analyze the results](#)
- [To graph the reaction pathway for DFTB+ using a Pipeline Pilot protocol \(optional\)](#)
- [To refine a transition state using DMol³](#)
- [To compare the reaction pathways for DFTB+ and DMol³ using a Pipeline Pilot protocol \(optional\)](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

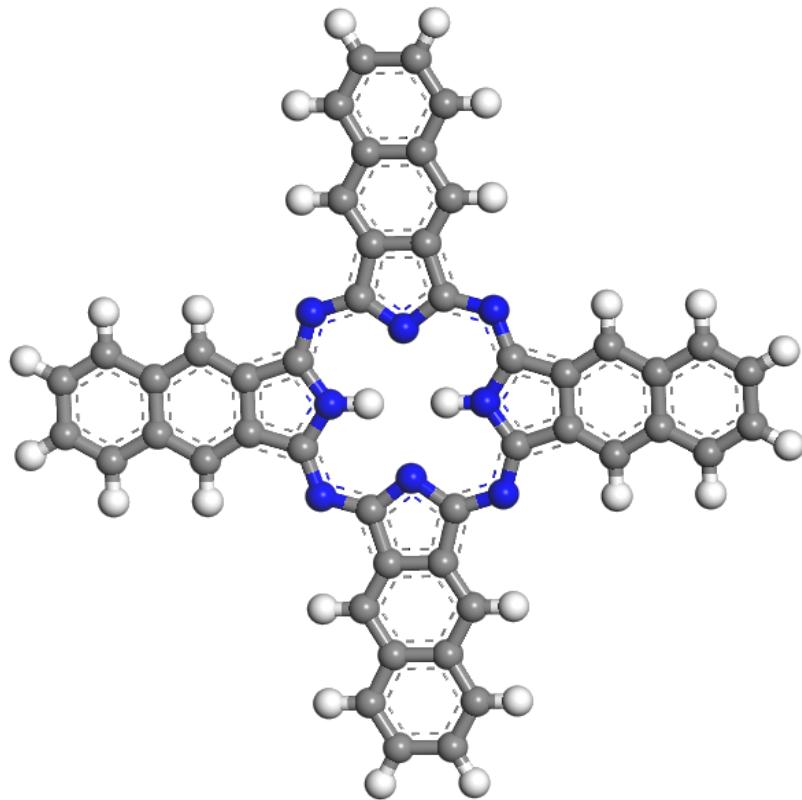
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MEP** as the project name, click **OK**.

This creates a new project with *MEP* listed in the Project Explorer.

2. To prepare the molecular structures for the calculation

In this section of the tutorial, you build the reactants and products in two different 3D Atomistic documents. The first step is to open a new 3D Atomistic document and sketch the reactant, naphthalocyanine.



Open a new 3D Atomistic Document and name it **reactant_start.xsd**. Starting from a porphyrin core, draw the reactant molecule shown above, with the central H atoms to the left and right. Click **Clean**  and save the document. Confirm that the molecule has 82 atoms with the chemical formula $C_{48}H_{26}N_8$.

Tip: You can create aromatic rings by pressing ALT while drawing six-membered carbon rings.

Ensure that the starting geometry of the reactant is reasonable by running a DFTB+ structure minimization.

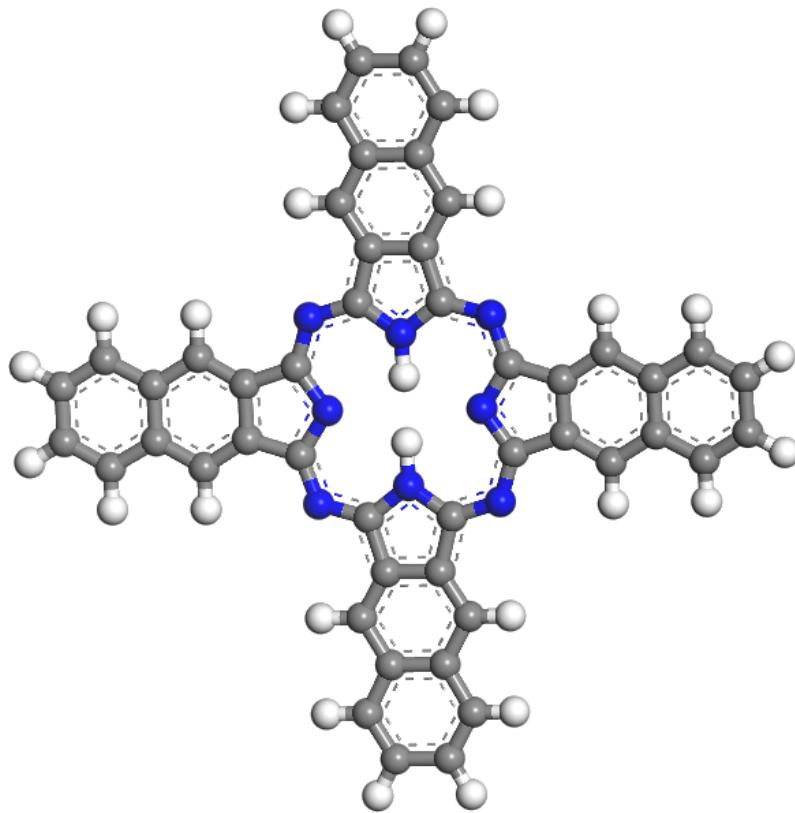
Open the **DFTB+ Calculation** dialog, change the **Task** to **Geometry Optimization** and click **Run**. When the optimization finishes, rotate the generated molecule to ensure that it is *completely flat*.

Copy the generated **reactant_start.xsd** file to the project root and rename the document **reactant.xsd**.

Tip: Alternatively, you can obtain the reactant structure from the Materials Studio examples by importing *Examples\Documents\3D Model\naphthalocyanine.xsd* into the root of your project and renaming it *reactant.xsd*.

DMol3: Calculating the Minimum Energy Path of a molecular switch

Next, create the product by modifying the reactant - this facilitates the subsequent creation of a reactant-product trajectory.



Create a copy of the **reactant.xsd** document by selecting it in the Project Explorer, press CTRL, and use the mouse to drag it onto the project root. Rename the new document **product.xsd**. On the **Atoms & Bonds** toolbar, click the **Bonds** arrow and select **Monitor Bonding** . Select the two central H atoms, press and hold SHIFT, click and hold the right mouse button, then drag the cursor along the bottom of the screen to rotate the atoms into the alternative set of trans positions (top and bottom) as shown above.

Without deselecting the central H atoms click **Clean** , click anywhere to clear the selection in the document, and save the document.

Tip: For the best visualization of reaction pathway calculations, keep monitor bonding turned on.

The next step is to create an initial trajectory with correct matching of all atoms.

Make sure that both documents **reactant.xsd** and **product.xsd** are open and that all other windows are closed. Select **Window | Tile Vertically** to display both structures side by side.

Open the **Tools | Reaction Preview** dialog and set **Reactant** and **Product** to the two structures that you have open on your desktop. Click **Match...** to open the **Find Equivalent Atoms** dialog.

The next step is critical to make sure that the reaction pathway makes chemical sense. However, since you drew the product from the reactant, there is an identical ordering of all the atoms in both structures. This makes it straight forward to achieve a correct match between reactant and product and to create an initial guess for the trajectory.

On the **Find Equivalent Atoms** dialog, click **Auto Find** to match reactant and product atoms. Select the first remaining unmatched atom in the file **reactant.xsd** and the corresponding first unmatched atom in the file **product.xsd**. Click **Set Match** and verify that all atoms are shown as matched. Repeat the last step until all atoms are matched. Close the **Find Equivalent Atoms** dialog.

On the **Reaction Preview** dialog, ensure selection of **Superimpose structures** and click **Preview**.

Rename the newly created trajectory **naphthalocyanine.xtd** and select **Monitor Bonding** . Save the trajectory and close the **Reaction Preview** dialog.

It is important to play the trajectory back and forth a few times now, to ensure correct matching of all the atoms. If this is not the case, you might sometimes see atoms "flying" through space without any connection to either reactant or product.

Tip: If you observe any misbehaving atoms while playing the trajectory, return to the *Reaction Preview / Match...* step to ensure correct selection of the equivalent atoms between reactant and product. When atoms do not move very far during a reaction, *Auto Find* can help you to speed up matching, but you might require some manual intervention depending on your system.

3. To calculate the reaction pathway using DFTB+ and analyze the results

The next stage of this investigation is to explore the energy landscape of the molecular switch using DFTB+.

Use the FlexTS module, you can access this on the DFTB+ and DMol³ dialogs through the Minimum Energy Path tasks. FlexTS crucially depends on highly accurate forces, so you must begin by tightening the self-consistent convergence thresholds for DFTB+ and by increasing the number of iterations to a safe number.

Open the **DFTB+ Calculation** dialog, select the **Electronic** tab, and click **More...** to open the **DFTB+ Electronic Options** dialog. Change **SCC tolerance** to **1e-10** and **Max. SCC cycles** to **100**. Close the dialog.

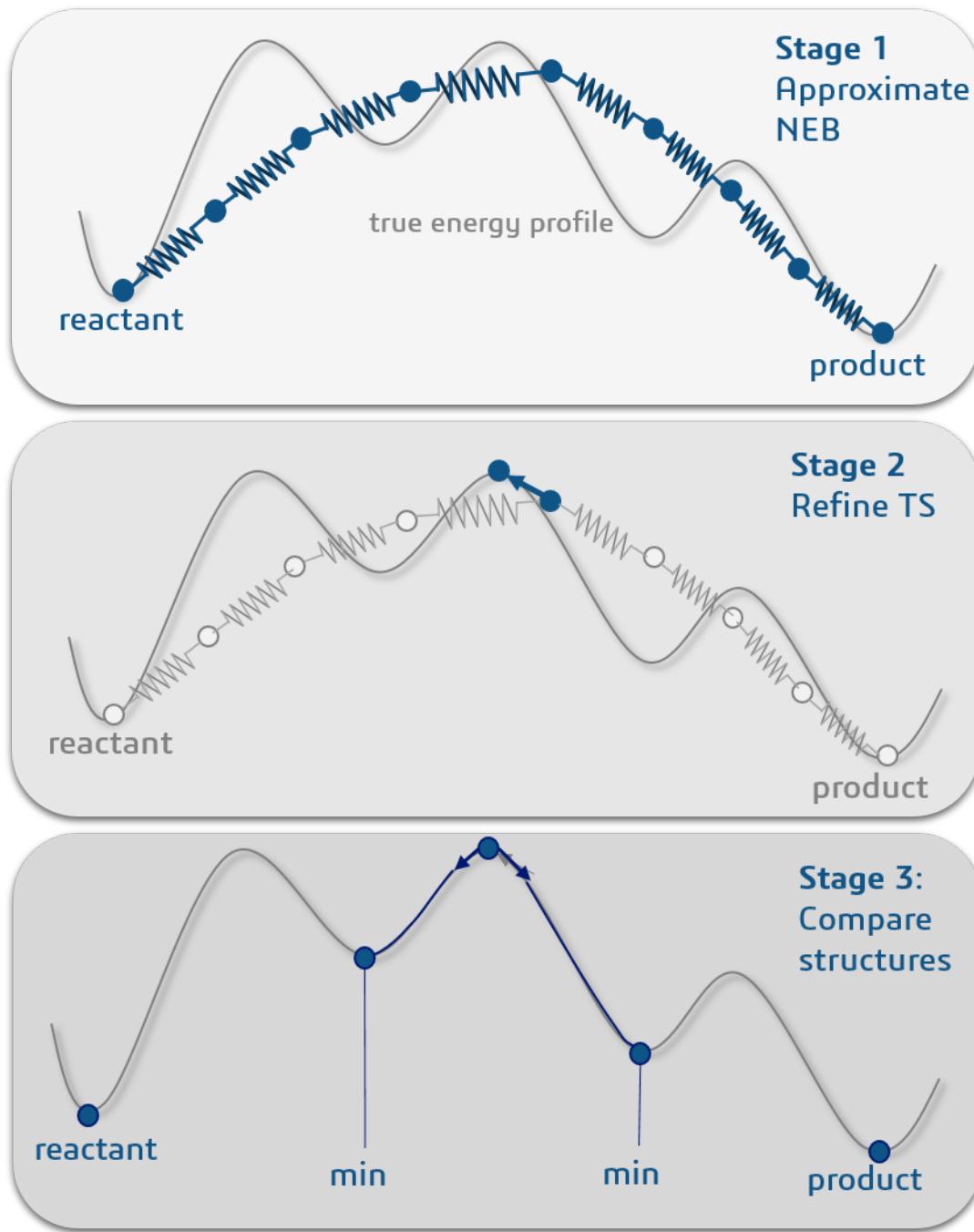
On the **DFTB+ Calculation** dialog, select the **Setup** tab and change the **Task** to **Minimum Energy Path**. Click **More...** to open the **DFTB+ Minimum Energy Path** dialog and inspect the different options.

The **Setup** tab contains basic information for running FlexTS, including three different modes:

DMol3: Calculating the Minimum Energy Path of a molecular switch

- **Full Path** consists of five stages:
 1. Optional optimization of the reactant and product states
 2. Nudged elastic band calculation to estimate the location of the transition states (TS)
 3. Refinement of the TS using a hybrid eigenvector following scheme based exclusively on energies and forces ([Kumeda et al. 2001](#))
 4. Displacement of the TS in the positive and negative direction of the transition vector followed by an optimization to identify the local minima corresponding to this particular reaction step
 5. Attempt to connect reactant and product states through individual steps using Dijkstra's algorithm

This procedure describes a single path cycle ([Carr et al, 2005](#)) as illustrated in the following image:



In the DFTB+ part of this tutorial, you use two successive path cycles to explore the naphthalocyanine molecular switch.

- **Nudged Elastic Band** interpolates the initial and final states in a reaction and optimizes an entire reaction path using a doubly nudged elastic band technique ([Trygubenko and Wales, 2004](#)) without further refinement of the transition state. Use this for extremely small barriers, to get a rough initial overview of the energy landscape, or to study barrierless reactions.
- **TS Path** begins with a guess for a single transition state and runs only stages (3) and (4) of the Full Path procedure to refine the transition state and to optimize the corresponding reactant and

product. Use this mode in the DMol³ section of the tutorial to get a more accurate estimate for the reaction barrier.

The other options on the *Setup* tab control:

- the number of path cycles
- whether to optimize reactants and product
- whether to include a geometry comparison when identifying local minima or transition states
- whether to use the initial trajectory as a guess for an NEB calculation (only when the active document is a trajectory)
- the basic parameters for the **Nudged Elastic Band** part of a FlexTS calculation

In general, for **Full Path** runs, choose *Determine the NEB parameters automatically*. This generates NEB parameters based on a predefined image density and maximal number of images. For certain cases, or for dedicated Nudged Elastic Band calculations, you might want to specify these numbers yourself.

The *Spring constant* controls the strength of the elastic band. In some cases, you can use this to speed up the calculation by allowing the system to relax to the actual minimum energy path more quickly. However, the exact spring constant value might be somewhat system-dependent.

Ensure that the **Run mode** is **Full Path**. For the **Number of path cycles**, specify a value of **2**.

Select the **Advanced** tab of the **DFTB+ Minimum Energy Path** dialog. Inspect the options available.

Most of the options on this tab are thresholds driving the detailed behavior of FlexTS.

Tip: The default options in Materials Studio FlexTS are set such that they provide good transition state convergence behavior in most standard cases. The particular scenario in this tutorial involves a reaction pathway that is significantly longer than the original guess. If such calculations do not converge, using more images can be helpful to get a better resolution of the path before attempting to find the transition state.

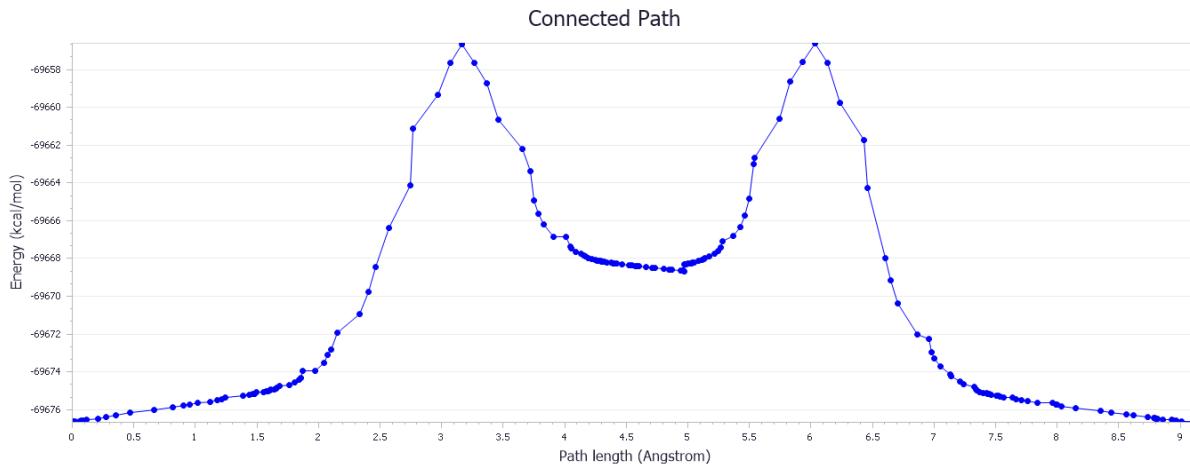
Select the **Setup** tab of the **DFTB+ Minimum Energy Path** dialog. Clear **Determine NEB parameters automatically** and increase **Images** to **12**.

Close the **DFTB+ Minimum Energy Path** dialog. On the **DFTB+ Calculation** dialog, select to the **Job Control** tab. Choose a suitable **Gateway location** and number of cores and click **Run**. Close the **DFTB+ Calculation** dialog.

This job takes some time to run. Once it completes, you can analyze the results.

In the **Project Explorer**, expand the **naphthalocyanine DFTB+ MEP** folder and inspect its contents.

The most important chart for this particular example is **naphthalocyanine Connected Path.xcd**. It contains the energy profile of the complete pathway found by FlexTS after successfully identifying all the steps required to connect reactant and product in a transition pathway.



You can see that this path has two separate steps with an intermediate minimum. You can open the corresponding trajectory file `naphthalocyanine Connected Path.xtd` to follow the pathway. The H-atoms in the molecular core do not jump in a concerted fashion but rather move step by step. This movement is symmetric in the sense that both individual barriers have the same shape (but inverted), and have matching reactant, product, and TS energies. You can use this symmetry to make the next steps easier.

Notes:

- The path length can depend on the drawing of the initial and final structure and may differ in your results.
- The default accuracy settings might lead to a path that is not completely symmetric, with small energy differences between reactant and product. This is expected, you can resolve it by using significantly more accurate convergence thresholds.

Tip: Make sure that you enable **Monitor Bonding**  for each document when investigating trajectories and other results.

The `naphthalocyanine Results.std` study table summarizes all the numbers and structures required to identify the transition states. The *All Segments* sheet of this study table contains one row for each of the barriers computed by the FlexTS run. The *Connected Path* sheet contains the individual steps involved in the actual path linking reactant and product. In this particular calculation, both tabs contain the same results but they might be in a different order.

The results study table also has a *Computational Settings* column, which contains all the non-default settings on the dialog in scripting format and allows you in principle to recreate the calculation. This column is particularly helpful when storing the results of multiple *Minimum Energy Path* calculations in a single study table. It keeps track of the different modules, electronic structure settings, charge, and spin settings and so one for each computed barrier individually.

If you focus on the *Connected Path* sheet, you can see the forward and reverse barriers listed in kcal/mol. Each row begins with a collection document that contains the reactant, TS, and product - ordered according to their relative energies. You can use these documents for further analysis. For example; as inputs for a refined accuracy calculation of the barrier, or as input for a Kinetics task in DMol³ or CASTEP.

Identify the forward and reverse barrier for the DFTB+ calculation.

DMol3: Calculating the Minimum Energy Path of a molecular switch

The energy difference between the reactant or product and the TS is around 20 kcal/mol. The energy difference between the two TS and the intermediate state is about 12 kcal/mol.

The naphthalocyanine MEP Report.txt document contains the text output of the FlexTS run. When inspecting this document, you can identify the different sections of a single path cycle and find that in this case the calculation required two path cycles to complete.

If required, you can investigate consistency to help to troubleshoot calculations. First, the NEB calculation must converge successfully to the threshold you specified. You can verify this by searching the document for the term **Energy per image**, which is in the header of the NEB section.

After the successful completion of the NEB calculation, FlexTS automatically optimizes the transition state guess for the images it identifies as candidates. You can find this section by searching for **Beginning of optimization cycle**. Each cycle consists of two steps; first converging the direction of the lowest-eigenvalue eigenvector of the Hessian matrix (for example, the uphill vector of the transition state) and then following that vector until it becomes no longer relevant. It is important to explicitly verify that the converged eigenvalue for each new direction is negative.

Finally, each FlexTS calculation returns a number of trajectories and linked charts. Each row of the **All Segments** tab of the results study table corresponds to one trajectory and one chart in the **Path** folder. The calculation returns an additional chart and trajectory the job folder if it identifies a connected path. The trajectory corresponds to the two downhill geometry optimizations from the transition state, taken from [stage 4 of the full path task](#). The **NEB** folder contains trajectories and charts for each nudged elastic band calculation run during a calculation. You can use this to study the convergence behavior of the initial stages of the calculation.

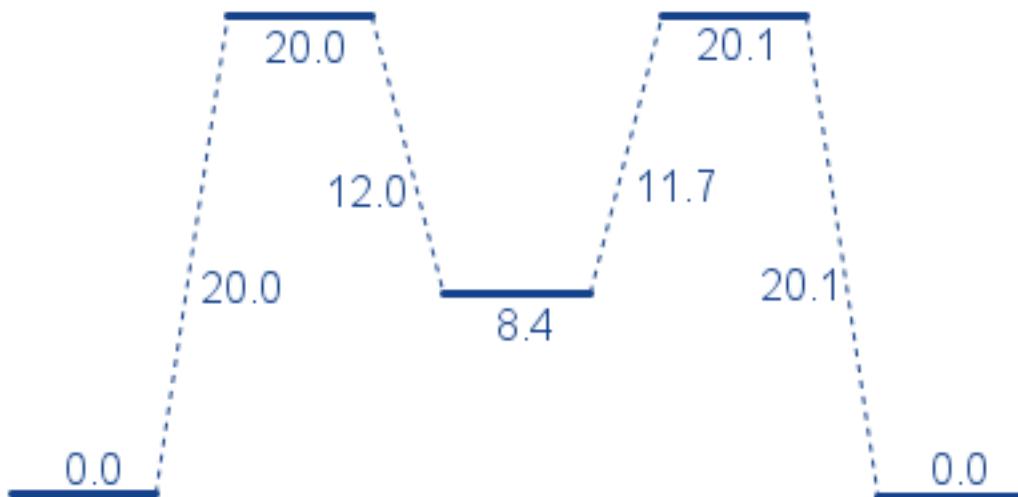
4. To graph the reaction pathway for DFTB+ using a Pipeline Pilot protocol (optional)

In this section, you use a Pipeline Pilot protocol to graph the multistep barrier results from the DFTB+ calculation. This optional section requires a Pipeline Pilot Server with the Materials Studio Collection and the Pipeline Pilot connector in Materials Studio.

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results.std** and make sure that the **Connected Path** sheet is active. Open the **Pipeline Pilot Protocols** dialog from the **Tools** menu and select the **Protocols\BIOVIA Materials Studio\Reaction Chemistry\Reaction Pathway Display** protocol. Click **Run** and close the dialog.

This protocol allows you to take the result from a FlexTS calculation and obtain a publication-quality graph that visually represents the location of different minima and transition states. Inspect the options that are available. You can control the canvas size, font size, and optionally turn off labels for barriers and stationary points.

Once the results are returned, open the **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results Reaction Pathway Display\ naphthalocyanine Results.png** file.



Minima and transition states plot

This plot shows the two-step process in a standardized visual way that practitioners can understand immediately. It can also form the basis of more complicated figures, though you may want to switch off some of the labels for more advanced processing. The energy units are always in kcal/mol.

Note: The energies in this plot correspond to the final energies after optimizations beginning at the transition state. They might not correspond exactly to the energies of the initial reactants and products at the start of the FlexTS calculation.

5. To refine a transition state using DMol³

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results.std** and double-click the structure document in the first row of the **Connected Path** sheet.

This collection document contains all the relevant information to serve as a starting point for a DMol³ Minimum Energy Path calculation. You can run a complete path cycle based on the Reactant and Product physical systems specified, regenerating an entire reaction step in this particular system. In this case, use the TS found in the DFTB+ calculation as a starting guess for a TS Path run.

Open the **DMol3 Calculation** dialog and change the **Task** to **Minimum Energy Path**, the **Quality** to **Fine**. Select the density functional by changing **Functional** to **GGA - PBE**.

On the **Electronic** tab, click **More...** to open the **DMol3 Electronic Options** dialog. Decrease the **SCF tolerance** to **1e-8** and increase the **Max. SCF cycles** to **100**. Close the **DMol3 Electronic Options** dialog and select the **Setup** tab of the **DMol3 Calculation** dialog.

Click **More...** to open the DMol3 Minimum Energy Path dialog and inspect the options available on the dialog.

The DMol³ Minimum Energy Path task works identical to its twin in DFTB+. The main difference is that the energy units used for input are in Ha. These units are converted to kcal/mol, as used by FlexTS internally and by Materials Studio in general.

In this example, use the TS found in DFTB+ to initialize our DMol³ transition state search. There is only one option to change to achieve this.

On the **DMol3 Minimum Energy Path** dialog, change the **Run mode** to **TS Path**, and close the dialog.

On the **Job Control** tab of the **DMol3 Calculation** dialog, select a suitable gateway and a number of processors and click **Run**.

This calculation takes some time to complete.

The DMol³ Minimum Energy Path task works differently to the other tasks in DMol³. In particular, this task runs FlexTS which in turn works with the DMol³ calculation engine. This means that there is no input file that you can inspect or modify directly. Instead, DMol³ input files are generated on the fly when required by FlexTS.

When the calculation finishes, download and inspect the results. You can find a similar result to one of the single barriers in the initial DFTB+ calculation. Now with a more accurate energy barrier of about 12 kcal/mol between reactant or product and TS, and around 4 kcal/mol between the intermediate minimum and the transition state. Each row of the study table document also contains the computational settings used for this calculation, which can be useful as reference later.

You can use the collection document in the final result study table for further processing, for example in a DMol³ Kinetics calculation to generate input for reaction mechanisms in Cantera.

You might also want to inspect the report document naphthalocyanine 1 MEP Report.txt that tracks the FlexTS calculation. At the bottom of this document, you can find the number of energy and gradient calls for the DMol³ calculation. This allows you to assess the method against an equivalent transition search calculation. The overall number should be significantly less than six times the number of atoms required to compute the Hessian matrix of the structure to provide the basic input for a TS Optimization in DMol³. Meanwhile this calculation has refined the transition state and calculated the reactants and products corresponding to this particular reaction step.

6. To compare the reaction pathways for DFTB+ and DMol³ using a Pipeline Pilot protocol (optional)

Next, use the protocol that generated the line plot above to graphically compare the barriers predicted by DMol³ and DFTB+. To achieve this, create a single study table that contains the results for both methods, one in each tab. We begin by making a copy of the first results study table containing the DFTB+ path and remove all unnecessary data.

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results.std** and save it as **naphthalocyanine comparison.std**. Activate the **All Segments** tab, right-click the tab name, and select **Delete**. Rename the **Connected Path** tab to **DFTB+** and insert a new tab **DMol3** to the right.

You now have a study table with two tabs, one of which is empty.

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine 1 DMol3 MEP\ naphthalocyanine 1 Results.std** and copy its entire content into the newly created **DMol3** tab in the comparison study table.

This table now contains two separate pathways with all the information required to plot it in a single panel.

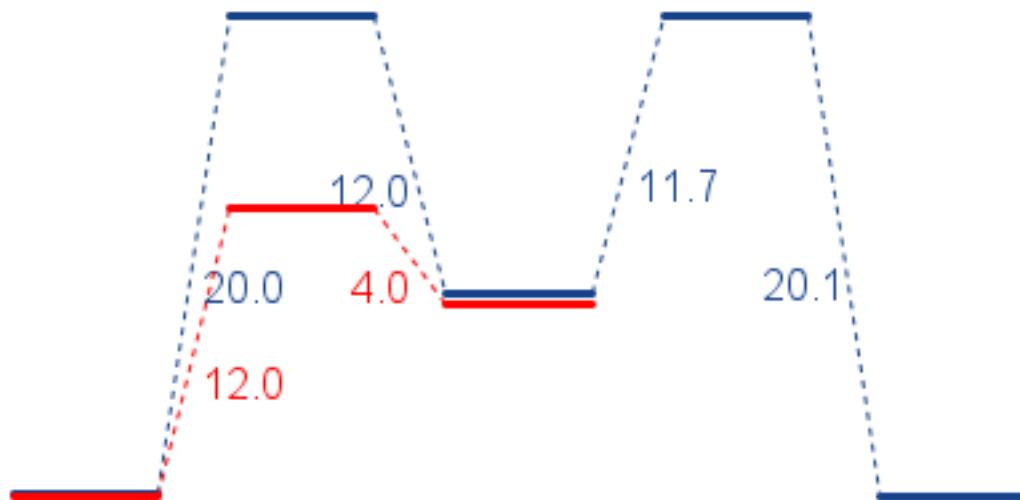
Open the **Pipeline Pilot Protocols** dialog and select the **Protocols\BIOVIA Materials Studio\Reaction Chemistry\Reaction Pathway Display** protocol. For **Sheets** select **AllSheets**, choose **Sheet for Reference Energy**, and select **False** for **Labels | Stationary Points**. Click **Run** and close the dialog.

Tip: Your results study table might require reversal of the path being plotted. If your graph does not look like the example below, select *True* for *Plot Path in Reverse* and regenerate the graph.

The first option makes sure that all the sheets that are now in the study table are used to plot the graph. With more than one line on the graph, you may end up in a situation where there are too many overlapping labels. To avoid that scenario, you only display the barrier heights for comparing our methods, but turn off the energies of the stationary points. You might also choose to process the graph further to add numbers by hand.

The two calculations were performed with different Hamiltonians, which means that each sheet in the study table has its own reference energy. This is why you selected a sheet-based reference energy, as it ensures that each method has its own energy origin.

When the protocol returns the results, inspect the graph created as a PNG file.



Note: The relative energies of the minima in the DFTB+ are extremely close while the actual barriers are significantly higher. While it is extremely efficient and quick to use DFTB+ to obtain the initial pathways, always use a suitable DFT calculation with DMol³ to verify the actual barrier height.

In this specific use case, you ran the same reaction with two different methods, but you can use the same protocol to compare different pathways for the same reaction as well.

You might want to create an image that contains both steps in the DFT path. To do this, manually amend the study table and copy the correct barrier heights and energies of all the stationary states.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

- P. Liljeroth, J. Repp, G. Meyer, "Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules", *Science* **317** 1203 (2007).
- Y. Kumeda, D. J. Wales, L. J. Munro, "Transition states and rearrangement mechanisms from hybrid eigenvector-following and density functional theory. Application to C₁₀H₁₀ and defect migration in crystalline silicon" *Chem. Phys. Lett.* **341** 185 (2001).
- J. M. Carr, S. A. Trygubenko, D. J. Wales, "Finding pathways between distant local minima", *J. Chem. Phys.* **122** 234903 (2005).

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S. A. Trygubenko, D. J. Wales, "A doubly nudged elastic band method for finding transition states" *J. Chem. Phys.* **120** 2082 (2004).

Chapter 9: DMol³ tutorials

The following tutorials illustrate how to utilize DMol³'s capabilities.

- [Computing band structure and density of states with DMol³](#)
- [Geometry optimization for solids using delocalized internal coordinates in DMol³](#)
- [Calculating the Minimum Energy Path of a molecular switch](#)
- [Kinetics of a Diels-Alder reaction](#)
- [Calculating the free energies of chemical reactions](#)
- [Calculating the Optical Properties of Coumarin](#)
- [Simulating electron transport with DMol3](#)
- [Transition state searching using LST/QST tools](#)
- [Calculating barriers of simple chemical reactions using DMol³'s LST/QST and NEB tools](#)
- [Effective Screening Medium \(ESM\) Calculations in DMol³](#)

Computing band structure and density of states with DMol³

Purpose: To introduce the electronic properties of band structures and density of states.

Modules: Materials Visualizer, DMol³

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Extended periodic systems can be characterized by their energy bands, which are analogous to orbital eigenvalues in molecular systems. Unlike the orbital eigenvalues, the energy of each band varies at different points in *reciprocal space*. The bands are conventionally plotted in the reciprocal space to show the dispersion of eigenvalues in different directions. There are a limited number of unique high symmetry directions in reciprocal space, so only a finite number of points are needed to characterize the bands. By observing the energy gaps between bands at various points, it is possible to draw conclusions about the nature of a material; whether it is an insulator, a conductor, or a semiconductor.

Another way of characterizing the electronic structure of a material is by the density of states (DOS). The DOS counts the relative number of energy levels in each energy range. In a molecule, there are distinct energy eigenvalues, so the DOS has a value of 1 at each of these values and a value of 0 elsewhere. In contrast, for a crystal the energy levels constitute a continuum, and DOS charts provide a useful tool for qualitative analysis of the electronic structure of the material. Examining the DOS also allows you to see whether a system is conducting or insulating. In addition, the partial density of states (PDOS) allows you to characterize the DOS in terms of the contributions from particular atomic orbitals, s, p, d, or f.

Introduction

In this tutorial, you will use DMol³ to compute and analyze the band structure, DOS, and PDOS of a semiconductor.

This tutorial covers:

- [Getting started](#)
- [To set up the DMol³ calculation](#)
- [To control the job settings and running the job](#)
- [To analyze the band structure](#)
- [To analyze the DOS and PDOS](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **AlAs_DOS** as the project name, click the **OK** button.

The new project is created with *AlAs_DOS* listed in the Project Explorer. Now you will import the input file you will be studying.

The next step is to import the structure that you will analyze. Materials Studio includes a wide range of prebuilt structures. In this tutorial, you will perform calculations on AlAs (a semiconductor).

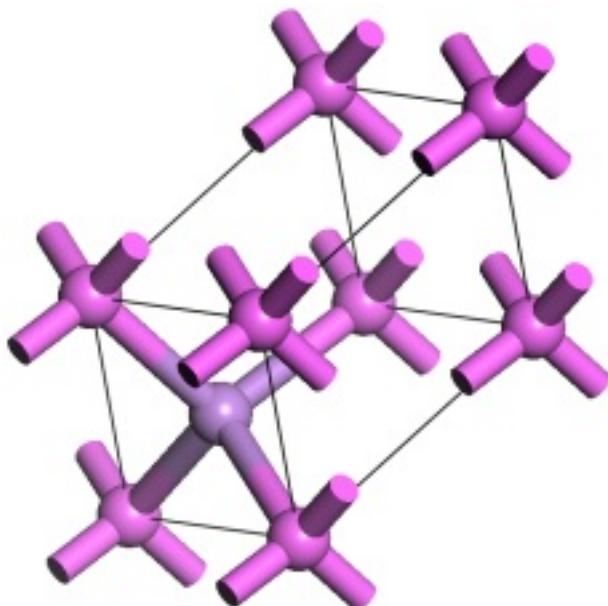
Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Structures\semiconductors\AlAs.xsd**, then click the **Open** button.

The structure of AlAs is displayed. The crystal structure in the 3D Viewer is the conventional unit cell, which shows the cubic symmetry of the lattice.

2. To set up the DMol³ calculation

DMol³ uses the full symmetry of the lattice, if any exists. The primitive lattice, containing 2 atoms per unit cell, can be used instead of the conventional cell, which contains 8 atoms. The charge density, bond distances, and total energy per atom will all be the same no matter how the unit cell is defined. By using fewer atoms in the unit cell, the computation time will be decreased.

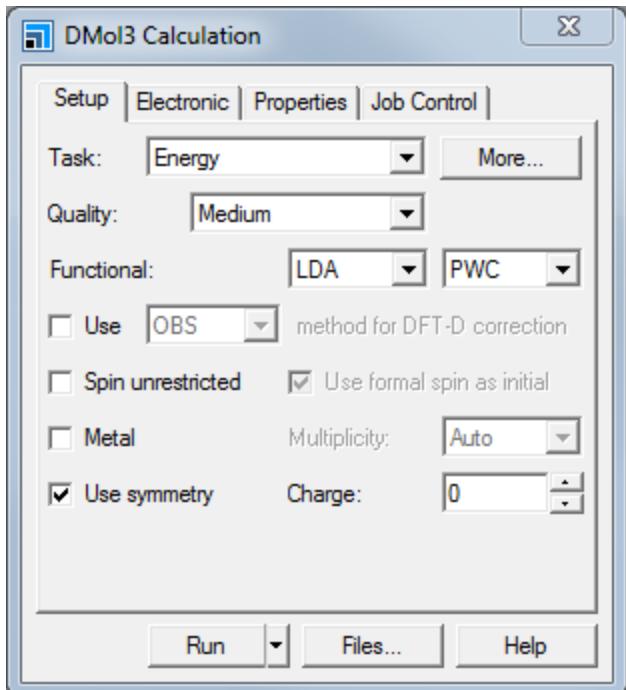
Choose **Build | Symmetry | Primitive Cell** from the menu bar.



The primitive cell of AlAs

Click the **DMol3** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.



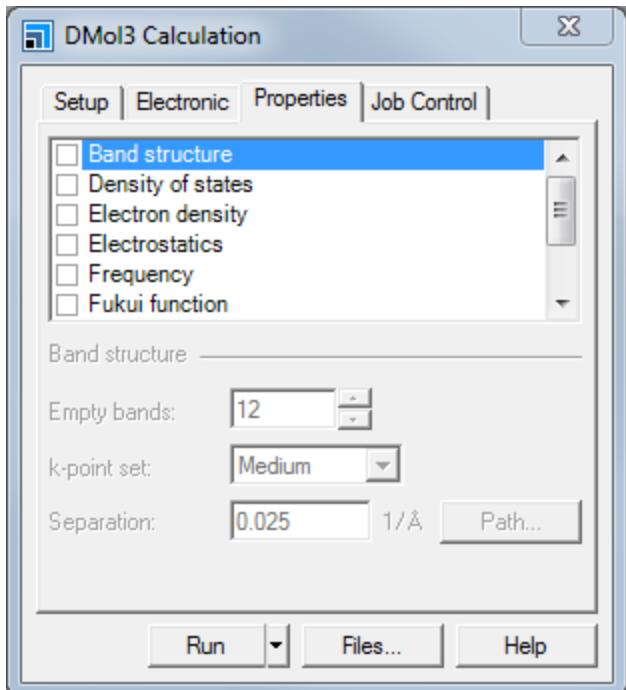
DMol3 Calculation dialog, Setup tab

Select **Energy** from the **Task** dropdown list. Set the **Functional** to **LDA** and **PWC**, and the **Quality** to **Medium**.

You will use all the default options for the *Medium* quality setting, there is no need to change any of the other calculation parameters.

Select the **Properties** tab.

This tab allows you to calculate certain properties after the structure is optimized.



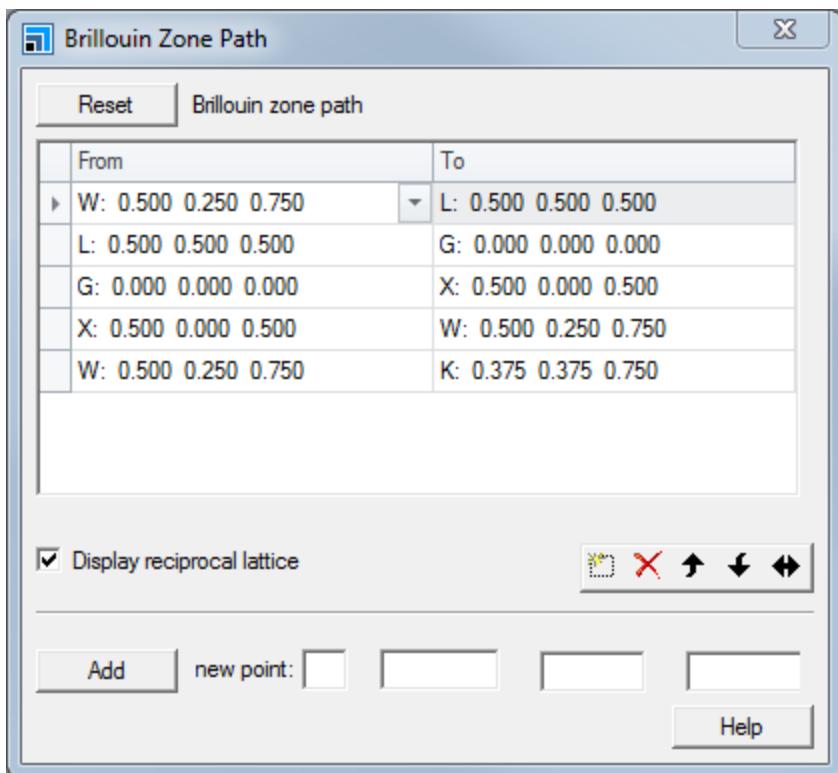
DMol3 Calculation dialog, Properties tab

Check the **Band structure** checkbox.

Notice that the default number of *Empty bands* to be included is 12 and the default value of *k-point set* is Medium. These values are suitable for most applications. However, you should examine the k-point set in more detail.

Click the **Path...** button to display the Brillouin Zone Path dialog. Click the **Create** button.

The button name changes to **Reset** when the Brillouin Zone has been created.



Brillouin Zone Path dialog

The structure in the 3D Viewer is updated to display the reciprocal lattice in light blue and the Brillouin zone paths in magenta, the k-points are labeled with the letters reported on the Brillouin Zone Path dialog.

Each row of the table indicates a path through symmetry-unique points in the Brillouin zone. The coordinates are given in fractional coordinates in reciprocal space. In row 1, for example, a path will be traced from [0.5, 0.25, 0.75] to [0.5, 0.5, 0.5]. The energy will be computed at a number of points along the path, and the results will be displayed as a plot of electron energy vs k-vector. By convention, each of the high symmetry points in Brillouin zone is assigned a letter. As you can see, for example, W corresponds to [0.5, 0.25, 0.75]. The gamma point, Γ , represented here by G, corresponds to [0, 0, 0].

Using the controls at the bottom of the panel, you can add or delete rows or you can change the value of the coordinates. You could also change the number of divisions along each segment of the path by changing the value of *k-point set* on the *Properties* tab. However, you do not need to change any of these values for this tutorial.

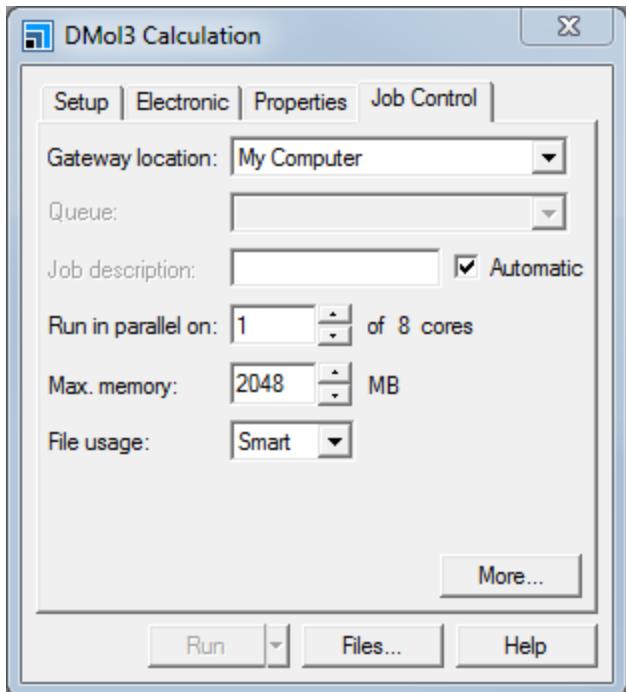
Close the Brillouin Zone Path dialog.

On the **Properties** tab check the **Density of states** and **Calculate PDOS** checkboxes to compute the full and partial density of states.

3. To control the job settings and running the job

You will use the commands on the *Job Control* tab to control the DMol³ calculation.

Select the **Job Control** tab.



DMol3 Calculation dialog, Job Control tab

Here, you can choose the gateway location where you will run your calculation and set various options, such as the job description, whether the job will be launched using multiple cores, and the number of cores to employ. You can access further job options by clicking the *More...* button, including live update settings and controls that determine what happens when the job completes.

You are now ready to run your DMol³ calculation.

Click the **Run** button and close the dialog.

The Job Explorer opens, containing information about status of the calculation.

A text document called **Status .txt**, containing the DMol³ run status opens. This document is updated regularly until the calculation is complete.

4. To analyze the band structure

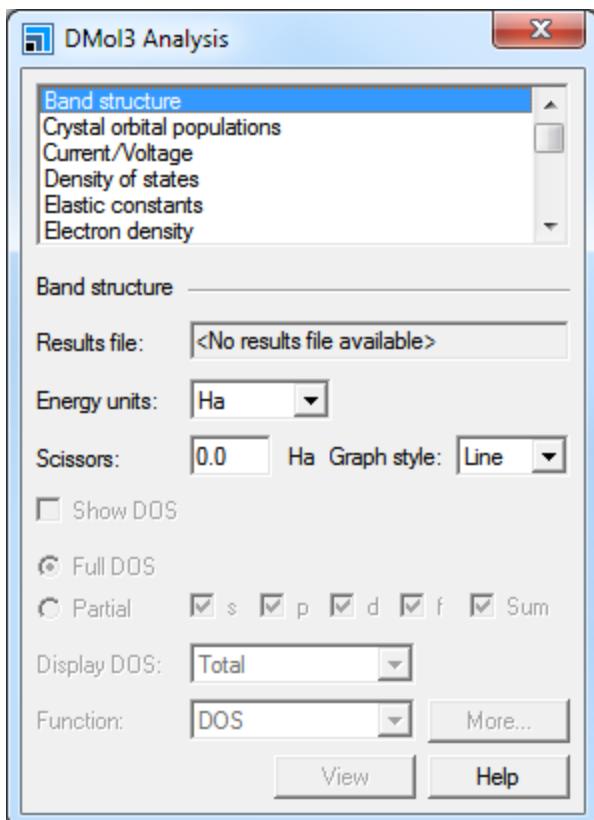
When the calculation is complete, the results are returned to the **AlAs DMol3 Energy** folder in the Project Explorer.

In the **AlAs DMol3 Energy** folder, double-click on **AlAs.xsd**.

The AlAs structure is displayed. The crystal structure is the same as that of the original, but this structure has results associated with it from running a DMol³ calculation. In the remainder of this tutorial, you will analyze the band structure and DOS results.

Click the **DMol3** button  on the **Modules** toolbar and choose **Analysis** or select **Modules | DMol3 | Analysis** from the menu bar.

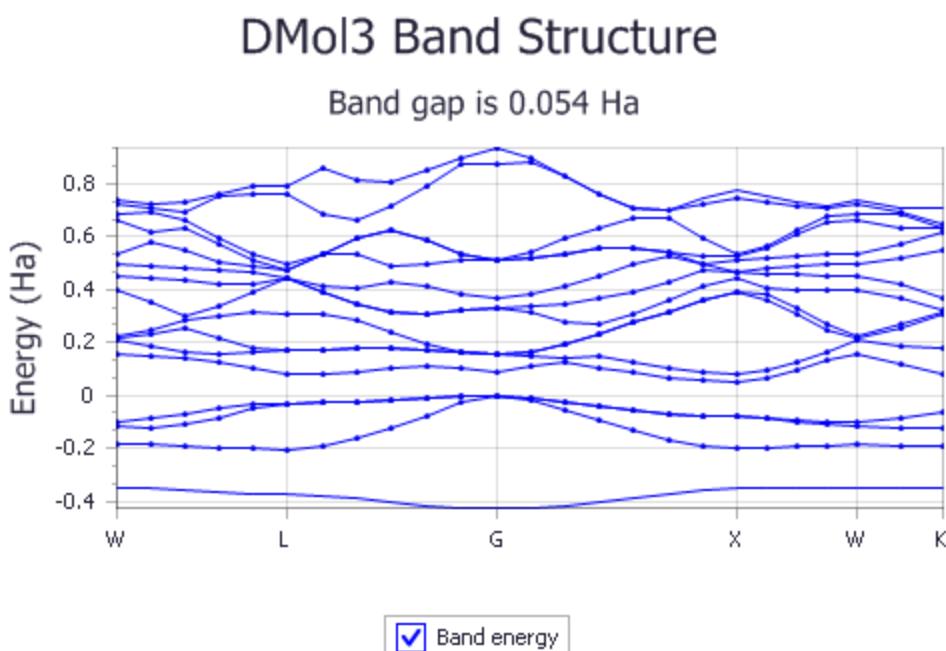
This opens the DMol3 Analysis dialog.



DMol3 Analysis dialog, Band structure selection

Select **Band structure** from the list and click the **View** button.

A band structure plot is displayed.



DMol³ band structure for AlAs

The energies of the bands are plotted with respect to the Fermi level, which is assigned a value of zero. Notice that the band gap at the [Γ point](#), (G), is only about 0.1 Hartree, indicating that this is a semiconductor. You can use the zoom controls to expand this area of the chart and measure the band gap more precisely. The actual band gap is reported in the chart as 0.054 Ha (1.5 eV) and you can see from the plot that AlAs has an indirect band gap in qualitative agreement with experimental findings [\[1\]](#). The absolute value of the band gap is underestimated by the density functional approach, with the experimental band gap at low temperatures being about 2.2 eV.

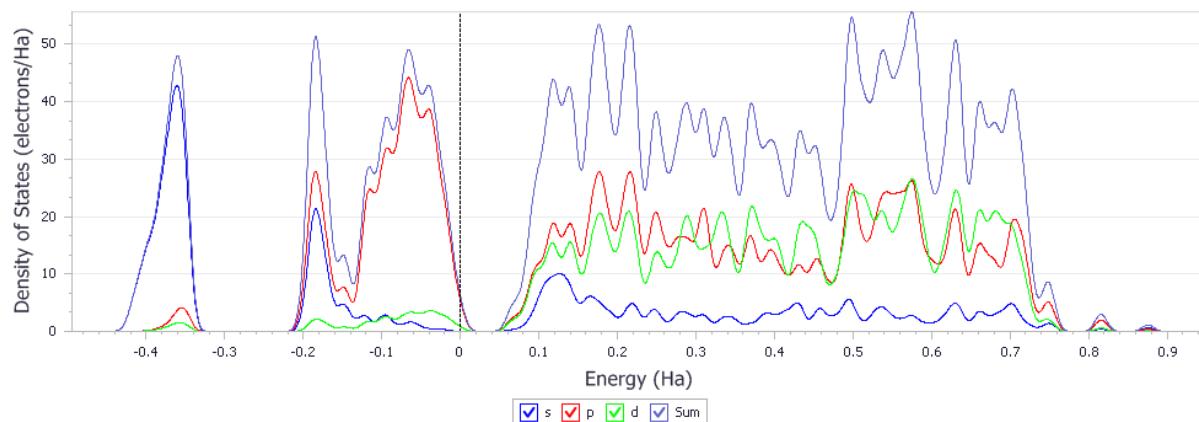
5. To analyze the DOS and PDOS

In the **AlAs DMol3 Energy** folder, double-click on **AlAs.xsd**.

Select **Density of states** on the DMol3 Analysis dialog. Click the **Partial** radio button and check the **s**, **p**, **d**, and **Sum** checkboxes. Click the **View** button.

A PDOS plot is displayed.

DMol3 Partial Density of States



DMol³ PDOS for AlAs

Examine the number of energy states at the Fermi level, where Energy = 0. An insulator will have a distinct gap, while a conductor will have many states. The plot here is typical of a semi-conductor. Notice that you can see how many of the states arise from each type of orbital, s, p, or d.

It also is possible to see how many of the states are associated with a particular atom in the structure.

In the **AlAs DMol3 Energy** folder, double-click on **AlAs.xsd**.

Select one of the Al atoms by clicking on it (the Al atoms are at the corners of the cell).

Recreate the PDOS chart using the same procedure as above.

Now, select the As atom in AlAs and create another PDOS plot for this atom.

Compare the results for Al, As, and for the entire unit cell.

Tip: In order to improve the quality of DOS and PDOS plots you can change the integration method employed for the density of states calculation.

Click the *More...* button on the DMol3 Analysis dialog when *Density of states* is selected, this opens the *DMol3 DOS Analysis Options* dialog. Select [Interpolation](#) from the *Integration method* dropdown list and [Fine](#) as the *Accuracy level*. Click the *OK* button and then the *View* button on the DMol3 Analysis dialog. This will produce more accurate DOS, with sharper features and more clearly defined band gap.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

[1] [Semiconductors Information](#)

Geometry optimization for solids using delocalized internal coordinates in DMol³

Purpose: To introduce the use of the delocalized internal coordinate optimizer for periodic systems and the volume visualization tools.

Modules: Materials Visualizer, DMol³

Time:   

Prerequisites: Working with isosurfaces and slices Visualizer Tutorial

Background

DMol³'s delocalized internal coordinate optimization scheme for molecules provides good performance for large molecular systems. This scheme has been extended to periodic systems in DMol³ in Materials Studio.

The new optimizer, built on the delocalized internal coordinates, also has the capability to handle:

- Highly coordinated systems such as close packed solids
- Fragmented systems, such as molecular crystals, in which the internal coordinates do not span the optimization space
- The inclusion of Cartesian constraints during the optimization process

In-house validation work shows that this state-of-the-art delocalized internal coordinate optimization scheme for periodic systems is typically 2-5 times more efficient than the Cartesian approaches that are the standard in solid-state calculations today.

Introduction

In this tutorial you will use the DMol³ optimizer, employing delocalized internal coordinates to perform a geometry optimization on a zeolite structure.

This tutorial covers:

- [Getting started](#)
- [To set up the DMol³ calculation](#)
- [To control the job settings and run the job](#)
- [To examine the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

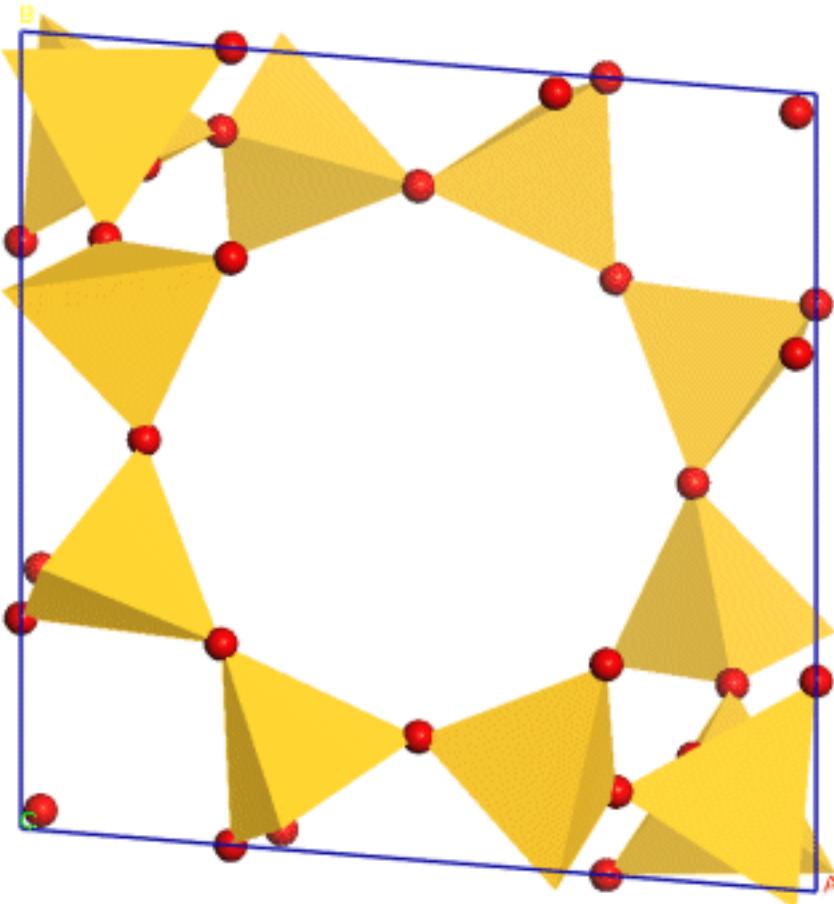
Open the **New Project** dialog and enter **Chabazite** as the project name, click the **OK** button.

The new project is created with *Chabazite* listed in the Project Explorer. The next step is to import the zeolite sheet structure that you want to optimize. Materials Studio has a wide range of prebuilt zeolite structures. In this tutorial you will optimize chabazite.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Examples\Documents\3D Model\CHA.xsd**, then click the **Open** button.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Click the **Polyhedron** radio button and close the dialog.

The structure of CHA is displayed as polyhedra in the 3D Viewer.

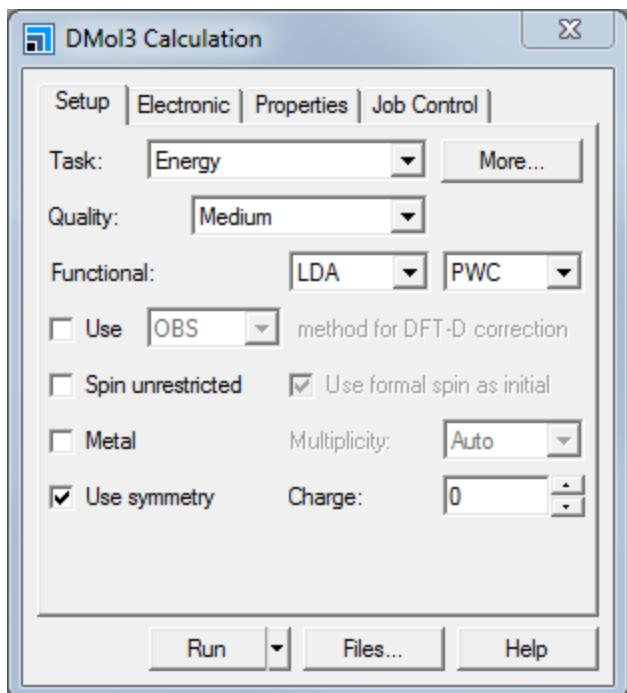


A unit cell of chabazite

2. To set up the DMol³ calculation

Click the **DMol3**  button on the **Modules** toolbar and select **Calculation** or choose **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.

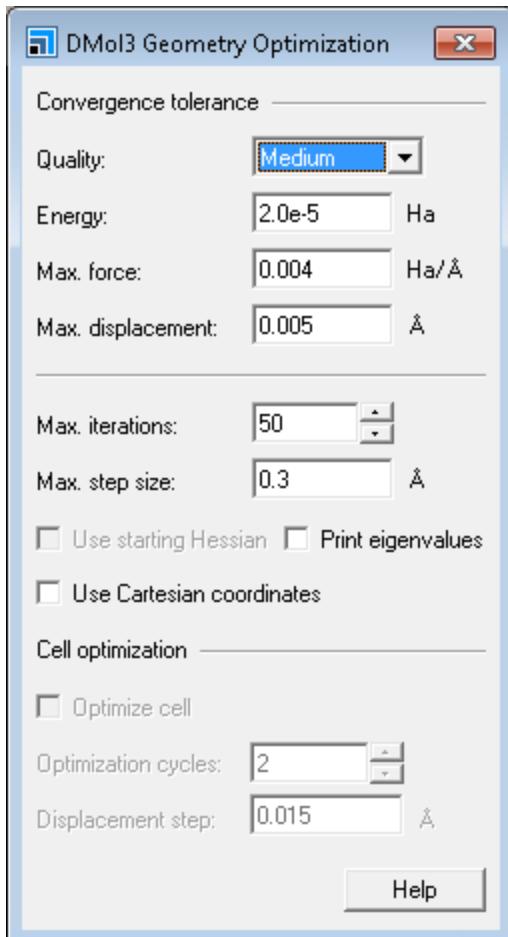


DMol3 Calculation dialog, Setup tab

Set the **Task** to **Geometry Optimization**. Change the **Functional** from LDA, PWC to **LDA, VWN**.

The LDA/VWN functional is adequate for covalent solids like a zeolite.

Click the **More...** button to open the DMol3 Geometry Optimization dialog,

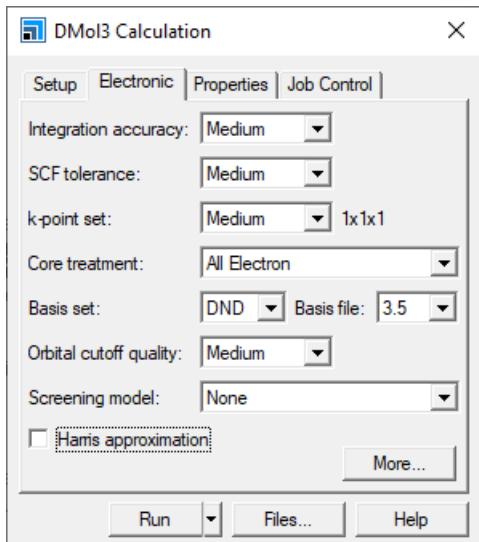


DMol3 Geometry Optimization dialog

You can set your convergence tolerance by changing the *Quality* level or by editing the values individually. The default **Medium** setting for the *Quality* selects various options such as basis set, integration grid, and convergence thresholds. These are selected to yield reliable results in most cases, while keeping computational costs reasonable.

Leave the **Quality** at **Medium** and close the dialog. On the **DMol3 Calculation** dialog, select the **Electronic** tab.

The *Electronic* tab on the DMol3 Calculation dialog is displayed. This tab contains parameters associated with the electronic Hamiltonian.



DMol3 Calculation dialog, Electronic tab

You will explore some of the options that are available to reduce the computational cost of a calculation. The options you will change on this tab are the *k-point set* and the *Orbital cutoff quality*.

Set the **k-point set** to **Gamma** and the **Orbital cutoff quality** to **Coarse**. Click the **More...** button to display the DMol3 Electronic Options dialog.

On the **Orbital Cutoff** tab the orbital cutoff is set to **3.5 Å**.

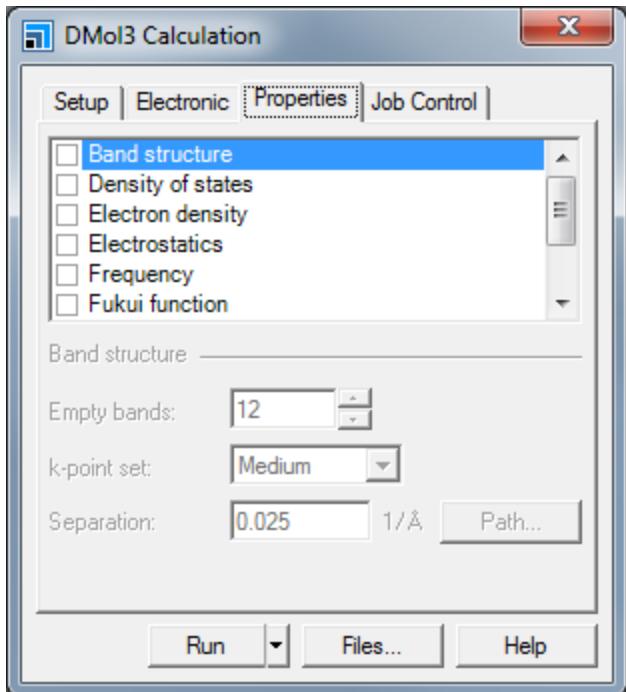
This text box allows you to customize the orbital cutoff value, giving access to more precise values than the *Orbital cutoff quality* dropdown list on the Electronic tab of the DMol3 Calculation dialog.

Close the DMol3 Electronic Options dialog.

Tip: The DMol3 Electronic Options dialog also allows you to exercise greater control over the SCF and k-point electronic Hamiltonian parameters.

Select the **Properties** tab on the DMol3 Calculation dialog.

The *Properties* tab is displayed and this allows you to calculate certain properties after the structure is optimized.



DMol3 Calculation dialog, Properties tab

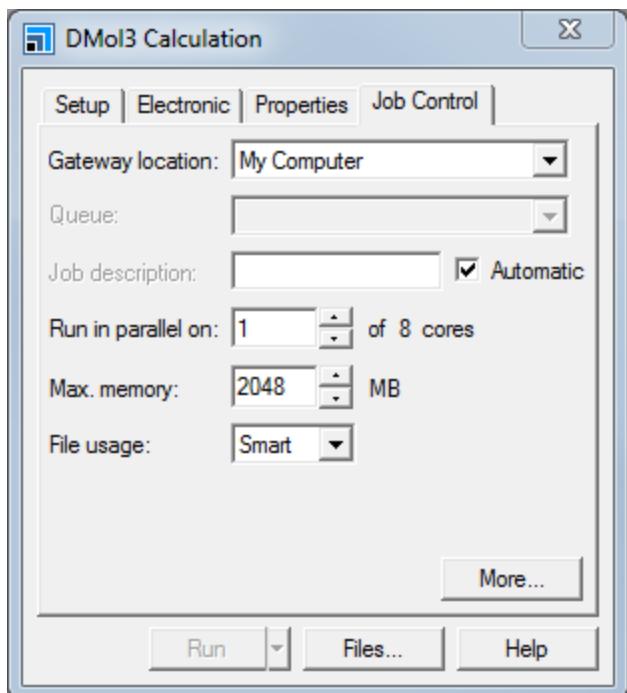
Check the **Electron density** and **Electrostatics** checkboxes.

3. To control the job settings and run the job

You will use the commands on the *Job Control* tab to control the DMol³ calculation.

Select the **Job Control** tab on the DMol3 Calculation dialog.

The *Job Control* tab is displayed.



DMol3 Calculation dialog, Job Control tab

From this tab, you can choose the gateway location where you will run your calculation and set various options such as the job description, whether the job will be launched using multiple processors, and the number of processors to employ. You can access further job options by clicking the *More...* button to open the DMol3 Job Control Options dialog. You can specify live update settings and what happens when the job completes.

You are now ready to run your DMol³ geometry optimization.

Click the **Run** button and close the dialog.

The Job Explorer opens, containing information about status of the calculation.

A text document called **Status .txt** containing the DMol3 Run Status opens. This is a live document that is updated regularly until the calculation is complete. Shortly after that, two chart documents are displayed, **CHA Energies .xcd** and **CHA Convergence .xcd**, which refer to the optimization and convergence status of the calculation. These can be useful visual aids to indicate the progress of your calculation.

4. To examine the results

When the calculation is complete, the results are returned to the **CHA DMol3 GeomOpt** folder in the Project Explorer.

In the **CHA DMol3 GeomOpt** folder, double-click on **CHA.xtd**.

The zeolite CHA structure is displayed in a 3D viewer. This is a trajectory document containing the geometry optimization progress. Its history can be viewed using the controls on the Animation toolbar.

If the **Animation toolbar** is not visible, select **View | Toolbars | Animation** from the menu bar.

On the Animation toolbar, click the **Play** button  to view the sequence of changes in the optimization process. When you have finished viewing the animation, click the **Stop** button .

Tip: Click the **Animation Mode** arrow  on the Animation toolbar and select **Options** to open the Animation Options dialog. You can use this to view individual frames, change the playback speed, and the start and end frames.

The final total energy can be viewed in the **.outmol** file document.

Use the **Project Explorer** to change the focus to **CHA.outmol**. Scroll down the document to find the total energy.

The **.xsd** document contains the optimized structure.

In the **Project Explorer**, double-click on **CHA.xsd** in the **CHA DMol3 GeomOpt** folder.

To visualize the properties that you calculated, you need to analyze the output documents.

Click the **DMol3**  button on the **Modules** toolbar and select **Analysis** or choose **Modules | DMol3 | Analysis** from the menu bar.

This opens the DMol3 Analysis dialog.

Select **Electron density** and check that the correct **.outmol** file is displayed in the **Results** box. Set the **Density field** to **Total density** and check the **View isosurface on import** checkbox. Click the **Import** button.

The total electron density is displayed on the zeolite.

Zoom in and rotate to inspect the structure.

You can change the display style of the isosurface but first you should change the atom display style.

Open the **Display Style** dialog and, on the **Atom** tab, choose the **Stick** display style. Select the **Isosurface** tab.

You can change the transparency of your displayed isosurface with the *Transparency* ruler. You can also change the display style of your isosurface by checking the *Dots* or *Solid* options.

Change the **Transparency** by dragging the ruler to the next mark.

You can also control the size of the isosurface.

Change the **Isovalue** to **0.1** and press **TAB**. Change it back to **0.2** and press **TAB** again.

Once you have the electron density isosurface, you can map other calculated properties onto it.

On the **DMol3 Analysis** dialog, select **Potentials** and uncheck the **View isosurface on import** checkbox. Click the **Import** button and close the dialog.

On the **Display Style** dialog, select the **Isosurface** tab. Select **DMol3 electrostatic potential Ha*electron(-1)** from the **Mapped field** dropdown list and close the dialog.

The electrostatic potential is mapped onto the electron density isosurface. You can change the color of the mapped field by using the Color Map dialog.

Right-click in the 3D Viewer and select **Color Maps** from the shortcut menu.

This opens the Color Maps dialog; you can change the color scheme, mapped values, and number of bands displayed.

Change the **Spectrum** to **Blue-White-Red**. Click the **right-arrow** for **From** and select **Mapped Minimum**. Click the **right-arrow** for **To** and select **Mapped Maximum**. Close the dialog.

The colors on the isosurface change to reflect the minimum and maximum values associated with the field you have mapped onto the electron density.

You can access more volumetric visualization tools from the Volume Visualization toolbar.

Select **View | Toolbars | Volume Visualization** from the menu bar.

You can add a slice to the structure.

Click the **Create Slices** arrow  and select **Best Fit** to open the **Choose Fields to Slice** dialog. Select **DMol3 electrostatic potential** and click the **OK** button.

A slice is displayed through the electrostatic potential. This slice uses the minimum and maximum values of the entire field. To see the maximum and minimum in the specific area covered by the slice, you need to use the Color Maps dialog again.

Click the **Color Maps** button  and select the slice.

When you select a slice, a dashed yellow line is displayed around the edge of it and a cross is displayed in the middle of the selected slice.

Click the **right-arrow** for **From** and select **Mapped Minimum**. Click the **right-arrow** for **To** and select **Mapped Mean**. Change the **Spectrum** to **Blue-White-Red**.

There are some high maximum values in this section of the grid that you do not need to view and this is why you selected *Mapped Mean* rather than *Mapped Maximum*. You can remove the display of certain values from the field by using the Color Maps dialog.

Click the **Red right-arrow** for the color bar.

All the data points above the mean value are removed from the slice. You can also remove individual colors from the color bar by clicking on them, change the colors from the *Spectrum* dropdown and increase the number of bands.

Click the || button on the right of the color bar so that colors are displayed above the mean value.
Close the **Color Maps** dialog.

You can change the display styles of the slice from the *Slice* tab on the Display Style dialog.

Open the **Display Style** dialog and, on the **Slice** tab, drag the **Transparency** to the right.

As you drag the *Transparency* ruler, the transparency of the slice changes.

When you have finished working with the slices and isosurfaces, you can remove them by selecting them in the 3D Viewer and pressing **DELETE**.

Select the slice and press **DELETE**. Repeat this for the **isosurface**.

More information about manipulating slices, including translation and rotation of them can be found in the Creating and customizing slices topic.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Calculating the Minimum Energy Path of a molecular switch

Purpose: Introduces the use of FlexTS together with DMol³ and DFTB+ to compute and refine a multi-step reaction pathway.

Modules: Materials Visualizer, DMol³, DFTB+, FlexTS, optionally Pipeline Pilot Connector

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial, Sketching a porphyrin Visualizer Tutorial

Background

The modeling of chemical reactions requires an efficient way to identify and validate chemical transition states; a universal problem in theoretical chemistry. Chemical reaction pathways frequently have multiple steps, requiring the correct identification of intermediate states for the simulation of reaction pathways.

Introduction

This tutorial introduces you to the main working modes of the FlexTS module, using a hierarchical method to investigate the tautomerization barriers of the molecular switch naphthalocyanine ([Liljeroth, Repp, Meyer, 2007](#)). You start by exploring the entire reaction pathway using the DFTB+ module in Materials Studio, which shows two separate equivalent steps in the tautomerization reaction. Then you use the DMol³ module to accurately determine the transition state for one of the barriers, which fully determines the energy landscape of the entire switch.

This tutorial covers:

- [Getting started](#)
- [To prepare the molecular structures for the calculation](#)
- [To calculate the reaction pathway using DFTB+ and analyze the results](#)
- [To graph the reaction pathway for DFTB+ using a Pipeline Pilot protocol \(optional\)](#)
- [To refine a transition state using DMol³](#)
- [To compare the reaction pathways for DFTB+ and DMol³ using a Pipeline Pilot protocol \(optional\)](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

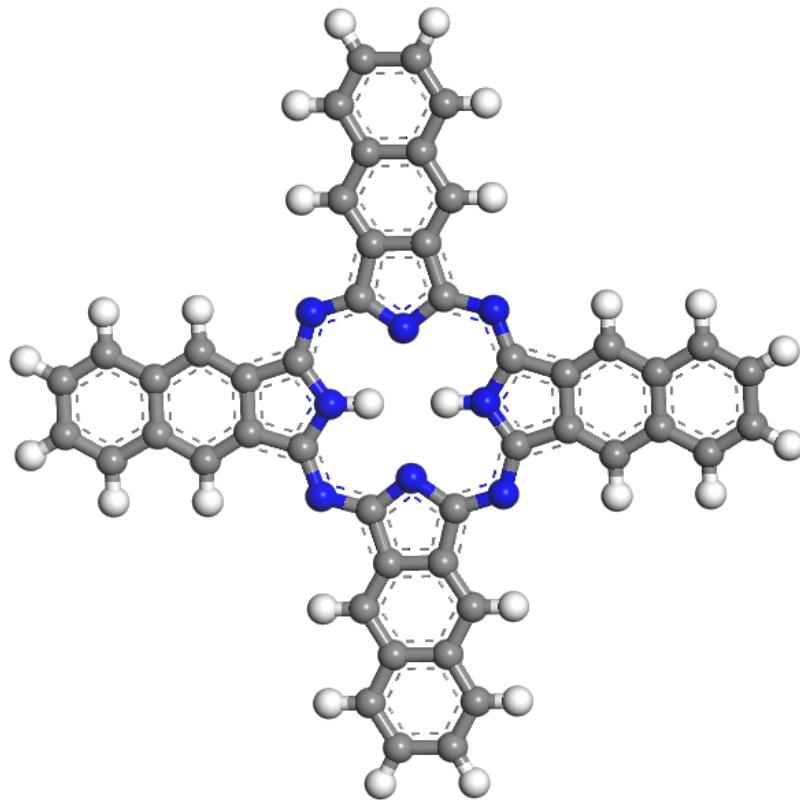
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MEP** as the project name, click **OK**.

This creates a new project with *MEP* listed in the Project Explorer.

2. To prepare the molecular structures for the calculation

In this section of the tutorial, you build the reactants and products in two different 3D Atomistic documents. The first step is to open a new 3D Atomistic document and sketch the reactant, naphthalocyanine.



Open a new 3D Atomistic Document and name it **reactant_start.xsd**. Starting from a porphyrin core, draw the reactant molecule shown above, with the central H atoms to the left and right. Click **Clean**  and save the document. Confirm that the molecule has 82 atoms with the chemical formula $C_{48}H_{26}N_8$.

Tip: You can create aromatic rings by pressing ALT while drawing six-membered carbon rings.

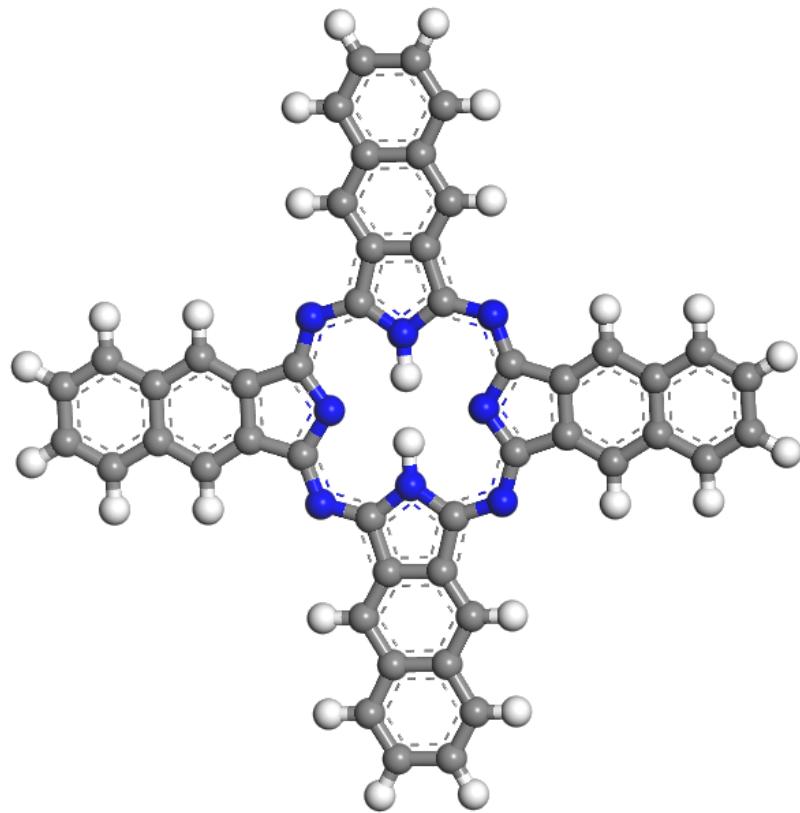
Ensure that the starting geometry of the reactant is reasonable by running a DFTB+ structure minimization.

Open the **DFTB+ Calculation** dialog, change the **Task** to **Geometry Optimization** and click **Run**. When the optimization finishes, rotate the generated molecule to ensure that it is *completely flat*.

Copy the generated **reactant_start.xsd** file to the project root and rename the document **reactant.xsd**.

Tip: Alternatively, you can obtain the reactant structure from the Materials Studio examples by importing *Examples\Documents\3D Model\naphthalocyanine.xsd* into the root of your project and renaming it *reactant.xsd*.

Next, create the product by modifying the reactant - this facilitates the subsequent creation of a reactant-product trajectory.



Create a copy of the **reactant.xsd** document by selecting it in the Project Explorer, press CTRL, and use the mouse to drag it onto the project root. Rename the new document **product.xsd**. On the **Atoms & Bonds** toolbar, click the **Bonds** arrow and select **Monitor Bonding** . Select the two central H atoms, press and hold SHIFT, click and hold the right mouse button, then drag the cursor along the bottom of the screen to rotate the atoms into the alternative set of trans positions (top and bottom) as shown above.

Without deselecting the central H atoms click **Clean** , click anywhere to clear the selection in the document, and save the document.

Tip: For the best visualization of reaction pathway calculations, keep monitor bonding turned on.

The next step is to create an initial trajectory with correct matching of all atoms.

Make sure that both documents **reactant.xsd** and **product.xsd** are open and that all other windows are closed. Select **Window | Tile Vertically** to display both structures side by side.

Open the **Tools | Reaction Preview** dialog and set **Reactant** and **Product** to the two structures that you have open on your desktop. Click **Match...** to open the **Find Equivalent Atoms** dialog.

DMol3: Calculating the Minimum Energy Path of a molecular switch

The next step is critical to make sure that the reaction pathway makes chemical sense. However, since you drew the product from the reactant, there is an identical ordering of all the atoms in both structures. This makes it straight forward to achieve a correct match between reactant and product and to create an initial guess for the trajectory.

On the **Find Equivalent Atoms** dialog, click **Auto Find** to match reactant and product atoms. Select the first remaining unmatched atom in the file **reactant.xsd** and the corresponding first unmatched atom in the file **product.xsd**. Click **Set Match** and verify that all atoms are shown as matched. Repeat the last step until all atoms are matched. Close the **Find Equivalent Atoms** dialog.

On the **Reaction Preview** dialog, ensure selection of **Superimpose structures** and click **Preview**.

Rename the newly created trajectory **naphthalocyanine.xtd** and select **Monitor Bonding** . Save the trajectory and close the **Reaction Preview** dialog.

It is important to play the trajectory back and forth a few times now, to ensure correct matching of all the atoms. If this is not the case, you might sometimes see atoms "flying" through space without any connection to either reactant or product.

Tip: If you observe any misbehaving atoms while playing the trajectory, return to the *Reaction Preview / Match...* step to ensure correct selection of the equivalent atoms between reactant and product. When atoms do not move very far during a reaction, *Auto Find* can help you to speed up matching, but you might require some manual intervention depending on your system.

3. To calculate the reaction pathway using DFTB+ and analyze the results

The next stage of this investigation is to explore the energy landscape of the molecular switch using DFTB+.

Use the FlexTS module, you can access this on the DFTB+ and DMol³ dialogs through the Minimum Energy Path tasks. FlexTS crucially depends on highly accurate forces, so you must begin by tightening the self-consistent convergence thresholds for DFTB+ and by increasing the number of iterations to a safe number.

Open the **DFTB+ Calculation** dialog, select the **Electronic** tab, and click **More...** to open the **DFTB+ Electronic Options** dialog. Change **SCC tolerance** to **1e-10** and **Max. SCC cycles** to **100**. Close the dialog.

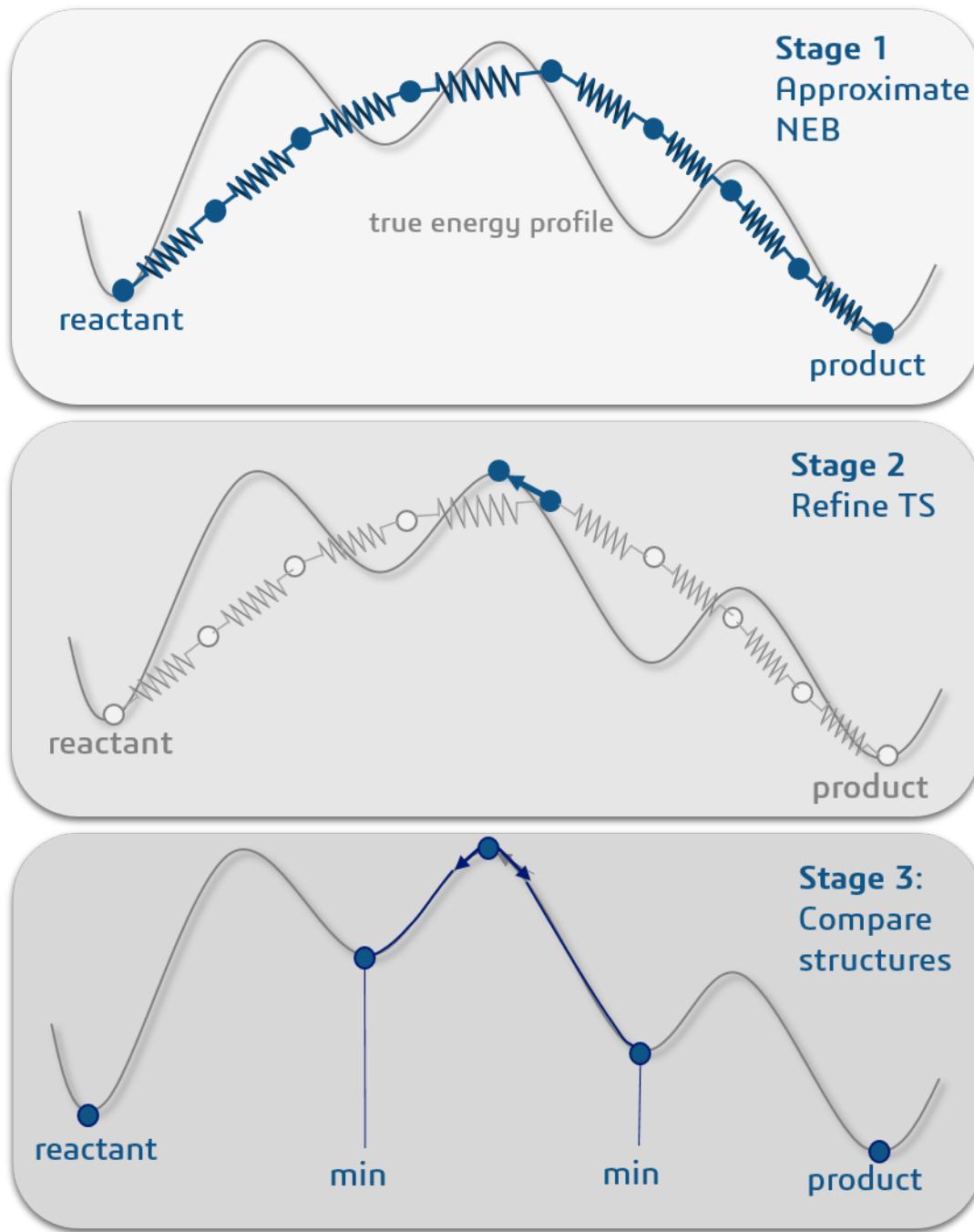
On the **DFTB+ Calculation** dialog, select the **Setup** tab and change the **Task** to **Minimum Energy Path**. Click **More...** to open the **DFTB+ Minimum Energy Path** dialog and inspect the different options.

The **Setup** tab contains basic information for running FlexTS, including three different modes:

- **Full Path** consists of five stages:

1. Optional optimization of the reactant and product states
2. Nudged elastic band calculation to estimate the location of the transition states (TS)
3. Refinement of the TS using a hybrid eigenvector following scheme based exclusively on energies and forces ([Kumeda et al. 2001](#))
4. Displacement of the TS in the positive and negative direction of the transition vector followed by an optimization to identify the local minima corresponding to this particular reaction step
5. Attempt to connect reactant and product states through individual steps using Dijkstra's algorithm

This procedure describes a single path cycle ([Carr et al, 2005](#)) as illustrated in the following image:



In the DFTB+ part of this tutorial, you use two successive path cycles to explore the naphthalocyanine molecular switch.

- **Nudged Elastic Band** interpolates the initial and final states in a reaction and optimizes an entire reaction path using a doubly nudged elastic band technique ([Trygubenko and Wales, 2004](#)) without further refinement of the transition state. Use this for extremely small barriers, to get a rough initial overview of the energy landscape, or to study barrierless reactions.
- **TS Path** begins with a guess for a single transition state and runs only stages (3) and (4) of the Full Path procedure to refine the transition state and to optimize the corresponding reactant and

product. Use this mode in the DMol³ section of the tutorial to get a more accurate estimate for the reaction barrier.

The other options on the *Setup* tab control:

- the number of path cycles
- whether to optimize reactants and product
- whether to include a geometry comparison when identifying local minima or transition states
- whether to use the initial trajectory as a guess for an NEB calculation (only when the active document is a trajectory)
- the basic parameters for the **Nudged Elastic Band** part of a FlexTS calculation

In general, for **Full Path** runs, choose *Determine the NEB parameters automatically*. This generates NEB parameters based on a predefined image density and maximal number of images. For certain cases, or for dedicated Nudged Elastic Band calculations, you might want to specify these numbers yourself.

The *Spring constant* controls the strength of the elastic band. In some cases, you can use this to speed up the calculation by allowing the system to relax to the actual minimum energy path more quickly. However, the exact spring constant value might be somewhat system-dependent.

Ensure that the **Run mode** is **Full Path**. For the **Number of path cycles**, specify a value of **2**.

Select the **Advanced** tab of the **DFTB+ Minimum Energy Path** dialog. Inspect the options available.

Most of the options on this tab are thresholds driving the detailed behavior of FlexTS.

Tip: The default options in Materials Studio FlexTS are set such that they provide good transition state convergence behavior in most standard cases. The particular scenario in this tutorial involves a reaction pathway that is significantly longer than the original guess. If such calculations do not converge, using more images can be helpful to get a better resolution of the path before attempting to find the transition state.

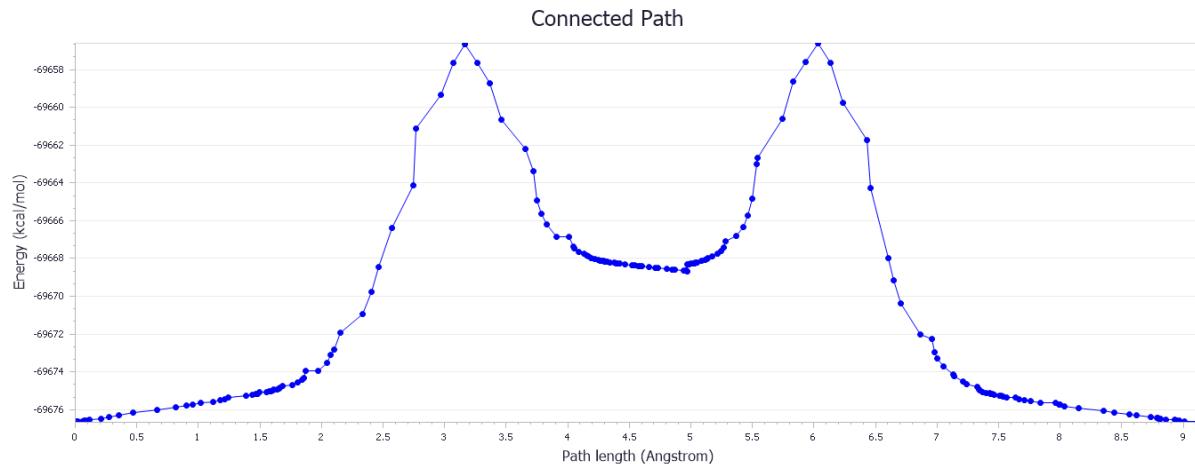
Select the **Setup** tab of the **DFTB+ Minimum Energy Path** dialog. Clear **Determine NEB parameters automatically** and increase **Images** to **12**.

Close the **DFTB+ Minimum Energy Path** dialog. On the **DFTB+ Calculation** dialog, select to the **Job Control** tab. Choose a suitable **Gateway location** and number of cores and click **Run**. Close the **DFTB+ Calculation** dialog.

This job takes some time to run. Once it completes, you can analyze the results.

In the **Project Explorer**, expand the **naphthalocyanine DFTB+ MEP** folder and inspect its contents.

The most important chart for this particular example is **naphthalocyanine Connected Path.xcd**. It contains the energy profile of the complete pathway found by FlexTS after successfully identifying all the steps required to connect reactant and product in a transition pathway.



You can see that this path has two separate steps with an intermediate minimum. You can open the corresponding trajectory file `naphthalocyanine Connected Path.xtd` to follow the pathway. The H-atoms in the molecular core do not jump in a concerted fashion but rather move step by step. This movement is symmetric in the sense that both individual barriers have the same shape (but inverted), and have matching reactant, product, and TS energies. You can use this symmetry to make the next steps easier.

Notes:

- The path length can depend on the drawing of the initial and final structure and may differ in your results.
- The default accuracy settings might lead to a path that is not completely symmetric, with small energy differences between reactant and product. This is expected, you can resolve it by using significantly more accurate convergence thresholds.

Tip: Make sure that you enable **Monitor Bonding**  for each document when investigating trajectories and other results.

The `naphthalocyanine Results.std` study table summarizes all the numbers and structures required to identify the transition states. The *All Segments* sheet of this study table contains one row for each of the barriers computed by the FlexTS run. The *Connected Path* sheet contains the individual steps involved in the actual path linking reactant and product. In this particular calculation, both tabs contain the same results but they might be in a different order.

The results study table also has a *Computational Settings* column, which contains all the non-default settings on the dialog in scripting format and allows you in principle to recreate the calculation. This column is particularly helpful when storing the results of multiple *Minimum Energy Path* calculations in a single study table. It keeps track of the different modules, electronic structure settings, charge, and spin settings and so one for each computed barrier individually.

If you focus on the *Connected Path* sheet, you can see the forward and reverse barriers listed in kcal/mol. Each row begins with a collection document that contains the reactant, TS, and product - ordered according to their relative energies. You can use these documents for further analysis. For example; as inputs for a refined accuracy calculation of the barrier, or as input for a Kinetics task in DMol³ or CASTEP.

Identify the forward and reverse barrier for the DFTB+ calculation.

The energy difference between the reactant or product and the TS is around 20 kcal/mol. The energy difference between the two TS and the intermediate state is about 12 kcal/mol.

The naphthalocyanine MEP Report.txt document contains the text output of the FlexTS run. When inspecting this document, you can identify the different sections of a single path cycle and find that in this case the calculation required two path cycles to complete.

If required, you can investigate consistency to help to troubleshoot calculations. First, the NEB calculation must converge successfully to the threshold you specified. You can verify this by searching the document for the term **Energy per image**, which is in the header of the NEB section.

After the successful completion of the NEB calculation, FlexTS automatically optimizes the transition state guess for the images it identifies as candidates. You can find this section by searching for **Beginning of optimization cycle**. Each cycle consists of two steps; first converging the direction of the lowest-eigenvalue eigenvector of the Hessian matrix (for example, the uphill vector of the transition state) and then following that vector until it becomes no longer relevant. It is important to explicitly verify that the converged eigenvalue for each new direction is negative.

Finally, each FlexTS calculation returns a number of trajectories and linked charts. Each row of the **All Segments** tab of the results study table corresponds to one trajectory and one chart in the **Path** folder. The calculation returns an additional chart and trajectory the job folder if it identifies a connected path. The trajectory corresponds to the two downhill geometry optimizations from the transition state, taken from [stage 4 of the full path task](#). The **NEB** folder contains trajectories and charts for each nudged elastic band calculation run during a calculation. You can use this to study the convergence behavior of the initial stages of the calculation.

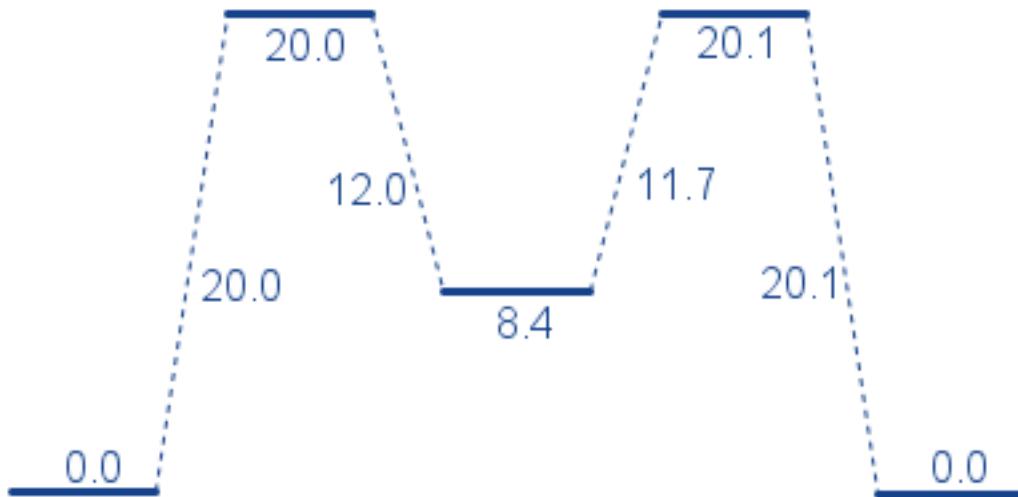
4. To graph the reaction pathway for DFTB+ using a Pipeline Pilot protocol (optional)

In this section, you use a Pipeline Pilot protocol to graph the multistep barrier results from the DFTB+ calculation. This optional section requires a Pipeline Pilot Server with the Materials Studio Collection and the Pipeline Pilot connector in Materials Studio.

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results.std** and make sure that the **Connected Path** sheet is active. Open the **Pipeline Pilot Protocols** dialog from the **Tools** menu and select the **Protocols\BIOVIA Materials Studio\Reaction Chemistry\Reaction Pathway Display** protocol. Click **Run** and close the dialog.

This protocol allows you to take the result from a FlexTS calculation and obtain a publication-quality graph that visually represents the location of different minima and transition states. Inspect the options that are available. You can control the canvas size, font size, and optionally turn off labels for barriers and stationary points.

Once the results are returned, open the **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results Reaction Pathway Display\ naphthalocyanine Results.png** file.



Minima and transition states plot

This plot shows the two-step process in a standardized visual way that practitioners can understand immediately. It can also form the basis of more complicated figures, though you may want to switch off some of the labels for more advanced processing. The energy units are always in kcal/mol.

Note: The energies in this plot correspond to the final energies after optimizations beginning at the transition state. They might not correspond exactly to the energies of the initial reactants and products at the start of the FlexTS calculation.

5. To refine a transition state using DMol³

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results.std** and double-click the structure document in the first row of the **Connected Path** sheet.

This collection document contains all the relevant information to serve as a starting point for a DMol³ Minimum Energy Path calculation. You can run a complete path cycle based on the Reactant and Product physical systems specified, regenerating an entire reaction step in this particular system. In this case, use the TS found in the DFTB+ calculation as a starting guess for a TS Path run.

Open the **DMol3 Calculation** dialog and change the **Task** to **Minimum Energy Path**, the **Quality** to **Fine**. Select the density functional by changing **Functional** to **GGA - PBE**.

On the **Electronic** tab, click **More...** to open the **DMol3 Electronic Options** dialog. Decrease the **SCF tolerance** to **1e-8** and increase the **Max. SCF cycles** to **100**. Close the **DMol3 Electronic Options** dialog and select the **Setup** tab of the **DMol3 Calculation** dialog.

Click **More...** to open the DMol3 Minimum Energy Path dialog and inspect the options available on the dialog.

The DMol³ Minimum Energy Path task works identical to its twin in DFTB+. The main difference is that the energy units used for input are in Ha. These units are converted to kcal/mol, as used by FlexTS internally and by Materials Studio in general.

In this example, use the TS found in DFTB+ to initialize our DMol³ transition state search. There is only one option to change to achieve this.

On the **DMol3 Minimum Energy Path** dialog, change the **Run mode** to **TS Path**, and close the dialog.

On the **Job Control** tab of the **DMol3 Calculation** dialog, select a suitable gateway and a number of processors and click **Run**.

This calculation takes some time to complete.

The DMol³ Minimum Energy Path task works differently to the other tasks in DMol³. In particular, this task runs FlexTS which in turn works with the DMol³ calculation engine. This means that there is no input file that you can inspect or modify directly. Instead, DMol³ input files are generated on the fly when required by FlexTS.

When the calculation finishes, download and inspect the results. You can find a similar result to one of the single barriers in the initial DFTB+ calculation. Now with a more accurate energy barrier of about 12 kcal/mol between reactant or product and TS, and around 4 kcal/mol between the intermediate minimum and the transition state. Each row of the study table document also contains the computational settings used for this calculation, which can be useful as reference later.

You can use the collection document in the final result study table for further processing, for example in a DMol³ Kinetics calculation to generate input for reaction mechanisms in Cantera.

You might also want to inspect the report document naphthalocyanine 1 MEP Report.txt that tracks the FlexTS calculation. At the bottom of this document, you can find the number of energy and gradient calls for the DMol³ calculation. This allows you to assess the method against an equivalent transition search calculation. The overall number should be significantly less than six times the number of atoms required to compute the Hessian matrix of the structure to provide the basic input for a TS Optimization in DMol³. Meanwhile this calculation has refined the transition state and calculated the reactants and products corresponding to this particular reaction step.

6. To compare the reaction pathways for DFTB+ and DMol³ using a Pipeline Pilot protocol (optional)

Next, use the protocol that generated the line plot above to graphically compare the barriers predicted by DMol³ and DFTB+. To achieve this, create a single study table that contains the results for both methods, one in each tab. We begin by making a copy of the first results study table containing the DFTB+ path and remove all unnecessary data.

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine Results.std** and save it as **naphthalocyanine comparison.std**. Activate the **All Segments** tab, right-click the tab name, and select **Delete**. Rename the **Connected Path** tab to **DFTB+** and insert a new tab **DMol3** to the right.

You now have a study table with two tabs, one of which is empty.

Open the study table **naphthalocyanine DFTB+ MEP\ naphthalocyanine 1 DMol3 MEP\ naphthalocyanine 1 Results.std** and copy its entire content into the newly created **DMol3** tab in the comparison study table.

This table now contains two separate pathways with all the information required to plot it in a single panel.

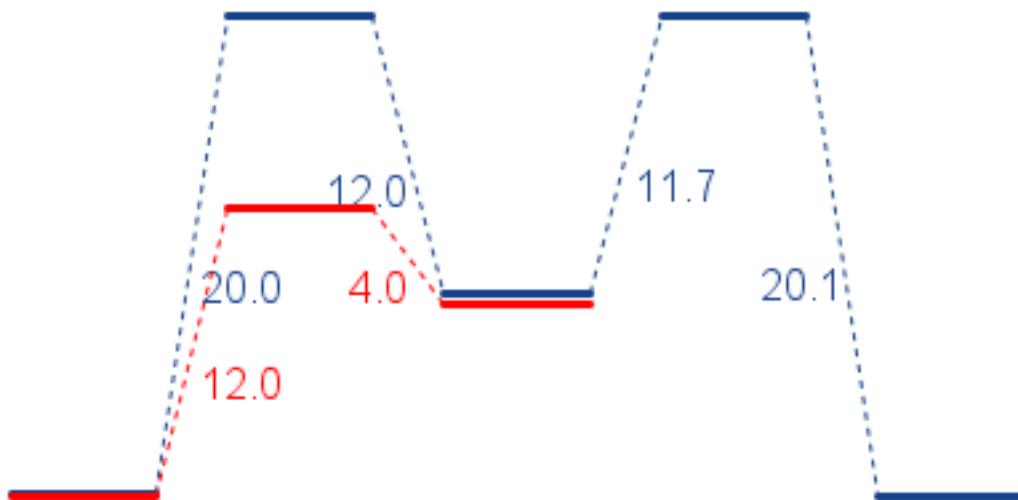
Open the **Pipeline Pilot Protocols** dialog and select the **Protocols\BIOVIA Materials Studio\Reaction Chemistry\Reaction Pathway Display** protocol. For **Sheets** select **AllSheets**, choose **Sheet for Reference Energy**, and select **False** for **Labels | Stationary Points**. Click **Run** and close the dialog.

Tip: Your results study table might require reversal of the path being plotted. If your graph does not look like the example below, select *True* for *Plot Path in Reverse* and regenerate the graph.

The first option makes sure that all the sheets that are now in the study table are used to plot the graph. With more than one line on the graph, you may end up in a situation where there are too many overlapping labels. To avoid that scenario, you only display the barrier heights for comparing our methods, but turn off the energies of the stationary points. You might also choose to process the graph further to add numbers by hand.

The two calculations were performed with different Hamiltonians, which means that each sheet in the study table has its own reference energy. This is why you selected a sheet-based reference energy, as it ensures that each method has its own energy origin.

When the protocol returns the results, inspect the graph created as a PNG file.



Note: The relative energies of the minima in the DFTB+ are extremely close while the actual barriers are significantly higher. While it is extremely efficient and quick to use DFTB+ to obtain the initial pathways, always use a suitable DFT calculation with DMol³ to verify the actual barrier height.

In this specific use case, you ran the same reaction with two different methods, but you can use the same protocol to compare different pathways for the same reaction as well.

You might want to create an image that contains both steps in the DFT path. To do this, manually amend the study table and copy the correct barrier heights and energies of all the stationary states.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

- P. Liljeroth, J. Repp, G. Meyer, "Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules", *Science* **317** 1203 (2007).
- Y. Kumeda, D. J. Wales, L. J. Munro, "Transition states and rearrangement mechanisms from hybrid eigenvector-following and density functional theory. Application to C₁₀H₁₀ and defect migration in crystalline silicon" *Chem. Phys. Lett.* **341** 185 (2001).
- J. M. Carr, S. A. Trygubenko, D. J. Wales, "Finding pathways between distant local minima", *J. Chem. Phys.* **122** 234903 (2005).

S. A. Trygubenko, D. J. Wales, "A doubly nudged elastic band method for finding transition states" *J. Chem. Phys.* **120** 2082 (2004).

Kinetics of a Diels-Alder reaction

Purpose: To introduce the Reaction Kinetics task and demonstrate the calculation of reaction rates.

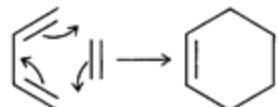
Modules: Materials Visualizer, DMol³, DFTB+

Time: 

Prerequisites: [Transition-state searching using LST/QST tools](#)

Background

This tutorial is based on the Diels-Alder ethene (C_2H_4) with butadiene (C_4H_6) reaction:



This reaction has a large number of derivatives, generally producing six membered rings, hence its practical utility. Extensive studies have examined this reaction and its reverse (the retro Diels-Alder reaction). The high stereo-specificity of the reaction, and other characteristics, have established that the mechanism is a concerted pericyclic reaction.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculations](#)
- [To create the reaction trajectory](#)
- [To calculate the transition state](#)
- [To calculate the rate coefficient parameters](#)
- [To calculate the rate coefficient](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **kinetics** as the project name, click the **OK** button.

The new project is created with *kinetics* listed in the Project Explorer.

2. To prepare the structures for the calculations

Creating models of the reactant and products and mapping between the two models is often the key step in determining transition states and calculating rate coefficients.

To get the relevant structures, use the *Material from Chemical Name or SMILES Pipeline Pilot* protocol.

From the menu bar, select **Tools | Pipeline Pilot Protocols**.

Materials Studio connects to your Pipeline Pilot Server and opens the *Pipeline Pilot Protocols* dialog.

In the **Protocols explorer**, expand the **Protocols | BIOVIA Materials Studio | Reaction Chemistry** node, and then double-click the **Material from Chemical Name or SMILES** protocol.

The dialog displays the parameters for the protocol.

Select **SMILES** and add **C1CC=CCC1** and **C=CC=C.C=C** to the list of SMILES and close the dialog.

Click **Run** to start the protocol.

The protocol runs and returns the requested structures.

Change the name of the results folder to **DA** and rename the documents **C1CC=CCC1.xsd** to **Cyclohexene.xsd** and **C6H10.xsd** to **Butadiene+Ethene.xsd**.

Note: If you do not have access to Pipeline Pilot and the Materials Studio Collection, you can access these output files from the *Examples* folder.

Create a folder named **DA** and select it. Select *File | Import...* to open the Import Document dialog, navigate to *Examples\Documents\3D Model*, select *Cyclohexene.xsd* and *Butadiene+Ethene.xsd*, and then click *Open*.

The Diels-Alder reaction requires that the diene has the *s-cis* conformation. The protocol returned butadiene in the ground state *s-trans* conformation. To change the conformation into the *s-cis* conformation, rotate the torsion angle around the carbon-carbon single bond.

Click the **Measure/Change** arrow  and select **Torsion** from the list. Select the **butadiene** carbon-carbon single bond. Choose the **Selection tool**  and select the torsion monitor. In the **Properties Explorer**, change the value of the **Angle** property to **0** degrees.

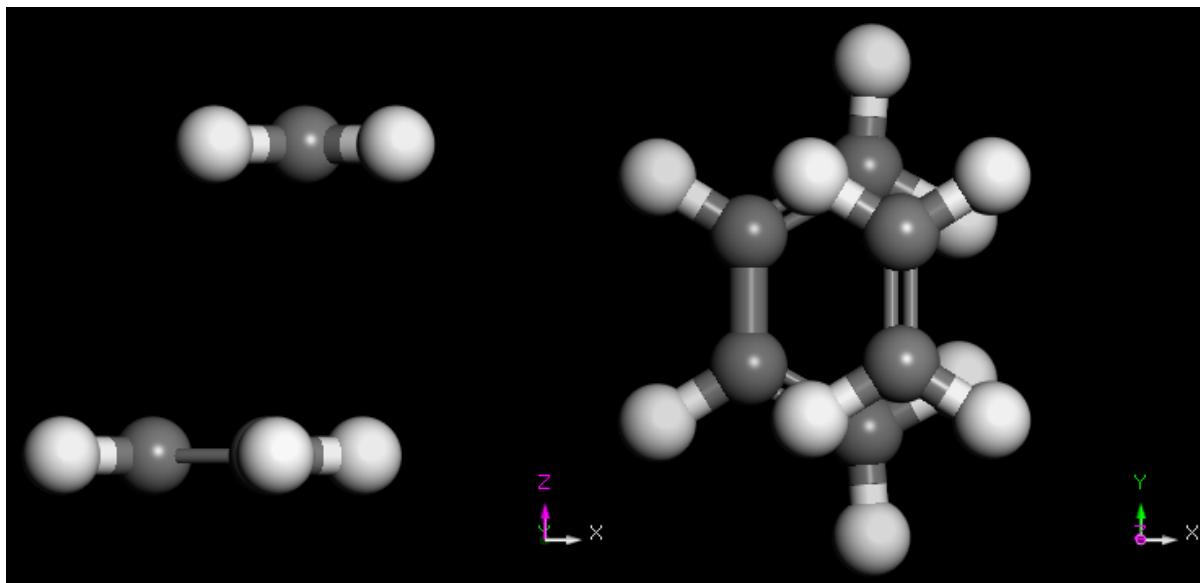
Remove the torsion monitor.

You need to move the ethene molecule to a suitable location relative to the butadiene.

Click **Home**  to reset the view. Select the **butadiene** molecule, click the **Align onto View** arrow , and select **Align With Screen**, followed by **Align Vertical**.

Select the **ethene** molecule, click the **Align onto View** arrow , and select **Align with Screen**, followed by **Align Vertical**.

Use the movement tools to move the **ethene** molecule to a location above the **butadiene**. Create a distance measurement and ensure that the ethene is about **3 Å** above the butadiene, as shown below. Delete the distance measurement.



Butadiene and ethene arrangement, side on (left) and top down (right)

3. To create the reaction trajectory

To perform a transition-state search with DMol³ or DFTB+, you need to create pairs between all the atoms in the reactant and product documents. Use the *Reaction Preview* tool to match atoms in the structures.

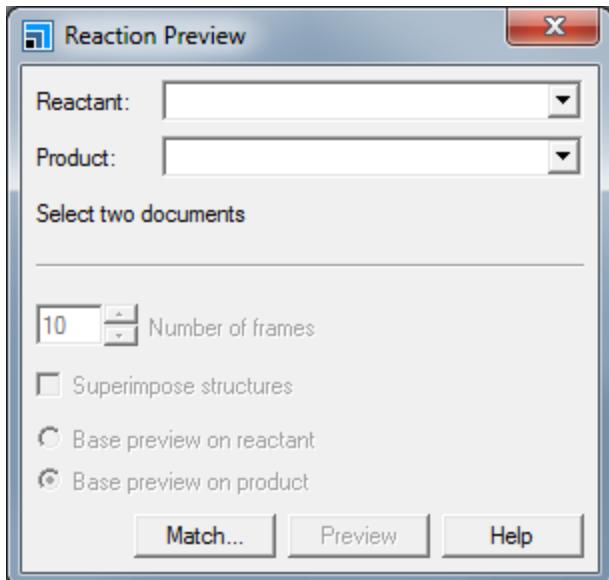
First, display the reactant and product structures side-by-side.

Open the **Cyclohexene.xsd** and **Butadiene+Ethene.xsd** documents. Choose **Window | Tile Vertically** to view both structures at the same time. To ease identification, rotate the **cyclohexene** such that the double bond has the same orientation as the **butadiene** single bond.

Now, you are ready to start pairing atoms in the reactant and product structures.

From the menu bar, select **Tools | Reaction Preview**.

This opens the Reaction Preview dialog.



Reaction Preview dialog

Select **Butadiene+Ethene.xsd** as the **Reactant** list and select **Cyclohexene.xsd** as the **Product**, and then click **Match...** to open the Find Equivalent Atoms dialog.

You can see that no atoms have matches.

Tip: To make it easier to select the correctly matching atoms, change the *Display Style* in both documents to *Ball and Stick*. You can also change the *Projection to Perspective* on the Display Options dialog to assist in identifying equivalent atoms.

For each atom in the **Butadiene+Ethene.xsd** view, select the equivalent atom in the **Cyclohexene.xsd** view and click **Set Match**.

Begin with the hydrogen atoms at the center of the butadiene fragment, these are equivalent to the hydrogens on the cyclohexene double bond.

When you have prepared all the matches, click once anywhere in each 3D Atomistic document to clear the selection of all atoms and bonds.

Close the Find Equivalent Atoms dialog.

You can preview the reaction between butadiene and ethene to form cyclohexene.

On the Reaction Preview dialog, select **Base preview on reactant** and click **Preview**. Close the dialog.

This produces a trajectory document, named **Butadiene+Ethene-Cyclohexene .xtd**. Animating this trajectory gives you an approximate view of the reactive collision.

On the **Animation** toolbar, click the **Animation Mode** arrow  , and select **Bounce**. Then, click **Play** .

Rotate the structure in the trajectory as it plays so that you can view the changes in geometry during the reaction.

If the reaction appears incorrect, repeat the previous matching step and regenerate the preview.

4. To calculate the transition state

You are now ready to prepare the calculation of the transition state.

Ensure that the **Cyclohexene-ButadieneEthene.xtd** trajectory document is in focus. Close the other documents.

You can predict the minimum energy path from both the DMol³ and the DFTB+ modules. It can save time to do the initial transition state search using DFTB+ and then optimize it using DMol³.

Open the **DFTB+ Calculation** dialog. On the **Setup** tab, change the **Task** to **Minimum Energy Path**. Make sure that the **Quality** is **Fine**. Select **Use dispersion method** and select the **D4** option.

Click **More...** to open the DFTB+ Minimum Energy Path dialog.

Make sure that the **Run mode** is **Full Path**. Clear **Determine NEB parameters automatically**, for the **Images** specify **40**, and for **Iterations** specify **120**. Close the dialog.

Click **Run** and close the dialog.

Wait for the simulation to complete.

After the job completes, you can view the text results in the **Butadiene+Ethene-Cyclohexene MEP Report.txt** file and the result in the **Butadiene+Ethene-Cyclohexene Results.std** study table document. If the transition search was successful, the study table contains a single row with the data for the returned transition. The *Estimated lowest Hessian eigenvalue* for the transition state is typically about -260 kcal/mol. To get a better estimate of the reaction energies, you can optimize the transition state using DMol³.

From the study table document, open the **Structure** document.

Select the **TS** structure, right-click, and select **Extract To Atomistic Documents**.

This creates an atomistic document **TS . xsd** containing the transition state structure.

Open the **TS . xsd** document. Close the other documents.

Next, prepare the DMol³ simulation.

Open the **DMol3 Calculation** dialog. On the **Setup** tab, change the **Task** to **Minimum Energy Path**. Make sure that the **Quality** is **Fine**. For the **Functional**, choose **m-GGA** and **SCAN**. Select **Spin unrestricted**.

Tip: On the *Electronic* tab, you can choose to change the *Basis set* to **DNP+**. This setting generates more accurate results but takes significantly longer.

On the **Electronic** tab, click **More...** to open the **DMol3 Electronic Options** dialog. On the **SCF** tab, select **Use smearing**, and then close the dialog.

On the **Setup** tab, click **More...** to open the **DMol3 Minimum Energy Path** dialog. For the **Run mode**, select **TS Path**. On the **Advanced** tab, in the **RMS force convergence** section, for the **Stationary points** specify **5.0e-5 Ha/Å**. Close the dialog.

Click **Run** and close the **DMol3 Calculation** dialog.

After the job completes, you can view the text results in the **TS MEP Report.txt** file. The **TS Results.std** file contains the reactants, product, and proposed transition state.

Tip: You can inspect the energy of each component of the reaction (reactant, product, and TS) in the collection document in the Properties Explorer. You can also edit these energies. Select the component of interest, choose **Energy** from the *Filter* list, and double-click the *TotalEnergy* property (in kcal/mol) to open the Edit Property dialog. For example, you might want to change this energy if you have additional information from another calculation.

5. To calculate the rate coefficient parameters

The next step is to run a reaction kinetics calculation to obtain the parameters required to find the rate coefficient. To do this, you need a collection document with the reactant, product, and transition states, with a Hessian available for each structure.

Right-click the **DA** folder and select **New | 3D Atomistic Collection Document**. Rename the document **DA reaction.xod**, and then open the document.

In the **TS Results.std** study table, open a view of the structure document, it contains a collection containing the **Reactant**, **TS**, and **Product** structures. Copy and paste the content to the new collection document.

Ensure that the **DA reaction.xod** collection document is in focus. Close the other documents.

To calculate the correct rate coefficient, the reaction kinetics task needs to determine the type of reaction. That is, whether it is an isomerization reaction, an association dissociation reaction, or an exchange reaction. The reaction kinetics task attempts to assign motion groups to the reactive fragments. However, you can also specify the motion groups on the reactants and products using the Motion Groups dialog.

Note: The TS search task sometimes switches the Reactant and Product labels.

Confirm that the butadiene+ethene system is labeled **Reactant**. If this is not the case, switch the **Reactant** and **Product** labels in the document.

From the menu bar, select **Modify | Motion Groups** to open the Motion Groups dialog.

Select the **ethene** structure in the system labeled **Reactant** and click **Create from selection** to create a motion group.

Select the **butadiene** structure in the same system and create a second motion group.

Select the system labeled **TS** and create a motion group.

Repeat this for the system labeled **Product**.

Close the dialog.

You now have four motion groups assigned in total, one each for the product and transition state, and two for the reactant.

Open the **DMol3 Calculation** dialog. On the **Setup** tab. Change the **Task** to **Reaction Kinetics**.

Click **More...** to open the DMol3 Reaction Kinetics dialog. Clear selection of **Optimize transition state**, **Reuse Hessian for reaction and products**, and **Use coarse-grained parallelization**. Close the dialog.

Click **Run** and close the **DMol3 Calculation** dialog.

When this job completes, it produces an updated **DA reaction.xod** document.

Before performing a reaction kinetics analysis, ensure that your input structures are reasonable by performing a vibrational analysis.

From the menu bar, select **Tools | Vibrational Analysis** to open the Vibrational Analysis dialog.

Double-click the **TS** structure to select it and click **Calculate**.

A true transition state only has one imaginary (negative) frequency. Similarly, a true minimum has no imaginary (negative) frequencies.

Notes: If a structure has too many imaginary (negative) frequencies, this indicates that the structure had not sufficiently converged. To correct this, you can run the *Minimum Energy Path* task again on the result of the previous *Minimum Energy Path* calculation, using a lower value for *Stationary points* on the *Advanced* tab.

If you encounter a problem with the Reactant or Product, you can save some time by extracting the structure and running a separate geometry optimization on it, requesting the *Frequency* property. Then, replace the structure in the collection document with the re-optimized structure.

6. To calculate the rate coefficient

Next, analyze the output **DA reaction.xod** to calculate the rate coefficient.

With the DA_reaction.xod in focus, open the **DMol3 Analysis** dialog and select **Reaction kinetics**. Define the temperature range **From 200.0 K To 1000.0 K**. Clear selection of **Apply tunneling correction** and click **Calculate**.

This produces a study table, containing the parameters of the Arrhenius equation for the rate of reaction.

$$k = Ae^{-E_a/RT}$$

You can compare the calculated parameters with experimental values obtained from shock tube experiments for the dissociation reaction ([Tsang, 1965](#)). DMol³ also provides the parameters for the association reaction.

Note: By using some combination of a higher-quality basis set (DNP+) and a hybrid functional, you can obtain results that are closer to experimental values. However, these calculations take significantly longer.

Parameter	Dissociation Tutorial (SCAN(DNP))	Dissociation Tutorial (SCAN0(DNP+))	Dissociation Experiment	Association Tutorial (SCAN(DNP))
A	$3.8 \times 10^{14} \text{ s}^{-1}$	$7.5 \times 10^{13} \text{ s}^{-1}$	$1.05 \times 10^{15} \text{ s}^{-1}$	$1.3 \times 10^{-15} \text{ cm}^3/\text{molecule/s}$
E _a /R	27369 K	31376 K	33565 K	6136 K
k(298K)	$3.6 \times 10^{-26} \text{ s}^{-1}$	$1.0 \times 10^{-32} \text{ s}^{-1}$	$1.273 \times 10^{-34} \text{ s}^{-1}$	$1.3 \times 10^{-24} \text{ cm}^3/\text{molecule/s}$

Select **File | Save Project** from the menu bar, then **Window | Close All**.

This is the end of the tutorial.

References

Tsang, W. *J. Chem. Phys.*, **42**, 1805 (1965).

Calculating the free energies of chemical reactions

Purpose: Introduces DMol³ as a tool for predicting thermodynamic properties of molecular systems.

Modules: Materials Visualizer, DMol³

Time: 

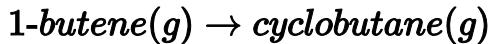
Prerequisites: [Geometry optimization for solids using delocalized internal coordinates in DMol³](#)

Background

The results of a vibrational analysis calculation can be used to compute important thermodynamic properties such as enthalpy (H), entropy (S), free energy (G) and heat capacity at constant pressure (C_p) as functions of temperature. The DMol³ total energy yields the total electronic energy at 0 K. The various translational, rotational, and vibrational components are used to compute H , S , G , and C_p at finite temperatures, as discussed below.

Introduction

In this tutorial, you will use DMol³ to calculate the free energy of a simple reaction, the isomerization of 1-butene to cyclobutane:



The heat of combustion of each hydrocarbon has been measured and subtraction of the results gives [1]:



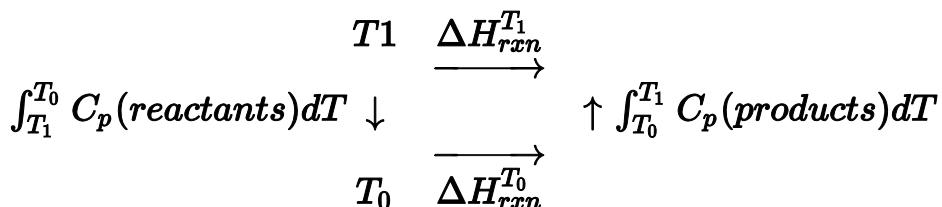
The entropy of each substance is reported in the same document [1] as $\Delta S_{\text{exp}}^{298.15K} = -9.8 \text{ cal/mol/K}$. These results can be used to calculate the free energy at $T = 298.15 \text{ K}$ using:

$$\Delta G_{\text{exp}}^{298.15K} = \Delta H_{\text{exp}}^{298.15K} - T \Delta S_{\text{exp}}^{298.15K}$$

resulting in:



To determine the reaction enthalpy or free energy from first principles calculations, the thermodynamic cycle is used, as shown below, where the reaction enthalpy at temperature T_1 can be calculated if the reaction enthalpy at T_0 and the heat capacities of the products and reactants between the two temperatures are known:



resulting in the following equation:

$$\Delta H_{rxn}^{T_1} = \int_{T_1}^{T_0} \sum_{reactants} C_p dT + \Delta H_{rxn}^{T_0} + \int_{T_0}^{T_1} \sum_{products} C_p dT$$

The results obtained from a geometry optimization using DMol³ give the total electronic and ionic energy (E_{tot}) of the system. The enthalpy difference is given by:

$$\Delta H = \Delta U - P\Delta V$$

Note: In certain cases, the possible changes in volume of the system must be included.

The internal energy (U) of the system arises from the electronic, vibrational, translational, and rotational contributions, and is given by the following equation:

$$\Delta U = \Delta E_{tot} + \Delta E_{vib} + \Delta E_{trans} + \Delta E_{rot}$$

The Gibbs free energy difference is given by:

$$\Delta G = \Delta H - T\Delta S$$

where ΔS is given by the following equation:

$$\Delta S = \Delta S_{vib} + \Delta S_{trans} + \Delta S_{rot}$$

DMol³ can calculate all the above terms once the ground-state structure is determined and the vibrational frequencies for the 3N - 6(5) normal modes are obtained using statistical mechanics.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculations](#)
- [To optimize the geometry and performing a vibrational analysis calculation](#)
- [To calculate free energies at finite temperature from data contained in the DMol³ output document](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **butene** as the project name, click the **OK** button.

The new project is created with *butene* listed in the Project Explorer.

2. To prepare the structures for the calculations

In this section of the tutorial, you will build the reactants and products in separate documents. The first step is to create two new 3D Atomistic documents.

Click the **New** arrow  on the **Standard** toolbar and select **3D Atomistic Document** from the dropdown list. Repeat this procedure so that two new 3D Atomistic documents are created.

Ensure that the first 3D Atomistic document is active. Select the **Sketch Atom** tool  from the **Sketch** toolbar. Draw a chain of four carbon atoms, then press **ESC** to cancel sketching. Click on one of the terminal C-C bonds to increase the bond order to two.

To complete the structure, you need to add hydrogens and arrange the structure into a sensible initial geometry.

Click the **Adjust Hydrogen** button  and then the **Clean** button  on the **Sketch** toolbar.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Atom** tab select the **Ball and stick** option.

You should rename this document to avoid confusion later.

Rename the new document **1-butene.xsd**.

Now build the other molecule involved in the reaction, cyclobutane.

Click in the 3D Viewer for **3D Atomistic (2).xsd** to make it the active document. Click the **Sketch Ring** arrow  on the **Sketch** toolbar and select **4 Member** from the dropdown list. Click once in the document to insert a cyclobutane ring.

Click the **Adjust Hydrogen**  and **Clean**  buttons.

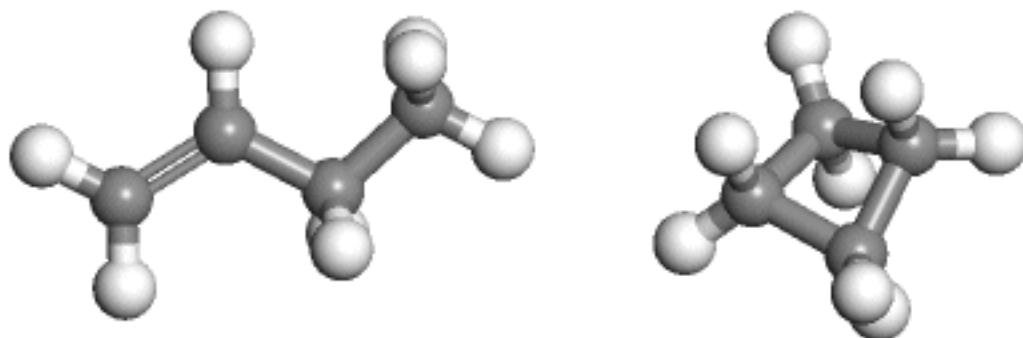
On the Display Style dialog, select the **Ball and stick** option and close the dialog.

You should rename this document.

Rename the second new document **cyclobutane.xsd**.

Click the **3D Viewer Selection Mode** button  on the **3D Viewer** toolbar.

When you have finished, you should have the two molecules shown below in separate 3D Atomistic documents.



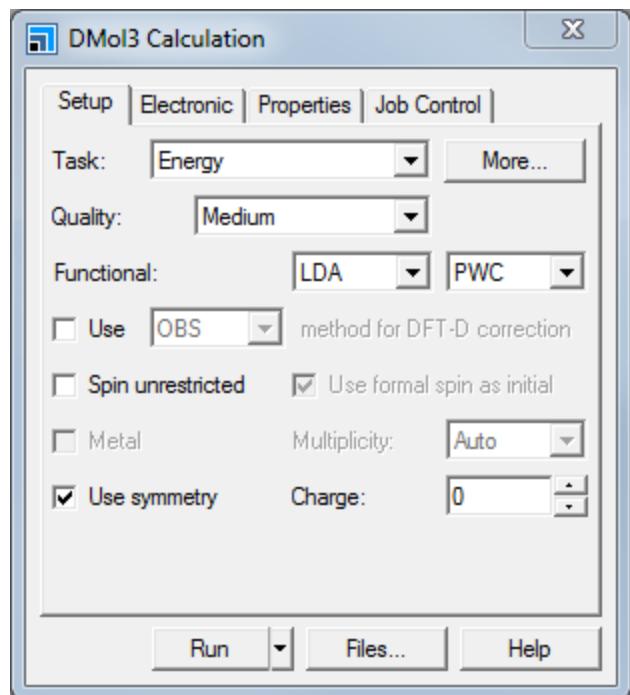
The structures of 1-butene and cyclobutane

3. To optimize the geometry and perform a vibrational analysis calculation

Prior to performing the vibrational analysis calculation, you should optimize the structures of both molecules. You will do this using the geometry optimization functionality in DMol³.

Make **1-butene.xsd** the active document. Click the **DMol3** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the DMol3 Calculation dialog.



DMol3 Calculation dialog, Setup tab

Set the **Task** to **Geometry Optimization**. Make sure that the **Quality** is set to **Medium** and change the **Functional** to **GGA** and **BLYP**.

You have just specified the basis set and the Hamiltonian to be used in this calculation. A gradient corrected functional such as BLYP is important for computing accurate thermodynamic properties.

On the **Electronic** tab, click the **More...** button to open the DMol3 Electronic Options dialog. Check the **Use smearing** checkbox on the **SCF** tab and make sure that the value of **Smearing** is set to the default, **0.005**. Close the dialog.

Smearing populates the energy levels around the Fermi level according to a thermal distribution and can help to improve SCF convergence in many cases.

On the **Properties** tab on the DMol3 Calculation dialog, check the **Frequency** checkbox.

This causes a vibrational analysis to be performed after the structure optimization has converged. The results of this analysis are used to compute enthalpy (*H*), entropy (*S*), free energy (*G*), and heat capacity at constant pressure (*C_p*) as functions of temperature. The DMol³ total energy yields the total electronic energy at 0 K. The various translational, rotational, and vibrational components are used to compute *H*, *S*, *G*, and *C_p* at finite temperatures. In this tutorial, you are mainly interested in the finite temperature corrections for the free energy.

You are now ready to run the calculations on 1-butene and cyclobutane.

Ensure that **1-butene.xsd** is the active document and click the **Run** button.

Make **cyclobutane.xsd** the active document and click the **Run** button again. Close the dialog.

The progress of the jobs during the computations is presented in the form of chart and text documents. When the jobs are complete, all of the results files are returned to the client.

The calculation for cyclobutane is much quicker than the one for 1-butene because DMol³ makes use of the D_{2D} symmetry of the molecule.

4. To calculate free energies at finite temperature from data contained in the DMol³ output document

The optimized structure for 1-butene is contained in the **1-butene DMol3 GeomOpt/1-butene.xsd** file. The text output of the computation is contained in the **1-butene.outmol** file. Before calculating the free energy for the isomerization reaction, you will display the calculated thermodynamic properties in a chart document.

Select **File | Save Project** from the menu bar, then **Window | Close All**.

In the Project Explorer, double-click on **1-butene.xsd** in the **1-butene DMol3 GeomOpt** folder.

Select **Modules | DMol3 | Analysis** from the menu bar to open the DMol3 Analysis dialog and select **Thermodynamic properties** from the dropdown list. Ensure that **1-butene.outmol** is the **Results file** and click the **View** button and close the dialog.

The calculated thermodynamic properties are displayed in a chart document.

You will now calculate the free energy for the reaction from the data in the corresponding DMol³ output documents.



In the Project Explorer, double-click on **1-butene.outmol** in the **1-butene DMol3 GeomOpt** folder.

The output of the calculation for 1-butene is displayed in a Text Viewer.

Press **CTRL + F** and search for **Geometry optimization completed**. Write the value for the **Total Energy** displayed above the table for the last step in the **E_{total}** row for **1-butene** in the table below.

The text document should look similar to this:

```

opt==   Cycle    15      Total Energy -157.1555609   Energy change -0.0000179   Max Gradient 0.001173   Max Displacement 0.001386
                                                 Step 15
+-----+-----+-----+-----+-----+-----+
| Parameter | value | tolerance | units | OK? | <-- DELOC
+-----+-----+-----+-----+-----+
| delta E | -0.179057E-04 | 0.200000E-04 | Ha | Yes | <-- DELOC
| F|max | 0.117269E-02 | 0.211671E-02 | au | Yes | <-- DELOC
| dR|max | 0.138633E-02 | 0.944863E-02 | au | Yes | <-- DELOC
+-----+-----+-----+-----+-----+
Geometry optimization completed successfully in 15 steps.
  
```

Section of the DMol³ .outmol document containing the total energy in Hartree for 1-butene

	1-Butene	Cyclobutane
E _{total} (Hartree)		
G ^{298.15K} _{total} (kcal/mol)		
G _{total} (Hartree)		
E _{Tcorr} ^{298.15K} = E _{total} + G _{total} (Hartree)		

Note: The atomic energy unit Hartree is very large, such that physically important differences are often of the order of mH or even μ H. To avoid undesirable rounding errors, it is important to record all of the significant figures provided in the DMol³ output document.

Scroll to the end of the **1-butene.outmol** document.

At the end of **1-butene.outmol** you will find a table containing the finite temperature corrections for the standard thermodynamic quantities (entropy, heat capacity, enthalpy, and free energy) computed from 25 to 1000 K in steps of 25 K. All these quantities include the zero-point vibrational energy (ZPVE).

Record the **G** value for 1-butene at **298.15** K in kcal/mol in the second row of the table.

The text document should look similar to this.

STANDARD THERMODYNAMIC QUANTITIES computed from 25.00 to 1000.00 in steps of 25.00					
T (K)	Entropy S (cal/mol.K)	Heat_Capacity Cp	Enthalpy H (kcal/mol)	Free_Energy G	
(ZPVE is included)					
1 25.00	42.588	8.023	65.971	64.906	
2 50.00	48.362	8.838	66.180	63.762	
3 75.00	52.152	9.945	66.415	62.504	
4 100.00	55.165	11.037	66.677	61.161	
5 125.00	57.738	12.058	66.966	59.749	
6 150.00	60.024	13.047	67.280	58.276	
7 175.00	62.111	14.065	67.619	56.749	
8 200.00	64.060	15.155	67.984	55.172	
9 225.00	65.912	16.335	68.377	53.547	
10 250.00	67.698	17.604	68.801	51.877	
11 275.00	69.438	18.947	69.258	50.163	
12 298.15	71.021	20.237	69.712	48.537	

The computed G_{total} value at 298.15 K should be about +49 kcal/mol.

Now convert G_{total} from kcal/mol to Hartree (1 Hartree = 627.51 kcal/mol).

Write down the **G** value for 1-butene at **298.15** K in Hartree in the third row of the table above.

Since the DMol³ .outmol document provides the corrections for H , S , and G for finite temperature, you can simply add up the values in rows 1 and 3 of the table above to obtain the finite temperature-corrected value for G for 1-butene.

Add the values in rows **1** and **3** for 1-butene together and enter the result in row **4** of the table.

Repeat the procedure above for cyclobutane to fill the remaining cells of the table.

You can now calculate the ΔG value in kcal/mol for the isomerization of 1-butene to cyclobutane using the following formula:

$$\Delta G_{reaction}^{298.15K} = 627.51 [E_{Tcorr}^{298.15K}(\text{cyclobutane}) - E_{Tcorr}^{298.15K}(\text{butene})]$$

The resulting computed free energy for the reaction should be about +10.75 kcal/mol, very close to the experimental value. The positive sign of the free energy indicates that this reaction will not occur spontaneously at room temperature.

Note: You may get slight variations from the values shown in this tutorial. This is mainly due to slight structural differences resulting from using the *Medium* convergence level in the DMol³ geometry optimization.

Select **File | Save Project** from the menu bar, then **Window | Close All**.

This is the end of the tutorial.

References

<http://www.wiredchemist.com/chemistry/data/entropies-organic>

Calculating the Optical Properties of Coumarin

Purpose: Demonstrates how to calculate optical properties using DMol³.

Modules: Materials Visualizer, DMol³

Time:  

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Coumarin and its derivatives represent a family of compounds, originally found in plants, which are optically active. Coumarin (2H-chromen-2-one) is often used as a reference standard compound for dealing with latex and liposomes.

Introduction

In this tutorial, you calculate the optical properties of coumarin both in vacuum and in the presence of water. You perform geometry optimization and subsequent TD-DFT calculations with and without the COSMO solvation model.

This tutorial covers:

- [Getting started](#)
- [To create and optimize the input structure](#)
- [To calculate the optical spectra of coumarin in the gas phase](#)
- [To calculate the optical spectra of coumarin in the presence of water](#)
- [To optimize the geometry of an excited state](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

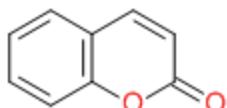
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DMol3_optical** as the project name, click **OK**.

The new project is created with *DMol3_optical* listed in the Project Explorer.

2. To create and optimize the input structure

You can use the sketching tools to draw the Coumarin molecule.



Open a new **3D Atomistic Document** and sketch the structure of coumarin. Use the **Adjust Hydrogen** and **Clean** tools to amend the structure.

Rename the new document **coumarin.xsd**.

For flexible molecules, you could preoptimize the structure with a good quality forcefield such as COMPASS. However, as this molecule is very rigid, you can move on to performing the initial geometry optimization.

Click **DMol3**  on the Modules toolbar and choose **Calculation** to open the DMol3 Calculation dialog.

Next, run a geometry optimization using the PBE functional.

On the **Setup** tab, select **Geometry Optimization** from the **Task** list and select **GGA PBE** as the **Functional**.

To improve the accuracy of the calculation, modify the basis set. Calculation of optical properties requires the use of the 4.4 basis file.

Select the **Electronic** tab, for the **Basis set** select **DNP** and for the **Basis file** select **4.4**.

You are now ready to run the initial geometry optimization.

On the DMol3 Calculation dialog, click **Run**.

Depending on the speed of your computer, the calculation may take several minutes to complete. When the calculation completes, the results return to Materials Studio. These include the optimized structure, **Coumarin . xsd**, a trajectory containing the frames from each optimization step, and various chart and text documents containing information about the calculation.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To calculate the optical spectra of coumarin in the gas phase

In this section of the tutorial, you perform a single point energy calculation and calculate the optical spectrum of coumarin in vacuum.

Open the optimized **coumarin.xsd**.

On the **DMol3 Calculation** dialog, select the **Properties** tab. Select the **Optics** checkbox and change the **Calculate lowest states** value to **25**.

This calculates the 25 lowest excited states, their energies, and properties such as transition intensities. Increasing the number of states in the calculation increases the calculation time.

Note: You can also calculate linear polarizability. This requires that you calculate all available excitations and is very memory and time intensive.

On the **Setup** tab, select **Energy** from the **Task** list. Click **Run** and close the dialog.

As this is a single point energy calculation, it returns fewer documents. You can use DMol3 Analysis to calculate the optical spectrum.

Open the **coumarin DMol3 Energy\coumarin.xsd** document. Click **DMol3**  on the Modules toolbar and choose **Analysis** to open the DMol3 Analysis dialog.

Select the **Optics** property and click **View spectrum**. Close the dialog.

A chart displays, **coumarin Optical Spectrum.xcd**.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To calculate the optical spectra of coumarin in the presence of water

DMol³ enables you to include the effect of a solvent when calculating optical properties using the COSMO approach. Optimize coumarin with COSMO switched on and then recalculate the optical spectra. You can do this in one step.

Change focus to the original **coumarin.xsd** that you sketched. Open the **DMol3 Calculation** dialog, on the **Setup** tab change the **Task to Geometry Optimization**.

You can use COSMO (COnductor-like Screening MOdel) to mimic a range of solvents. In COSMO, the solute molecule forms a cavity in the dielectric continuum of given permittivity representing the solvent.

Select the **Electronic** tab and select the **COSMO** option in the **Screening model** list. Click **More...** to open the DMol3 Electronic Options dialog, select the **Solvent** tab.

You are going to use water as the solvent.

Ensure that you select **Water** from the **Solvent** list and close the dialog. On the DMol3 Calculation dialog, click **Run**.

This calculation is likely to take several minutes to complete. When the calculation has finished, you can analyze the results to generate the optical spectrum.

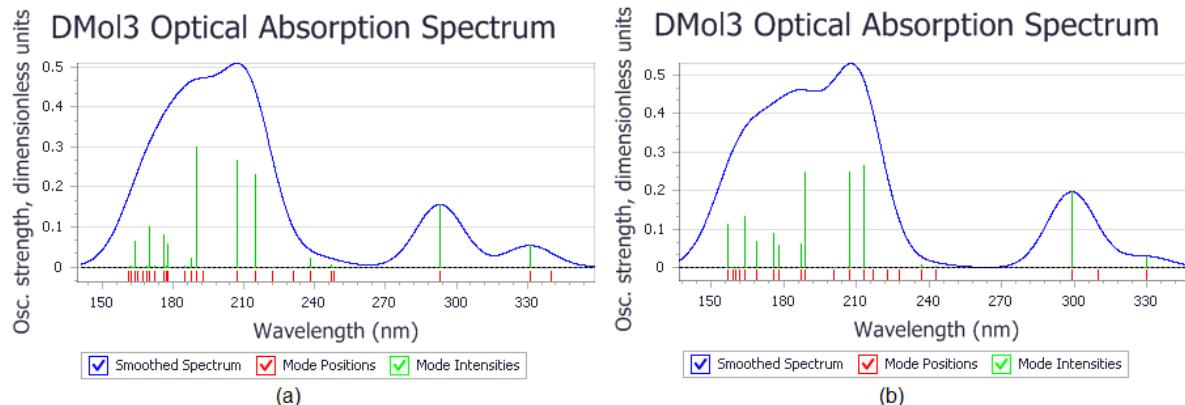
Open **coumarin DMol3 GeomOpt (2)\coumarin.xsd** and open the **DMol3 Analysis** dialog. Select the **Optics** property and click **View spectrum**.

You can view both spectra side-by-side so you can compare them.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Open both chart documents and select **Window | Tile Vertically**.

You can see that the spectra are slightly different with the solvent effect shifting the highest absorption band. The solvent-induced shift in absorption is usually small (about 5-15 nm).



The charts show the optical spectra for (a) the molecule in vacuum and (b) the molecule in the solvent.

5. To optimize the geometry of an excited state

An additional exercise that you can carry out in this tutorial is to optimize the geometry of an excited state and compare it with the geometry of the ground state. These types of calculations are significantly more time-consuming than the TD-DFT evaluation of excitation energies for a fixed molecular geometry. So, the best approach is to perform them separately from the previous steps.

Excited state optimization produces not only modified geometries but also the energies that are relevant to studies of fluorescence, for example. Excitation energies reported in a TD-DFT calculation correspond to the absorption spectrum; that is the energies of absorbed photons. You can interpret the final excitation energy in the DMol³ output file for an excited state geometry optimization as an energy of the emitted photon, as registered in a fluorescence spectroscopy experiment. The energy difference between the last reported ground state dissociation energy and the same value for the optimized ground state geometry represents the energy to dissipate after a fluorescence event through electron-phonon coupling.

You can perform these calculations both in the gas phase and in the presence of water; this calculation is similar to steps 3 and 4 above.

First, you calculate the emission energy in a vacuum.

Open **coumarin DMol3 GeomOpt\coumarin.xsd**.

On the **Properties** tab of the **DMol3 Calculation** dialog, select the **Optics** checkbox and select the **Optimize geometry for** checkbox. Keep the **Singlet** state setting and select the **1st** excitation.

Choose the **Setup** tab and select the **Energy** task.

Choose the **Electronic** tab and make sure that the **Screening model** list is **None**.

This produces an optimized geometry of the lowest energy singlet excitation of the molecule in a vacuum.

Click **Run**.

When the calculation is complete, the results folder contains **coumarin_S1_GO** files in addition to the files generated in the previous steps of the tutorial. You can examine the geometry of the excited state in **coumarin_S1_GO.xsd** and compare it to the optimized geometry of **coumarin.xsd**. You can see that there are significant changes in some of the bond lengths. For example, the C=O double bond

DMol3: Calculating the Optical Properties of Coumarin

weakens and it is about 0.1 Å longer than in the ground state, while the C-O bonds in the ring structure become stronger and shorter.

Next, you calculate the emission energy in water.

Open **coumarin DMol3 GeomOpt (2)\coumarin.xsd**.

On the **Electronic** tab of the **DMol3 Calculation** dialog, select the **COSMO** option in the **Screening model** list.

Click **Run**.

You can also analyze the energetics of the excitation before and after the excited state optimization. The vertical absorption energy corresponds to the excitation energy at the beginning of the TDDFT optimization.

Open the **coumarin_S1_GO.outmol** output file and search for the section beginning **Done calculating TDDFT forces**.

The next three lines contain essential information about the ground and excited state energetics of this conformation.

Make a note of the value of **Excitation energy**.

This is the absorption energy.

Find the last occurrence of **Done calculating TDDFT forces** and make a note of the **Excitation energy**.

This corresponds to the emission energy of the excited state back into the ground state.

For coumarin in vacuum, you can find that the emission is about 1.57 eV lower than the absorption. When coumarin is solvated in water, the emission is only about 0.80 eV lower than the absorption.

This is the end of the tutorial.

Simulating electron transport with DMol³

Purpose: To introduce DMol³ calculations on transport devices.

Modules: Materials Visualizer, DMol³

Time: 

Prerequisites: Building transport devices for electron transport calculations Visualizer Tutorial

Background

The Electron Transport task in DMol³ applies the non-equilibrium Green's function (NEGF) formalism to model electron transport between two electrodes. The Electron Transport task allows you to calculate transmission functions and current voltage characteristics.

Introduction

In this tutorial you will use the DMol³ module to calculate transport properties for a lithium island connected to two hydrogen chain electrodes.

This tutorial covers:

- [Getting started](#)
- [Initial preparation](#)
- [To set up the electron transport job](#)
- [To analyze the transmission function](#)
- [To analyze the current voltage characteristics](#)
- [To analyze the charge density and potential](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

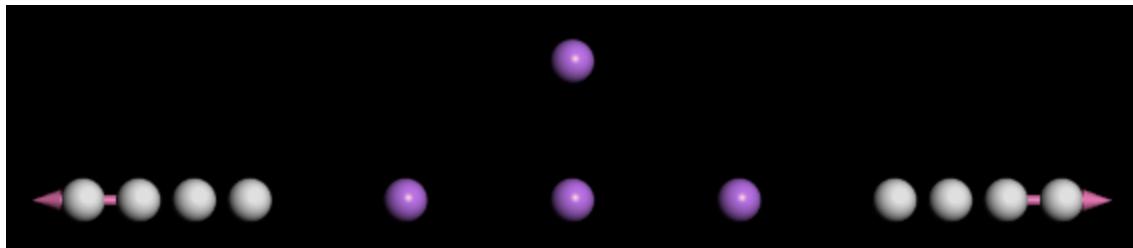
Open the **New Project** dialog and enter **DMol3 Transport** as the project name, click **OK**.

The new project is created with DMol3 Transport listed in the Project Explorer.

2. Initial preparation

The first step is to import the device structure.

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Examples\Documents\3D Model\HChainLi4.xsd**, click **Open**.



Device structure

The device comprises two hydrogen chains and four lithium atoms in a central island.

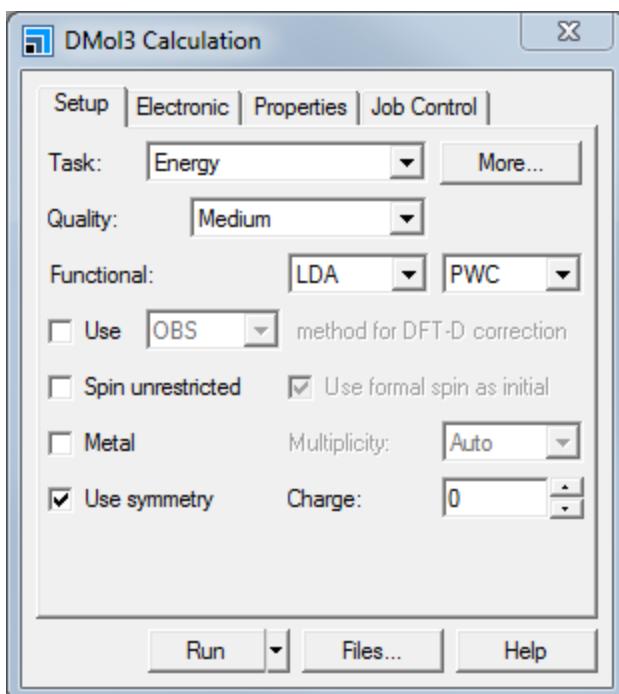
3. To set up the electron transport job

You now have a device structure ready for use with the DMol³ Electron Transport task.

Begin by setting up a calculation for the transmission of the device.

Click the **DMol3**  button on the **Modules** toolbar and select **Calculation** or choose **Modules | DMol3 | Calculation** from the menu bar.

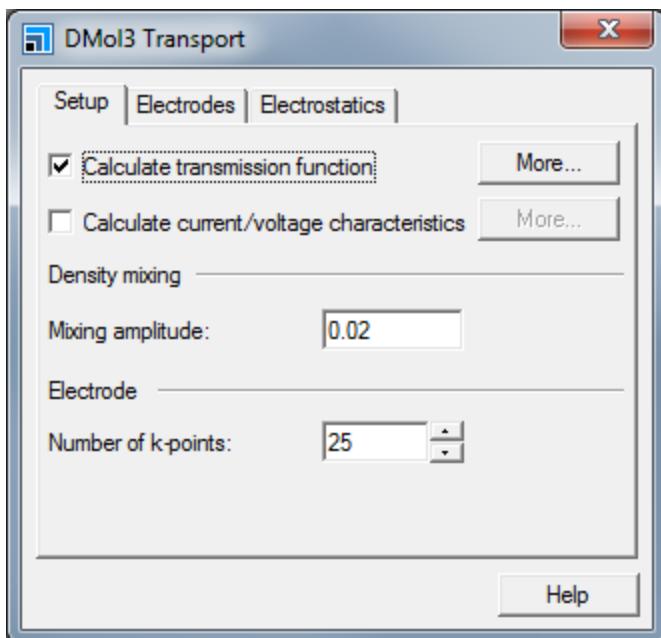
This opens the DMol3 Calculation dialog.



DMol3 Calculation dialog, Setup tab

On the **Setup** tab select **Electron Transport** in the **Task** dropdown list.

Click **More...** to open the **DMol3 Transport** dialog.



The DMol3 Transport dialog contains settings specific to the Electron Transport task.

Make sure the **Calculate transmission function** checkbox is checked.

This will request calculation of the transmission functions between the electrodes. The range and number of steps for the transmission function can be modified to fit the device. The energy range is given relative to the lowest Fermi energy for the electrodes.

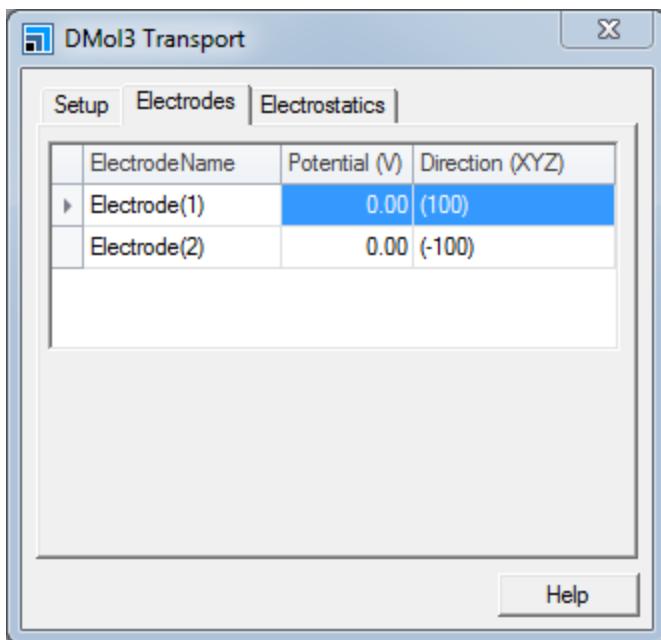
On the **Setup** tab of the DMol3 Transport dialog, click **More...** for **Calculate transmission function** to open the DMol3 Transmission dialog. Set **From** to **-2**, **To** to **3**, and the number of **Steps** to **1001**. Close the dialog.

Since a transport device is an open system it does not conserve charge during the SCF cycle and is often prone to charge fluctuations. As a result the mixing parameter used for the charge mixing should be smaller than the normal mixing parameter used in DMol³.

On the **Setup** tab of the DMol3 Transport dialog set the **Mixing amplitude** to **0.015**

As part of the calculation each electrode will be modeled as a periodic structure in order to calculate the Fermi level and other properties needed to describe the electrodes during the device calculation. You should ensure that the number of k-points used for the calculation is large enough to properly predict the Fermi level and the electronic structure of the electrodes. For this calculation the default value of **25** will be enough.

Select the **Electrodes** tab.



The Electrodes tab shows information about the hydrogen electrodes and allows you to modify settings for them. You will change the name of the electrode so that they are more easily identifiable later.

Change the name of **Electrode(1)** to **source** and **Electrode(2)** to **drain**. Close the DMol3 Transport dialog.

The names of the electrode objects are also modified in the 3D Atomistic document.

Note: If you use the Properties Explorer to change the name of electrodes, the electrode will use any settings related to the new name. If no settings exist the default settings will be applied. When the name is changed on the DMol3 Transport dialog the current settings will be used with the new name.

Since the convergence of the SCF cycle can be problematic for transport calculations it is prudent to increase the maximum number of SCF cycles.

On the **Electronic** tab of the DMol3 Calculation dialog click **More...** to open the DMol3 Electronic Options dialog.

On the **SCF** tab set the **Max. SCF cycles** to **500**.

You are now ready to start the transport job.

Click **Run**.

A text document named **Status . txt** is displayed, reporting the status of the calculation. This document is updated regularly until the calculation is complete, it can be a useful aid to indicate the progress of your calculation. The transmission calculation should only take a few minutes.

You will now set up a current calculation for the same device.

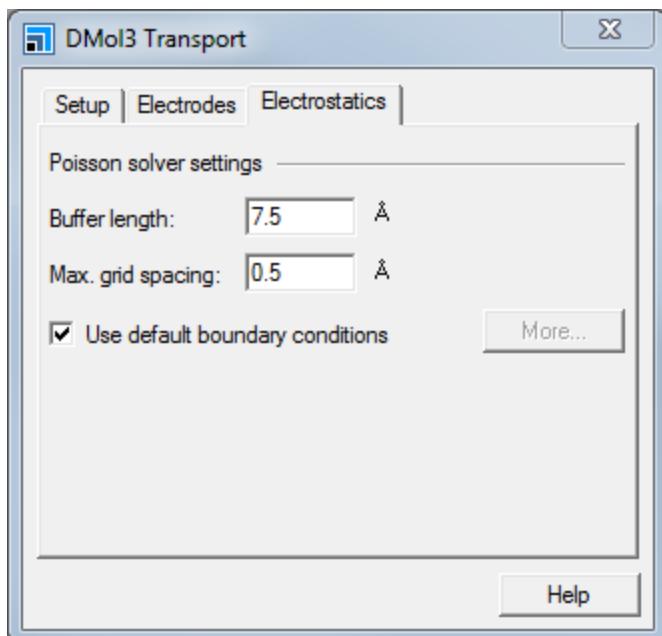
Close all of the output files and make the original **HChainLi4.xsd** the active document.

Open the DMol3 Transport dialog, on the **Setup** tab uncheck the **Calculate transmission function** checkbox and check the **Calculate current/voltage characteristics** checkbox. Click **More...** for **Calculate current/voltage characteristics** to open the DMol3 Current/Voltage dialog.

Set **Vary potential for source**, set the potential range **From** to **0**, **To** to **1.5**, and the number of **Steps** to **16**. Close the dialog.

For a biased calculation the quality of the calculation can be improved by decreasing the grid spacing for the Poisson solver.

On the DMol3 Transport dialog select the **Electrostatics** tab.



On the **Electrostatics** tab of the DMol3 Transport dialog, set the **Max. grid spacing** to **0.3**.

You can calculate the charge density and electrostatic potential to improve your understanding of the device.

Select the **Properties** tab of the DMol3 Calculation dialog, select the **Electron density** property, and check the **Deformation density** check box.

Select the **Electrostatics** property and click **Grid...** to open the **DMol3 Grid Parameters** dialog. Set the **Grid resolution** to **Fine**.

You are now ready to launch the job.

Click **Run** and close the dialog.

The current calculation can take up to a few hours depending on the computational resources used.

4. To analyze the transmission function

When the transmission calculation is complete the results are returned in the HChainLi4 DMol3 Transport folder in the Project Explorer.

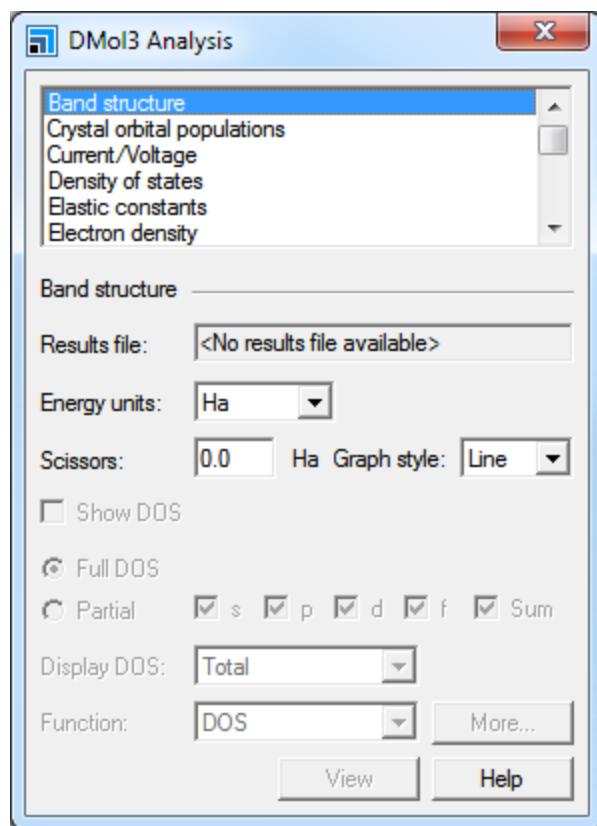
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

In the **HChainLi4 DMol3 Transport** folder double-click on **HChainLi4.xsd**

You will now analyze the results using the DMol3 Analysis module.

On the **Modules** toolbar, click **DMol3**  and select **Analysis** or choose **Modules | DMol3 | Analysis** from the menu bar.

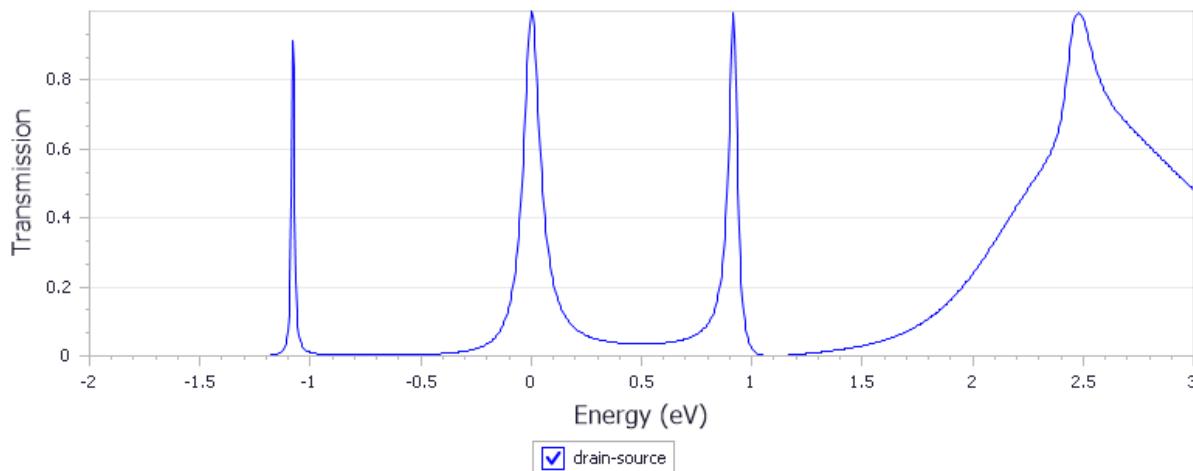
This opens the DMol3 Analysis dialog.



Select **Transmission** from the list and click **View**. Close the dialog.

A plot of the transmission function is shown.

DMol3 Transmission



The transmission for the device will have peaks where the Li island have states. If the states are delocalized on both the island and electrode leads then the peak will be broadened by the electrodes while if the state is strongly localized on the island the peak will be sharp. The energies of the transmission function are plotted relative to the lowest chemical potential of the electrodes.

5. To analyze the current voltage characteristics

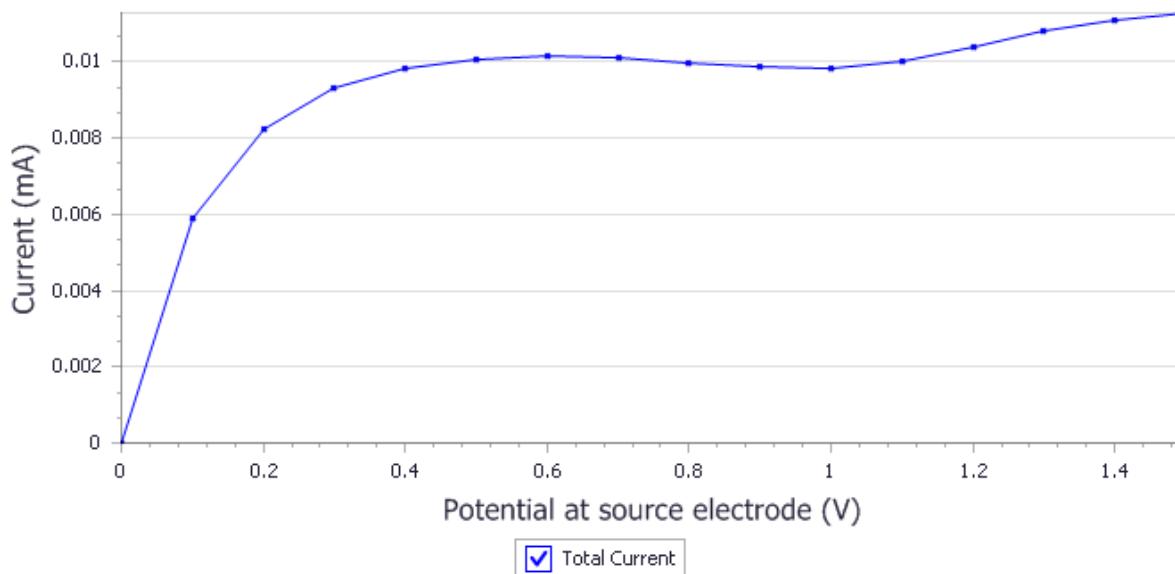
When the current calculation is complete the results are returned in the **HChainLi4 DMol3 Transport (2)** folder in the Project Explorer.

In the **HChainLi4 DMol3 Transport (2)** folder double-click on **HChainLi4.xsd**.

Open the **DMol3 Analysis** dialog, select **Current/Voltage** and click **View**. Close the dialog.

A plot of the current voltage characteristics is shown.

DMol3 Current Voltage



Since the device is symmetric along the transport direction we expect the current for positive and negative bias to only differ by a sign. The current is measured at the drain electrode and the voltage is varied at the source electrode. We use the convention that a positive current indicates that current is passing out of the device at the electrode where the current is measured.

6. To analyze the charge density and potential

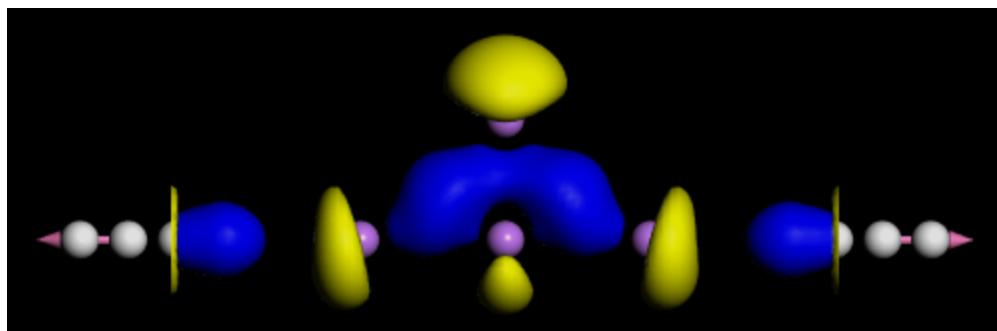
In the **HChainLi4 DMol3 Transport (2)** folder double-click **HChainLi4.xsd**.

Open the **DMol3 Analysis** dialog and select **Electron density**.

In the **Density field** dropdown list select **Deformation density** and click **Import**.

In the **HChainLi4.xsd** document open the **Display style** dialog. On the **Isosurface** tab set the **Isovalue** to **0.015** and the **Type** to **+/-**.

The **HChainLi4.xsd** document now contains an isosurface representing the deformation density for the device.



In the **HChainLi4 DMol3 Transport (2)** folder double-click on **HChainLi4.xsd**.

Open the **DMol3 Analysis** dialog and select **Potentials**.

In the **Potential field** dropdown list select **Biased electrostatic potential**. In the **Bias potential** dropdown list select **1.0 V**.

Click **Import** to import the field.

The potential field is best viewed as a slice through the device.

On the **Volume visualization** tool bar click the **Create slice** button:

Choose **Parallel to A & B axis**, and select **DMol3 electrostatic potential Ha*electron(-1)(1.0000 V)**.

The potential is given in atomic units and will have large values close to the atoms. To view the potential drop over the device the range of the color map needs to be changed.

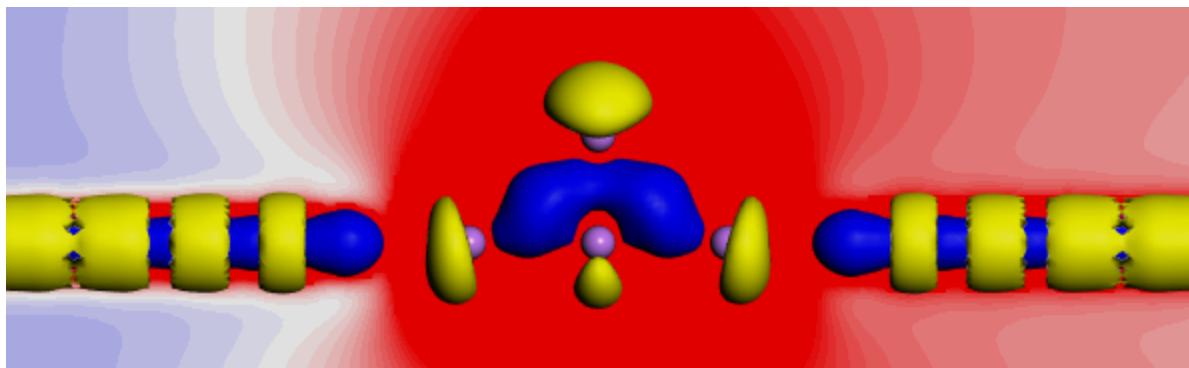
On the **Volume visualization** tool bar click the **Color maps** button:

Set **From** to **-0.05** and **To** to **0.05**. Change the **Spectrum** to **Blue-White-Red**.

The range of the field for both charge density and electrostatic potential are set to the range of the defined device. The range can be expanded to include the extended sections of the device created during the DMol calculation.

In the **HChainLi4.xsd** document open the Display Style dialog, and on the **Field** tab set the **Display range** for **A** to **0.25** and **0.75**.

The **HChainLi4.xsd** document now shows a potential slice through the center of the device. Notice how the potential drops over the Li island section of the device.



This is the end of the tutorial.

Transition-state searching using LST/QST tools

Purpose: Introduces the use of DMol³ and the Reaction Preview tool to perform a transition-state search calculation. The transition state of a simple reaction is calculated and validated.

Modules: Materials Visualizer, DMol³

Time:  

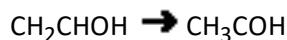
Prerequisites: [Geometry optimization for solids using delocalized internal coordinates in DMol³](#)

Background

Exploring the potential energy surface of any reaction requires both structural and energetic, or kinetic and thermodynamic, snapshots of each step in the reaction process. Of particular importance is the rate determining step, which usually involves finding the elusive transition-state structure. A few techniques have been well validated for finding a transition-state structure and among the better known of these are linear synchronous transit (LST) and quadratic synchronous transit (QST) which works well for simple reactions. For complex reaction pathways, use the *Minimum Energy Path* task in DMol³, which is covered in a [separate tutorial](#).

Introduction

This tutorial aims to introduce to you the LST/QST tool in DMol³. In this tutorial, you will learn how to use the LST/QST tool to find a transition-state structure for a hydrogen transfer reaction from vinyl alcohol to acetaldehyde.



This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculation](#)
- [To define the atom pairing](#)
- [To calculate the transition state using the LST/QST/CG method](#)
- [To refine the transition state](#)

Note: Completion of this tutorial entails running a DMol³ transition-state search. Depending on the configuration of your compute server, this calculation could take a considerable amount of time.

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **vinylOH** as the project name, click the **OK** button.

The new project is created with *vinylOH* listed in the Project Explorer.

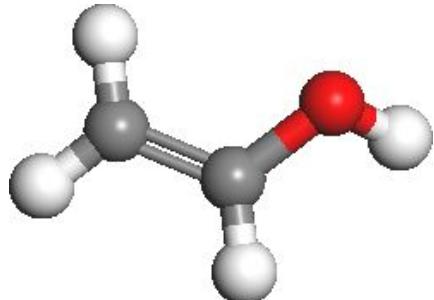
2. To prepare the structures for the calculation

In this section of the tutorial, you will build the reactants and products in two different 3D Atomistic documents. The first step is to open a new 3D Atomistic document and sketch the reactant, vinyl alcohol.

Click the **New** button  on the **Standard** toolbar and select **3D Atomistic Document** from the dropdown list.

Use the **Sketch** tools to draw a vinyl alcohol molecule. Click the **Adjust Hydrogen** button  and then the **Clean** button .

Move the structure so it looks similar to the one shown below (shown in ball and stick display style).



Rename the new document **reactant.xsd**.

Choose the **Selection** tool  on the **3D Viewer** toolbar. Double-click on any of the atoms in the vinyl alcohol structure to select all of the atoms.

Now all the vinyl alcohol atoms are selected and colored yellow.

Press **CTRL + C**.

This copies the contents of the document to the clipboard.

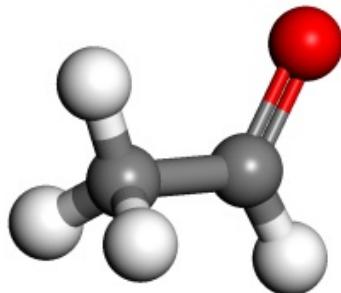
Use the **New** button to create a new 3D Atomistic document. Press **CTRL + V**.

The structure is pasted into the new 3D Atomistic document. Now you have to change the bonding and rearrange the atoms to obtain the product structure.

In the new 3D Atomistic document, select the **O-H** bond and press **DELETE**. Click the **Sketch Atom** button, then click the lone **H** atom followed by the terminal **C** atom.

Click once on the **C-O** bond to change the bond type from single to double. Click twice in succession on the **C-C** bond to toggle the bond type from double to triple to single. Click the **Clean** button.

The structure should look similar to the one shown below.



Before continuing, you need to change the name of the document.

Rename the document **product.xsd.**

3. To define the atom pairing

For DMol³ to perform a transition-state search, all the atoms in the reactant and product documents need to be paired. This is performed using the Reaction Preview functionality on the *Tools* menu.

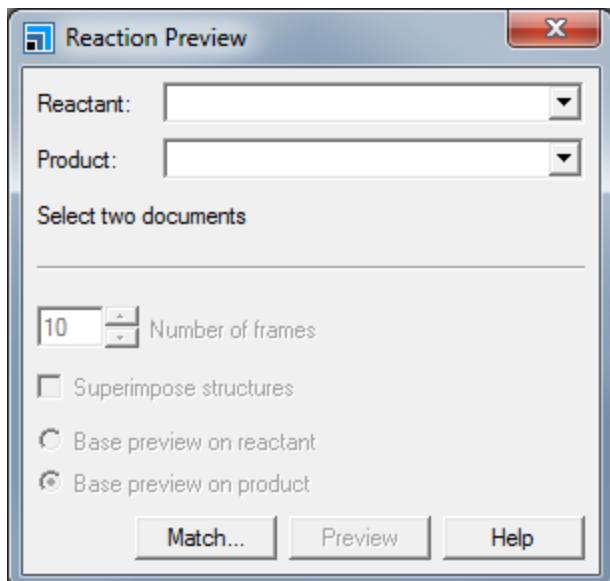
First, you should display the reactant and product structures side-by-side.

Select **Window | Tile Vertically from the menu bar.**

Now you are ready to start pairing atoms in the reactant and product structures.

Select **Tools | Reaction Preview from the menu bar.**

This opens the Reaction Preview dialog.



Reaction Preview dialog

Select the **reactant.xsd and **product.xsd** documents from the **Reactant** and **Product** dropdown tree views. Click the **Match...** button to open the Find Equivalent Atoms dialog.**

You should see that one atom is matched and six atoms are unmatched.

Double-click on **2xC in the reactant column.**

The corresponding folder in the product column also opens. The reactant column should contain **1:C** and **2:C**. These should map directly onto their counterparts in the products window, but take the following steps to make sure.

Click on **1:C** in the reactant pane and **1:C** in the product pane.

The carbon atoms in both panes should be selected and these should be identical in the two 3D Atomistic documents.

If they represent equivalent atoms, click the **Auto Find** button.

The Find Equivalent Atoms algorithm matches all of the remaining heavy atoms.

Tip: If some unmatched atoms remain, repeat the manual pairing step above on the next unmatched atom pair, but now click on *Set Match* instead. Repeat this procedure for the rest of the unmatched atom pairs or click on *Auto Find*.

You can review the matched atoms list between reactant and product.

Click on one of the atoms in the list in either the reactant or product column to review the proper pairing until you are satisfied with the matches.

Click anywhere in each 3D Atomistic document to deselect everything and **close** the Find Equivalent Atoms dialog.

To perform a transition-state search with the DMol³ LST/QST functionality, you need to create a pathway between the reactant and product as it is required as input to the DMol³ calculation.

Click on the project root in the Project Explorer. On the Reaction Preview dialog, increase the **Number of frames** to **100** and check the **Superimpose structures** checkbox. Click the **Preview** button and close the dialog.

Within a few seconds, a new 3D Atomistic Trajectory document entitled **reactant-product.xtd** is displayed. You will run the DMol³ calculation on this file. You can animate the trajectory document using the tools on the *Animation* toolbar. The animation looks best in *Bounce* mode. You can switch on bond monitoring so that it recalculates the bonds after each step.

Select **Build | Bonds** from the menu bar to open the Bond Calculation dialog. Check the **Monitor bonding** checkbox and close the dialog.

Click the **Play** button .

When you have finished watching the animation, click the **Stop** button.

4. To calculate the transition state using the LST/QST/CG method

Note: The **reactant_product.xtd** file contains important information needed by DMol³ where the first frame is reactant and the last frame is product.

You are now ready to set up the DMol³ calculation to calculate the transition state.

DMol3: Transition-state searching using LST/QST tools

Open the **DMol3 Calculation** dialog, on the **Setup** tab change the **Task** to **TS Search**. Make sure that the **Quality** is set to **Medium** and set the **Functional** to **GGA** and **BP**.

Click the **More...** button to display the DMol3 Transition State Search dialog. Make sure the **Search protocol** is set to **Complete LST/QST** and set the **Quality** to **Medium**. Check the **Optimize reactants and products** checkbox and close the dialog.

You have just specified the Hamiltonian to be used and the quality level of the calculation. The quality determines both the basis set used - in this case, it is DND - and the orbital cutoff. You can check these parameters by clicking on the *Electronic* tab. Now you need to optimize the convergence behavior by applying some thermal smearing.

On the **Electronic** tab, ensure that **Medium** is selected from the **SCF Tolerance** dropdown list. Click the **More...** button to open the DMol3 Electronic Options dialog. On the **SCF** tab, check the **Use smearing** checkbox and close the dialog.

The electronic Hamiltonian settings are the same as for the geometry optimization calculation. This time you need to calculate the *Frequency* property.

On the **Properties** tab of the DMol3 Calculation dialog, check the **Frequency** checkbox.

Finally, you should set the *Job Description*.

On the **Job Control** tab uncheck the **Automatic** checkbox. Type in **TS** as the **Job description**.

You are now ready to run the calculation.

Click the **Run** button and close the dialog.

Note: During the calculation, several different documents and a LST/QST graph are displayed in the workspace. These report the status of the calculation. In particular, an LST/QST graph monitors the progress of the TS search by showing a plot of energy vs. path coordinate for LST, QST, and CG (conjugate gradient).

After job completion, you can view text results in the **TS.outmol** file.

If the document is not automatically displayed, double-click on **TS.outmol** in the Project Explorer. Press **CTRL + F** and search for **Energy of barrier**.

The energy of reaction is about $-14 \text{ kcal mol}^{-1}$ and the energy barrier should be around 52 kcal mol^{-1} . Also note down the energy of the transition state, which we will use in the next section.

At a transition state one imaginary frequency appears in the IR spectrum. This frequency corresponds to the reaction mode, which can be animated.

You can view the transition state by opening the document **TS.xsd**.

If the document is not displayed automatically, double-click on **TS.xsd** in the Project Explorer.

A 3D Viewer opens displaying the structure of the transition state for this reaction obtained using the BP/DND level of theory.

Select **Tools | Vibrational Analysis** from the menu bar to display the Vibrational Analysis dialog and click the **Calculate** button.

The calculated normal modes appear in the grid on the dialog. There is one imaginary frequency at about -2000 cm^{-1} .

Select the imaginary frequency and click the **Animation** button. When the trajectory animation begins, click the **Stop** button. Select **Build | Bonds** from the menu bar to open the Bond Calculation dialog. Check the **Monitor bonding** checkbox and close the dialog. Click the **Play** button.

A new window is opened and the corresponding reaction mode is animated with the bonds recalculated for each frame.

Stop the animation and close the Vibrational Analysis dialog.

The **TS Search** task also generates a collection document containing the reactant, transition state, and products. You can look at the energies of the reactant, transition state, and products by labeling by their total energy.

Change focus to **TS.xod**. Right-click and select **Label** from the shortcut menu, click the **Remove All** button. Change the **Object type** to **Energy**, select **TotalEnergy** and click the **Apply** button. Close the Label dialog.

Tip: The displacements of the reactant, transition state, and product in the Y-axis indicate their relative energy differences.

Note: You can also animate the vibrational modes directly from the collection document.

5. To refine the transition state

Now the transition state found in the previous section will be refined.

Select **File | Save Project** then **Window | Close All** from the menu bar. Double-click on **TS.xsd** in the Project Explorer.

Open the **DMol3 Calculation** dialog and change the **Task** to **TS Optimization**. Leave everything else unchanged and click the **Run** button.

Note: This calculation will only start if you have selected an appropriate normal mode on the **Tools | Vibrational Analysis** dialog, as in the [previous section](#). This mode will be followed during the transition state optimization.

The transition-state optimization is now launched.

The calculation finishes after a short time since you were already very close to the fully optimized transition state. Examine the **.outmol** file of the TS optimization and search for the total final energy.

Search the **.outmol** file for the line beginning with **Geometry optimization completed successfully**. Write down the total energy, which is reported 13 lines earlier.

Compare the total energy with the energy of transition state of the LST/QST/CG optimization. Using the conversion factor $1\text{ Hartree} = 627.51\text{ kcal mol}^{-1}$, you will find that the energies differ by only about 0.6 kcal mol^{-1} , the optimized energy barrier therefore is about 53 kcal mol^{-1} .

Note: The actual energies obtained in your calculations may deviate by few kcal mol⁻¹ from the numbers quoted above and vibrational frequencies can be different by few tens of cm⁻¹. In order to obtain more accurate and better reproducible results you should set the **Quality** to **Fine** and investigate the convergence of the results with respect to the calculation parameters.

Finally you can animate the reaction mode corresponding to the imaginary frequency again as described in [section 4](#).

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Calculating barriers of simple chemical reactions using DMol³'s LST/QST and NEB tools

Purpose: Introduces minimum energy path calculations using DMol³ in Materials Studio.

Modules: Materials Visualizer, DMol³

Time: 

Prerequisites: [Transition-state searching using LST/QST tools](#)

Background

The calculation of a reaction path is an important part of studying reactivity. The simplest way to calculate a reaction path is to start at a saddle point and take successive steps in the direction of the negative gradient. This steepest descent approach leads to a minimum energy path (MEP). If the coordinate system is mass-weighted, this is called an intrinsic reaction coordinate (IRC).

The MEP (or IRC path) might be quite complicated and can have several minima. The highest saddle point is of most interest, as the overall reaction rate depends on the height of this reaction barrier. Following the reaction path can reveal intermediate structures and can connect the reaction barrier to the correct reactant and product.

DMol³ uses the nudged elastic band (NEB) method to determine whether transition states link directly to predefined minima. The NEB method introduces a fictitious spring force that connects neighboring points on the path. This ensures continuity of the path and projection of the force so that the system converges to the MEP. Researchers have used the NEB method widely in solid-state physics and applied it to molecules as well. The advantage of the NEB algorithm is that it provides a fast qualitative examination of the MEP.

Tip: For a fully connected implementation of a nudged elastic band that includes transition state searches and verification, use the *Minimum Energy Path* task in DMol³ as described in [this tutorial](#).

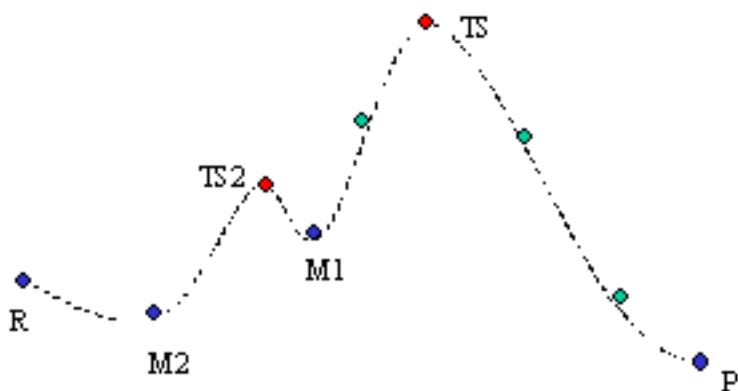


Figure 1

DMol3: Exploring the minimum energy path of chemical reactions using DMol3's LST/QST and NEB tools

Consider the complex reaction pathway in [Figure 1](#). An LST/QST transition state (TS) search algorithm takes the two endpoints R and P as input and locates one of the local maxima on the reaction coordinate. Assume that in this example it locates the highest energy barrier, TS.

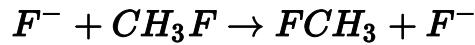
The *TS Confirmation* algorithm takes these three points as input and return a trajectory that contains at least one point in the vicinity of the new minima; in this case, M1 or M2. [Figure 1](#) shows these points as blue (minima) and red (maxima). In general, the path also contains a few points that do not correspond to stationary points (green).

Note: A conventional NEB is intended to start from two end points and yield the TS and the entire reaction pathway, giving a lot of green points. In contrast, the algorithm implemented in DMol³ is intended to start at the TS and to locate the alternative minima in the direction of reactants and products. It only attempts to answer the question "Does this TS really connect the presumed reactant with the presumed product, or are there alternative minima on the reaction path?".

The optimization consists of two phases, termed 'macroiteration' and 'microiteration'. DMol³ assumes that springs hold the points loosely in place. Macroiterations consist of an optimization over all the images; microiterations consist of the optimization of the molecule or crystal in a direction orthogonal to the reaction pathway. The calculation completes when both the macroiterations and microiterations converge.

Introduction

This tutorial aims to introduce to you to the NEB tool in DMol³. You can use DMol³'s LST/QST to find a transition-state structure for a simple symmetrical S_N2 reaction; fluorine exchange on methyl fluoride:



Then, you use the *TS Confirmation* tool to map the energy path between reactants, intermediates, and products.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures for the calculation](#)
- [To prepare the input trajectory document for the transition-state calculation](#)
- [To calculate the transition state using LST/QST](#)
- [To perform an NEB calculation using TS Confirmation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **LSTQST** as the project name, click the **OK** button.

The new project is created with **LSTQST** listed in the Project Explorer.

2. To prepare the structures for the calculation

In this section of the tutorial, sketch the reactants and products in two different 3D Atomistic documents. The first step is to open a new 3D Atomistic document and sketch the reactant, a fluoride ion, at a defined distance from a methyl fluoride molecule.

Click **New**  on the **Standard** toolbar to open the New Document dialog. Choose **3D Atomistic** and click **OK**.

Sketch a single carbon atom and click **Adjust Hydrogen** . Change one of the hydrogen atoms to a fluorine.

Click **Clean** .

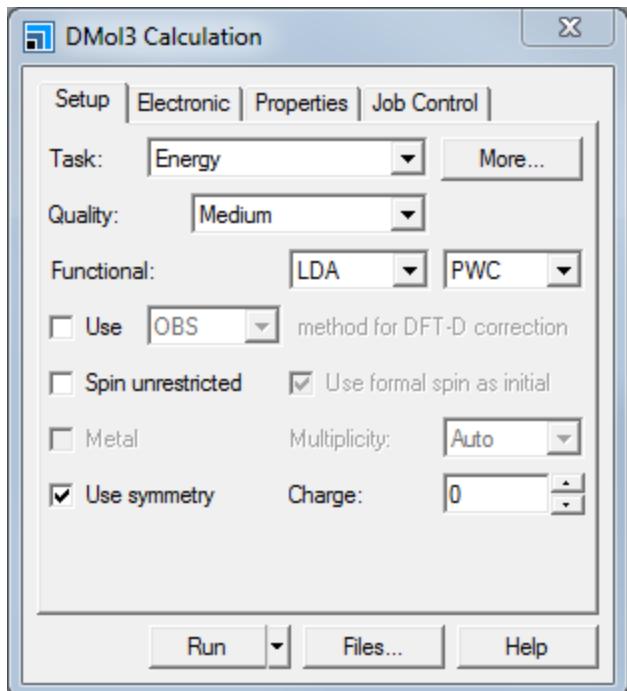
The selected hydrogen atom changes to fluorine and the geometry of the structure has a reasonable initial configuration.

Rename the new document **methylfluoride.xsd**.

Before you continue preparing the structures, perform a rough geometry optimization of this molecule.

Click **DMol3**  on the **Modules** toolbar and choose **Calculation**, or select **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.



DMol3 Calculation dialog, Setup tab

Perform an optimization with relatively coarse parameter values. To achieve more accurate results, increase the size of the basis set.

On the **Setup** tab, change the **Task** from **Energy** to **Geometry Optimization** and the **Quality** from **Medium** to **Coarse**. Leave the **Functional** at the defaults of **LDA** and **PWC**. Click **Run** and close the dialog.

DMol3: Exploring the minimum energy path of chemical reactions using DMol3's LST/QST and NEB tools

The calculation takes about 15 seconds to complete, depending on the speed of the processor in your computer server.

The progress of the calculation updates in the form of chart and text documents. When the calculation completes, the final optimized structure saves in the document `methylfluoride.xsd` in a new folder called `methylfluoride DMol3 GeomOpt`. The text output of the computation saves in the `methylfluoride.outmol` file. The results folder also contains the `methylfluoride.xtd`, a 3D Atomistic Trajectory document containing the progress of the minimization.

Now, finish defining the inputs for the LST/QST calculation.

In the Project Explorer, select **methylfluoride DMol3 GeomOpt/methylfluoride.xsd** and right-click, then select **Copy** from the shortcut menu.

In the Project Explorer, right-click the project name and choose **Paste** from the shortcut menu.

You have made a copy of the optimized methyl fluoride molecule. Before continuing to sketch, rename the document.

Rename the **methylfluoride (2) .xsd** document to **SN2reactant.xsd** and open **SN2reactant.xsd**.

You need to add a second fluorine atom at a defined distance from the carbon atom.

Click the **Sketch Atom** arrow  and choose **Periodic Table...** from the list to open the Periodic Table dialog.

Select **F** and click **OK**. Click the **carbon** atom of the methyl fluoride and sketch a new carbon-fluorine bond opposite to the other C-F bond. Press **ESC** to stop sketching.

Now, use the *Measure/Change* tool to position the fluorine atom so that it is approximately 3 Å from the carbon atom.

Click the **Measure/Change** arrow  and select **Distance** from the list. Select the newly created C-F bond, hold down the left mouse button, and drag the mouse until the distance increases to approximately 3 Å.

The final step is to delete the new C-F bond.

Click **3D Viewer Selection Mode** . Hold down **CTRL** and click the **distance monitor** and then the elongated C-F bond to select them. Press **DELETE**

Now create the product from the reactant structure.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**. In the Project Explorer, select **SN2reactant.xsd** and right-click. Select **Copy** from the shortcut menu.

In the Project Explorer, right-click the project name and choose **Paste** from the shortcut menu.

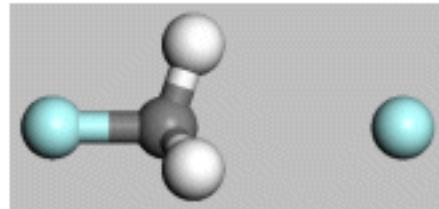
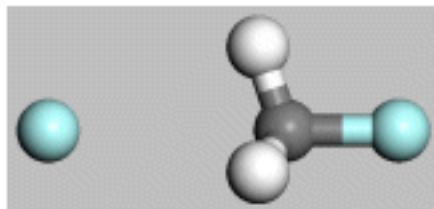
Rename the **SN2reactant (2) .xsd** document to **SN2product**.

Open the documents **SN2reactant.xsd** and **SN2product**, then select **Window | Tile Horizontally** from the menu bar. Rotate the structures so that in one 3D Viewer, the non-bonded fluorine atom is on the right, and in the other, it is on the left.

Tip: You can use the left and right arrow keys to rotate the structures about the y-axis in increments of 45 degrees.

Right-click in either of the 3D Viewers and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Atom** tab, choose the **Ball and stick** option. Click in the other 3D Viewer and choose **Ball and stick** again. Close the dialog.

Your two model documents look similar to those shown below.



The **SN2reactant.xsd** and **SN2product.xsd** structures displayed in ball and stick style

You have prepared the structures that you need and you are ready to create the input 3D Atomistic Trajectory document for the LST/QST calculation.

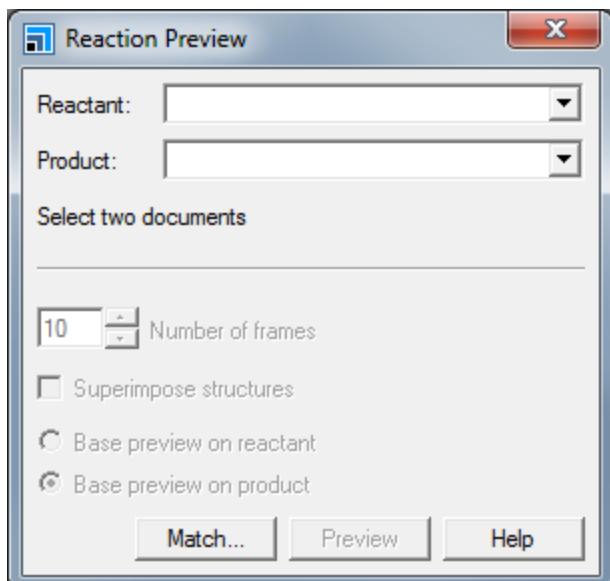
3. To prepare the input trajectory document for the transition-state calculation

For DMol³ to perform an LST/QST calculation, you must pair all the atoms in the reactant and product documents and create a trajectory document. You can do this using the Reaction Preview tool.

From the menu bar, select **Tools | Reaction Preview**.

This opens the Reaction Preview dialog.

DMol3: Exploring the minimum energy path of chemical reactions using DMol3's LST/QST and NEB tools



Reaction Preview dialog

Select **SN2reactant.xsd** and **SN2product.xsd** as the **Reactant** and **Product**, respectively. Click **Match....**

This opens the Find Equivalent Atoms dialog, showing that one atom has a match and 5 atoms do not have matches.

Expand the **2xF** folder in the reactant column.

The corresponding folder in the product column also opens. The reactant column contains **5:F** and **6:F**. For the LST/QST calculation, these must map directly onto their counterparts in the product column.

Note: Depending on how you sketched the original structure, you could have either **5:F** or **4:F**. These are interchangeable throughout the rest of this tutorial.

With both 3D Atomistic documents in view, click **5:F** in the reactant column, then click **5:F** in the product column.

This selects the corresponding atoms in both 3D Viewers and you can see that they are not equivalent in the two documents.

Click **6:F** in the product column.

This is the equivalent atom to **5:F** in the reactant column, so you can now match these atoms.

Click **Set Match**.

The atoms move into the **matched atoms** folder.

Repeat this procedure for the rest of the unmatched atom pairs.

You can review the matched atoms list between reactant and product.

Expand the **6 matched atoms** node in the reactant column. Click one of the atoms on the list in either the reactant or product column to review the pairing. Close the Find Equivalent Atoms dialog when you are satisfied.

To perform an LST/QST calculation, you need to create a trajectory path between the reactant and product as the input to the DMol³ calculation.

On the **Reaction Preview** dialog, increase the **Number of frames** to **25**. Check the **Superimpose structures** checkbox. Click **Preview** and close the dialog.

A new 3D Atomistic Trajectory document called **SN2reactant-SN2product.xtd** displays. You run the DMol³ calculation on this document. You can animate the 3D Atomistic Trajectory document using the tools on the *Animation* toolbar. If this is not visible, you can open it from the *View* menu.

Tip: The animation looks best when viewed in *Bounce* mode.

From the menu bar, select **Build | Bonds** to open the Bond Calculation dialog. On the **Bonding Scheme** tab, check the **Monitor bonding** checkbox and close the dialog.

If the **Animation** toolbar is not visible, select **View | Toolbars | Animation** from the menu bar.

Click the **Animation Mode** arrow  and choose **Bounce**. Click **Play** .

When you have finished watching the animation, click **Stop** .

4. To calculate the transition state using LST/QST

You are now ready to prepare the DMol³ LST/QST calculation.

Open the **DMol3 Calculation** dialog, on the **Setup** tab, change the **Task** from **Geometry Optimization** to **TS Search**. For the **Functional**, select **LDA** and **PWC**.

With the LST/QST tool, you can quickly and reliably locate the transition states of a chemical reaction. This tutorial aims to demonstrate the power of the NEB method for confirming a transition state or finding additional minima on the MEP. Therefore, use a rough parameter set for the LST/QST calculation. Specifically, you are using LDA functionals. Due to their inherent tendency toward overbinding, LDA functionals tend to seriously underestimate reaction barriers. Sometimes, DMol³ even finds a minimum where you might expect a transition state. Therefore, for a rigorous transition-state search, you would use bigger basis sets and gradient-corrected functionals. Refer to the DMol³ tutorial [Transition-state searching using LST/QST tools](#) for an overview of how to perform a more accurate reaction barrier calculation.

On the **Setup** tab of the DMol3 Calculation dialog, change the **Charge** to **-1**. On the **Electronic** tab, select **DN** as the **Basis set**.

Click **More...** to display the DMol3 Electronic Options dialog. On the **SCF** tab, check the **Use smearing** checkbox. On the **Orbital Cutoff** tab, select **Custom**. For the **Global orbital cutoff**, specify **5.0 Å**. Click **Assign** and close the dialog.

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This procedure increased the finite range cutoff of the atomic basis set. DMol³ takes the atomic orbitals as zero beyond this distance from their atomic center. Decreasing the cutoff reduces the computation time required for a calculation, but introduces some approximations. Increasing the cutoff distance results in a more accurate calculation. In this case, longer range cutoffs improve the relatively weak interactions between the carbon and fluorine at the transition state.

During the LST/QST search, you might create structures for which the self-consistent field (SCF) cycle of a DMol³ energy calculation may prove difficult to converge. By using the smearing option, you are allowing for fractional orbital occupancy, which improves the SCF convergence behavior.

On the **Properties** tab of the DMol3 Calculation dialog, select the **Frequency** checkbox.

This performs a vibrational analysis after the LST/QST calculation has finished.

You are now ready to run the calculation.

Click **Run** and close the dialog.

Wait until the calculation completes.

Note: During the calculation, several different documents display, including an LST/QST chart. These report the status of the calculation. In particular, the LST/QST chart monitors the progress of the *TS Search* by showing a plot of Energy vs. Path Coordinate for LST, QST, and CG (conjugate gradient).

Select **SN2reactant-SN2product TSSearch.xcd**.

By inspecting the energy plot, you can see that the Conjugate Gradient (CG) Search has located a minimum. Although it is marked as a transition state, the structure is lower in energy than the reactants and products. Now, find out whether this is really a transition state. At a transition state, one imaginary frequency appears in the IR spectrum. This frequency corresponds to the reaction mode and you can animate it.

Double-click **SN2reactant-SN2product.xsd** in the **SN2reactant-SN2product DMol3 TSSearch** folder in the Project Explorer. From the menu bar, select **Tools | Vibrational Analysis** to open the Vibrational Analysis dialog. On the **Analysis** tab, click **Calculate**.

The calculated normal modes appear in the table. There is one imaginary frequency at about -330 cm⁻¹.

Select the imaginary frequency and click **Animation**. Close the dialog.

A new window opens and the corresponding reaction mode animates. It is possible that there are other minima on the minimum energy path that the LST/QST search missed. You now attempt to locate these minima using the *TS Confirmation* tool.

From the menu bar, click **Stop**  . Select **File | Save Project**, followed by **Window | Close All**.

5. To perform an NEB calculation using TS Confirmation

The **SN2reactant-SN2product.xtd** trajectory document contains all the structures generated during the transition-state search. You can use this as the input to the NEB calculation.

Make **SN2reactant-SN2product.xtd** the active document.

You are now ready to prepare the NEB calculation.

Open the **DMol3 Calculation** dialog. On the **Setup** tab, change the **Task** to **TS Confirmation**. Click **More...** to open the DMol3 TS Confirmation dialog.

You can specify several convergence criteria for the *TS Confirmation* calculation here.

From the **Quality** list, select **Coarse** and close the dialog.

This speeds up the calculation by calculating only 6 images.

On the **Properties** tab of the DMol3 Calculation dialog, clear the **Frequency** checkbox. Click **Run** and close the dialog.

During the calculation, several different documents and a transition state confirmation chart display. These report the status of the calculation. In particular, the **SN2reactant-SN2product TSConfirmation.xcd** chart monitors the progress of the calculation by showing a plot of Energy vs. MEP Path and highlighting possible stationary points on this path.

Wait until the calculation is complete before continuing.

In the **SN2reactant-SN2product DMol3 TSConf** folder, double-click **SN2reactant-SN2product TSConfirmation.xcd**.

The *TS Confirmation* has found two new minima (marked by asterisks in the graph) that are lower in energy than the transition state found in the *TS Search*. Now review these minimum energy structures.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

Certain chart documents dynamically link to the associated trajectory documents. This allows you to use the *Chart Viewer* tools to pick a point on the chart and display the appropriate frame in the trajectory document.

In the Project Explorer, double-click **SN2reactant-SN2product.xtd** and then on **SN2reactant-SN2product TSConfirmation.xcd**. From the menu bar, select **Window | Tile Vertically**.

Click **Chart Viewer Selection Mode**  and click the minimum points in the chart.

The structure in the 3D Viewer updates accordingly. The two minima correspond to the M1 and M2 points on the reaction pathway, see [Figure 1](#). In fact, the starting geometries with a fluorine atom 3 Å from the carbon is not the lowest energy structure. Instead a state exists with the fluorine loosely bound to the CH₃F.

The transition state connects these loosely bound structures. Ideally, they would be symmetric and exactly equal in energy. Due to the limited accuracy of the parameters used in the calculation, your results are not symmetric. You could try to produce a symmetric curve using Medium or Fine settings in DMol³.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

This is the end of the tutorial.

Effective Screening Medium (ESM) Calculations in DMol³

Purpose: Introduces the use of the Effective Screening Medium in DMol³, to model structures under a given electric potential bias with periodic boundaries.

Modules: Materials Visualizer, DMol³

Time:



Prerequisites: Sketching simple molecules, Opening and Viewing 3D Atomistic Documents

Introduction

Dual-carbon batteries (DCBs) attract great interest as part of the concerted effort to develop energy storage technologies, thanks to their sustainability. The use of carbon as the active material of DCBs presents several challenges involving capacity and stability. We need a method that can perform first principle calculations on model systems under potential bias, to allow quantification of the behavior of DCBs under realistic conditions.

The Effective Screening Medium, ESM (Otani, 2006), approach applies a periodic boundary condition for the electrostatic solution along the surface normal direction (z-direction) of a slab model. This avoids the need for a large vacuum region in the z direction. The ability to add a metallic medium to the model allows calculations with charged slab systems simulating gate effects, as well as biased systems.

The tutorial is based on the paper of Yilmaz et al. (2023), which applies the ESM method to investigate the effect of bias on the interface between graphene and a hexafluorophosphate ion.

This tutorial covers:

- [Getting started](#)
- [To prepare the molecular structures for the calculation](#)
- [To optimize the geometry under applied bias and without bias](#)
- [To control the job settings and run the job](#)
- [To charge the system](#)
- [To analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

If Materials Studio is not already open, double-click on the **Materials Studio** icon  on your desktop to start the program or, alternatively, select **BIOVIA | Materials Studio 2025** from the list of programs on the Windows **Start** menu.

Open the New Project dialog, enter **ESM** as the name, and click the **OK** button.

The new project is created with **ESM** listed in the Project Explorer.

2. To prepare the molecular structures for the calculation

The first step is to import the graphite structure so that you can create the host system that represents the anode.

Materials Studio includes a structure library that contains many different types of structures from ceramic materials to organic compounds. This tutorial helps you to perform calculations on graphite.

Click **Import**  on the **Standard** toolbar.

This opens the Import Document dialog.

Navigate to **Structures\ceramics** and select the file **graphite.xsd**. Click **Open**.

To convert the graphite structure into graphene, you need to remove one of the layers and increase the lattice constant perpendicular to the graphene layer.

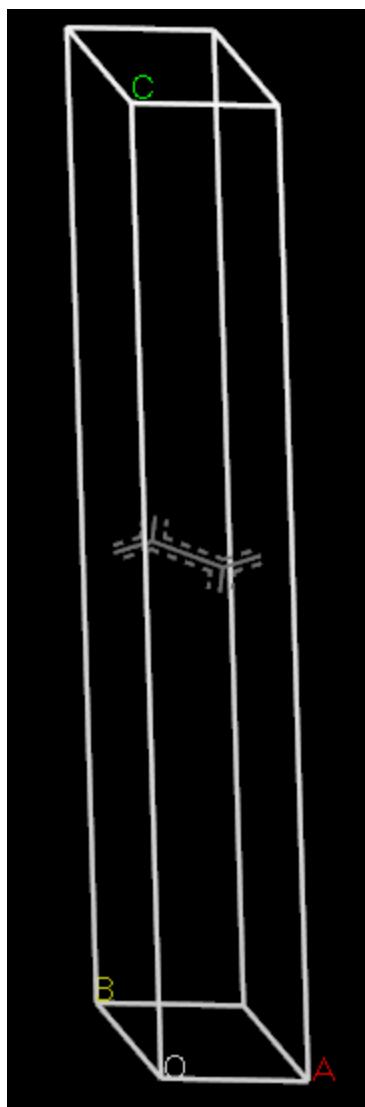
From the menu bar, select **Build | Symmetry | Make P1**.

Rotate the cell so that you can see the vertical layers. Select and delete the top layer of atoms in the graphite cell.

From the menu bar, select **Build | Symmetry | Find Symmetry....** On the Find Symmetry dialog, click **Find Symmetry**, and then **Impose Symmetry**.

Right-click the document and select **Lattice Parameters**. Change the value of **c** to **20 Å**.

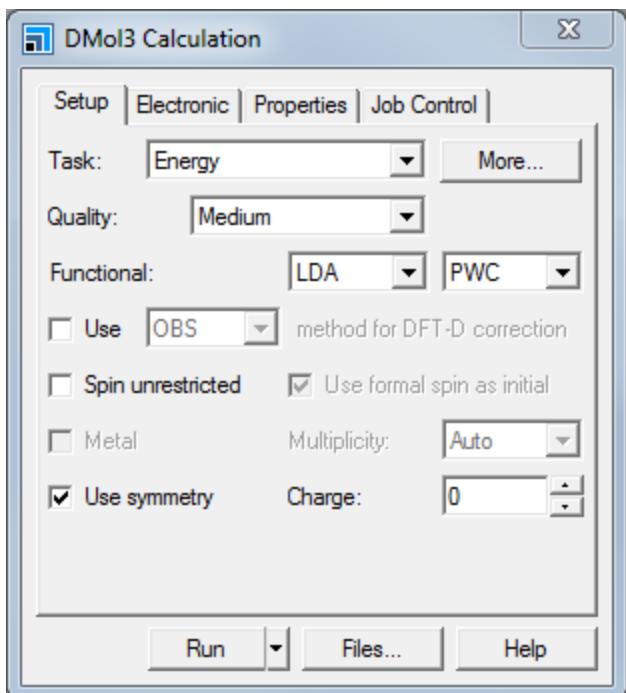
Rename the document **graphene.xsd**.



Before manipulating the structure any further, optimize the geometry of the cell.

Click **DMol3**  on the **Modules** toolbar and select **Calculation** or choose **Modules | DMol3 | Calculation** from the menu bar.

This opens the DMol3 Calculation dialog.



DMol3 Calculation dialog, Setup tab

Set the **Task** to **Geometry Optimization**. Change the **Quality** to **Fine**, the **Functional** to **GGA, PBE**, and select **Metal**.

Click **More...** to open the DMol3 Geometry Optimization dialog. Check **Optimize cell** and close the dialog.

Click **Run** on the DMol3 Calculation dialog.

This optimizes the graphene structure, including the lattice parameters. Once the job finishes, you can use the optimized structure to create the graphene super cell.

The current implementation of ESM requires orthorhombic cells, so you need to redefine the lattice to change the γ angle from 120° to 90° .

Make sure that **graphene DMol3 GeomOpt\graphene.xsd** is the active document.

From the menu bar, select **Build | Symmetry | Redefine Lattice** to open the Redefine Lattice dialog.

Define **A** as **1 1 0**, **B** as **-1 1 0**, and **C** as **0 0 1**, and click **Redefine**.

This changes the γ value from 120° to 90° .

Right-click the document and select **Lattice Parameters**. Change the value of **c** to **20 Å**. On the **Advanced** tab, select **Orientation standard** as **C along Z, B in YZ plane**, and then click **Re-orient to standard**.

Press **CTRL + S** to save your changes.

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Now, you can create the super cells.

Copy and paste the **graphene DMol3 GeomOpt\graphene.xsd** document into the root of the Project folder and rename it **graphene (3x2).xsd**.

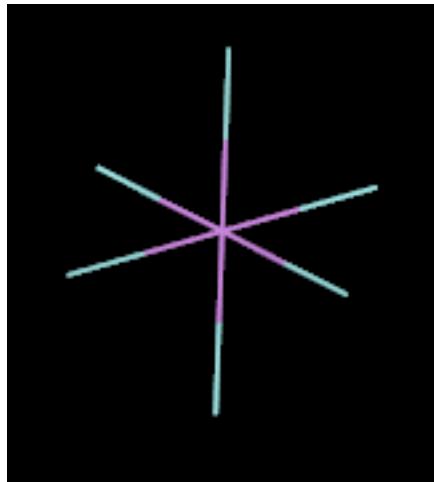
Open **graphene (3x2).xsd** and, from the menu bar, select **Build | Symmetry| Supercell**. Specify **A** as **3**, **B** as **2**, and **C** as **1**, and then click **Create Supercell**. Close the dialog.

Next, create the PF_6^- molecule to add to the graphene surface.

In a new **3D Atomistic Document**, sketch a molecule of **hexafluorophosphate**. In the toolbar, click **Clean** .

In the **Project Explorer**, rename the 3D Atomistic Document to **PF6.xsd**.

On the **DMol3 Calculation** dialog, select **Spin unrestricted**, and then click **Run** to optimize the PF_6^- geometry.



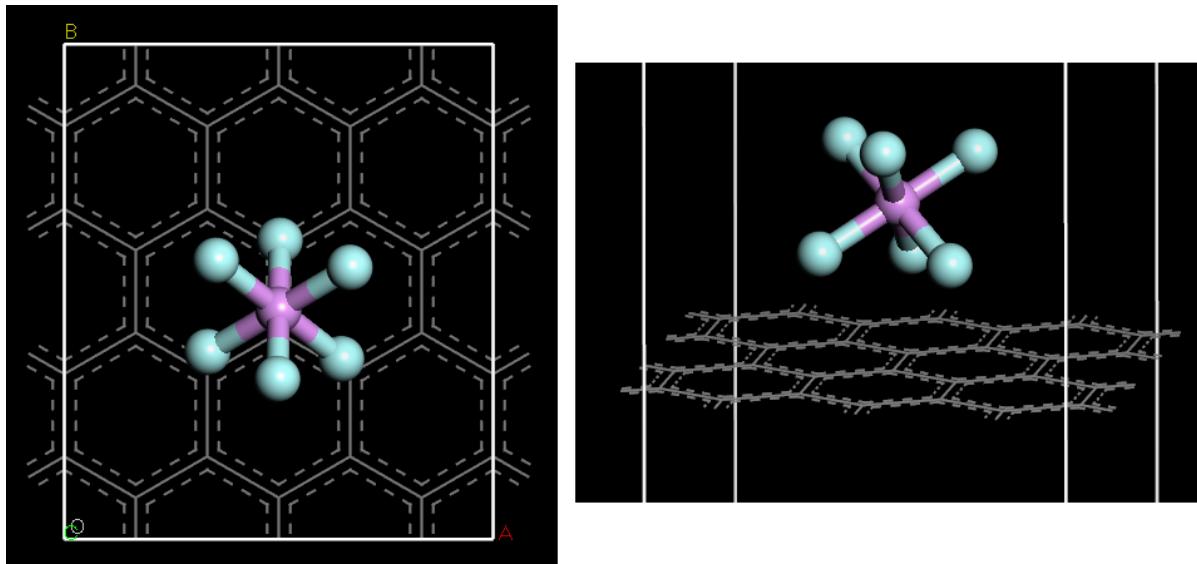
Finally, place the PF_6^- molecule on top of the Graphene layer.

Create a copy of the **graphene (3x2).xsd** document and name it **graphene (3x2)(PF6).xsd**.

Select the optimized version of the PF_6^- molecule in **PF6 DMol3 GeomOpt\PF6.xsd**, and then copy and paste it into **graphene (3x2)(PF6).xsd**.

Change the display style for the PF_6^- molecule only to **Ball and stick**.

Move and rotate the molecule until it is roughly positioned as in the figures below. Place the molecule on the top side of the graphene layer, facing the metal boundary, with the three lower fluorines placed directly above three carbon atoms. Ensure that the distance between the phosphorus atom and the graphene surface is about 3.5 Å.



3. To optimize the geometry under applied bias and without bias

Now you can run a geometry optimization on the complete system.

On the **DMol3 Calculation** dialog, click **More...** to open the DMol3 Geometry Optimization dialog.

Clear selection of **Optimize cell** and specify **Max. iterations** as **200**. Close the dialog.

Check and select **Use Grimme method for DFT-D** and clear selection of **Use symmetry**.

On the **DMol3 Calculation** dialog, select the **Electronic** tab.

This tab contains parameters associated with the electronic Hamiltonian. You can activate the Effective Screening Medium (ESM) model here.

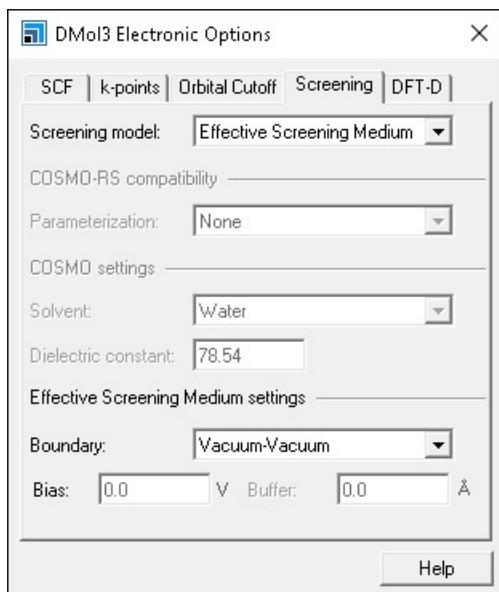
For the **Screening model**, choose **Effective Screening Medium**.

Next, specify the detailed settings for the screening model.

Click **More...** to open the DMol3 Electronic Options dialog. Select the **Screening** tab.

You need to choose which screening model to apply the Effective Screen Medium (ESM) model.

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The **Boundary** setting allows you to specify the boundary conditions to use for the calculations. DMol³ offers the following options:

- **Vacuum-Vacuum**
- **Metal-Vacuum**
- **Metal-Metal**

The choice of boundary condition depends on the nature of your problem. For more details about the ESM boundary conditions, see Effective Screening Medium in the DMol³ theory topics.

Here, you need to use the Metal-Vacuum boundary conditions.

Select **Metal-Vacuum** as the **Boundary** and close the DMol3 Electronic Options dialog.

Finally, request the properties that you want to analyze later.

Select the **Properties** tab on the **DMol3 Calculation** dialog.

Select **Electron density** and request the **Deformation density** information. Also select **Population analysis** and **Electrostatics** properties.

4. To control the job settings and run the job

You can now run the DMol³ geometry optimizations.

For the neutral structure **graphene (3x2)(PF6).xsd**, click **Run**.

After completing the geometry optimization calculation, the Project Explorer has a folder that contains the results for the neutral system **graphene (3x2)(PF6) DMol3 Geometry Optimization**. You can see that the system has shifted along the z-axis to center the structure around z=0. To ensure that the neutral system is centered the same way as the charged system, run a single energy calculation to recenter the neutral system.

From the **graphene (3x2)(PF6) DMol3 GeomOpt** results folder, open the optimized **graphene (3x2)(PF6).xsd** structure document.

On the **DMol3 Calculation** dialog, for the **Task** select **Energy**, and click **Run**.

Next, you need to introduce a fractional charge of 0.035e to each system to study how it behaves under bias. First, clean the Materials Studio workspace.

From the menu bar, select **File | Save Project** followed by **Window | Close All**.

5. To charge the system

By introducing a fractional charge to the system, you can simulate the effect of a gate bias that introduces charge to the system. However, instead of explicitly adding a bias you can introduce a charge; the system returns the gate bias required to induce that charge.

You can directly modify the charge in the DMol³ input file to specify the required charge.

From the **graphene (3x2)(PF6) DMol3 GeomOpt** results folder, open the optimized **graphene (3x2)(PF6).xsd** structure document.

On the DMol3 Calculation dialog, click **Files...** and click **Save Files**.

This creates a new folder containing input files for the DMol³ task.

Rename the folder **Charge(0.035e)**. Open the **.input** file and change the **Charge** to **-0.035**, then save the file.

On the **DMol3 Job Files** dialog, click **Run Files** to start the manually modified job.

Close the **DMol3 Calculation** dialog.

6. To analyze the results

To visualize the properties that you calculated, you need to analyze the output documents.

From the menu bar, select **File | Save Project** followed by **Window | Close All**. Open the neutral **graphene (3x2)(PF6) DMol3 GeomOpt\graphene (3x2)(PF6) DMol3 Energy\graphene (3x2)(PF6).xsd** document in the results folder.

From the **Modules** toolbar, select **DMol3** , and then select **Analysis**. Or, from the menu bar, choose **Modules | DMol3 | Analysis**.

This opens the DMol3 Analysis dialog. Start by investigating the Mulliken charges for the structures.

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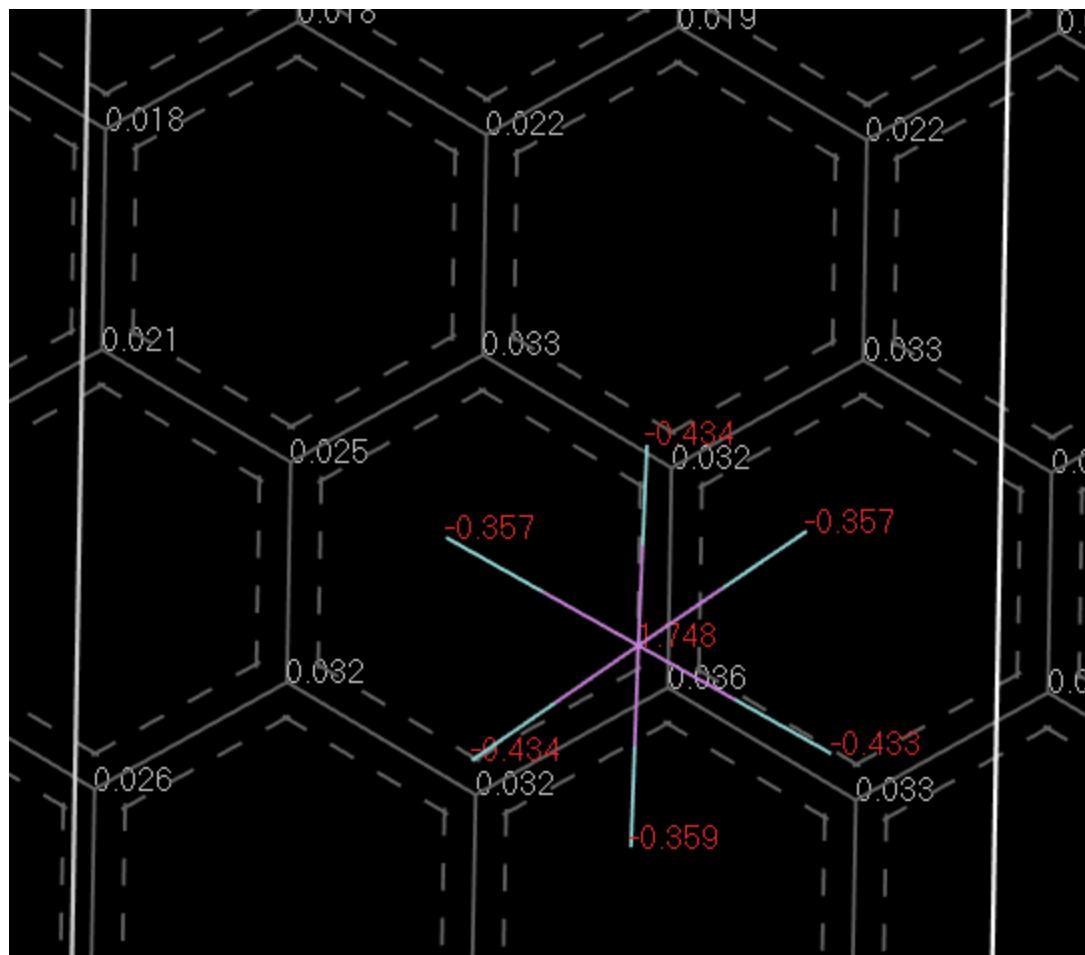
On the **DMol3 Analysis** dialog, select **Population analysis**, and then click **Assign Mulliken charges to structure**.

Right-click in the structure document and select **Label**. On the Label dialog, select **Charge** and click **Apply**.

Double-click any atom of the PF_6^- molecule, for the **Color** choose **red**, select **Charge**, and click **Apply**. Close the Label dialog.

Change the display style for PF_6^- molecule to **Line**. Zoom and rotate the structure so that you can examine the charges.

You can see that the graphene layer becomes positively charged, with the charge centering around the locations where the PF_6^- molecule docks to the surface. For example, away from the docked molecule, the C atoms of graphene have charges of about 0.02. Directly below the docked molecule, the C atoms have charges up to about 0.035.



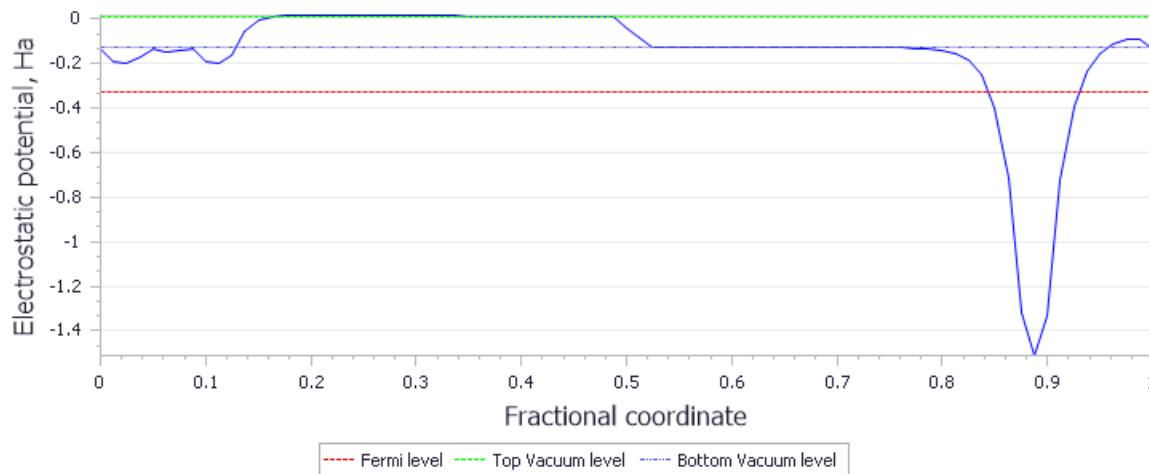
The accumulation of negative charges on the PF_6^- molecule and positive charges on the graphene surface generate a dipole effect that you can observe in the potential profile of the cell.

With the neutral **graphene (3x2)(PF6).xsd** document still in focus, on the **DMol3 Analysis** dialog, select **Potentials** and clear selection of **View isosurface on import**. Click **Import**.

When the potential analysis runs on the result from a job using the ESM method, it automatically generates a potential profile plot that averages the potential along slices of the cell.

Average potential profile along C axis

Work Functions: Top 0.338 Ha Bottom 0.202 Ha



You can see that the potential is zero on the right side of the structure, the metal side, and has a negative value on the left side, the vacuum side. Since the potential plot includes the potential around the atoms, it is hard to visually compare the neutral and charged systems. To compare the neutral and charged systems, subtract the potential for the neutral system from that of the charged system, so that you can visualize the change in potential.

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Create a new **Study Table** document in the project root.

In the neutral potential profile plot, **graphene (3x2)(PF6) DMol3 GeomOpt\graphene (3x2)(PF6) DMol3 Energy\graphene (3x2) (PF6) Potential Profile.xcd**, right-click, and select **Copy**. Then, paste into the top left empty cell in the study table.

Name the first column **Fractional Coordinate** and the second column **Neutral Potential (Ha)**.

Remove the remaining non-empty columns.

Create a potential profile plot for the charged **graphene (3x2)(PF6) DMol3 GeomOpt\Charge (0.035e)\graphene (3x2)(PF6) DMol3 Energy\graphene (3x2)(PF6).xsd** result structure.

Copy the potential information from the chart and paste it into the next empty column of the same study table. Name the column for the potentials of the charged system **Charged Potential (Ha)**.

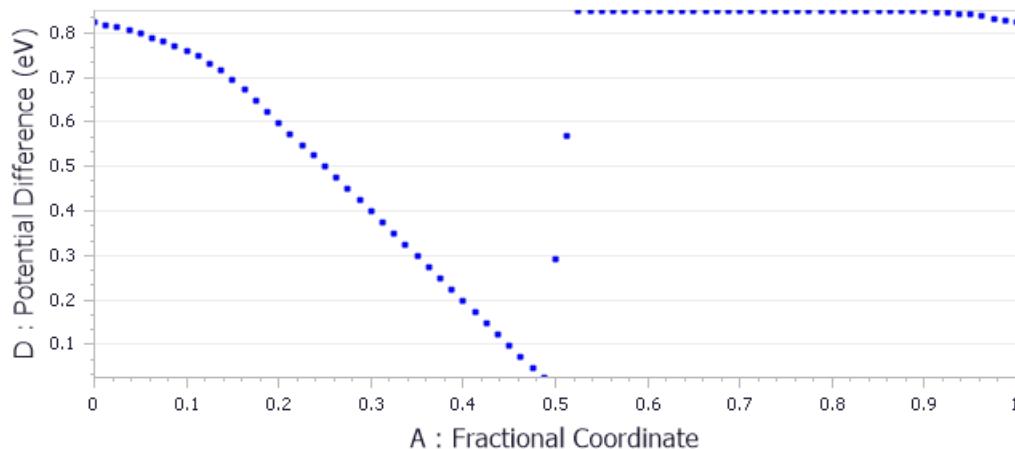
Remove the column containing the duplicate fractional coordinate values as they are the same as for the neutral system.

Remove the remaining non-empty columns.

Tip: Before you delete the coordinates column for the charged potentials, check that they match the neutral coordinates. If the charged coordinates have an extra row at the beginning, shift the values so that they match the neutral coordinates.

Select the first empty column and click  on the toolbar to define a function for the column. For the **Expression**, enter **(C-B)*27.2114**, and for the **Name**, specify **Potential Difference (eV)**. Click **OK**.

Select **Column A** and **Column D** and, from the toolbar, click **Quick Plot** .



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You can see how the potential difference goes to zero at the metal surface since the metal surface has a potential of 0 eV by definition. The charge injection introduces a bias of about 0.85 eV and the potential drop happens between the graphene surface and the metal gate.

You can access volumetric visualization tools from the Volume Visualization toolbar.

From the menu bar, select **View | Toolbars | Volume Visualization**.

For example, you can add a slice to the structure showing the potential for the slice of the cell.

With the charged **graphene (3x2)(PF6).xsd** document in focus, click the **Create Slices** arrow  and select **Best Fit**.

A slice displays the electrostatic potential in the cell.

From the menu bar, select **File | Save Project** followed by **Window | Close All**.

This is the end of the tutorial.

[1] B. Yimaz et al, First-Principles Investigation of Charged Germagraphene as a Cathode Material for Dual-Carbon Batteries, *ChemSusChem* **16** (2023) e202201639; <https://doi.org/10.1002/cssc.202201639>

Chapter 10: Forcite tutorials

The following tutorials illustrate how to utilize Forcite's capabilities.

- [Geometry optimization of urea with and without symmetry constraints](#)
- [Hydrogen Physisorption on a Tungsten Surface](#)

Some [Forcite Plus](#) tutorials are also available.

Geometry optimization of urea with and without symmetry constraints

Purpose: Illustrates the effect of symmetry when optimizing a structure using Forcite.

Modules: Materials Visualizer, Forcite, COMPASS

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

Background

Forcite in Materials Studio is a classical molecular mechanics tool, designed by BIOVIA scientists and software engineers to perform a range of tasks. These include fast energy calculations and geometry optimizations for single molecules as well as periodic systems. In geometry optimizations of crystal structures Forcite retains the symmetry of the systems, which is of particular importance in work relating to structure determination.

Introduction

In the determination of crystal structures, it is important that both the symmetry elements are found to be correct *and* that the structure is at an energy minimum. This means that an optimized structure should not change very much during a later geometry optimization without symmetry constraint.

This tutorial aims to demonstrate the use of symmetry when performing the geometry optimization of a crystal structure. For this tutorial, use the crystal structure of urea, a widely used chemical and pharmaceutical intermediate.

This tutorial covers:

- [Getting started](#)
- [To perform a geometry optimization of the structure and cell with symmetry](#)
- [To remove the symmetry and carry out a further geometry optimization](#)
- [To compare the results of the two runs](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **urea** as the project name, click **OK**.

This creates a new project with *urea* listed in the Project Explorer. Load the crystal structure of the system to study - urea.

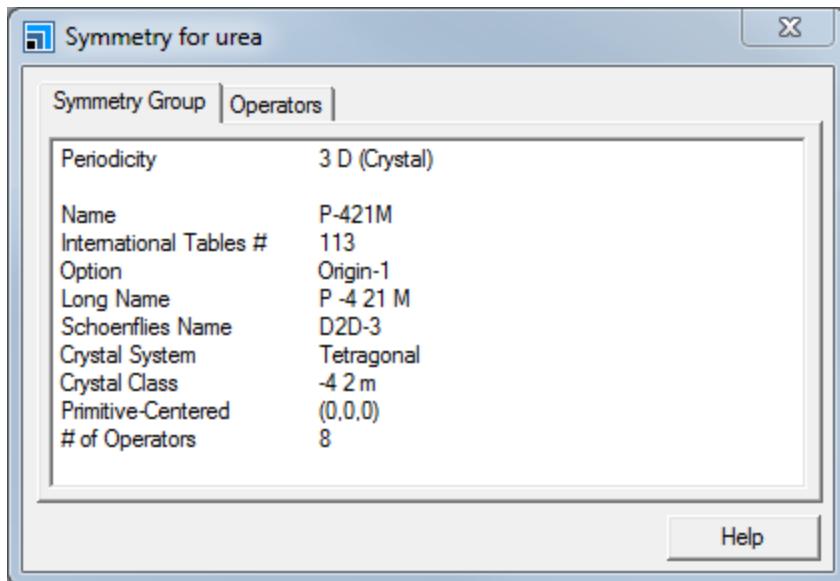
Click **Import**  to open the Import Document dialog. Navigate to the **Structures/molecular-crystals/misc** folder and double-click **urea.xsd**.

Forcite: Geometry optimization of urea with and without symmetry constraints

The crystal structure of urea is displayed in a 3D Atomistic Document called `urea.xsd`. Validate the symmetry of the structure.

Click **Show Symmetry**  on the **Symmetry** toolbar, or choose **Build | Symmetry | Show Symmetry** from the menu bar.

This opens the Symmetry dialog.



Symmetry dialog

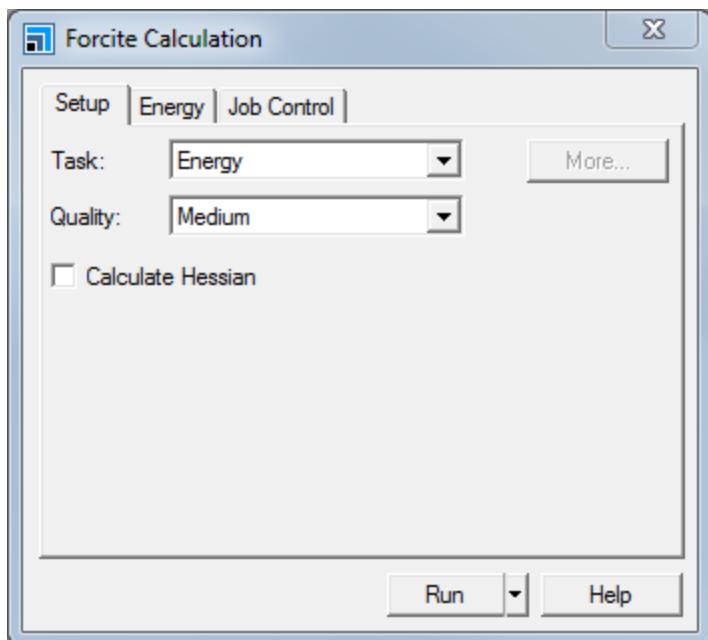
It shows that the space group is P-421M.

2. To perform a geometry optimization of the structure and cell with symmetry

The next step is to carry out a geometry optimization of urea using the COMPASS forcefield.

Click **Forcite**  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog.



Forcite Calculation dialog, Setup tab

Change the **Task** from Energy to **Geometry Optimization** and the **Quality** to **Fine**.

Click **More...** to display the Forcite Geometry Optimization dialog. Check the **Optimize cell** checkbox and close the dialog.

On the **Energy** tab, choose **COMPASSIII** from the **Forcefield** dropdown list. Leave all the other settings unchanged.

Click **Run** and close the dialog.

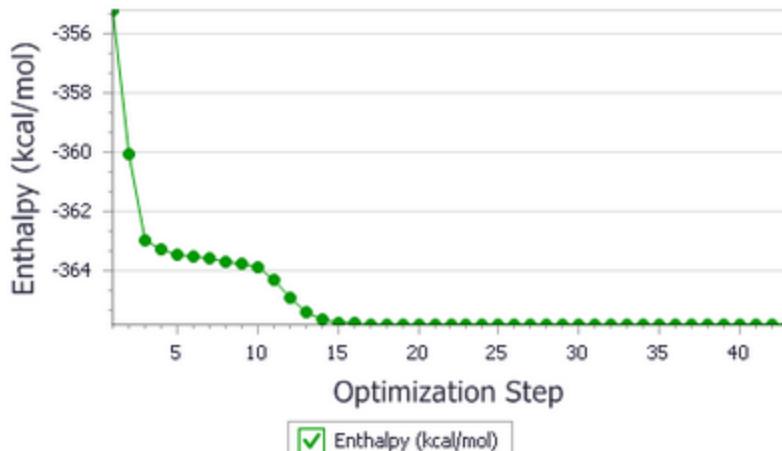
A new folder, entitled urea Forcite GeomOpt, opens in the Project Explorer. The calculation takes less than 1 minute to complete, that is, to reach the stipulated convergence criteria, since the library structure is already close to optimum. When completed, the `urea .xsd` document near the top of the new folder contains the optimized structure.

There are six other documents in the urea Forcite GeomOpt folder. The `urea .txt` document contains all the text information for the job. This includes the structure and energy parameter values for the initial and final structures. The `Status .txt` document contains the last job execution status. The urea Energy chart shows the variation of the total energy during the optimization. The urea Convergence chart shows the variation of the convergence criteria, namely Energy Change, Gradient Norm, and Stress Norm as a function of the Optimization step. The simulation stops as soon as all the required criteria are met. The urea Cell chart shows the variation of the cell parameters, and the urea Density chart shows the variation of the system density.

Open the chart document **urea Energies.xcd**.

It looks similar to this.

Forcite Geometry Optimization - Energy



Make sure that the symmetry has not changed.

Make **urea Forcite GeomOpt/urea.xsd** the active document and open the **Symmetry** dialog.

The space group is still P-421M. Before completing this section of the tutorial, save the project and tidy up the workspace area.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To remove the symmetry and carry out a further geometry optimization

Now repeat the same procedure without symmetry constraints. Begin by importing another copy of the urea structure.

Open the **Import Document** dialog, navigate to **Structures/molecular-crystals/misc/**, and import **urea.xsd**.

This opens a second 3D Atomistic Document containing the urea structure, called **urea (2).xsd**. Remove the symmetry from the crystal structure.

Select **Build | Symmetry | Make P1** from the menu bar.

Confirm that the symmetry is now P1.

On the **Symmetry** dialog, confirm that the Space group is **P1**. Close the dialog.

To reflect the changed symmetry, rename **urea (2).xsd**.

Right-click **urea (2).xsd** in the **Project Explorer** and select **Rename** from the shortcut menu. Change the name to **urea_P1**.

The next step is to carry out a geometry optimization on **urea_P1**, using the same settings as before.

Open the **Forcite Calculation** dialog.

Forcite retains all of the previous parameters. You want to run the calculation in the same way as before, so there is no need to make any changes to the settings.

Click **Run** and close the dialog.

A new folder, entitled **urea_P1 Forcite GeomOpt**, opens in the Project Explorer. Again, the calculation finishes very quickly. When it is complete, save the project and close all of the open windows once more.

Select **File | Save Project** on the menu bar, then **Window | Close All**.

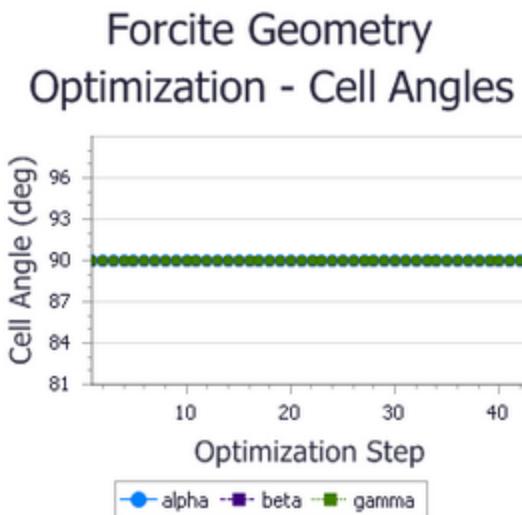
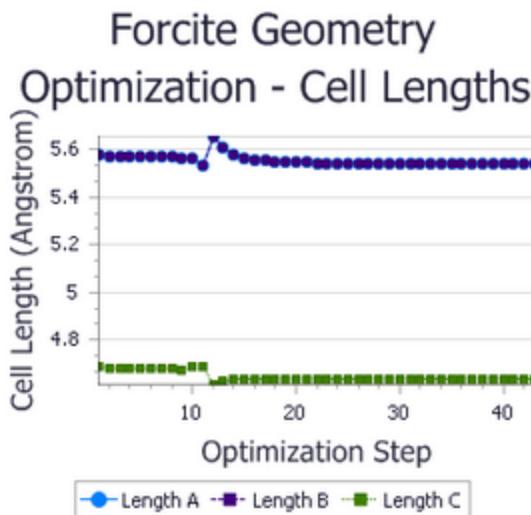
4. To compare the results of the two runs

The final step is to compare the results of the two calculations.

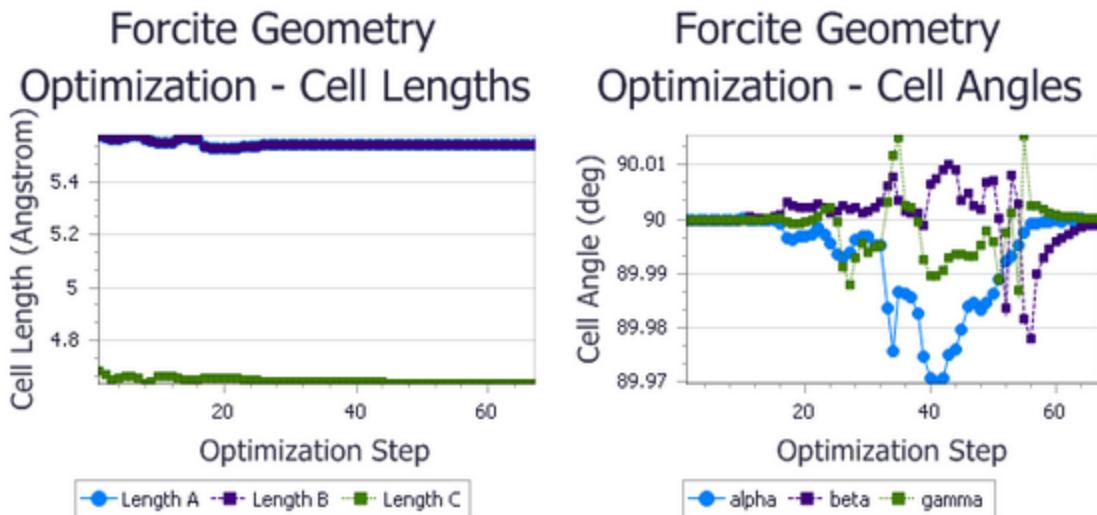
Locate and open the text output documents **urea.txt** and **urea_P1.txt** and open them. Scroll down to the final structure **Total energy**.

The values are almost identical at -365.83 kcal/mol. Now compare the two cell optimizations.

Locate and open the chart documents **urea Cell.xcd** and **urea_P1 Cell.xcd**.



P-421M urea cell

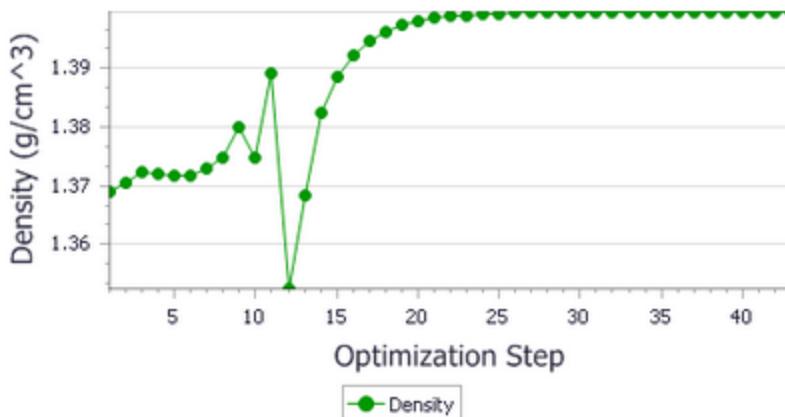


P1 urea cell

In the case of urea with full symmetry, the cell lengths decreased slightly and the angle remained constant at 90 ° in line with the symmetry constraints. In the case of the P1 structure, with no symmetry constraints, the cell angles vary during the simulation. While the exact variations are very sensitive to machine details, the angles finally converge again to 90 °. So, overall the cell angles are also very similar in both cases.

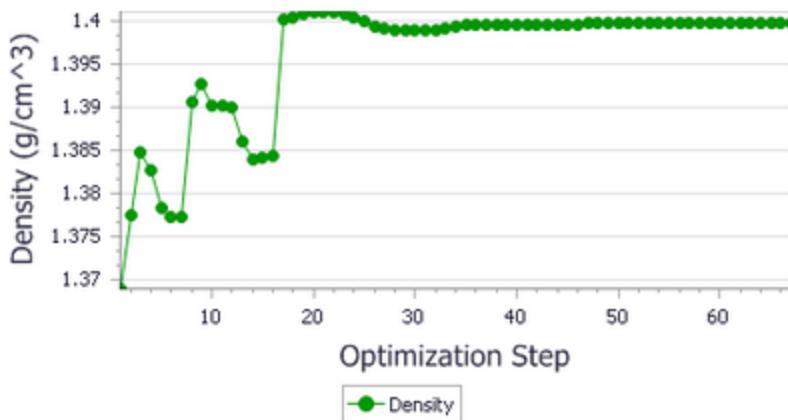
Locate and open the charts **urea Density.xcd** and **urea_P1 Density.xcd**.

Forcite Geometry Optimization - Density



P-421M urea density

Forcite Geometry Optimization - Density



P1 urea density

In both cases, the density of the urea cell has increased slightly as a result of the optimization. Once again, exact variations depend on machine details, but the final value is slightly below 1.40 g/cm³.

You can conclude that the course the geometry optimization takes in each case is quite different but that both calculations converge to the very similar values in the end.

You have learned that symmetry elements are maintained during Forcite geometry optimization and that the presence or absence of these elements strongly affects the course of the calculation. Once a structure is close to its minimum energy conformation it may, as in this case, converge to give very similar cell parameters and energies with and without symmetry constraints.

This is the end of the tutorial.

Hydrogen physisorption on a tungsten surface

Purpose: Introduces the use of Forcite to generate an optimized structure of a molecule on a surface.

Modules: Materials Visualizer, Forcite

Time: 

Prerequisites: [Geometry optimization of urea with and without symmetry constraints](#)

Background

Forcite in Materials Studio is a classical molecular mechanics tool, designed by BIOVIA scientists and software engineers to perform a range of tasks including fast energy calculations and geometry optimizations for single molecules as well as periodic systems. It provides access to different forcefields and is easy to use for the novice as well as providing the widest range of customization options for the experienced user.

Introduction

A detailed knowledge of surface interactions and reactions plays a key role in the design of many materials and processes. An important first step in such a study is the preparation of a model of molecules physisorbed to the surface with optimized geometry (that is, energy minimized). The different steps involved in the modeling approach include:

- Construction of the surface from the pure crystal.
- Addition of the molecules near to the surface.
- Definition of the potentials (by the forcefield) to study the gas-solid interaction.
- Geometry optimization.

This tutorial aims to explain the different steps involved in the study of the physisorption of a gas onto a surface. The system in this tutorial is an example inspired by a case study of the adsorption of H₂ onto a tungsten surface (see the [White \(1996\)](#) paper). In this particular case, you can consider the use of molecular mechanics as a precursor to computationally more expensive quantum mechanical methods. Once you have optimized the model with Forcite, you can use DMol³ or CASTEP to study the chemisorption reaction.

This tutorial covers:

- [Getting started](#)
- [To build a metallic surface from the pure crystal](#)
- [To place the gas phase molecule on the surface](#)
- [To perform a Forcite geometry optimization](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **H2_W** as the project name, click **OK**.

The new project is created with *H2_W* listed in the Project Explorer. The next step is to load the crystal structure that you want to cleave, in this tutorial you work with pure tungsten (W).

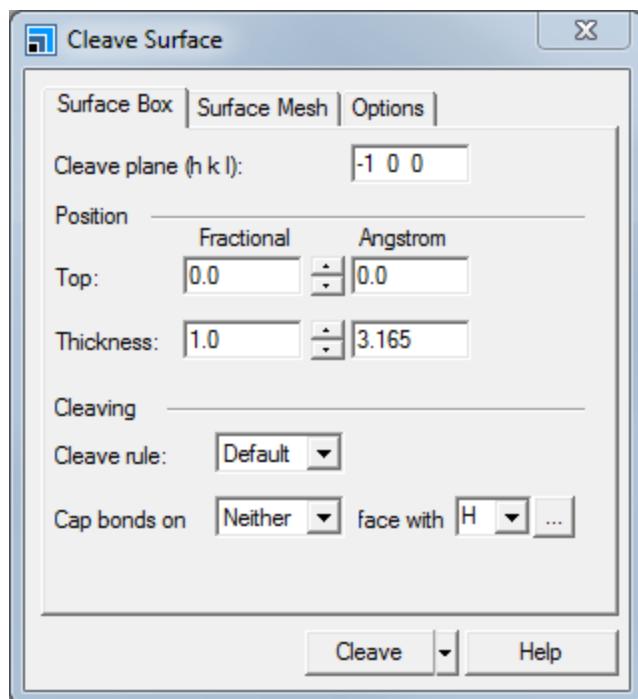
Click **Import**  to open the Import Document dialog. Navigate to the **Structures/metals/pure-metals** folder and double-click **W.xsd**.

The crystal structure of tungsten is displayed in a 3D Atomistic Document called **W.xsd**.

2. To build a metallic surface from the pure crystal

Select **Build | Surfaces | Cleave Surface** from the menu bar.

This opens the Cleave Surface dialog.



Cleave Surface dialog, Surface Box tab

Blue dashed lines display on the crystal indicating the plane to cleave. The Surface Box tab also displays this information, at the top. The default plane is $-1\ 0\ 0$, which is equivalent to the $(1\ 0\ 0)$ surface, so you do not need to change this setting.

Change the thickness of the cell, to ensure that the final model includes all the significant interactions between the gas molecule and the tungsten atoms.

Increase the **Fractional Thickness** to **2.0**.

The thickness is now 6.33 Å. Now that you have configured the surface parameters, you can cleave the cell.

Click **Cleave** and close the dialog.

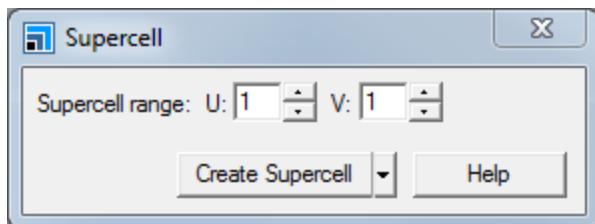
Forcite: Hydrogen physisorption on a tungsten surface

A new 3D Atomistic document, `w (-1 0 0).xsd`, opens and displays a 2D periodic structure as a white square with the tungsten atoms.

You have now built a 2D cell out of a 3D crystal. However, before you place the gas molecules onto the surface, you need to increase the lateral extent of the surface. This avoids artificial interactions between the gas molecule and its periodic images during the optimization step.

Select **Build | Symmetry | Supercell** from the menu bar.

This opens the Supercell dialog.



Supercell dialog

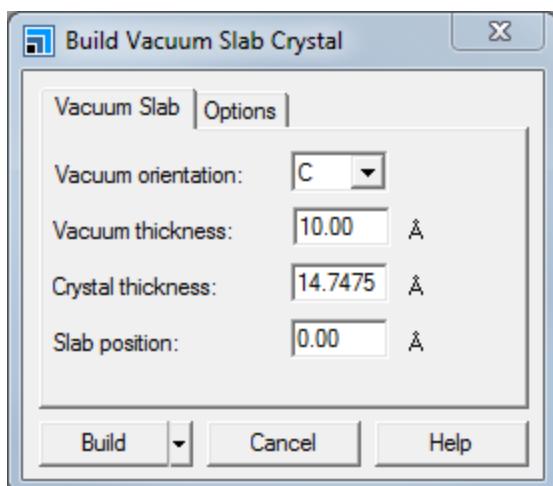
Increase the **Supercell range** for **U** and **V** to **4**. Click **Create Supercell** and close the dialog.

This builds a larger surface, consisting of 16 of the original cells, this model has 2D periodicity. Convert it to a 3D lattice using the *Build Vacuum Slab* functionality.

A slab is a 3D periodic cell with the surface at the bottom and a vacuum above it. This enables you to put molecules onto the surface, in the vacuum, so that the molecule does not see a periodic image of the surface above it.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar.

This opens the Build Vacuum Slab Crystal dialog.



Build Vacuum Slab Crystal dialog, Vacuum Slab tab

This dialog allows you to specify the orientation, thickness, and position of the region of vacuum.

Change the **Slab position** from **0.00** to **1.00 Å**. Increase the **Vacuum thickness** to **20.00 Å**. Click **Build**.

The `W (-1 0 0)` 3D Atomistic document updates to display a rectangular box with the surface at the bottom. The tungsten atoms are inside the cell, making it easier to visualize them.

3. To place the gas phase molecule on the surface

The next stage in this tutorial is to build a hydrogen molecule and then position it on the surface. To do this, sketch a hydrogen molecule in a new 3D Atomistic document, copy and paste it into the slab and dock it on the surface.

Create a new 3D Atomistic document and sketch and clean an H_2 molecule.

The next step is to copy and paste this into the document containing the slab.

Select **Edit | Copy** from the menu bar. Double-click on **W (-1 0 0).xsd** in the Project Explorer, then choose **Edit | Paste**.

Tip: You can also use the standard Windows shortcut keys **CTRL + C** to copy and **CTRL + V** to paste.

The hydrogen molecule appears in the cell. A second "ghost" molecule also appears, as a result of the periodic boundary conditions. You can remove this periodic image later.

You can use the Close Contacts tool to monitor how close the hydrogen is to the surface.

Select **Build | Close Contacts** from the menu bar to open the Close Contact Calculation dialog. Select **Monitor close contacts** and close the dialog.

Now, select the hydrogen molecule and translate and rotate it until it docks onto the metal surface.

Select the **hydrogen** molecule. Hold down the **SHIFT** and **ALT** keys and the **right** mouse button. Move the mouse to translate the molecule.

Tip: If you have a three button mouse or a mouse with a wheel, you can use the wheel or middle button with SHIFT to translate without holding down ALT.

As you move the hydrogen atom, a pink dashed line appears to indicate a close contact. Use these controls to position the hydrogen molecule slightly above the tungsten surface, with the pink line showing.

You can remove the "ghost" molecule in the adjacent unit cell by changing the display style.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Lattice** tab, select **In-Cell** from the **Style** list. On the **Atom** tab, select **Ball and stick**. Close the dialog.

Click anywhere in the 3D Viewer to clear the selection of everything.

4. To perform a Forcite geometry optimization

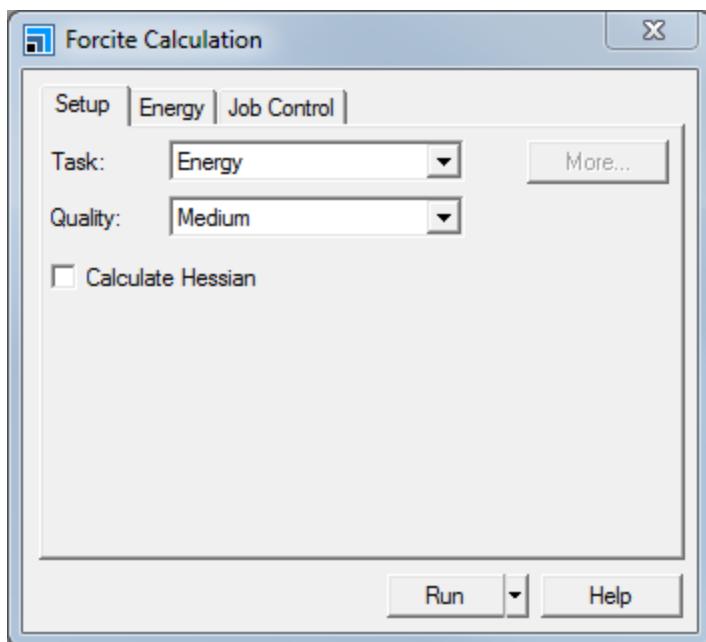
The final step in this tutorial is to calculate the actual physisorption of the hydrogen molecule on the tungsten surface.

Forcite: Hydrogen physisorption on a tungsten surface

Make **W (-1 0 0).xsd** the active document. Use the **Reset View**  tool on the **3D Viewer** toolbar to place the model in the center of the window.

Click **Forcite**  on the **Modules** toolbar and select **Calculation** or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog.



Forcite Calculation dialog, Setup tab

Change the **Task** from Energy to **Geometry Optimization** and the **Quality** to **Fine**.

Click **More...** to display the Forcite Geometry Optimization dialog. Change the **Maximum number of iterations** to **1000**. Ensure that **Optimize cell** is not selected. Close the dialog.

The minimization algorithm used by default is the **Smart** algorithm; it is a cascade of methods using successively Steepest descent and Conjugate gradient algorithms.

On the **Energy** tab, for the **Forcefield** select **Universal**.

The final step before performing the geometry optimization is to fix the coordinates of the metallic atoms. By doing this, you assume that the surface structure is similar to the bulk and not significantly modified by the hydrogen atoms. For a more accurate and detailed study, you might need to relax the surface of the crystal before performing the geometry optimization.

Hold down **ALT** and double-click **any tungsten atom**.

This highlights all the tungsten atoms.

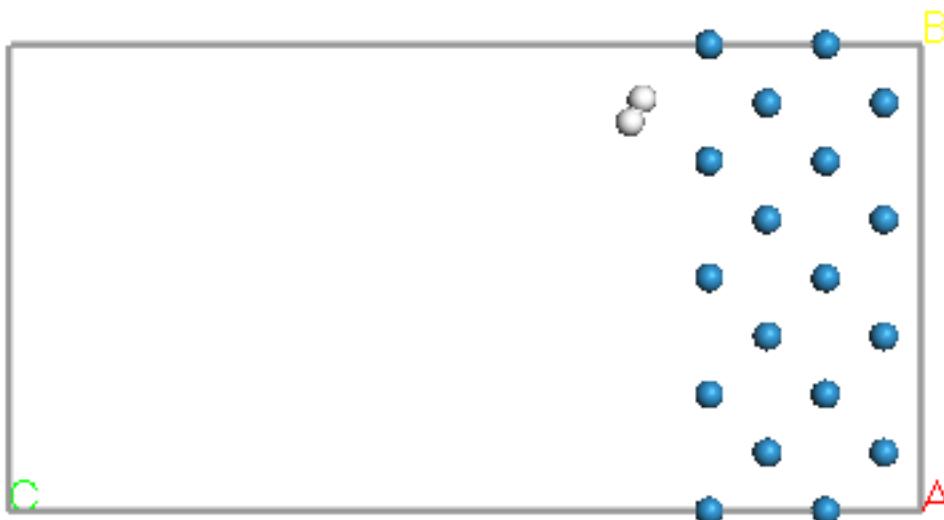
Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. On the **Atoms** tab, select **Fix Cartesian position** and close the dialog.

Click anywhere in the **3D Viewer** to clear the selection of all the atoms.

You are now ready to run the simulation.

Click **Run** on the Forcite Calculation dialog.

A new folder, entitled W (-1 0 0) Forcite GeomOpt, opens in the Project Explorer. The calculation usually takes less than one minute to complete, and reach the stipulated convergence criteria. When completed, the W (-1 0 0).xsd document near the top of the new folder contains the optimized structure that looks similar to that shown below.



There are four other documents in the W (-1 0 0) Forcite GeomOpt folder. The W (-1 0 0).txt document contains all the text information for the job, in particular the structure and energy parameter values for the initial and final structure. The Status .txt document contains the last job execution status. The W (-1 0 0) Energy chart shows the variation of the total energy during the optimization. The W (-1 0 0) Convergence chart shows the variation of the convergence criteria, namely the Energy Change and Gradient Norm as a function of the Optimization step. The simulation stopped as soon as all the required criteria were met.

You have now prepared a structure that would be well suited for further simulations, such as the dissociation reaction, using the DMol³ or CASTEP modules.

This is the end of the tutorial.

References

White, J.A.; Bird, D.M.; Payne, M.C. *Phys. Rev. B*, **53**, 1997 (1996),
<http://dx.doi.org/10.1103/PhysRevB.53.1667>.

Chapter 11: Forcite Plus tutorials

The following tutorials illustrate how to utilize the Forcite Plus capabilities.

- [Finding low energy configurations of a molecule on a surface](#)
- [Using Materials Studio to edit a forcefield](#)
- [Calculating the diffusivity of a gas in a polymer](#)
- [Polymer interactions with a metal oxide surface](#)
- [Calculating the Miscibility of Two Polymers](#)
- [Running a confined shear simulation](#)
- [Calculating the solvation free energy of propionic acid in *n*-octanol](#)
- [Calculating the melting temperature of a metal using the coexistence method](#)

Some [Forcite](#) tutorials are also available.

Finding low energy configurations of a molecule on a surface

Purpose: Demonstrates the use of molecular dynamics and geometry optimization in looking for low energy minima.

Modules: Materials Visualizer, Forcite Plus, QSAR, COMPASS

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial and [Geometry optimization of urea with and without symmetry constraints](#)

Background

The potential energy surface of a small molecule can be very complex, with many local energy minima and one global energy minimum. There are several methods available to determine the global minimum, including Monte-Carlo algorithms and different forms of molecular dynamics. Quench molecular dynamics performs a standard molecular dynamics calculation with an additional geometry optimization step, in which a geometry optimization is performed on every frame in the trajectory file. Effectively, molecular dynamics samples many different low energy configurations.

Introduction

This tutorial uses Forcite Plus to perform molecular dynamics on a system comprising a small organic molecule, o-chlorophenol, and a metal-oxide surface, titanium dioxide. This tutorial cleaves the titanium dioxide surface from the rutile form of the TiO_2 crystal structure, places the molecule on the surface, optimizes it, and runs quench molecular dynamics. A study table allows you to look for the lowest energy conformation and, finally, calculate the binding energy.

This tutorial covers:

- [Getting started](#)
- [To sketch and optimize chlorophenol](#)
- [To build and optimize the \$\text{TiO}_2\$ surface](#)
- [To equilibrate the molecule on the surface](#)
- [To sample configurations using quench dynamics](#)
- [To calculate the binding energy](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

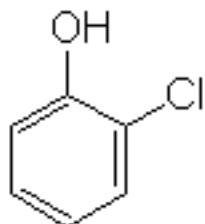
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Cl_phenol** as the project name, click **OK**.

This creates a new project with *Cl_phenol* listed in the Project Explorer.

2. To sketch and optimize chlorophenol

You are going to sketch the molecule ortho-chlorophenol.



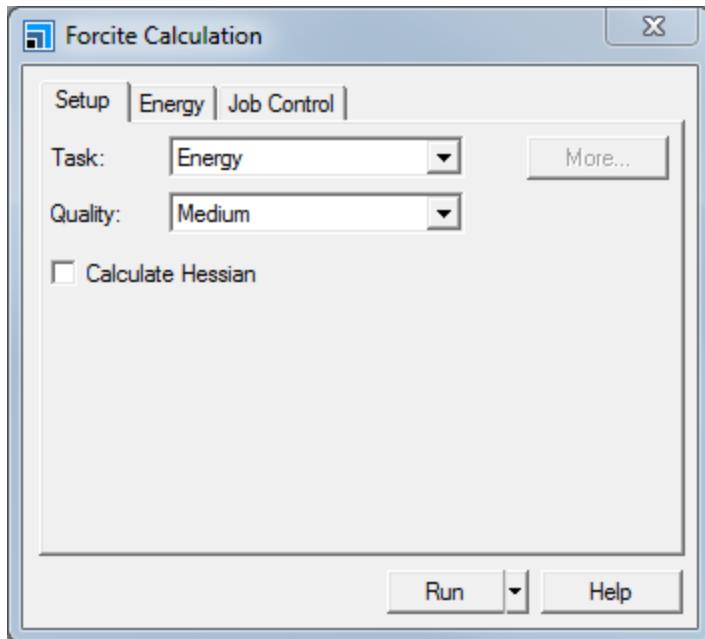
Create a new **3D Atomistic Document**. Sketch a molecule of ortho-chlorophenol, make sure that you use the **Adjust Hydrogen** and **Clean** tools.

In the Project Explorer, rename the 3D Atomistic Document **chlorophenol.xsd**.

The molecule you have sketched does not have an accurate geometry, so optimize the geometry using a classical simulations tool. Classical simulations tools require a forcefield that describes the forces between atoms in terms of a sum of functions in the distances, angles, and so on, between atoms of various types. Use the Forcite classical simulations engine and the COMPASS forcefield.

Click **Forcite**  on the **Modules** toolbar and select **Calculation** from the dropdown list, or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog.



Forcite Calculation dialog, Setup tab

On this dialog, you can choose what type of calculation to perform, the *Quality* controls different settings depending on the task chosen. On the *Energy* tab, you can select the forcefield, charging method, and customize the treatment of non-bond terms.

Change the **Task** to **Geometry Optimization**. On the **Energy** tab, change the **Forcefield** to **COMPASSIII**.

COMPASS is a well validated forcefield with its own charges. Hence, when you chose COMPASS, the **Charges** selection automatically changes to **Forcefield assigned**. The non-bond settings default to **Atom based**. This is suitable for small molecules but when you introduce the TiO₂ surface in later, you will change these to **Ewald**.

Click **Run**.

This launches the job and displays it in the Job Explorer. The job creates a new folder called **chlorophenol Forcite GeomOpt** in the Project Explorer. When the job completes, a notification displays and the results folder contains 6 files.

- **chlorophenol.xsd** - contains the optimized geometry of the initial structure
- **chlorophenol - Calculation** - an xml state file containing the settings for the job. Clicking on this file opens the Forcite Calculation dialog with the settings specified in the calculation.
- **chlorophenol Convergence.xcd** - plots the evolution of the energy change and gradient normal change.
- **chlorophenol Energies.xcd** - plots the evolution of the enthalpy. The dramatic drop indicates an initial bad geometry successfully refined.
- **Status.txt** - contains the live update status.
- **chlorophenol.txt** - a text version of the initial settings, and a breakdown of energies for the initial and final structure

3. To build and optimize the TiO₂ surface

Materials Studio has an extensive structure library containing many common metal oxides. Three forms of titanium dioxide exist. Here, work with the rutile form.

In the Project Explorer, right-click the project root and select **Import...** from the shortcut menu to open the Import Document dialog. Navigate to **Structures\metal-oxides** and import **TiO2_rutile.xsd**.

Before cleaving the surface, optimize the geometry of the crystal structure.

On the **Setup** tab on the Forcite Calculation dialog, click **More...** to open the Forcite Geometry Optimization dialog. Select the **Optimize cell** checkbox and close the dialog.

As this is a 3D periodic structure, you can choose to either optimize the cell and atomic positions or only the atomic positions. In this case, optimize the cell and atomic positions.

In the Properties Explorer, change the **Filter** to **Lattice 3D**.

The rutile form of titanium dioxide belongs to the P42/MNM space group. Forcite optimizes the structure within the symmetry constraints.

Click **Run** and close the Forcite Calculation dialog.

This creates a new folder, **TiO2_rutile Forcite GeomOpt**. When the calculation is complete, the new folder contains the same set of documents as the chlorophenol folder. In addition, since this is a periodic structure, Forcite also reports the change in cell parameters and density.

Note: The `TiO2_rutile.txt` output file reports that there are missing parameters for some energy contributors. These do not affect the outcome of the tutorial, but you can avoid the messages by manually applying forcefield types and then deleting all the bonds in the structure. **Step 2** of the [Polymer interactions with a metal oxide surface](#) tutorial uses this approach.

Now you have optimized the structure, cleave the crystal to show the active 110 surface.

Tip: If you do not know the active surface, you can use the Morphology module to find it.

Select **File | Save Project** from the menu bar, followed by **Window | Close All** from the menu bar.

Open the optimized `TiO2_rutile.xsd` document. Choose **Build | Surfaces | Cleave Surface** to open the Cleave Surface dialog. Change the **Cleave plane** to **1 1 0** and press **TAB**.

In `TiO2_rutile.xsd`, this displays a blue box showing the cleave plane as a solid blue line and the depth as dotted lines.

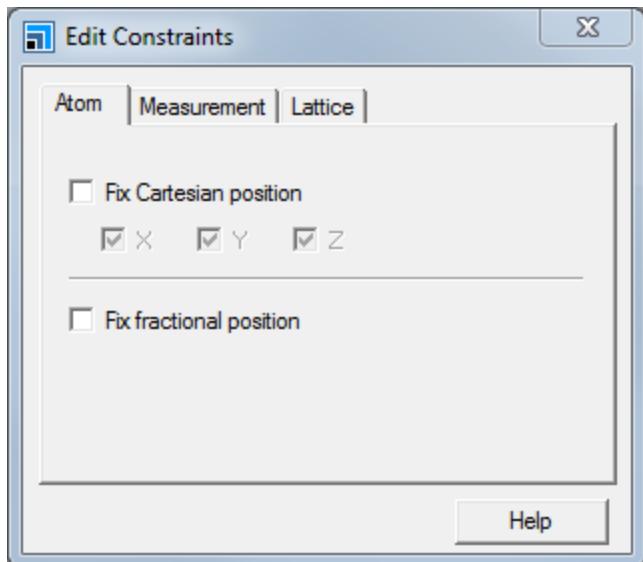
Use the spinners to increase the **Fractional Top** to **0.4** and the **Fractional Thickness** to **3.0**. Click **Cleave** and close the dialog.

A new 3D Atomistic Document, `TiO2_rutile (1 1 0).xsd` opens. The surface, denoted by a solid white rectangle, contains a mixture of titanium and oxygen atoms.

You are now going to optimize the surface. As you have already optimized the bulk crystal structure, you can constrain the geometry of the bottom layers as these represent the bulk structure.

Click the **3D Viewer Selection Mode** tool. Orient your structure with the surface at the top of the screen. Select the bottom mixed Ti and O layer and the partial O layers immediately above and beneath it. Choose **Modify | Constraints** from the menu bar.

This opens the Edit Constraints dialog.

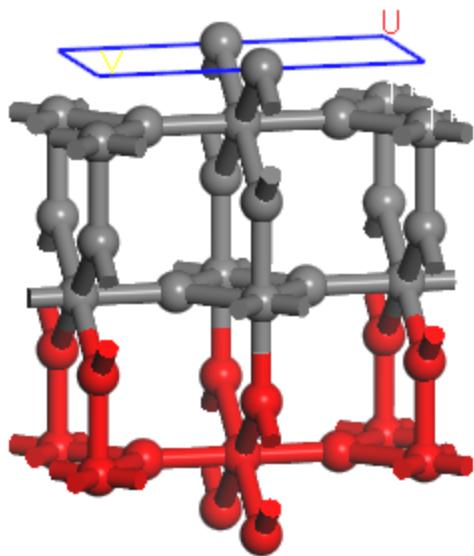


Edit Constraints dialog, Atom tab

Select the **Fix Cartesian position** checkbox and close the dialog.

Click in the 3D Viewer to clear all selections. Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. In the **Coloring** section on the **Atom** tab, change the **Color by** option to **Constraint**.

The structure looks similar to the one below, with the constrained atoms colored red and the unconstrained atoms colored gray.



TiO₂ surface in Ball and stick display style.

On the Display Style dialog, change the **Color by** option back to **Element** and close the dialog.

You are now ready to optimize the surface.

Open the Forcite Calculation dialog and click **Run**.

Once again, the new folder contains the results files. The final step in this section is to determine how large to make the surface. The surface must be large enough to accommodate the organic molecule while minimizing interactions with ghost molecules. Therefore, begin by using a distance monitor to calculate the length of chlorophenol.

Open the optimized **chlorophenol.xsd**. Click the **Measure/Change** arrow and select **Distance**. Select the **Cl** atom and the opposite **H** atom.

This displays a distance monitor with a value around 5.6 Å. Assuming that a 2 Å region around each molecule is sufficient to minimize intermolecular interactions, this indicates a unit cell size of 5.6 + 2 × 2 or about 9.6 Å. Now you need to determine how many copies of the current surface you must generate to achieve this.

Make the optimized rutile surface active. In the Properties Explorer, change the **Filter** to **Lattice 2D**.

The cell parameters are around 3.0 and 6.3 Å for U and V respectively. Therefore, a supercell of 3 × 2 is sufficient to accommodate the organic molecule.

Choose **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Change **U** to **3** and **V** to **2**. Click **Create Supercell** and close the dialog.

You have now created your surface. Before continuing, save the project.

Choose **File | Save Project** from the menu bar.

4. To equilibrate the molecule on the surface

The next stage is to place the molecule on the surface and optimize the structure. Create a new document in the root project folder and using that for the calculations.

With the enlarged optimized surface active, choose **File | Save As...** from the menu bar to open the Save As dialog. Navigate to the root project folder, change the **File name** to **ChloroTiO2_110**, and click **Save**.

This saves a copy of the surface in the root project folder. You now need to paste the organic molecule onto the surface.

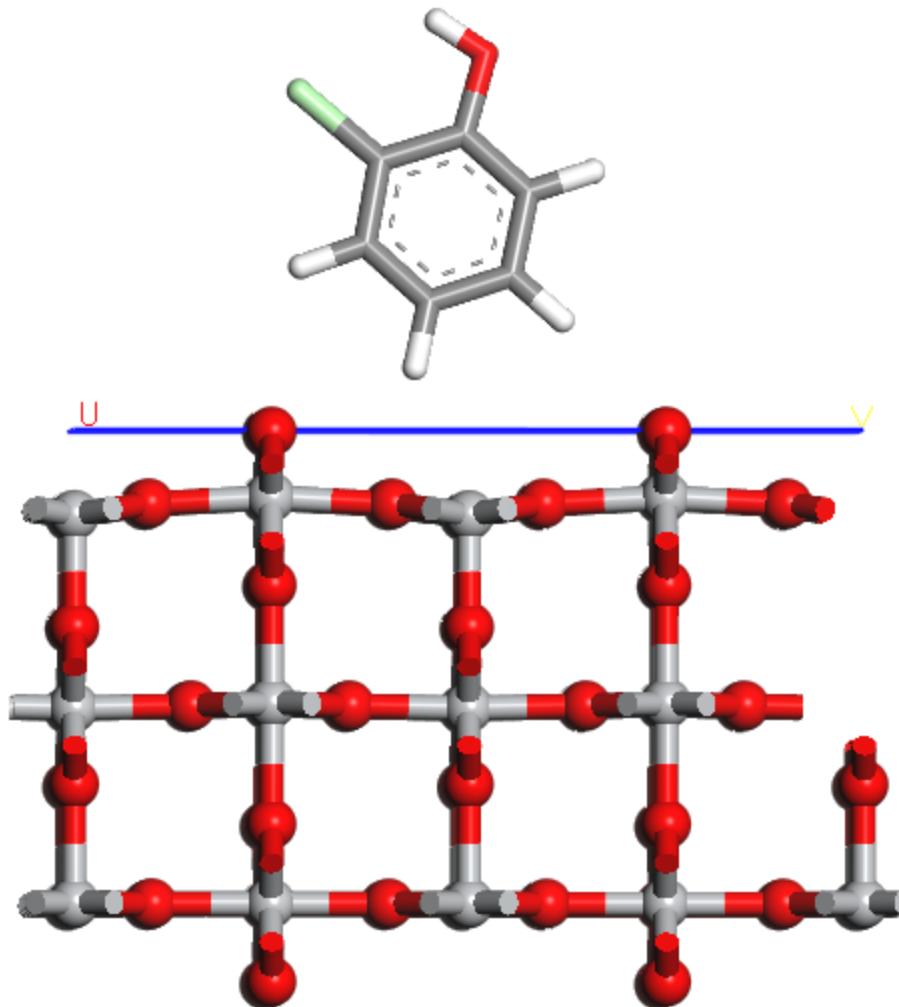
Select the optimized **chlorophenol.xsd**. Choose the **3D Viewer Selection Mode** tool and select the distance monitor. Press **DELETE**. Press **CTRL + C** and change focus back to **ChloroTiO2_110.xsd**. Press **CTRL + V**.

This pastes chlorophenol into the document containing the surface. Now orient the molecule so that it lies perpendicular to the surface.

Hold down the **SHIFT** and **ALT** keys, right-click, and position the chlorophenol so that it is hovering over the surface.

Tip: If you are using a mouse with a wheel or a middle button, you can translate the fragment by holding down SHIFT and the middle mouse button or wheel.

The initial starting structure looks similar to the image below.



Chlorophenol hovering over the TiO_2 surface.

Note: Take care to ensure that the chlorophenol molecule does not penetrate the surface. Use the CPK display style to verify this before attempting to optimize the system.

When investigating the different interactions of the molecule with the surface, constrain the surface atoms.

Use the **3D Viewer Selection Mode** tool to select all the atoms in the TiO_2 surface. Open the **Edit Constraints** dialog, clear and reselect the **Fix Cartesian position** checkbox. Close the dialog.

Now optimize the structure.

Click **Run** on the Forcite Calculation dialog.

This creates a new results folder containing the optimized structure. The molecule orients itself approximately flat on the surface.

This is one energy minimum for the structure however it is only a guess at the minimum energy adsorption site. To calculate the global energy minimum, you could try around 20 different starting configurations to make sure you have covered as much of the phase space as possible.

Forcite Plus: Finding low energy configurations of a molecule on a surface

Alternatively, you could use a quench molecular dynamics approach to sample many different configurations. Before continuing, save the project and close all the documents.

Choose **File | Save Project** followed by **Window | Close All** from the menu bar.

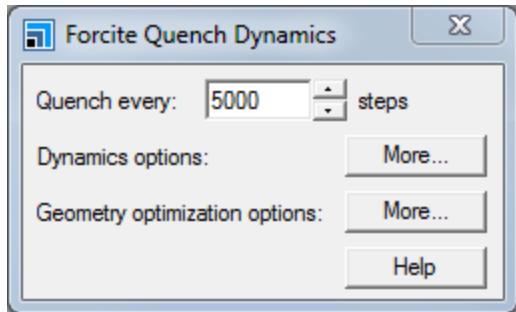
5. To sample configurations using quench dynamics

You are now ready to run a molecular dynamics simulation.

Reopen the optimized **ChloroTiO2_110.xsd**.

On the Forcite Calculation dialog, change the **Task** to **Quench** and click **More....**

This opens the Forcite Quench Dynamics dialog.

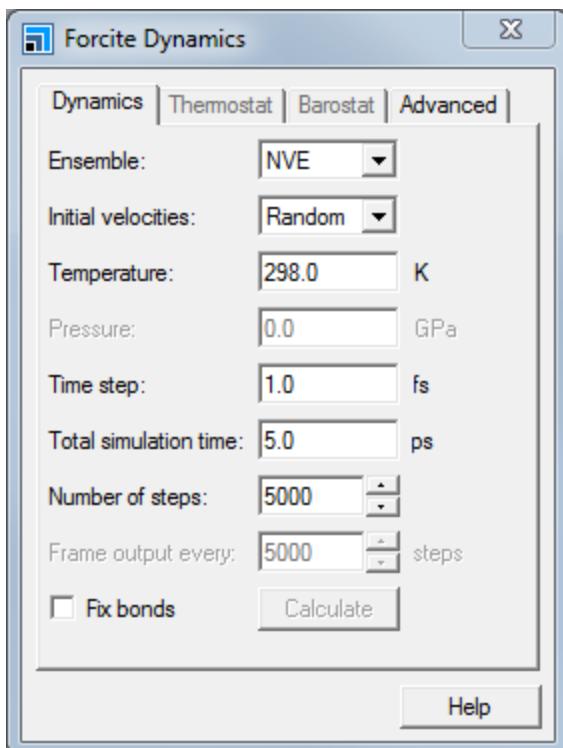


Forcite Quench Dynamics dialog

This gives you access to the basic quenching options. However, additional Dynamics options allow you to specify the temperature and so on.

Click **More...** for **Dynamics options**.

This opens the Forcite Dynamics dialog.



Forcite Dynamics dialog, Dynamics tab

Note: The *Frame output every steps* option depends on the *Quench every* option on the Forcite Quench Dynamics dialog.

Specify the **Temperature** as **350 K**.

This temperature represents a trade-off between a system with too much kinetic energy, where the molecule desorbs from the surface, and a system with not enough kinetic energy for the molecule to move around the surface. You might need to perform several calculations at different temperatures to determine the correct temperature. For this tutorial, 350 K is a good temperature.

Use the default number of 5000 steps to run the dynamics at 350 K, providing 5 ps of simulation time. Currently, a quench, or geometry optimization, is performed every 5000 steps. For this simulation, it would only perform one quench. Therefore, change the quench value to every 250 steps.

Close the Forcite Dynamics dialog. On the Forcite Quench Dynamics dialog, change the **Quench every** to **250** steps and close the dialog. On the Forcite Calculation dialog, click **Run** and close the dialog.

This creates another new folder, **ChloroTiO2_110 Forcite Quench**, in the Project Explorer, containing the usual updated results files plus these:

Forcite Plus: Finding low energy configurations of a molecule on a surface

- `ChloroTiO2_110.xsd` - The input structure
 - `ChloroTiO2_110 Quench Energy.xcd` - Chart containing the energies of the quenched structures
 - `ChloroTiO2_110 Quench.std` - Study table containing the results of the quench dynamics including a breakdown of the energies.
 - `ChloroTiO2_110 Quench.xtd` - Trajectory document containing the quenched structures
 - `ChloroTiO2_110.xtd` - Trajectory document containing the original, non-quenched, structures
 - `ChloroTiO2_110.txt` - Text document containing initial settings and a summary of the results.
- First, investigate the initial, non-quenched trajectory.

In the Project Explorer, double-click to open **ChloroTiO2_110.xtd**.

The `.xtd` document is the trajectory containing the frames from the dynamics run. You can animate the trajectory using the animation toolbar.

Choose **View | Toolbars | Animation** to display the **Animation** toolbar, click **Play** .

The trajectory document plays and you can visualize the movement of the chlorophenol molecule on the surface. The chlorophenol molecule might appear to move away from the surface. This is an artifact of the 2D periodic boundary conditions. You can change the visualization to remove this artifact.

Click **Stop** . Click the **Animation Mode** arrow  and select **Options** from the dropdown list to open the Animation Options dialog. Select the **Recalculate atom visibility every frame** checkbox and close the dialog. Click **Play**.

The chlorophenol molecule moves around on the surface.

Click **Stop** to stop the animation.

Next you can examine the quenched trajectory.

Change focus to **ChloroTiO2_110 Quench.xtd** and click **Play**.

There are several low energy conformations but which of these is the lowest energy? You can either consult the Forcite text output document or use the study table.

Stop the animation and change focus to the **ChloroTiO2_110 Quench.std** study table document.

The first column of the study table contains the structures, then the remaining columns contain the trajectory and energy breakdowns. The total energy is in column D, labeled as Hamiltonian.

Select column **D, Hamiltonian**. Click **Quick Plot** .

This plots the total energy against the row number.

Click the **Chart Viewer Selection Mode** tool. With the study table visible, click a point in the chart.

Selecting a point in the chart highlights the corresponding row in the study table. You can use this method to identify the low energy conformations. Alternatively, you can use the Sort tool on the study table.

Make the study table active and select the **Hamiltonian** column again. Click **Sort Ascending** .

This orders the rows in the study table, with the lowest energy row first. You can visualize the frames by double-clicking the structures in column A.

Double-click to open the lowest energy frame in column A.

You can also use a 3D Atomistic Collection Document to overlay all the structures to see if there is a preferential binding site on the surface.

Make the study table document active. Select the structure column **A**, move your mouse over any cell in this column, right-click, and select **Extract To Collection** from the shortcut menu. Click **OK** on the warning dialog.

The default view allows you to visualize the placement of all the molecules.

Open the **Display Style** dialog, on the **Lattice** tab change the **Style** to **In-Cell**.

This overlays all the molecules on the 2D surface, so you can see whether there is a preferred orientation or adsorption site. There is effectively one binding mode.

6. To calculate the binding energy

You can calculate the binding energy between the molecule and surface using the following equation:

$$\text{Binding Energy} = E_{\text{total}} - (E_{\text{chlorophenol}} + E_{\text{TiO}_2\text{Surface}})$$

If you take each of these energies as the minimum possible (in other words, you use the energy of the geometry optimized configuration for each), you can obtain a consistent result for the binding energy at the limit of low temperature.

E_{total} is the energy of the chlorophenol-TiO₂ system, and you know this from your quench calculation. Since you have already put the study table in order of increasing energy, you can take the value of the Hamiltonian from row 1. This is about -23.2 kcal/mol.

You know the energy of chlorophenol from your initial geometry optimization. Open **chlorophenol Forcite GeomOpt/chlorophenol.txt** and find the value of the Total Energy reported at the end. This is about 5.85 kcal/mol.

Note: As the atoms in the surface are constrained, the energy of the forces between them remain constant throughout the simulation. Since these constant forces do not affect the overall motion of the sorbate, they are excluded from the calculation and so they are not reported. Hence, in the case of the constrained TiO₂ surface, the energy reported is zero.

Since the energy of the TiO₂ surface is zero, we conclude that the zero-temperature binding energy of chlorophenol on TiO₂ is -29.05 kcal/mol. To obtain a binding energy at a finite temperature, you would need to carry out a molecular dynamics calculation for both chlorophenol and for chlorophenol on the TiO₂ surface. Then you would use the average energy resulting from each calculation, including the kinetic energy.

Using the quench molecular dynamics method above you have found the preferred binding site for this structure and surface and calculated the binding energy. You could now functionalize this organic molecule further and look to see if there are different interactions or you could change the surface. You can try a longer run to sample more configurations if required.

This is the end of the tutorial.

Using Materials Studio to edit a forcefield

Purpose: Illustrates a workflow for editing forcefield parameters in Dreiding to improve the fit between calculated and experimental crystal structure data.

Modules: Materials Visualizer, Conformers, and Forceite Plus. DMol³ is optional.

Time: 

Prerequisites: [Using Conformers to probe geometry-energy relationships](#)

Background

The forcefield is the core of a classical simulations calculation as it embodies how each type of atom in the structure interacts with the atoms around it. For each atom in the system, a forcefield type is assigned which describes the local environment of the atom. A forcefield contains a variety of information describing properties such as equilibrium bond lengths and electrostatic interactions between pairs of forcefield types. Typically, forcefields attempt to be either general, to cover many systems, or parameterized, for a specific problem. A general forcefield, such as Dreiding, has many parameters for atoms in different environments. However, for specific cases, it will never perform as well as a forcefield that has been parameterized for that case alone. Therefore, it can be useful to be able to edit a forcefield for use with systems for which it has not been parameterized.

This can occur in many scenarios: you might want to parameterize a forcefield to mimic a sorption isotherm for a molecule in a zeolite framework, you might have experimental crystal data that you want to use to increase the accuracy of a Polymorph prediction calculation or you may want to alter a forcefield to better describe the density of a polymer. In all these cases, you need to edit the underlying forcefield and observe the effect of those changes.

Editing forcefields is a complex task as many of the interactions are coupled, either explicitly or implicitly. For example, the energy profile on rotating a torsion angle does not just depend on the torsion term but also the non-bond energies. Therefore, getting the correct parameters can take considerable time and involve many different calculations. The best approach is to make small systematic changes and see the effect on the system. As with all forms of parameterization, there will also be a trade-off between obtaining the result and overfitting.

Introduction

In this tutorial, you will modify a single torsion angle of a small molecule to improve the match between the optimized model and the crystal structure. Initially, you will optimize the crystal structure of an explosive material, triaminotrinitrobenzene (TATB), using the Dreiding forcefield. You will then modify the Dreiding forcefield to improve the match between the crystal structure and the forcefield optimized model structure. You will use a combination of the Conformers module to probe torsion-energy relationships, DMol³ to provide ab initio data, and Forceite to optimize the crystal structure.

This tutorial covers:

- [Getting started](#)
- [To optimize the crystal structure](#)
- [To examine the torsion angle](#)
- [To work with the non-bond terms](#)
- [To modify the van der Waals terms](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ff_edit** as the project name, click the **OK** button.

The new project is created with *ff_edit* listed in the Project Explorer. The next step is to load the crystal structure that you want to work with - the explosive TATNBZ.

Open the **Import Document** dialog and navigate to **Examples\Documents\3D Model** and double-click on **TATNBZ.xsd**. Rename the structure **TATNBZ_crystal.xsd**.

2. To optimize the crystal structure

You will perform all the editing work on the isolated molecule before applying the modified forcefield to the crystal structure to verify your changes. You should make a copy of the isolated molecule.

In the **Project Explorer**, right-click on the project root and select **New | 3D Atomistic** from the shortcut menu.

In **TATNBZ_crystal.xsd**, click on an atom in one of the molecules, right-click and choose **Select Fragment**. Press **CTRL + C**. Change to the new atomistic document and press **CTRL + V**. In the **Project Explorer**, rename the new atomistic document to **TATNBZ_molecule.xsd**.

If you examine the crystal structure you should see that the nitro groups are in the plane of the benzene ring. You will now optimize the structure with the standard Dreiding forcefield using Forcite.

Ensure that **TATNBZ_crystal.xsd** is the active document. Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** from the dropdown list to open the Forcite Calculation dialog.

Change the **Task** to **Geometry Optimization**. On the **Energy** tab, change the **Forcefield** to **Dreiding** and change the **Charges** to **Charge using Gasteiger**.

You could use a more complex charging method such as applying ESP charges using DMol³, but the Gasteiger charges will be suitable for development of a customized forcefield.

Click the **Run** button. When the job completes, open the optimized **TATNBZ_crystal.xsd**.

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You should see that the nitro groups are no longer in plane with the benzene ring. The off-plane nature of the nitro groups of the optimized structure can affect the way these molecules pack together in a crystal, so obtaining a planar nitro group is important.

There is a single torsion between the nitro group and the benzene ring which will control the planarity of the group. Modifying the parameters that control this torsion this will be the focus of this tutorial.

3. To examine the torsion angle

Now that you have identified the torsion angle that you want to change, you can begin to look in more detail at the energy profile for that torsion angle. A Conformers calculation will give you the energy profile by calculating single point energies as the torsion is rotated through 360°.

Right-click in **TATNBZ_molecule.xsd** and select **Label** from the shortcut menu to open the Label dialog. Ensure the **Object type** is set to **Atom** and choose **Name** from the **Properties** list. Click the **Apply** button.

Use the **Measure/Change** tool to define a torsion on the nitro group for the atom sequence **O5-N5-C5-C4**.

On the **Label** dialog, click the **Remove** button and close the dialog.

You will use the Conformers module to systematically rotate the torsion and calculate the energy at each point.

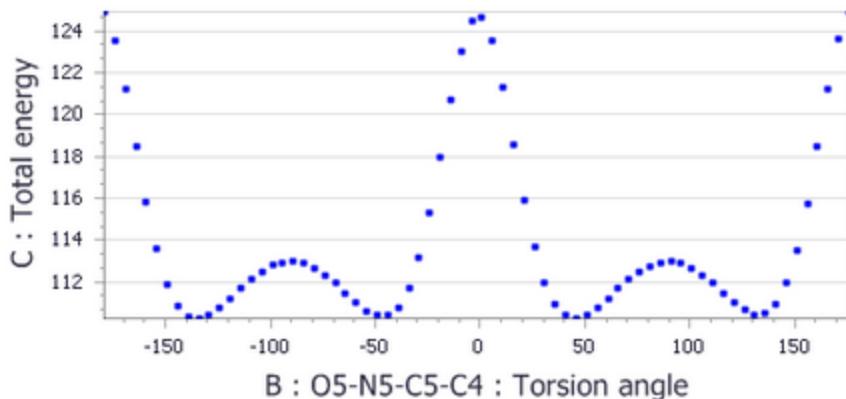
Click the **Conformers** button  on the **Modules** toolbar and select **Calculation** from the dropdown list to open the Conformers Calculation dialog. Click the **Torsions...** button to open the Conformers Torsions dialog.

Change the **# Steps** to **72** and close the dialog.

On the **Energy** tab, change the **Forcefield** to **Dreiding** and select **Charge using Gasteiger** from the **Charges** dropdown list. Click the **Run** button and close the dialog.

When the calculation completes, you can plot the torsion-energy to see the energy profile.

Select columns **B** and **C** in the study table and click the **Quick Plot** button . Rename the chart document **Dreiding_Original.xcd**.



Torsion-Energy plot for the nitro-benzene torsion angle calculated by Dreiding

You can see from the torsion-energy plot that there are large maxima at 0° and 180° giving a barrier to rotation of about 14 kcal mol⁻¹. From examining the crystal structure, you would expect there to be energy minima at 0° and 180° not maxima as shown by the torsion-energy plot.

You could also compare this potential energy surface with that predicted by DMol³. As you already have a study table containing the conformers, you can use the DMol³ Model to calculate the energy for each conformer.

Note: As this calculation requires accurate energies, you will use fine settings and this calculation is likely to take more than one hour. A study table with the calculated results has been provided in the Examples\StudyTables folder. If you wish to use this instead, please skip the next two steps.

In the study table, select column A. Click the **Models** button  to open the Models dialog. Locate the **DMol³ Molecular Energy** model and double-click to edit it.

For this calculation, you need accurate energies. So you should use a good functional and a fine convergence level.

On the **Inputs** tab of the **Model Editor - DMol3 Molecular** dialog, change the **Functional** to **BLYP** and the **Quality level** to **Fine**. Click the **Save** button and close the dialog. Click the **Run** button on the Models dialog.

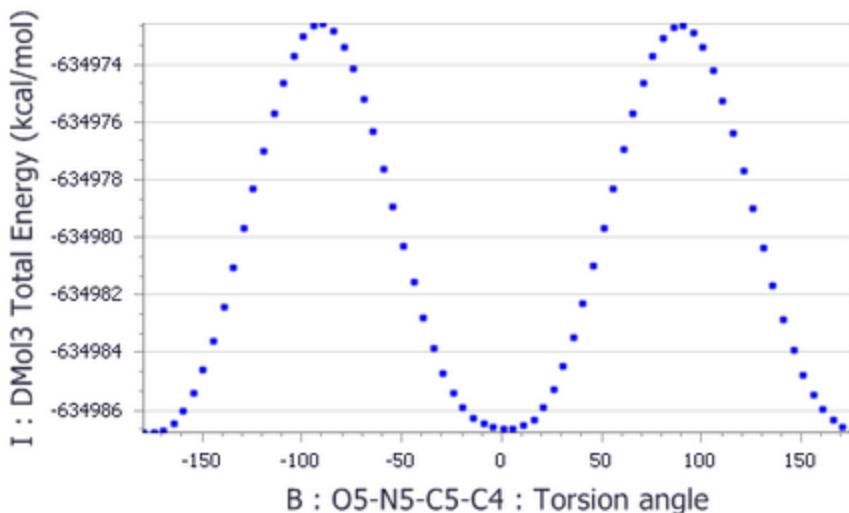
The Fine quality level not only changes the SCF convergence criteria but other settings such as the basis set. This calculation will take some time to complete and you are recommended to run it remotely or overnight. You must wait for the calculation to complete before moving to the next step or import the example study table.

Open the study table, or import the example study table from **Examples\StudyTables\TATNBZ_conformers.std**.

You will see that the Total Energy (DMol3 Molecular) is in Hartree so you need to convert this to kcal mol⁻¹ (1 Hartree = 627.51 kcal mol⁻¹). Assuming that the Total Energy column is in column D, you need to define a function of D×627.51. Once converted, you should plot the energies as you did for the original conformers plot.

Click the **Define Function** button  to open the Define Function dialog. In the **Expression** text area, type **D*627.51**. Enter **DMol3 Total Energy (kcal/mol)** as the **Name** and click the **OK** button. Select the column containing the torsions, and the newly created column and click the **Quick Plot** button.

Note: The absolute energies will be very high as they are not optimized with DMol³. However, you are only interested in the relative barrier height, not the absolute energies.



Dihedral-energy plot of the DMol³ single point energies

From the chart, you should see that the barrier height is approximately 14 kcal mol⁻¹. Later in the tutorial, you will try to get the same approximate barrier height from the forcefield calculations.

Now that you have the energy profile predicted by Conformers and DMol³, you can compare this with the torsional term in Dreiding. The Forcefield Manager is used to create an editable copy of a standard forcefield.

Click the **Forcite** button  on the **Modules** toolbar and select **Forcefield Manager** from the dropdown list. In the **Standard Forcefields** section, select **Dreiding**. Click the **>>** button. Close the dialog.

A copy of the Dreiding forcefield is made in the project and the **Dreiding.off** forcefield is opened for you to edit. The forcefield document consists of four tabs:

Summary - contains summary text describing the forcefield.

Types - contains the forcefield types and properties associated with them.

Interactions - contains the main interactions such as valence and non-bond terms.

Equivalences - contains the definitions of the equivalences for the interactions.

Before editing the forcefield, you can change the name of the forcefield document.

In the **Project Explorer**, change the name of the forcefield document to **Dreiding_new.off**.

You are now ready to explore the forcefield document.

In **Dreiding_new.off**, select the **Types** tab.

This contains the forcefield types available in Dreiding, a description of the type, element, and van der Waals parameters for each forcefield type. The display of other properties can be switched on using the checkboxes on the Forcefield Type Properties dialog, for example hybridization, charge, and hydrogen bond.

There are many forcefield types describing the different local environments for each element, with some elements having more than one forcefield type. Scrolling through all of these would be tedious so you can filter those displayed by their forcefield type. Filter boxes are displayed in yellow in the forcefield document.

In the yellow **Type Filter** box, type **C_*** and press **ENTER**.

Only the atom types associated with the carbon atoms are now displayed in the Types dialog.

Change the **Type Filter** back to *****.

You can also filter by the forcefield types present in a 3D Model document.

Check **Filter by selection in** and select **TATNBZ_molecule.xsd** from the dropdown list.

You will see a warning dialog. This is because there are no forcefield types assigned to the atoms in the molecule. You can assign forcefield types using the Forcite Calculation dialog.

Open the **Forcite Calculation** dialog. On the **Energy** tab, click the **More...** button associated with **Forcefield** to open the Forcite Preparation Options dialog. Uncheck **Calculate automatically** for **Forcefield types** and change focus to **TATNBZ_molecule.xsd**. Click the **Calculate** button. Check **Calculate automatically** again. Close both Forcite dialogs.

This calculates the forcefield types on the atoms in **TATNBZ_molecule**. You need to refresh the forcefield types in the forcefield document.

Change focus back to **Dreiding_new.off**. Reselect **TATNBZ_molecule.xsd**.

You should now see the four forcefield types that represent the atoms in the document and a dummy forcefield type.

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Type	Description	Element Symbol	van der Waals Form
C_R	carbon, aromatic	C	LJ_12_6
H_A	hydrogen, involved in hydrogen bonding	H	LJ_12_6
N_R	nitrogen, aromatic	N	LJ_12_6
O_2	oxygen, sp2	O	LJ_12_6
X	Dummy forcefield type	X	Ignore

Dreiding_new forcefield document showing forcefield type information

You are interested in the torsion angle between the aromatic carbon, C_R and aromatic nitrogen, N_R.

Change to the **Interactions** tab. Change the **Show interaction to Torsion**.

There are six different combinations of the torsion terms. You can change the *Functional Form* filter to view the different options.

Click the **Functional Form** filter and select **Dihedral**.

The value of the parameters used in the Dihedral functional form describing the torsion are displayed. The parameters are all documented in the online help.

Select one of the displayed rows and press **F1**.

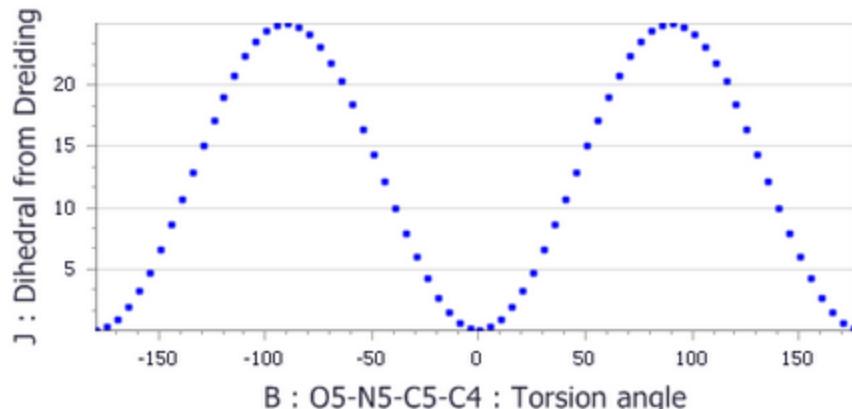
The help is displayed showing the different functional forms. The functional form for the Dihedral Torsion is:

$$E = \frac{1}{2} \sum_j B_j (1 - d_j \cos[n_j \phi])$$

You can use the Conformers study table that you generated earlier to plot the variation of the pure torsional term and compare the functional form for the whole energy expression derived from Conformers and DMol³. For the forcefield interaction, you will replace B_j in the above equation with 25, d with 1 and n_j with 2. You will use the value of the angle from column B in the study table, converted to radians.

Change focus to **TATNBZ_conformers.std** and open the **Define Function** dialog. In the **Expression** text area, type **(25*(1-1*cos(2*B*0.0174532925)))/2**. Set the **Name** to **Dihedral from Dreiding** and click the **OK** button. Select columns **B** and **J** and click the **Quick Plot** button.

The chart generated should match the one below, showing minima and maxima that correspond to the DMol³ plot but with a higher energy barrier than expected.



Dihedral-energy plot using the pure dihedral contribution from the forcefield editor for X_C_R_N_R_X torsion.

From the above plot, you can see that the dihedral torsion looks reasonable. This suggests that the problem must lie somewhere else. In the next section, you will look at exploring the non-bonded terms to see how they affect torsion energy.

4. To work with the non-bond terms

From the previous calculations, you observed that the energy contribution for the pure dihedral differed significantly from that of the observed energy change on rotation of the torsion. You can use the forcefield editor to switch off contributions from the different types of interaction in a system to see the effect they have. As you are only changing a terminal torsion angle, the contributions that change, apart from the energy of the torsion itself, are the non-bond energies. Therefore, you will switch off the non-bond energies to see what effect they have on the torsion-energy plot.

As it is likely that the oxygen atom of the nitro group is strongly hydrogen bonded to the adjacent amine, it makes sense to disable the hydrogen bond term first.

Change to **Dreiding_new.off**. On the **Interactions** tab, click the **More...** button.

This opens the Forcefield Preferences dialog where you can set general preferences for the forcefield.

Uncheck the **Hydrogen Bond** checkbox in the Interactions list.

Tip: You do not need to save the forcefield document before you use it with modules such as Conformers or Forcite. You are advised to save it if you are making lots of changes.

You now need to run another Conformers calculation with the new forcefield to see the effect of switching off the hydrogen bond interactions.

Open **TATNBZ_molecule.xsd** in the project root. Open the **Conformers Calculation** dialog and select the **Energy** tab. Select **Browse...** from the **Forcefield** dropdown list to open the **Choose Forcefield** dialog. Select **Dreiding_new.off** and ensure that **Charges** is set to **Charge using Gasteiger**.

In the *Forcefield* box, you will now see \Dreiding_new. The back slash indicates that the forcefield has been selected from the project and is not a standard forcefield.

Note: This forcefield will be transferred to the server when the calculation is run and will be returned in the new job results folder.

On the **Conformers Calculation** dialog, click the **Run** button.

When the job has completed, open **TATNBZ_molecule.std** and generate a plot of columns **B** and **C**. Compare this with **Dreiding_Original.xcd**.

You should see that disabling the hydrogen bond interaction has little effect on the torsion-energy plot. Next, try disabling the electrostatic interactions.

Change to **Dreiding_new.off**. On the **Forcefield Preferences** dialog, uncheck the **Electrostatic** checkbox in the Interactions list. Change the focus back to **TATNBZ_molecule.xsd** in the project root. Open the **Conformers Calculation** dialog, and change to the **Energy** tab.

Your edited version of Dreiding is still the chosen forcefield so you can just run the calculation.

Run the Conformers calculation. When the job has completed, plot the torsion and energy and compare with **Dreiding_Original.xcd**.

You should see that the low energy maxima have decreased in height compared with having electrostatics switched on. You should also see that the overall energy has increased by a few kcal mol⁻¹. Finally, you should switch off the van der Waals interactions to see the effect.

Change to **Dreiding_new.off** and uncheck the **van der Waals** checkbox in the Interactions list on the Forcefield Preferences dialog. **Run** the Conformers calculation on **TATNBZ_molecule.xsd**. In the output study table, plot the torsion and energy and compare with **Dreiding_Original.xcd**.

When you switch off the van der Waals terms, you should see a major effect on the energy torsion-energy plot. The profile should closely resemble the plot you generated from the Dihedral interaction. This shows that the van der Waals terms are playing a major part in the energy profile of this torsion angle. Modifying the van der Waals terms will be the focus of the next section.

Change to **Dreiding_new.off**. Check the **van der Waals**, **Hydrogen Bond**, and **Electrostatic** checkboxes in the Interaction list and close the **Forcefield Preferences** dialog.

The change on removing the van der Waals potential is related to the close distance between the oxygen atoms on the nitro groups and the hydrogen atoms on the amine groups. By modifying the van der Waals term to have a shorter equilibrium distance, and so less repulsive at shorter distances, you should see that the Conformers plot begins to match more closely that predicted by DMol³.

Change focus to **TATNBZ_molecule.xsd** in the project root. Use the **Measure/Change** tool to add a **Distance** monitor between an oxygen atom and the adjacent hydrogen atom.

The distance should be about 1.8 Å. You will use this information when modifying the van der Waals terms in the next section.

5. To modify the van der Waals terms

The van der Waals terms in Dreiding are generated automatically based on combinations of parameters for each forcefield type. As the parameters are stored on each forcefield type, they are displayed in the

forcefield document on the **Types** tab. You can also add your own specific custom van der Waals terms for pairs of atoms and these will be used instead of automatically calculated terms.

On **Dreiding_new.off**, change to the **Types** tab. Click the yellow filter box for **van der Waals Form** and select **LJ_12_6**.

Note: You will notice that you can either choose to show the functional form or to *Ignore* the interaction. If you choose *Ignore*, the interaction is not calculated in the energy expression. Choosing *Ignore* for the *van der Waals* forcefield type would ignore all van der Waals interactions that contain that type. Although this may seem drastic for this example, ignore can be useful if you want to switch off individual interactions.

You can set either a functional form or choose to ignore the van der Waals parameters. Dreiding uses a simple Lennard-Jones 12-6 form for calculating the van der Waals parameters where D0 is the well-depth and R0 is the equilibrium distance.

Note down the values of D0 and R0 for both H_A and O_2.

You should see that the well depth for H_A is very shallow compared with that of O_2. The combination of parameters is usually calculated using an arithmetic mean. However, as the well depth for hydrogen is very small, in this case a geometric combination of the well depth parameter gives a better representation of the van der Waals interaction.

The geometric mean is calculated as the square root of the product of well-depths and is equal to 0.0031 for H_A and O_2.

Change to the **Interactions** tab. Change the **Show interaction to van der Waals**. Change the **Functional Form** to **LJ_12_6**.

You will note that there are no specific van der Waals terms defined for Dreiding. To introduce a specific van der Waals term the forcefield type sequence must be specified first.

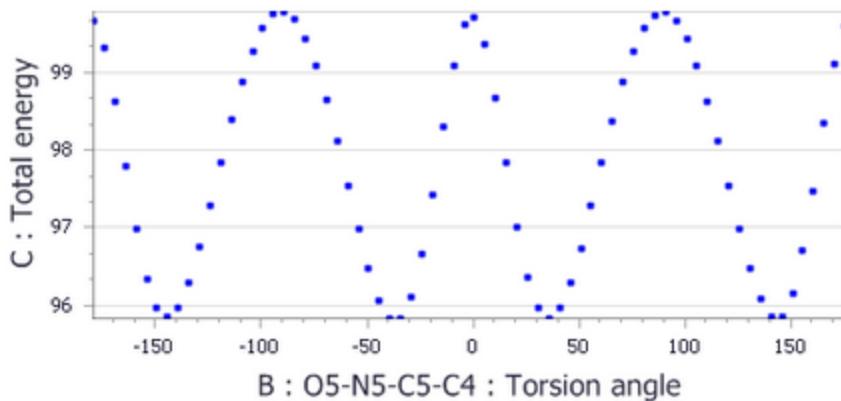
Click in the **Fi** box for the first empty row and choose **H_A** from the dropdown list. Click in the **Fj** box and choose **O_2** from the dropdown list. Click in the **Functional Form** box and choose **LJ_12_6**. Set the value of **D0** to **0.0031**.

For this test, you should leave the R0 calculated using the arithmetic mean. This gives a value of 3.29.

Set the value of **R0** to **3.29**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd** in the project root. Generate the torsion-energy plot.

You should see that the height of the minima has changed by about 0.5 kcal mol⁻¹ but has not had a large overall effect on the plot. The other way to change the functional form is to decrease the value of the equilibrium distance. Previously, you calculated the distance from an oxygen to hydrogen atom in the molecule. This was about 1.8 Å compared with a R0 of 3.29 Å. This suggests that the repulsive part of the van der Waals potential is making a significant contribution to the torsional potential. To rectify this you should decrease the value of R0. Although it is tempting to set the equilibrium value to that of the distance measured, this could overfit the interaction which may lead to changes in the overall structure. In reality, choosing the right number can involve some guesswork but it is better to start higher and decrease, running multiple Conformers calculations. For the purposes of this tutorial, an R0 of 2.7 Å is used.

On **Dreiding_new.off**, change the value of **R0** to **2.7**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.



Dihedral-energy plot for the adjusted van der Waals parameters from the forcefield editor for X C_R N_R X torsion.

The plot shows that changing the equilibrium position has a significant effect on the energy profile of the torsion angle with the maximum at 0 and 180 degrees decreased substantially in energy. However, the overall energy barriers are now significantly lower than those predicted in the DMol³ calculations previously. To compensate for this, you should increase the torsion energy barrier.

On **Dreiding_new.off**, change the **Show Interaction** to **Torsion** and the **Functional Form** filter to **Dihedral**. Change the **X N_R C_R X** value of **B** to **50**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.

You see that the new torsion-energy plot is now similar to that predicted by the ab-initio calculations with torsion barriers of a similar magnitude and in the same locations. There are still two low energy minima either side of 0 and 180 degrees and these will cause distortion of the structure. However, changing the values of the H_A O_2 van der Waals interaction will no longer have much effect.

This suggests that the small repulsion terms must be caused by another atom interacting with the oxygen on the nitro group.

Change focus to **TATNBZ_molecule.xsd** in the project root. Add a **Distance** monitor between an oxygen atom and the nearest nitrogen on an amine group.

The distance should be around 2.5 Å. As with the oxygen-hydrogen interaction, this is smaller than the equilibrium distance in the forcefield. The distance means the van der Waals repulsions will be large and this could be causing the small maxima in the potential energy surface.

Change focus back to **Dreiding_new.off**. Change to the **Types** tab and note down the **D0** and **R0** values for **N_R** and **O_2**.

As with the hydrogen and oxygen van der Waals terms, you will calculate the new D0 term using a geometric mean and set the R0 to 2.7 Å.

Change to the **Interactions** tab and show only **van der Waals** interactions. Click the yellow filter box for **Functional Form** and select **LJ_12_6**. Click in the empty **Fi** box and choose **N_R**. Click in the empty **Fj** box and choose **O_2**. Click in the **Functional Form** box and choose **LJ_12_6**. Set the value of **D0** to **0.086** and the value of **R0** to **2.7**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.

There should be no extra minima present and the shape of the chart should look similar to that of the DMol³ generated plot previously with slightly flatter minima. However, as you have changed the functional form of the van der Waals parameters for oxygen and nitrogen, the energy barrier for the dihedral is now too high. From the DMol³ calculation, you want this to be approximately 14 kcal mol⁻¹.

Change focus back to **Dreiding_new.off**. On the **Interactions** tab, select the **Torsion** interaction. On the **Functional Form**, select **Dihedral**. Change the value of **B** for **X N_R C_R X** to **35**. Run the **Conformers** calculation on **TATNBZ_molecule.xsd**. Generate the torsion-energy plot.

This should give an energy barrier of about 14 kcal mol⁻¹. You could continue to tweak the parameters to improve the forcefield further but this should be good enough to test with the crystal structure.

Open the original **TATNBZ_crystal.xsd**. Open the **Forcite Calculation** dialog. Change to the **Energy** tab and choose **\Dreiding_new.off** as the forcefield. Click the **Run** button.

When the calculation completes, you should see that the nitro groups are nearly aligned in the plane of the benzene rings as they are in the crystal structure.

From here, you could run a Polymorph Prediction calculation with the new forcefield.

This is the end of this tutorial.

Calculating the diffusivity of a gas in a polymer

Purpose: Introduces the use of forcefield methods to calculate the diffusion coefficient of a gas in a dense material.

Modules: Materials Visualizer, Forcite Plus, Amorphous Cell, COMPASS, optionally Pipeline Pilot Connector

Time: 

Prerequisites: Using the polymer builder Visualizer Tutorial

Background

The diffusivity of a gas in an organic solvent, polymer, or zeolite can be calculated by running a molecular dynamics simulation and determining the mean square displacement of the gas in the material. This allows you to calculate the self-diffusivity coefficient of the gas and gives an insight into the overall diffusivity. As you are performing a molecular dynamics calculation, you can analyze the effect of temperature, pressure, density, and the size and structure of the penetrant on diffusion.

Introduction

In this tutorial, you will calculate the diffusivity of methane in poly(cis-1,4-butadiene) (PBD) by constructing an amorphous cell containing methane and PBD. After you have constructed the cell, you will perform a molecular dynamics simulation and calculate the mean square displacement of the methane molecule. Although the tutorial will only demonstrate a short calculation, you will become familiar with the methodology involved. Optionally, you could run the entire workflow through a Pipeline Pilot protocol. The tutorial is based on a paper published by Meunier (2005), which examined the diffusion of gases in diene polymers.

This tutorial covers:

- [Getting started](#)
- [To set up the initial structures](#)
- [To build an amorphous cell](#)
- [To relax the cell](#)
- [To run and analyze molecular dynamics](#)
- [To run the entire workflow in Pipeline Pilot](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **gas_polymer** as the project name, click the **OK** button.

The new project is created with *gas_polymer* listed in the Project Explorer.

2. To set up the initial structures

The first stage is to build and optimize a methane molecule and the PBD polymer so that you can construct your amorphous cell. To make it easier to select the methane molecules later, use a different display style.

Use the **Homopolymer** building tools to create a **20** repeat unit polymer of **c_butadiene** from the **dienes** library.

Create a new **3D Atomistic Document** and sketch a methane molecule. Change the **Display style** for atoms to **CPK**. Rename the new document **methane**.

Tip: Do *not* import methane from the Example structures library. The example does not have the structure defined as a Molecule in the document hierarchy, this will cause issues later when you attempt to select all methane molecules.

In this tutorial you will use charge groups in the calculation of the electrostatic and van der Waals interactions. Charge groups are small atomic fragments that have a net charge of zero. This means that the electrostatic interactions between two groups can be evaluated with a straightforward distance-based cutoff, avoiding the computationally more expensive Ewald method.

If need be, charge groups can be set up by hand, but automatically assigned charge groups are usually satisfactory. First, configure Forcite to use charge groups instead of the default summation methods for non-bond calculations.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog. On the **Energy** tab select **COMPASSIII** from the **Forcefield** dropdown list. Set both the **Electrostatic** and **van der Waals** summation methods to **Group based**.

Click the **More...** button for **Forcefield** to open the Forcite Preparation Options dialog. Ensure that the **Charges** are set to **Forcefield assigned** and that **Calculate automatically** is checked for both **Forcefield types** and **Charge groups**. Close the dialog.

Before building the amorphous cell, you will optimize the geometry of both molecules.

On the **Setup** tab of the Forcite Calculation dialog, select **Geometry Optimization** from the **Task** dropdown list. Change the **Max. iterations** to **2000**.

Now optimize the methane molecule.

Make **methane.xsd** the active document and click the **Run** button on the Forcite calculation dialog.

A new folder, **methane Forcite GeomOpt**, is created in the Project Explorer. When the calculation is complete, the minimized structure is stored in the new folder. Continue the minimization with the polymer.

Make **Polyc_butadiene.xsd** the active document and click the **Run** button. Close the Forcite Calculation dialog.

The same process is repeated and the minimized structure is returned to **Polyc_butadiene Forcite GeomOpt\Polyc_butadiene.xsd**.

You can now inspect the charge groups assigned automatically by the calculation.

Forcite Plus: Calculating the diffusivity of a gas in a polymer

Make **Polyc_butadiene Forcite GeomOpt\Polyc_butadiene.xsd** the active document. Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Change the **Color by** option to **Charge Group**. When verified, change the **Color by** option back to **Element**. Repeat for **methane Forcite GeomOpt\methane.xsd** and close the dialog.

Note: The torsion degrees of freedom in the polymer will be modified by Amorphous Cell. These will be optimized later, after the cell is constructed.

Before proceeding with the amorphous cell construction, clear the workspace.

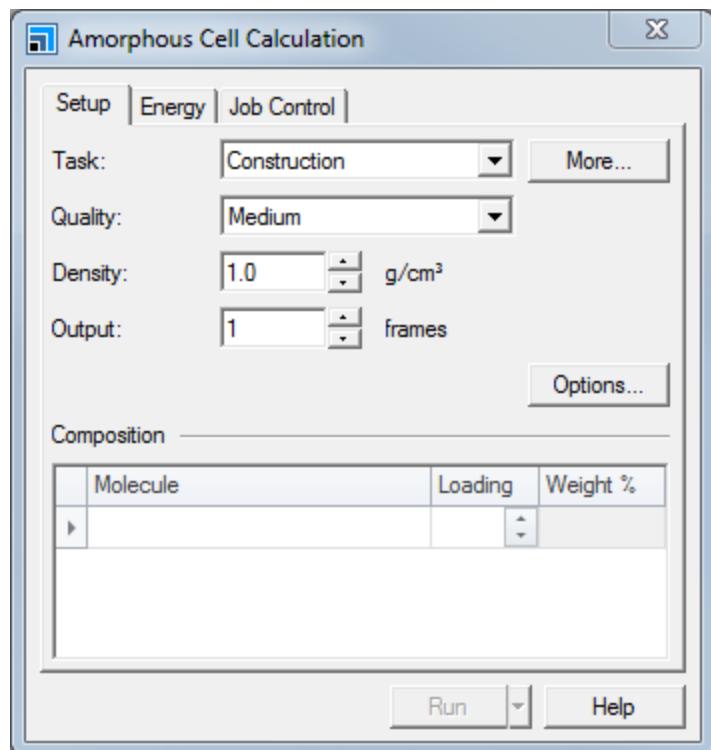
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To build an amorphous cell

Once you have prepared the two structures, you can build multiple copies of them in a cell using the Amorphous Cell module.

Click the **Amorphous Cell** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the Amorphous Cell Calculation dialog.



Amorphous Cell Calculation dialog, Setup tab

The first step is to define the composition in terms of number of molecules of each component. You want the cell to contain four molecules of methane and ten of PBD at a density of 0.89 g/cm^3 .

Set the **Density** to **0.89 g/cm³**.

In the **Molecule** column of the Composition grid select the document **methane Forcite GeomOpt\methane.xsd** containing the optimized structure of methane. In the **Loading** column enter **4**.

In the next row select **Polyc_butadiene Forcite GeomOpt\Polyc_butadiene.xsd** and a loading of **10**.

The estimated extensions of the cell are displayed at the bottom of the dialog, based on the loadings and the density. In this case a cube with cell lengths of about 27 Å will be constructed. Orthorhombic and tetragonal lattice types are also available, but are not used in the tutorial.

Amorphous Cell can optimize the structure as part of the construction. In this case you will optimize and equilibrate separately using Forcite and not use this feature.

Click the **Options...** button to open the Amorphous Cell Options dialog. Uncheck the **Optimize geometry** checkbox. Close the dialog.

Now select the same forcefield as used in Forcite.

On the **Energy** tab of the Amorphous Cell Calculation dialog select **COMPASSIII** from the **Forcefield** dropdown list.

The default job description in Amorphous Cell corresponds to the name of the first component, in this case **methane**, which is used as seedname in all output documents. In this tutorial you will change the default to **cell**.

On the **Job Control** tab uncheck the **Automatic** checkbox and enter **cell** into the text field. Click on the **gas_polymer** tree root in the Project Explorer and click the **Run** button. Close the dialog.

A new folder, **cell AC Construct**, is created and displayed in the Project Explorer. When the calculation is complete, a trajectory document, **cell.xtd**, is produced containing the amorphous cell.

Note: If you construct multiple frames, they are all stored in the **.xtd** document. They can be viewed and accessed using the Animation toolbar.

Double-click on **cell.xtd**.

The document contains a periodic cell with ten PBD oligomers and four methane molecules.

In the following steps it is most convenient to work with the model in a structure document (**.xsd**) rather than a trajectory document (**.xtd**). so you should make a copy of the structure in a new 3D Atomistic document.

Right-click in the trajectory document and select **Copy** to copy everything.

Select **File | New...** from the menu bar and choose **3D Atomistic** document and click the **OK** button. Right-click in the new document and select **Paste** to paste the copied structure. **Rename** the new document to **cell**.

Before performing the relaxation, clear the work area.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

4. To relax the cell

When you generate an amorphous cell, the molecules may not be equally distributed throughout the cell, creating areas of low density. To correct this, you must perform a short energy minimization to optimize the cell. After the minimization, you should run a short molecular dynamics simulation to equilibrate the cell. This procedure of minimization and molecular dynamics is known as relaxing the structure and should be carried out whenever you construct an amorphous cell.

To perform the geometry optimization, you must first configure Forcite to use charge groups for 3D periodic structures.

Re-open the newly created structure document **cell.xsd**. Open the **Forcite Calculation** dialog and select the **Energy** tab. Change both **Electrostatic** and **van der Waals** summation methods to **Group Based**.

Note: Forcite has separate settings for nonperiodic and periodic structures. The dialog always shows the settings corresponding to the periodicity of the active document, defaulting to nonperiodic.

Now you are ready to minimize the total energy of the cell.

On the Forcite calculation dialog, click the **Run** button.

When the job is complete, the final structure is stored in the folder **cell Forcite GeomOpt**. You will continue relaxing the structure by running molecular dynamics on it with a periodically changing temperature, also known as annealing the system. For the purpose of this tutorial you will just run one anneal cycle.

On the **Setup** tab of the Forcite Calculation dialog, select **Anneal** from the **Task** dropdown list and click the **More...** button to open the Forcite Anneal Dynamics dialog.

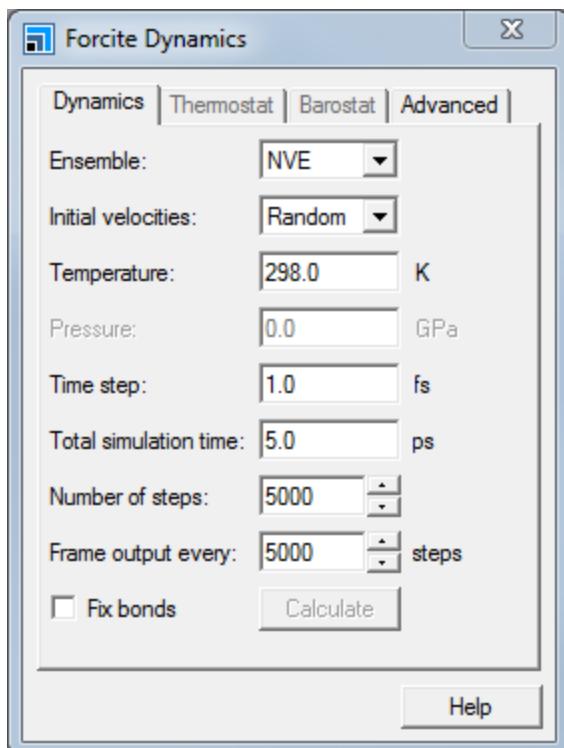
Set the number of **Annealing cycles** to **1**, the **Initial temperature** to **300 K**, and the **Mid-cycle temperature** to **500 K**. Close the dialog.

Now perform an anneal calculation on the optimized structure.

Make **cell.xsd** in the **cell Forcite GeomOpt** subfolder the active document. Click the **Run** button on the Forcite Calculation dialog.

The anneal task produces various output documents. The final structure after the last change of temperature is contained in the structure document **cell1.xsd** in the folder **cell Forcite Anneal**. You will proceed by running a short molecular dynamics simulation on this structure, now at constant temperature.

Make **cell.xsd** in the **cell Forcite Anneal** subfolder the active document. On the **Setup** tab of the Forcite Calculation dialog, select **Dynamics** from the **Task** dropdown list and click the **More...** button to open the Forcite Dynamics dialog.



Forcite Dynamics dialog, Dynamics tab

There are different types of molecular dynamics simulations available, classified by the ensemble names, **NVE**, **NVT**, **NPT**, and **NPH**. The letters refer to:

N = constant number of molecules

V = constant volume

E = constant energy

T = constant temperature

P = constant pressure

H = constant enthalpy

Note: The NPT ensemble should be used if the density (and hence the volume) chosen at construction needs adjusting to the outside pressure (usually atmospheric pressure); if the system has been build at a reasonable density, NVT can be used and the pressure should average to 1 atm or 0.0001 GPa.

You constructed the cell at a density of 0.89 g/cm³. Since this is also the average density of this system at 300 K and 1 atm, with the selected forcefield ([2005](#)), it is not necessary to relax the density further using NPT. Instead you can proceed using **NVT** dynamics.

Select **NVT** from the **Ensemble** dropdown list and change the **Temperature** to **300**.

For the purpose of this tutorial you will reduce the number of steps to **2000**. For such a short run the **Velocity Scale** thermostat is more suitable than the default.

Change the **Number of steps** to **2000**. On the **Thermostat** tab select **Velocity Scale** as the thermostat. Click the **Run** button on the Forcite Calculation dialog.

Forcite Plus: Calculating the diffusivity of a gas in a polymer

Note: In a realistic simulation, you would probably need to run at least 50000 steps (50 ps) to equilibrate the cell correctly. You can monitor the equilibration progress by looking up the energies in the live update chart, which should be constant apart from small fluctuations.

When the simulation completes a number of documents are returned. The final structure is contained in the structure document **cell.xsd** in the folder **cell Forcite Dynamics**.

Now clean up your workspace area again.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

5. To run and analyze molecular dynamics

When you equilibrated the system, you were only interested in the final structure. However, to calculate the mean square displacement of the methane molecules in the cell, you need to have many frames so that you can analyze where the methane molecules are moving. You will run another molecular dynamics simulation and generate a trajectory document which you can analyze using the Forcite Analysis tool.

To avoid too many subfolders, first move the working document to the top of the folder tree.

In the Project Explorer, double-click on **cell.xsd** in the **cell Forcite Dynamics** folder. In the Project Explorer **drag** this file to the top of the **gas_polymer** folder tree.

Previously, you ran dynamics at constant temperature (NVT), however for the production run, you will continue the simulation at constant energy (NVE). This is because some thermostats can interfere with the dynamics of the system, and potentially affect the diffusion coefficient that you will calculate later on. In order to collect enough data for the analysis, you should increase the number of steps and reduce the frame output interval. For the purpose of this tutorial you will just perform **5000** steps.

On the Dynamics tab of the Forcite Dynamics dialog select **NVE** from the **Ensemble** dropdown list. Change the **Number of steps** to **5000** and the **Frame output every** to **250**. Close the Forcite Dynamics dialog.

On the Forcite Calculation dialog click the **Run** button and close the dialog.

Tip: For a real production run you should increase the number of steps so that the simulation time is at least 50 ps.

As the calculation progresses, two chart documents are updated. One plots the total energy and various components with time and the other plots the temperature. As this is an NVE ensemble calculation, the total energy should be constant. There will be exchange of kinetic and potential energy, but provided the equilibration was long enough, there should be no net exchange. Likewise in an equilibrated system, the temperature will fluctuate around an average value of 300 K without systematic change.

When the calculation finishes, a trajectory **cell.xtd** containing 21 frames is returned on which the analysis will be performed.

Make **cell.xtd** the active document. Click the **Play** button  on the **Animation** toolbar. When you have finished watching the animation, click the **Stop** button .

To calculate the mean square displacement of the methane molecules, you need to distinguish them from the polymer molecules. This can be achieved by defining them as a set.

To select all the methane molecules, hold down **CTRL** and **double-click** on each molecule in turn.

Tip: To automatically select all molecules of a kind you can use the Find Patterns tool.

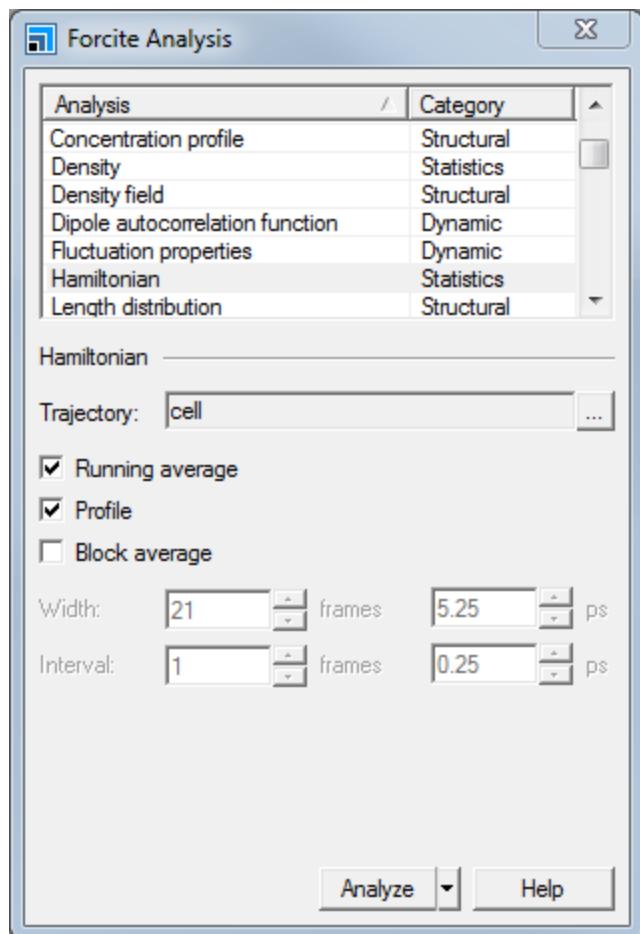
Now you can use the Edit Sets tool to create a set of the selected atoms.

Select **Edit | Edit Sets** from the menu bar to open the Edit Sets dialog. Click the **New...** button, enter the name **methane**, and click the **OK** button. Close the Edit Sets dialog. Click anywhere in the trajectory document to undo the selection.

Now that you have defined the methane molecules as a set, you can analyze their movement.

Click the **Forcite** button  on the **Modules** toolbar and select **Analysis** from the dropdown list.

This opens the Forcite Analysis dialog.



Forcite Analysis dialog

There are many different types of analysis that you can perform with Forcite and they are split into three categories; *Structural*, *Statistics*, and *Dynamic*. Mean square displacement is in the *Dynamic* section.

Select **Mean square displacement** from the list. Select **methane** from the **Sets** dropdown list and set the **Length** to **21**.

Click the **Analyze** button and close the dialog.

Note: Since the statistical accuracy of the MSD data decreases with the length of the time interval, by default the MSD is not calculated beyond half the number of frames.

The Forcite Analysis tool calculates the mean square displacement and generates a chart document, **cell Forcite MSD.xcd**, which contains a plot of the mean square displacement (MSD) of the methane molecules with time. A study table, **cell Forcite MSD.std**, is also produced. The value of the MSD for a given time reported in the chart is the average over all time intervals of that length and over all atoms in the set.

The mean square displacement typically has two regions. At short times the gas molecule collides inside a small pocket of free volume. Since the molecule is confined it does not diffuse on this time scale and the MSD levels off to a constant. On a longer time scale the molecule jumps out of the confined area to another pocket of free volume. The resulting motion of repeated jumps is diffusion, characterized by a mean square displacement that is linear in time. In practice, the statistics decreases with the time interval, often resulting in large fluctuations at the end.

The increase of MSD with time is related to the diffusion coefficient D :

$$D = \frac{1}{6N_\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$$

where N_α is the number of diffusive atoms in the system. The MSD in Forcite automatically calculates this quantity when generating the MSD data and lists the diffusion coefficient in the title of the chart document, **cell Forcite MSD.xcd**, as well as printing it in the Summary sheet of the study table **cell Forcite MSD.std**.

The diffusion coefficient is calculated in units of $\text{\AA}^2/\text{ps}$. To convert to the more commonly used unit cm^2/s , the resulting value must be divided by $1\text{e}4$.

Calculated values for the diffusion of methane in PBD have been reported in the range between $2.25 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ([Meunier, 2005](#)). This was obtained using ten chains of PBD polymer chains with 30 repeat units and four molecules of methane in an amorphous cell. The cell was equilibrated using a temperature cycle annealing method. Several cycles of NPT dynamics were performed with heating and cooling between 400 and 250 K (in 25 K steps), over 5 - 10 ps. Following equilibration NVT dynamics at simulation temperatures of 250 to 400 K in 25 K increments were performed over 3 ns. Using mean square displacement analysis the diffusion coefficient was obtained as a function of temperature.

Your calculated value may be very different to the reported values, since the run length was very short with limited statistics in the diffusive region. In practice, you should run longer simulations and also average over several molecular dynamics simulations started from independently generated structures to give an estimate of the precision of your calculation. The **Amorphous Cell** module can generate multiple independent frames at once, which may be helpful for production studies.

6. To run the entire workflow in Pipeline Pilot

The calculation of mass transport properties, such as diffusion, is a common application in many fields of materials science. To simplify studies, such as the one presented here, the Materials Studio Collection

in BIOVIA Pipeline Pilot includes a protocol that automatically computes the diffusion coefficients from a list of input structures. This optional section of the tutorial explains how to use this protocol.

Create a new **Study Table Document** and name it **gas_polymer.std**.

Locate the file **methane Forcite GeomOpt\methane.xsd** in the **Project Explorer**. Right-click on the file name and select **Insert Into**. Repeat this for **Polyc_butadiene Forcite GeomOpt\Polyc_butadiene.xsd**.

Right-click on column **B** in **gas_polymer.std**, select **Properties**, and enter the name **loading**. Enter values **4** and **10** in the first two rows of this column.

These steps prepare the input document for the mass and charge transport protocol in Pipeline Pilot, which we will load next.

From the main menu select **Tools | Pipeline Pilot Protocols** and select a suitable **Server location**.

Open the **Mass and Charge Transport** protocol in the **Protocols | BIOVIA Materials Studio | Battery** folder.

The protocol begins by creating amorphous cell lattices, as you did earlier in this tutorial. This is followed by an initial molecular dynamics run using the NPT ensemble, to establish a converged density, temperature, and initial set of velocities. Finally, a sampling run is performed to compute the diffusion coefficient and related transport properties.

The next step is to enter the required physical parameters in the protocol dialog.

Change **Temperature** to **300**, **Configurations** to **4**, and **Target Density** to **0.89**.

In the **Initialization** section, change **Time** to **2**.

In the **Sampling** section, change **Time** to **10**, **Frame Interval** to **0.05**, and **Min Rsq** to **0.9**.

Select appropriate options for the **Parallel Run On Grid** section if you are planning to run this on a queuing system.

Click **Run**.

This job runs four independent sets of calculations and averages the results. The results are returned as two PDF reports and a **Trajectories** folder containing the trajectory data. The file **gas_polymer Initialization Report.pdf** describes the chemistry of the input structures and provides plots of the temperature and density for each individual trajectory initialization. From this data, you will notice that the initialization is substantially too short to give converged results in this example. As discussed above, production accuracy calculations will require much longer runs.

The report **gas_polymer Sampling Report.pdf** returns the aggregated and average transport properties for all calculations, as well as an analysis of each individual trajectory. The initial section of the report contains data applicable to the entire system, such as the density and temperature. There is also a table with data for each molecule, including the diffusion coefficient and its relative concentration. The overall summary contains the standard errors obtained from averaging over the sample size. For each separate trajectory analysis, a plot of the MSD, the corresponding line fit, and the R^2 value of the fit are included to help assess the quality of the simulation.

Note: You may find some lines marked in red, these correspond to molecules where at least one of the fits to the MSD data returned an R^2 value below the initially specified target. To achieve better statistics, you can restart the job with the option **Extend Trajectories** enabled.

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If your study table contains charged molecules, the protocol will calculate the conductivity of your simulation cell, as well as the partial conductivity for each species. This functionality is designed, for example, to analyze electrolyte solutions for batteries.

This is the end of the tutorial.

References

M. Meunier "Diffusion coefficients of small gas molecules in amorphous cis-1,4-polybutadiene estimate by molecular dynamics simulations", *J. Chem. Phys.*, **123**, 134906 (2005).

Polymer interactions with a metal oxide surface

Purpose: Introduces concepts associated with the calculation of interactions between a polymer and a metal oxide surface. These include the construction of the amorphous polymer and metal oxide surface and the molecular dynamics simulations required to calculate the interaction energy.

Modules: Materials Visualizer, Amorphous Cell, Forcite Plus, COMPASS

Time:  

Prerequisites: Using the layer builder, Using the polymer builder Visualizer Tutorials

Background

Interactions at polymer surfaces and interfaces are critical to products including adhesives, coatings, contact lenses, composites, prosthetic devices, films, lubricants, paints, and printing inks. Properties of interest to researchers include the structure of the interface or interphase, how it differs from the bulk, surface tension, wetting, and the chemistry and mechanics of adhesion.

Introduction

This tutorial shows how to build a metal oxide surface with 2D periodic boundary conditions and to calculate the interaction energy of a polymer with that surface.

This tutorial covers:

- [Getting started](#)
- [To cleave and relax the surface](#)
- [To increase the surface area and change the periodicity](#)
- [To build the polymer](#)
- [To add the polymer to the surface using the layer builder](#)
- [To optimize the layer and run molecular dynamics](#)
- [To calculate the interaction energy](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **polymer_metal** as the project name, click **OK**.

This creates a new project with *polymer_metal* listed in the Project Explorer.

The first step is to import and cleave the 0 0 -1 plane of alumina, Al₂O₃.

Click **Import** on the toolbar . Navigate to **Structures\metal-oxides** and double-click **Al2O3.xsd**.

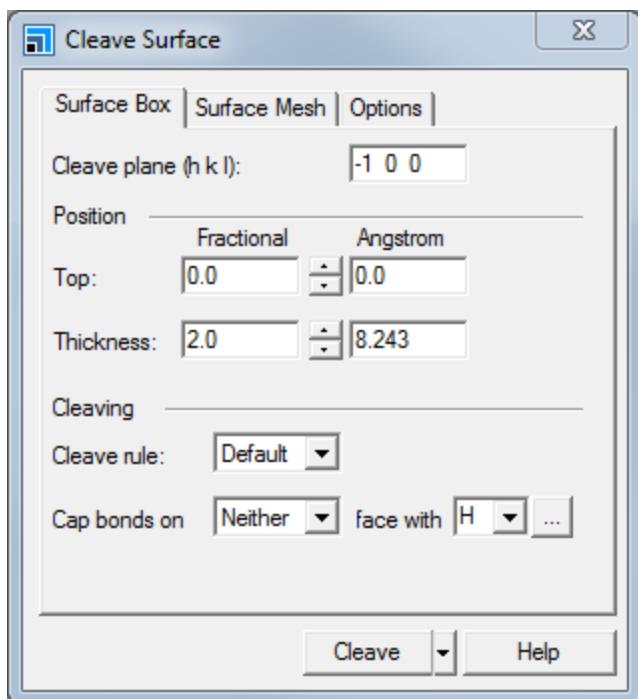
This opens a 3D Viewer containing the crystal cell of alumina.

2. To cleave and relax the surface

Cleave the crystal to provide a surface for the calculations later.

Select **Build | Surfaces | Cleave Surface** from the menu bar.

This opens the Cleave Surface dialog.



Cleave Surface dialog, Surface Box tab

Now you can specify the Cleave Plane and the Thickness.

Change the **Cleave plane (h k l)** from **-1 0 0** to **0 0 -1**. Press **TAB**.

As the non-bond cutoff distances in the forcefield settings are 9.5 Å, the thickness of your surface must be more than 9.5 Å. For the 0 0 -1 plane, it is approximately 13 Å.

Click **Cleave** and close the dialog.

This opens the new model document named **A12O3 (0 0 -1).xsd**, containing the cleaved surface.

Right-click in the new document and select **Lattice Parameters** from the shortcut menu to open the Lattice Parameters dialog.

The lengths of the U and V dimensions of the surface are 4.759.

Later, you can increase the surface area, but first relax the surface.

Close the Lattice Parameters dialog.

To relax the surface, you have to minimize the energy of it using molecular mechanics. Although the surface is ionic in nature, the typing of the model by the COMPASS forcefield requires bonds to exist between the aluminum and oxygen atoms. However, for calculations to proceed correctly, you must remove these bonds after the typing is complete.

Click **Forcite**  on the **Modules** toolbar and select **Calculation**.

This opens the Forcite Calculation dialog.

On the **Setup** tab, select **Geometry Optimization** from the **Task** dropdown list.

On the **Energy** tab, select **COMPASSIII** from the **Forcefield** dropdown list and click **More...** to open the Forcite Preparation Options dialog.

Usually, a Forcite run calculates the atom types automatically before each calculation. However, alumina is ionic so its Al-O bonds are not parameterized. Therefore, you need to preassign the forcefield types and prevent the simulation from recalculating them.

Clear the **Calculate automatically** checkbox and click **Calculate**. Close the Forcite Preparation Options dialog.

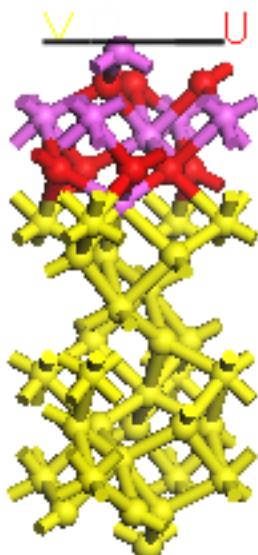
This assigns a forcefield type to each atom, you can display these by labeling the atoms.

On the **Energy** tab, select **Forcefield assigned** from the **Charges** dropdown list.

Only the top few layers of atoms in the surface interact with the polymer. The rest of the atoms are considered part of the bulk and therefore have little effect. This means that you can constrain the bulk atoms to prevent their minimization.

Rotate the model so that the surface is at the top. Click **Selection**  on the 3D Viewer toolbar. Select all the atoms apart from the two rows next to the surface by dragging a bounding box around the other atoms.

The structure looks similar to the image below.



Bulk atoms to constrain

Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. Select the **Fix Cartesian position** checkbox and close the dialog.

Click in the 3D Viewer to cancel selection of the atoms.

The final step before relaxing your surface is to remove the bonds between the aluminum and oxygen atoms.

Hold down **ALT** and double-click any bond. Press **DELETE**.

You are now ready to relax the surface.

On the **Forcite Calculation** dialog, click **Run** and close the dialog.

A new folder, entitled Al₂O₃ (0 0 -1) Forcite GeomOpt, opens in the Project Explorer. The calculation takes less than one minute to complete. When completed, the minimized structure is in the Al₂O₃ (0 0 -1).xsd document at the top of the new folder.

3. To increase the surface area and change the periodicity

The current surface area is very small. You can increase it by making a supercell.

Ensure that the optimized **Al₂O₃ (0 0 -1).xsd** in the Al₂O₃ (0 0 -1) Forcite GeomOpt folder is the active document.

Select **Build | Symmetry | Supercell** from the menu bar to open the **Supercell** dialog. Increase the **Supercell range** to **3** for both **U** and **V**. Click **Create Supercell** and close the dialog.

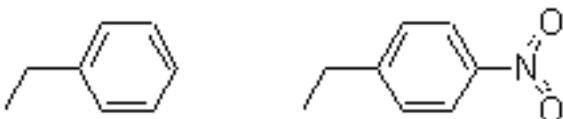
This displays the enlarged surface. You can use the Build Vacuum Slab Crystal dialog to change the periodicity from 2D to 3D.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. Change the **Vacuum thickness** to **0.0** and click **Build**.

If this displays a warning dialog, click **Yes**.

4. To build the polymer

The polymer that you are going to simulate is poly-p-nitrostyrene. This is not a prebuilt monomer but you can build it by editing a current monomer, styrene.



Structures of styrene and p-nitrostyrene

In the **Project Explorer**, right-click the project root and select **Import...** from the shortcut menu. Navigate back to **Structures\repeat-units\vinyls\styrene.xsd** and click **Open**.

To change the styrene monomer to p-nitrostyrene, add a nitro group para to the ethyl group on the phenyl ring. You can sketch the nitro group using the 3D Sketching tools or alternatively add it from the Fragment Browser.

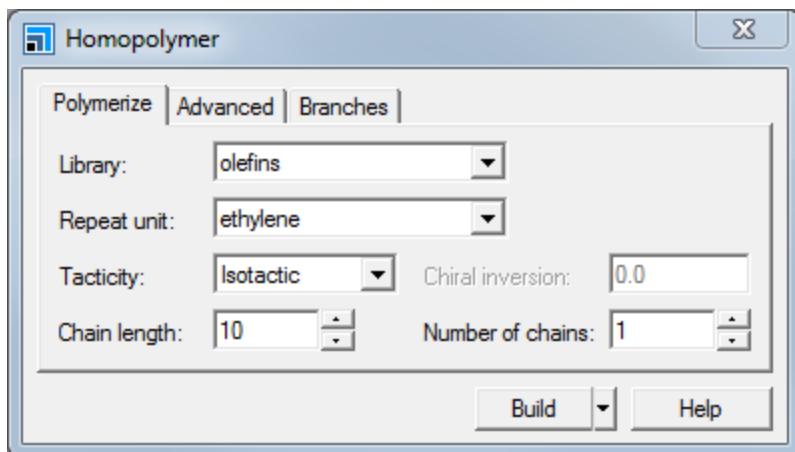
Click the **Sketch Fragment** arrow  on the **Sketch** toolbar and select **Fragment Browser**. Expand the **Functional Groups** node and select **Nitro**. Click once on the para hydrogen of the phenyl ring. Close the Fragment Browser dialog.

Change the name of the monomer before you continue.

In the **Project Explorer**, right-click **styrene.xsd** and select **Rename** from the shortcut menu. Change the name to **p-nitrostyrene**. Open the **Properties Explorer** and change the **Filter** to **Repeat Unit**. Change the **Name** to **p-nitrostyrene**.

You can use this monomer to build a homopolymer by using the polymer building tools.

Select **Build | Build Polymers | Homopolymer** from the menu bar to open the Homopolymer dialog.



Homopolymer dialog, Polymerize tab

Change the **Library** to **Current project** and the **Repeat unit** to **p-nitrostyrene**. Change the **Tacticity** to **Atactic** and the **Chain length** to **8**. Click **Build** and close the dialog.

You have generated your ideal polymer, entitled **Polyp-nitrostyrene.xsd**, though the adopted conformation is not very realistic. You can use Amorphous Cell used to obtain realistic polymer conformations, this generates chains containing sequences of backbone dihedrals typical of those found in actual melts or in ideal solutions.

Click **Amorphous Cell**  on the **Modules** toolbar and select **Calculation**.

This opens the Amorphous Cell Calculation dialog. You need to define what you want in your amorphous cell, in this case it is one copy of your polymer.

Choose **Confined Layer** from the **Task** dropdown list and select **Polyp-nitrostyrene.xsd** from the **Molecule** dropdown list in the **Composition** grid.

Note: In a real simulation, you would generate many different chains to average over configurational space.

Before building the cell, you need to specify the target density and the cell parameters for your confined layer.

Change to the **Al2O3 (0 0 -1).xsd** document containing the slab, right-click, and select **Lattice Parameters**. Note down the **a** and **b** parameters and close the dialog.

These parameters are around 14-15 Å. Therefore, specify that the **a** and **b** lattice parameters for the polymer are the same as the **U** and **V** parameters for the surface.

On the **Amorphous Cell Calculation** dialog, click **More...** to open the Amorphous Cell Confined Layer dialog. Select **Orthorhombic** from the **Lattice type** dropdown list and define the values of both **a** and **b** to the lattice parameters you wrote down and close the dialog.

On the **Setup** tab of the Amorphous Cell Calculation dialog, for the **Density** specify **0.8**. On the **Energy** tab, for the **Forcefield** select **COMPASSIII**. Click the **polymer_metal** project root in the Project Explorer and click **Run**. Close the dialog.

A new folder is created in the Project called Polyp-nitrostyrene AC Layer. The job completes in a few minutes and the amorphous structure is in the **Polyp-nitrostyrene.xtd** trajectory document.

Note: If you create more than one configuration, the other configurations are contained in the trajectory document and can be accessed from the Animation toolbar.

5. To add the polymer to the surface using the layer builder

Now that you have a minimized surface and polymer, use the Layer builder to place the polymer over the surface.

Select **Build | Build Layers** from the menu bar to open the Build Layers dialog. For **Layer 1**, select the optimized surface (**Al2O3 (0 0 -1).xsd** in the **Al2O3 (0 0 -1)** Forcite GeomOpt folder) and for **Layer 2** select the polymer you have confined in a cell and minimized (**Polyp-nitrostyrene.xtd**).

When you build the layered structure, the polymer can see both sides of the surface because of periodic boundary conditions. Therefore, add a large vacuum above the polymer so that it only sees one side of the surface.

On the **Layer Details** tab, increase the **Vacuum** for **Layer 2** to **30.0**.

On the **Matching** tab, select the lattice parameters for **Layer 1**. Click **Build**, on the warning dialog click **Yes**. Close the Build Layers dialog.

This opens the new document, entitled **Layer.xsd**, containing the surface, polymer, and vacuum. All further calculations performed use this structure as the starting point.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

6. To optimize the layer and run molecular dynamics

In the Project Explorer, double-click **Layer.xsd**.

A molecular dynamics simulation can equilibrate the system. Ideally, this would consist of a minimum of 30 ps of molecular dynamics to allow the system to fully equilibrate but, because of time constraints, you will only run 0.5 ps. As you minimized the surface in an earlier step, you can constrain the entire surface.

Select all the surface atoms. Open the **Edit Constraints** dialog and clear then select the **Fix Cartesian position** checkbox. Close the dialog and click in the 3D Viewer to cancel selection of the atoms.

Ensure that all the aluminum oxide atoms are constrained.

Right-click and select **Display Style** from the shortcut menu, on the **Atom** tab of the Display Style dialog select **Constraint** from the **Color by** dropdown list. All the Al_2O_3 atoms are red. If some are not, repeat the previous step. Change the **Color by** option back to **Element**. Close the dialog.

Optimize the geometry of the polymer layer with respect to the metal oxide surface before continuing.

Open the **Forcite Calculation** dialog and for the **Task** select to **Geometry Optimization**. Click **More...** to open the Forcite **Geometry Optimization** dialog and define the **Max. iterations** as **5000**, close the dialog. Click **Run**.

The generated optimized structure is now ready for the dynamic simulation. Molecular dynamics is one of the simulation types available in the Forcite module.

On the **Forcite Calculation** dialog, for the **Task** select **Dynamics**. Click **More...** to open the Forcite Dynamics dialog and define the **Number of steps** as **500**, close the dialog.

Click **Run** and close the Forcite Calculation dialog.

This calculation could take several minutes to run. As the calculation runs, this updates the charts containing temperature and energies. The text document **Status.txt** indicates the CPU time and the number of steps completed so far. When the calculation is complete, the final structure is present in the **.xsd** document.

7. To calculate the interaction energy

You can calculate the interaction energy by using the following equation.

$$E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{polymer}})$$

E_{total} is the energy of the surface and the polymer, E_{surface} is the energy of the surface without the polymer and E_{polymer} is the energy of the polymer without the surface. In the current structure, the surface atoms are fixed. Consequently E_{surface} vanishes, and E_{total} only contains the energy of the polymer and its interaction with the surface. However, in this case you can remove the constraints and evaluate all three terms explicitly.

Open the final structure from the dynamics calculation, **Layer.xsd**. Select all the atoms and open the **Edit Constraints** dialog, clear the **Fix Cartesian position** checkbox, and close the dialog.

You have to calculate single point energies for the total system, the polymer, and the surface.

Open the **Forcite Calculation** dialog. For the **Task** select **Energy** and click **Run**. When the job is complete, scroll down the output text document and note the **Total energy**.

This is E_{total} . To get the value for E_{polymer} , you need to calculate the single point energy of the polymer in the 3D lattice but without contributions from the surface. To do this, save the system as a different document so that you can remove the surface.

Change the focus back to your **Layer.xsd** document. Select **File | Save As...** from the menu bar, enter **polymer_only.xsd** and click **Save**. Change focus to **polymer_only.xsd** and select and delete all of the metal oxide atoms.

Now you need to perform a single point energy calculation on the polymer.

On the **Forcite Calculation** dialog, click **Run**. When the job is complete, scroll down the output text document and note the **Total energy**.

This is E_{polymer} . Finally, you need to calculate the energy of the surface.

Make **Layer.xsd** the active document and save it as **surface_only.xsd**. In **surface_only.xsd** select and delete the polymer.

Open the **Edit Constraints** dialog and verify that there are no constraints on the metal-oxide atoms, close the dialog.

On the **Forcite Calculation** dialog, click **Run**. When the job is complete, scroll down the output text document and note the **Total energy**.

This is E_{surface} . You can now use the above equation to calculate the interaction energy of the polymer and the surface. A negative number indicates that the polymer is binding to the surface.

This methodology gives basic instructions on how to calculate the energy of interaction between a polymer and a metal-oxide surface. However, if you were to perform an in-depth study of this type of interaction, you would be advised to use Materials Studio's scripting interface to vary structures and calculate the interaction energy for each variation.

This is the end of the tutorial.

Calculating the Miscibility of Two Polymers

Purpose: To demonstrate the use of the amorphous cell and molecular dynamics tool for calculation of polymer properties.

Modules: Materials Visualizer, Amorphous Cell, Forcite Plus, COMPASS

Time:  

Prerequisites: Using the polymer builder

Background

The prediction of polymer miscibility is a common use of atomistic simulation tools in polymer science. Blends of polymers are desirable since they are easier to produce than novel polymers and circumvent legislative problems. Frequently a pair (or more) of polymers with desirable properties are blended in the hope that the resultant mixture has improved characteristics. You can use Materials Studio to determine the solubility parameters, cohesive energy density, and the Flory-Huggins interaction parameter of any number of polymers.

In condensed phases (solids, liquids, solutions) strong attractive forces exist between molecules, so each molecule has a considerable (negative) potential energy compared to vapor phase molecules. This potential energy is the molar cohesive energy, $E_{coh} = -E_{pot}$, which by convention is positive. Expressed per unit of volume this gives the cohesive energy density (c):

$$c = \frac{E_{coh}}{V}$$

The cohesive energy density of a pure component is related to its solubility parameter δ :

$$\delta = \sqrt{c}$$

As a rule, components with similar solubility parameters are miscible, whereas dissimilar values lead to phase separation. The Flory-Huggins parameter expresses this rule:

$$\chi = \frac{\nu}{k_B T} (\delta_A - \delta_B)^2$$

Where ν is a reference volume used for χ . A value of χ smaller than a critical value χ_c indicates miscibility of components A and B. For larger values, the components do not mix.

This method provides a quick way to assess miscibility, but is an approximation as it does not consider the mixture explicitly. Another way to obtain the Flory-Huggins parameter also includes the cohesive energy of the mixture, by first calculating the energy of mixing per unit volume:

$$\frac{\Delta E_{mix}}{V} = \phi_A \left(\frac{E_{coh}}{V} \right)_A + \phi_B \left(\frac{E_{coh}}{V} \right)_B - \left(\frac{E_{coh}}{V} \right)_{AB}$$

Where ϕ_A and ϕ_B are the volume fractions of A and B in the mixed system. The resulting energy of mixing for a reference volume ν relates to the Flory-Huggins parameter χ as:

Calculating the Miscibility of Two Polymers

$$\chi = \frac{1}{\phi_A \phi_B} \left(\frac{\Delta E_{mix}}{k_B T} \right)$$

The results generated by this tutorial allow you to evaluate all of these properties.

Introduction

In this tutorial, you use the polymer building tools to construct two polymers. You then use Amorphous Cell and Forcite to create a cell containing an amorphous blend of the two polymers. Finally, you run a molecular dynamics simulation and analyze this to obtain the cohesive energy density.

This tutorial covers:

- [Getting started](#)
- [To build two syndiotactic homopolymers](#)
- [To optimize the geometries](#)
- [To use Amorphous Cell to construct an amorphous blend](#)
- [To run molecular dynamics on the cell](#)
- [To calculate the cohesive energy density](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

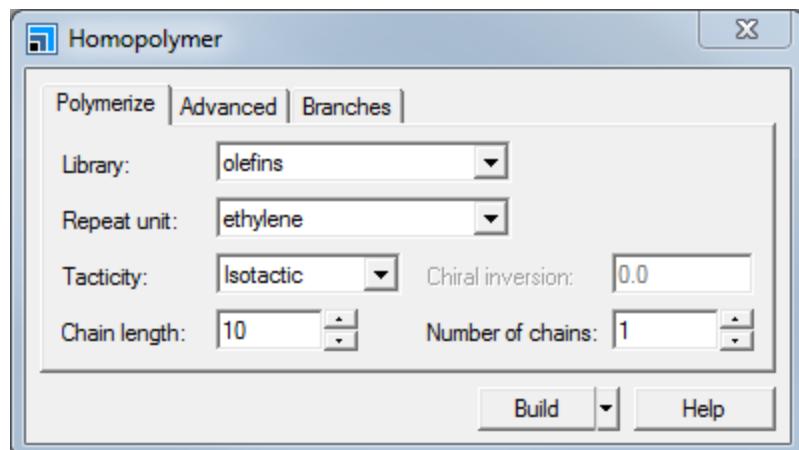
Open the **New Project** dialog and enter **miscibility** as the project name, click **OK**.

The new project is created with *miscibility* listed in the Project Explorer.

2. To build two syndiotactic homopolymers

The first stage in this tutorial is to use the polymer builder to build polystyrene and polypropylene.

From the menu bar, select **Build | Build Polymers | Homopolymer** to open the Homopolymer dialog.



Homopolymer dialog, Polymerize tab

You need to build an 18 repeat unit polypropylene polymer.

From the **Repeat unit** list, select **propylene**, and change the **Chain length** to **18**. From the **Tacticity** list, select **Syndiotactic**. Click **Build**.

A 3D Atomistic Document called **Polypropylene .xsd** opens. Now repeat this procedure for polystyrene. To ensure that both polymers have approximately the same volume, use 9 repeat units.

From the **Library** list, select **vinyls**, and for the **Repeat unit** select **styrene**. Change the **Chain length** to **9** and leave the other options as they are. Click **Build**, and close the dialog.

A second 3D Atomistic Document called **Polystyrene .xsd** opens.

3. To optimize the geometries

When Materials Studio constructs the polymers, there is no geometry optimization performed. Therefore, before you build your amorphous blend, perform an initial geometry optimization.

Click **Forcite**  on the **Modules** toolbar and select **Calculation** from the list or choose **Modules | Forcite | Calculation** from the menu bar.

This opens the Forcite Calculation dialog that allows you to perform a geometry optimization calculation.

The default maximum number of iterations is 500 but you do not need to perform this number as you only want to get a starting geometry. Therefore, perform 200 iterations.

On the **Setup** tab, change the **Task** to **Geometry Optimization**, and click **More...** to open the Forcite Geometry Optimization dialog. Change the **Max. iterations** to **200** and close the dialog.

In this tutorial, use the COMPASSIII forcefield.

On the **Energy** tab, select **COMPASSIII** from the **Forcefield** list.

Click **Run**.

If the Job Explorer is not already open, it displays. This provides basic information about the job as it progresses. A new folder also displays, named **Polystyrene Forcite GeomOpt**, and this is where Materials Studio returns the results of the calculation.

A status text document and two chart documents display, these allow you to monitor the progress of your job.

When the job finishes, the minimized **Polystyrene .xsd** structure displays in the **Polystyrene Forcite GeomOpt** folder. Forcite also produces a text document, **Polystyrene .txt**. This contains all the energy information about the calculation.

When the job has finished, you can minimize the energy of the other polymer.

In the **Project Explorer**, double-click **Polypropylene.xsd**. On the **Forcite Calculation** dialog, click **Run**.

When the job is complete, save the project, and then close all the windows.

From the menu bar, select **File | Save Project** followed by **Window | Close All**.

4. To use Amorphous Cell to construct an amorphous blend

Once you have built your polymers, you need to combine them in an amorphous cell.

Calculating the Miscibility of Two Polymers

Click **Amorphous Cell**  on the **Modules** toolbar and choose **Calculation** from the list or choose **Modules | Amorphous Cell | Calculation** from the menu bar.

This opens the Amorphous Cell Calculation dialog.

Initially, you need to define the polymers to add to your cell.

In the **Composition** grid, select the optimized **Polystyrene.xsd** for the first row in the **Molecule** column and the optimized **Polypropylene.xsd** for the second row. Set the **Loading** of both molecules to **10**. Set the target **Density** to **0.9 g/cm³**.

As you change the target density, the cell parameters adjust automatically. Since the loading is the same, and the molecules have approximately the same volume, the volume fractions in the mixture are 0.5.

Amorphous Cell automatically optimizes the geometry after construction. To avoid ring spearing during this optimization step, restrain the rings.

Click **Options...** to open the Amorphous Cell Options dialog. Check the **Restrain rings** option and close the dialog.

Use the COMPASS III forcefield.

On the **Energy** tab, select **COMPASSIII** as the **Forcefield**.

By default the job description is the name of the first component. So, to avoid confusion later, specify a different description for the job.

On the **Job Control** tab, clear selection of **Automatic**, and enter **PP-PS** as the **Job description**.

You can now start the calculation.

Click the **miscibility** root folder in the Project Explorer. Click **Run** and close the dialog.

After a few seconds, a new folder **PP-PS AC Construct** displays in the Project Explorer. As before, a summary of the job status displays in the Job Explorer.

The Job Explorer indicates any jobs that are running that are associated with this project. It shows useful information such as the server and job identification number. You can also use this explorer to stop the job if you need to.

To avoid nested folders later, collect the input structure for the next step in a study table.

Right-click the **miscibility** root folder in the Project Explorer, and select **New | Study Table Document**.

Materials Studio creates a new study table document. When the Amorphous Cell job completes, copy the result into the study table.

Ensure that the active view is on the new study table. In the Project Explorer, right-click the **PP-PS.xtd** trajectory from Amorphous Cell and choose **Insert Into**.

This inserts the amorphous cell into cell A1 of the study table. Open a view on this structure.

Double-click the entry in cell **A1** to open a study table detail view.

The next step uses this as input for a Forcite dynamics simulation.

5. To run molecular dynamics on the cell

Unless you request otherwise, Amorphous Cell performs a geometry optimization on a newly created cell. A minimization ensures equal distribution of the molecules throughout the cell, preventing pockets of vacuum. After building a cell, run a molecular dynamics simulation to equilibrate the system. This procedure of minimization and molecular dynamics is known as relaxing the structure, perform this whenever you construct an amorphous cell.

Once the cell is well equilibrated, you can perform the production run to generate the conformations to use in the cohesive energy density calculation.

In this case, perform two equilibration runs and a production run.

Open the **Forcite Calculation** dialog and change the **Task** to **Dynamics**.

Click **More...** to open the Forcite Dynamics dialog.

On the **Dynamics** tab, define the **Number of steps** and **Frame output every** to **20000**. Change the **Ensemble** to **NVT**. On the **Thermostat** tab, change the **Thermostat** to **Velocity Scale**.

On the **Job Control** tab, clear **Automatic**, and enter **NVT eq** as the **Job description**. Ensure that the study table detail view is active and click **Run**.

When the run completes copy the structure output to the study table.

Ensure that the active view is on the study table in the root folder. In the Project Explorer, right-click **NVT eq.xsd** in the Forcite Dynamics folder and choose **Insert Into**.

The structure inserts into cell A2 of the study table. Open a detail view for which to start the next simulation.

Double-click the entry in cell **A2** to open a study table detail view.

Proceed with an equilibration run using the NPT ensemble to ensure that the system is at the correct density under atmospheric pressure (1 atm = 1.013e-4 GPa).

On the **Dynamics** tab of the **Forcite Dynamics** dialog, change the **Ensemble** to **NPT**. For **Pressure**, specify **1.013e-4**. On the **Thermostat** tab, change the **Thermostat** to **NHL**. On the **Barostat** tab, change the **Barostat** to **Andersen**.

Use the more accurate NHL thermostat for this part of the simulation.

On the **Job Control** tab, enter **NPT eq** as **Job description**. Ensure that the detail view on A2 is active and click **Run**.

As before, copy the results to the study table.

Ensure that the active view is on the study table in the root folder. In the Project Explorer, right-click **NPT eq.xsd** in the Forcite Dynamics folder and choose **Insert Into**.

The structure inserts into cell A3 of the study table. Open a detail view for which to start the next simulation.

Double-click the entry in cell **A3** to open a study table detail view.

Calculating the Miscibility of Two Polymers

Finally, perform a production run to generate the frames for the cohesive energy density analysis.

On the **Dynamics** tab of the **Forcite Dynamics** dialog, for **Initial velocities** select **Current**. Change the **Number of steps** to **50000** and **Frame output every** to **500**.

This means that the trajectory document contains 101 frames.

On the **Job Control** tab, enter **NPT prod** as the **Job description**. Ensure that the detail view on A3 is active and click **Run**.

When the calculation finishes, save the project.

Choose **File | Save Project** from the menu bar.

6. To calculate the cohesive energy density

Once you have an equilibrated trajectory document, you can calculate the cohesive energy density using the Forcite Cohesive Energy Density task.

On the **Forcite Calculation** dialog, change the **Task** to **Cohesive Energy Density**.

You can either choose to apply the analysis to a single frame of the current document or you can choose a logical trajectory document. The logical trajectory option allows you to add together multiple dynamics runs on the same structure and analyze all of them. In this case, define a logical trajectory containing all the frames of the single dynamics run you have completed.

Open **NPT prod.xtd** output trajectory from the final Forcite Dynamics calculation.

Leave the **Frame filter** as **ALL** and click **More...** to open the Forcite Cohesive Energy Density dialog. Select **Include structure in study table** and close the dialog.

The study table containing the results of the calculation includes the structures for each frame analyzed.

Click **Run** and close the dialog.

The cohesive energy density calculation uses the client-server architecture and returns the results to the Polystyrene Forcite CED folder. The job returns several documents; including a trajectory, study table, and status and summary text documents.

In the text document **NPT prod.txt**, scroll down to find the line "--- Cohesive energy density & solubility parameters ---".

The text document contains the average cohesive energy density in J/m³. This corresponds to $(E_{coh}/V)_{AB}$ in the equation for the energy of mixing in the introduction.

As an optional step, to calculate the Flory-Huggins χ -parameter, you need two more simulations, of pure polystyrene and pure polypropylene. Repeat steps 4, 5, and 6 to calculate the cohesive energy densities of a system with 20 molecules of polystyrene, and again for 20 molecules of polypropylene. You can use the same study table to collect the output structures of intermediate steps in new columns B and C. You can compare the results with those in the table below.

Tip: To insert structures in another column, select any cell in the column before clicking *Insert Into*.

Tip: Double-click the settings of the previous Forcite jobs, to run with the same settings, including the job descriptions.

Species	CED (J/cm ³)	Solubility parameter (J/cm ³) ^{1/2}
PP-PS	233.8	15.291
PP	214.4	14.642
PS	268.8	16.394

You can use the equations in the introduction to estimate χ in both approximations. Using the volume of a PP repeat unit as reference volume (85.5 Å³, or 51.5 cm³/mol) the first equation gives $\chi = 51.5/(8.314 \times 298)(16.394 - 14.642)^2 = 0.0638$. For the second equation, first determine the energy of mixing per volume as, $E_{\text{mix}}/V = 0.5 \times 214.4 + 0.5 \times 268.8 - 233.8 = 7.8 \text{ J/cm}^3$. Using the same reference volume, this gives an energy of mixing $E_{\text{mix}} = 8.8 \times 51.5 = 401.7 \text{ J/mol}$. Finally, we obtain $\chi = 1/(0.5 \times 0.5) \times 401.7/(8.314 \times 298) = 0.6485$ in this approximation.

For a blend of two polymers where each polymer has the same number N of repeat units, the critical χ -parameter is $2/N$. For $N = 18$, the critical χ -parameter is $2/18 = 0.11$. Therefore the first model predicts miscibility, whereas the second model predicts phase separation.

This is the end of the tutorial.

References

A.F.M. Barton, "Solubility parameters", *Chem. Rev.*, **75**(6), 731-753 (1975).
<https://doi.org/10.1021/cr60298a003>.

Running a confined shear simulation

Purpose: Introduces the use of Forcite to calculate confined shear.

Modules: Materials Visualizer, Amorphous Cell, Forcite Plus, COMPASS

Time: 

Prerequisites: Using the polymer builder, [Finding low energy configurations of a molecule on a surface](#)

Background

The confined shear task in Forcite performs a simulation of shear flow of a fluid confined between semi-rigid walls or surfaces. The fluid can either be a liquid or an oligomer. The surfaces would normally be an inorganic oxide or metal - although in principle, you can use practically any chemically reasonable type of confining surface material.

This is achieved by imposing a user-defined velocity on the walls. The simulation shears two walls with an equal but opposite velocity and holds them in a fixed position relative to one another by harmonic springs.

Introduction

This tutorial shows you how to perform a confined shear simulation on a layered structure. It starts with building and defining the different layers using a combination of tools, such as Amorphous Cell and the Layer Builder. Once you have your layered structure, you can use the confined shear task to run the simulation.

This tutorial covers:

- [Getting started](#)
- [To set up the Fe layer](#)
- [To build a tridecane molecule](#)
- [To construct the layered system](#)
- [To equilibrate the layered system](#)
- [To run the confined shear simulation and analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ConfinedShear** as the project name, click **OK**.

This creates a new project with *ConfinedShear* listed in the Project Explorer.

2. To set up the Fe layer

The first stage is to import the metal from the structure library.

Click **Import**  on the toolbar to display the Import Document dialog. Select **3D Atomistic Files** from the file types list for the **File name**. Navigate to and select the file **Structures\metals\pure-metals\Fe.xsd** and click **Open**.

The next stage is to build a supercell out of your existing cell.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase the **Supercell range** to **7 7 3** and click **Create Supercell**. Close the dialog.

3. To build a tridecane molecule

To build a tridecane molecule, first build a dodecane molecule using the Polymer Builder.

Select **Build | Build Polymers | Homopolymer** from the menu bar to open the Homopolymer dialog. On the **Polymerize** tab, change the **Chain length** to **6**. Ensure selection of **ethylene** as the **Repeat unit**, from the **olefins Library**. Click **Build** and close the dialog.

The dodecane molecule is displayed in a new 3D Viewer. Modify the structure to add an extra methyl group at one end of the chain.

Choose the **Selection** tool  on the toolbar and select a terminal hydrogen at one end of the chain. Click the **Modify Element** arrow  and select **Carbon** from the dropdown list. Click anywhere in the 3D Viewer to cancel selection of the atom.

Click **Adjust Hydrogen**  and then **Clean** .

Before continuing, rename the new molecule to tridecane

Use the **Project Explorer** to rename Polyethylene.xsd to **tridecane.xsd**.

4. To construct the layered system

This section shows you how to build an amorphous cell containing the tridecane and then place this between two layers of iron using the Layer Builder.

Click **Amorphous Cell**  on the **Modules** toolbar and choose **Calculation**.

This opens the Amorphous Cell Calculation dialog.

Select **Confined Layer** from the **Task** dropdown list.

Define the number of tridecane molecules to load and the density of the cell, for this tutorial, this is **0.7 g cm⁻³**.

Select **tridecane.xsd** from the **Molecule** list and define the **Loading** as **25**. Specify **0.7 g/cm³** as the **Density**.

Click **More...** to open the Amorphous Cell Confined Layer dialog and select **Orthorhombic** from the **Lattice type** dropdown list.

Forcite Plus: Running a confined shear simulation

The cell parameters define the size of the lattice. As you want to make a layered structure, you need to change the **a** and **b** parameters so that they are the same as those of the metal layer.

Double-click **Fe.xsd** in the Project Explorer to make it the active document. Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu. Enter the **a** and **b** values displayed in the Lattice Parameters dialog in the **Lengths (Å)** section on the Amorphous Cell Confined Layer dialog. Close the Lattice Parameters and Amorphous Cell Confined Layer dialogs.

The default mode of the Amorphous Cell algorithm is to use the bonds between the backbone atoms as rotatable bonds. When you build a polymer, this defines the backbone atoms automatically as a path between the head and tail atoms. In this case, you have edited the structure and added an extra methyl group which does not have backbone atoms defined. Amorphous Cell can automatically find all flexible torsions which, in this case, would include the newly added torsion.

On the Amorphous Cell Calculation dialog, click **Options...** to open the Amorphous Cell Options dialog. Select the **Include non backbone torsions** checkbox and close the dialog.

Before launching the job, define the energy settings and specify a new job description.

On the **Energy** tab of the Amorphous Cell Calculation dialog, select **COMPASSIII** from the **Forcefield** dropdown list and **Group based** from the **Electrostatic** dropdown list for the summation method.

Click **More...** for **Forcefield** to open the Amorphous Preparation Options dialog. Verify selection of **Calculate automatically** for **Charge groups**. Close the dialog.

Amorphous Cell automatically calculates charge groups after assigning the charges. The default calculation method is *Divide-and-conquer*, which recursively divides the molecule into charge neutral groups.

Click **Run** and close the dialog.

When the job is complete, a document called **tridecane.xtd** is returned to the **tridecane AC Layer** folder in the project.

Once you have built the amorphous cell, you can add this to your layered structure.

Select **Build | Build Layers** from the menu bar to open the Build Layers dialog. On the **Define Layers** tab, define **Layer1** as **Fe.xsd**, **Layer2** as **tridecane.xtd**, and **Layer3** as **Fe.xsd**.

This builds a trilayer structure with the tridecane sandwiched between two iron layers.

Select the **Layer Details** tab on the Build Layers dialog.

This allows you to specify whether or not to add vacuums to either end of the layered structure.

Select the **Options** tab, select the **Configure for confined shear use** checkbox. Change back to the **Layer Details** tab and then the **Define Layers** tab.

For the confined shear simulation to work, the layers must have specific names, seen on the *Define Layers* tab. Also, this adds a 20 Å vacuum to the structure so that the non-bond interactions from the bottom wall do not influence the top wall.

Click **Build** and close the dialog.

After a few seconds, a new 3D Atomistic document, called `Layer.xsd`, opens containing your layered structure.

In the Project Explorer, drag this into the root of the project. Make `Layer.xsd` the active document and press the **UP** arrow key twice to rotate the view.

You can now see the layered structure.

5. To equilibrate the layered structure

Before performing the shear, first run a short geometry optimization and a long NVT dynamics to equilibrate the tridecane wax. As you only want to equilibrate the wax atoms, constrain the iron atoms.

In the 3D view, hold down **ALT** and double-click one of the Fe atoms. Select **Modify | Constraints** from the menu bar to open the Edit Constraints. Select the **Fix Cartesian position** checkbox and close the dialog.

Now you have constrained the position of the Fe atoms, you can relax the tridecane.

Select **Modules | Forcite | Calculation** from the menu bar to open the Forcite Calculation dialog.

On the **Setup** tab, change the **Task to Geometry Optimization**.

On the **Energy** tab, choose **COMPASSIII** as the **Forcefield**. Change the **Electrostatic** and **van der Waals** summation methods to **Group based**.

Click **More...** for **Forcefield** to open the Forcite Preparation Options dialog. Ensure selection of the **Calculate automatically** checkbox in the **Charge groups** section and close the dialog.

The charge groups for tridecane were already calculated by Amorphous Cell. Forcite completes the charge groups assignment on the structure by adding one to each Fe atom.

Click Run.

The initial relaxation of the structure removed any bad contacts generated from the Amorphous Cell building and layer building process. You can also run a molecular dynamics calculation to provide further equilibration. In this case, use a simulated annealing calculation that runs a set of short molecular dynamics calculations at different temperatures.

On the Forcite Calculation dialog, select the **Setup** tab. Change the **Task to Anneal** and click **More...** to open the Forcite Anneal Dynamics dialog.

On this dialog, you can specify the parameters for the temperature cycle. For this tutorial, leave the default values. For a real calculation, perform at least 50,000 steps of equilibration dynamics.

Close the Forcite Anneal Dynamics dialog and click **Run** on the Forcite Calculation dialog.

The calculation takes a few minutes to run. When it is complete, it returns three structure documents:

- `Layer.xsd` - contains the structure from the final frame of the annealing calculation
- `Layer_Anneal.xtd` - trajectory document with the lowest energy frame from each anneal cycle
- `Layer.xtd` - trajectory with all frames from the cycle

Use `Layer.xsd` as the input to the confined shear calculations.

Select **File | Save Project** followed by **Window | Close All** from the menu bar. Reopen the annealed **Layer.xsd**.

6. To run the confined shear simulation and analyze the results

Before performing the confined shear run, remove the constraints on the Fe atoms.

Select all the atoms in **Layer Forcite Anneal\Layer.xsd** and open the Edit Constraints dialog. On the **Atom** tab, clear the **Fix Cartesian position** checkbox and close the dialog.

Now you can set up the confined shear simulation.

On the **Setup** tab of the Forcite Calculation dialog, select **Confined Shear** from the **Task** dropdown list. Click **More...** to open the Forcite Confined Shear dialog.

Ensure that the **Wall velocity** is **0.05 Å/ps** and click **More...** to open the Forcite Dynamics dialog.

Change the **Number of steps** to **5000** and the **Frame output every** to **250**. Close the Forcite Confined Shear and Forcite Dynamics dialogs.

Note: If you run this tutorial with a simulation time of 250 ps, the polymer shearing occurs.

You are now ready to run your simulation.

Click **Run** and close the dialog.

The confined shear job starts and a new folder, **Layer Forcite ConfShear**, opens.

When the calculation completes, this returns the following documents:

- **Layer.xsd** - structure document containing the final output structure.
- **Layer Temperature.xcd** - chart document showing change in temperature with time.
- **Layer wall Stress.xcd** - chart document showing change in stress along the walls with time.
- **Layer Energies.xcd** - chart document showing change in energy with time.
- **Layer.txt** - summary of the calculation settings and results.
- **Status.txt** - contains the live update status.
- **Layer.xtd** - trajectory document containing frames snapshotting the progress of the shearing.

Analyze the changes in velocity in the z direction through the cell. This corresponds to the (0 0 1) h k l direction.

Double-click **Layer.xtd** in the Layer Forcite ConfShear folder.

Select **Modules | Forcite | Analysis** from the menu bar to open the Forcite Analysis dialog. Choose **Velocity profile** from the list and select **FLUID** from the **Sets** dropdown list. Make sure that the **Flow direction** is **A** and click **Analyze**.

This opens a chart document and study table document containing the velocity profile information.

This chart document contains the FLUID (tridecane) component of the velocity profiled across the z direction. The chart is zero between 0 and 9.9 Å and over 36.2 Å, as these regions correspond to the walls of metal atoms (where there is no polymer). The polymer region lies between 9.9 and 36.2 Å, in this

region the plot is noisy. A fully-equilibrated and well-averaged simulation run would show the velocity changing from a negative value at the bottom wall to a positive at the top wall.

A temperature profile can also give information about localized heating in the system.

On the Forcite Analysis dialog, choose **Temperature profile** and select **FLUID** from the **Sets** dropdown list. Select the **Specified direction (h k l)** checkbox and define the direction as **0 0 1**. Click **Analyze**.

This generates a chart for the temperature profile across the cell. In this example, the temperature is fairly constant with localized heating where chains are pulling across each other causing friction.

You also can calculate the concentration profile of the tridecane atoms to see how they vary across the cell.

On the Forcite Analysis dialog, select **Concentration profile** from the list. Select **FLUID** from the **Sets** dropdown list. Select the **Specified direction (h k l)** checkbox and specify the direction as **0 0 1**. Click **Analyze**.

This contains a plot of the concentration profile of the fluid in the z direction. The plot shows that the confined fluid has a higher density close to the wall surfaces indicating that the wax is sticking to the Fe surface under shear.

You can also average the concentration profile over a number of frames. This enables you to look for the time dependency of the profile.

Select **Frames to average** and specify a value of **6**. Click **Analyze** and close the dialog.

This generates a chart with multiple lines, where each line shows the averaged concentration profile. In this very short example, the concentration profile does not have time to vary dramatically.

A visual inspection of the trajectory also supports the view that the tridecane sticks to the walls.

Make the output **Layer.xtd** the active document and open the **Display Style** dialog. On the **Lattice** tab, change the **Style** to **In-Cell** and close the dialog.

This changes the display to translate all the atoms into the cell.

Press the **UP** arrow key twice to realign the view. Click the **Animation Mode** arrow  on the **Animation** toolbar and select **Options** to open the Animation Options dialog. Select the **Recalculate atom visibility every frame** checkbox and close the dialog.

Click **Play** .

As the animation progresses, the wax moves toward the metal walls.

Select **File | Save Project** from the menu bar.

This is the end of the tutorial.

Calculating the solvation free energy of propionic acid in *n*-octanol

Purpose: Introduces the use of Forcite to calculate the free energy of solvation.

Modules: Forcite Plus, COMPASS, Amorphous Cell

Time:



Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

The free energy to transfer a solute from its vapor phase to a solvent, or solvation free energy, is important for understanding a wide range of chemical and physical processes. For example, it determines the solubility, the amount that solvates in the solvent when it is in contact with the solute vapor. Knowledge of the relative solubilities of a compound in two or more solvents is key to the design of a solvent extraction process, a major separation technology. The most widely used parameter for relative solubility is $\log P$, which quantifies the partitioning in water and *n*-octanol. A positive value of $\log P$ indicates that the solute preferentially solvates in *n*-octanol, typical for apolar compounds. $\log P$ is used extensively as a predictor of the degree of adsorption of drugs and the activity of agrochemicals and environmental toxins in the body.

You can obtain the solvation free energy directly from a simulation, using the thermodynamic integration method. In this method, the interaction of the solute with the solvent gradually increasing from zero to full interaction (or vice versa), in a number of steps. For each coupling strength, this performs a simulation and calculates the derivative of the solvation free energy. Following calculation of all derivatives, you can obtain the free energy as the integral. Since each step requires a long simulation run (typically a few 100 ps), free energy calculations are computationally expensive.

In practice, you carry out solvation free energy calculations over three runs:

- Starting from a solute molecule in vacuum, the charges are gradually reduced to zero, while keeping all other interactions the same. The free energy change in this process is called the ideal contribution.
- Then, the chargeless molecule is coupled to the solvent by switching on the van der Waals interaction in a number of steps. The free energy change in this process is called the van der Waals contribution.
- Finally, the charges are reintroduced on the solute molecule, which is now submerged in the solvent. The free energy of this step is the electrostatic contribution. The total solvation free energy then follows as the sum of ideal, van der Waals, and electrostatic contributions.

Introduction

This tutorial shows you how to perform a solvation free energy calculation. You can calculate the solvation free energy of propionic acid (also known as propanoic acid) in *n*-octanol. Propionic acid is a liquid fatty acid found naturally in sweat, in milk products, and as a product of bacterial fermentation. In the form of its propionates, it is a mold inhibitor in bread and an ingredient in perfume.

This tutorial calculates the solvation free energy in octanol. Combined with the experimental solvation free energy in water of -6.36 kcal/mol ([Wolfenden, 1981](#)), you can determine the $\log P$ value of propionic acid.

Note: Since the calculations in this tutorial require very long simulation runs, the output of a long production run is provided for comparison. The example project `SolvationFreeEnergy.stp` is located in the `share\Examples\Projects\Forcite` directory, from the top level of your Materials Studio installation.

For Windows users who are not administrators, you can copy the `SolvationFreeEnergy.stp` project and associated `SolvationFreeEnergy_Files` folder to a location where you have write permissions. Then open the new copy of the `SolvationFreeEnergy.stp` project.

This tutorial covers:

- [Getting started](#)
- [Sketching a molecule of propionic acid and n-octanol](#)
- [Constructing an amorphous cell of propionic acid in n-octanol](#)
- [Equilibrating the structure](#)
- [Running the solvation free energy calculation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

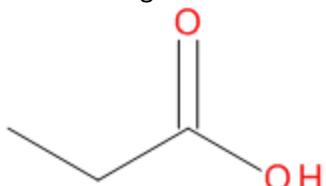
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **SolvationFreeEnergy** as the project name, click **OK**.

This creates a new project with `SolvationFreeEnergy` listed in the Project Explorer.

2. Sketching a molecule of propionic acid and n-octanol

The first stage is to create a structure for propionic acid:



Select **File | New...** from the menu bar to open the New Document dialog. Select **3D Atomistic** and click **OK**.

Rename the new document **Propionic acid**.

Using the tools on the Sketch toolbar, draw a propionic acid molecule, ensuring that you adjust the hydrogens and clean the structure. Right-click in the document and select **Display Style** to open the Display Style dialog. On the **Atom** tab, choose **CPK** as the **Display style** and close the dialog.

To prepare the molecule for subsequent calculations, optimize the geometry using charge groups. Once the charge groups are defined, they are available in subsequent calculations without the need to recalculate them.

Forcite Plus: Calculating the solvation free energy of propionic acid in n-octanol

Select **Modules** | **Forcite** | **Calculation** from the menu bar to open the Forcite Calculation dialog. Change the Task to **Geometry Optimization**.

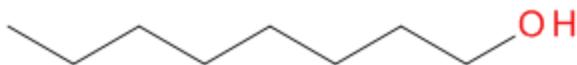
On the **Energy** tab, select **COMPASSIII** from the **Forcefield** dropdown list. Ensure selection of **Forcefield assigned** for the **Charges**. Specify **Group based** for both the **Electrostatic** and **van der Waals** summation methods.

Click **More...** for **Forcefield** to open the Forcite Preparation Options dialog. Click **More...** for **Charge groups** to open the Forcite Charge Groups dialog. For the **Method**, select **Divide-and-conquer**. Close both dialogs.

Click **Run** to start the calculation.

This creates a new folder, **Propionic acid Forcite GeomOpt**, in the Project Explorer. When the calculation completes, this stores the minimized structure in the new folder. The output structure has COMPASS charges assigned and is divided into neutral charge groups. You can verify this by coloring the molecule by Charge Group, and labeling the atoms by Charge.

Use the same procedure for n-octanol:



Select the project root and create a new **3D Atomistic Document**, rename it **n-Octanol**.

Sketch an octanol molecule, leaving display style at default settings.

As before, perform a geometry optimization using charge groups. This uses the same settings as above, so you can start the calculation immediately.

Ensure that **n-Octanol.xsd** is the active document, click **Run** on the Forcite Calculation dialog to start the calculation. Close the dialog.

This creates a new folder, **n-Octanol Forcite GeomOpt**, in the Project Explorer. On completion, this contains the optimized structure with charge groups assigned.

Select **File** | **Save Project** followed by **Window** | **Close All** from the menu bar.

3. Constructing an amorphous cell of propionic acid in n-octanol

Next, create an input structure for the Solvation Free Energy calculation using the Amorphous Cell module. The structure contains one molecule of propionic acid and several solvent molecules.

Select **Modules** | **Amorphous Cell** | **Calculation** from the menu bar to open the Amorphous Cell Calculation dialog.

In the **Composition** table, click in the **Molecule** column and select the optimized structure **Propionic acid.xsd** in the Propionic acid Forcite GeomOpt folder from the dropdown list. Ensure that the **Loading** is **1**.

Click the next row and select the optimized structure **n-Octanol.xsd**. Specify the **Loading** of n-Octanol as **100**.

The experimental density of octanol is 0.824 g/cm³. Construct the system at this density with a box length of about 3 nm. Use the same energy settings in the Amorphous Cell calculation as you used in Forcite.

On the **Setup** tab, define the **Density** as **0.824**. Click **Options...** to open the Amorphous Cell Options dialog. Select the **Include non backbone torsions** checkbox and close the dialog.

On the **Energy** tab, select **COMPASSIII** from the **Forcefield** dropdown list. Select **Group based** as the **Electrostatic** summation method.

In the Project Explorer, select the project root, then click **Run** to start the calculation. Close the dialog.

Note: Since valid charge groups are present on the input structures, Amorphous Cell does not recalculate them; undoing the automatic charge group calculation is not required. Group based summation for van der Waals interaction is not available in Amorphous Cell and can be replaced by Atom based summation.

This creates a new folder, **Propionic acid AC Construct**, in the Project Explorer. On completion, this contains the solvated molecule structure in a trajectory document. Amorphous Cell always outputs a trajectory document, in case multiple frames are requested. In the following, however, it is more convenient to proceed with a structure document, so copy the structure over first.

Select the project root and create a new **3D Atomistic Document**, rename it **PA_nOct**.

Right-click in the Amorphous Cell structure **Propionic acid.xtd** and select **Copy**. Right-click in the new document **PA_nOct.xsd** and select **Paste**.

Before continuing, save and close all the open documents.

Select **File** | **Save Project** followed by **Window** | **Close All** from the menu bar.

4. Equilibrating the structure

Before you start the Solvation Free Energy calculation, equilibrate the initial structure. The Amorphous Cell calculation performed a geometry optimization, but the structure might still contain stress points and density inhomogeneities that need dynamic relaxation. Running dynamics with a thermostat is a way to remove the excess heat from the system. The NHL thermostat is a good thermostat for both equilibration and production runs.

Forcite Plus: Calculating the solvation free energy of propionic acid in n-octanol

Make sure **PA_nOct.xsd** is the active document. Open the **Forcite Calculation** dialog and choose **Dynamics** as the **Task**, click **More...** to open the Forcite Dynamics dialog.

For the **Ensemble**, select **NVT**. Define the **Total simulation time** as **10 ps**. On the **Thermostat** tab, select **NHL** for **Thermostat** and define the **Q ratio** as **1.0**. Close the dialog.

Note: The default *Q ratio* of 0.01 ensures damping of the temperature oscillations that can occur with the Nosé thermostat, allowing faster equilibration. The NHL thermostat is an extension of the Nosé thermostat, with its own damping mechanism. This means you can use a higher *Q ratio* with NHL. For a *Q ratio* of 1, the impact of the thermostat is sufficiently weak that you can use the same value in both equilibration and production runs.

On the **Energy** tab, select **Group based** for both the **Electrostatic** and **van der Waals** summation methods.

Click **Run** to start the calculation and close the dialog.

This creates a new folder **PA_nOct Forcite Dynamics** in the Project Explorer. Chart and status text documents appear shortly after the calculation starts, recording the progress of the calculation. The equilibration might take a few minutes to complete, depending on the performance of your computer.

Tip: You can reduce the time required for the calculation by running the dynamics calculation in parallel, where multiple cores and licenses are available.

In a real calculation you would equilibrate for much longer, say 100 ps, followed by an equilibration with a barostat of about the same time to adjust the cell dimensions.

Note: If you want to continue with the next step without waiting for the equilibration to complete, you can import a prepared structure from the Examples folder, in **Examples\Projects\Forcite\SolvationFreeEnergy.stp** project. This structure was equilibrated with 100 ps NVT dynamics, followed by 100 ps NPT dynamics. Results might differ depending on which structure you continue from.

Before continuing, save all open documents and clear the work space.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

5. Running the solvation free energy calculation

Continue the calculation with the final structure of the equilibration run, as found in the **PA_nOct Forcite Dynamics** folder (or the equivalent structure from the Examples folder).

Open the **3D Atomistic** document (not the trajectory) in the Forcite dynamics folder, **PA_nOct.xsd**.

This 3D Atomistic document contains the final structure from the dynamics calculation.

Select **Modules | Forcite | Calculation** to open the Forcite Calculation dialog. Choose **Solvation Free Energy** as the **Task** and click **More...** to open the Forcite Solvation Free Energy dialog.

You can calculate the total solvation free energy as the sum of three contributions: *Ideal*, *van der Waals*, and *Electrostatic*.

Each contribution requires a separate Solvation Free Energy calculation. You can use the same input structure for all contributions, and run the calculations in any order. It is also possible to run all three contributions in a single calculation, which performs a sequence using the same settings in all runs.

This tutorial helps you to run through the individual contributions one-by-one, starting with the Ideal contribution and using the default Thermodynamic integration algorithm throughout. To reduce the time required for the calculations in the tutorial, decrease the number of time steps to 1000 for equilibration, and 5000 for production. In a real simulation, you would run much longer. The simulation in the Examples folder used 50000 steps equilibration and 100000 steps production. This tutorial varies the coupling parameter from 0 to 1, which means that the charges decrease from full COMPASS charges to zero. You can also run the coupling parameter in the reverse direction, and the result remains the same, on average. For the Ideal contribution, you may decrease the number of coupling parameter steps.

Define the **Contribution** as **Ideal**. Specify the **Equilibration steps** as **1000** and the **Production steps** as **5000**. Define the Coupling parameter **Steps** as **5**.

You can leave the Dynamics and Geometry Optimization settings, as well as the Energy tab settings, at their values specified in the previous steps. Before running the calculation, specify which molecule in the structure is the solute molecule, by creating a set.

In the structure, double-click any atom in the solute molecule to select the molecule. Click **Add** to create a set called *SoluteAtoms*.

Click **Run** to start the calculation.

This creates a new folder, **PA_nOct Forcite FreeEnergy**, in the Dynamics folder. After a short while a status text document appears, recording the progress of the calculation. The calculation of the Ideal contribution only takes a few minutes to complete, since it involves a single molecule in an empty box. On completion, the calculation returns a report document, a chart document, and a study table document.

Open the report document **PA_nOct.txt** and scroll down to the section containing the solvation free energy results.

The Ideal contribution of the Solvation free energy of propionic acid is about 25.5 kcal/mol. Since this is the free energy cost of removing charges on the molecule, it is close to minus the electrostatic energy of the optimized structure, as calculated above. You can verify this by looking up the electrostatic energy in the report document of the geometry optimization run of propionic acid (around -26.2 kcal/mol).

Note: The free energy values quoted in this tutorial are taken from a much longer run, available in the Examples folder. As the simulations in this tutorial are much shorter, your results may be different.

The solvation free energy is determined by integrating the free energy derivatives as calculated in the simulation. The chart shows the integral as a function of the coupling parameter.

Open the chart document **PA_nOct FreeEnergy.xcd**. Confirm that the value at coupling parameter 1 matches the reported solvation free energy.

The data in the chart is also contained in the study table document, in the column *A/lambda*). The actual free energy derivate values are contained in the column labeled *$\langle dE/d\lambda \rangle$*.

Forcite Plus: Calculating the solvation free energy of propionic acid in n-octanol

Open the study table document **PA_nOct.std**. Select the first column by clicking the header **A**. Hold down **CTRL** and click header **D** to select the fourth column. Click **Quick Plot** .

The plot shows a straight line from a value of about 50 kcal/mol to 0 at coupling parameter 1. The free energy corresponds to the area under the line, which in this case is half the initial value.

Before proceeding with the other contributions, save all open documents and clear the work space.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

Continue with the Electrostatic contribution to the Solvation free energy. As the free energy derivatives for electrostatics are approximately linear, you can use the same number of coupling parameter steps as for the Ideal contribution.

Open the same input structure document as used in the previous step, **PA_nOct.xsd**.

On the Forcite Solvation Free Energy dialog, choose **Electrostatic** as the **Contribution**.

Click **Run** to start the calculation.

This creates a new folder, **PA_nOct Forcite FreeEnergy (2)**, in the Dynamics folder. After a short while, a status text document appears recording the progress of the calculation. The calculation of the Electrostatic contribution takes much longer, since it involves all molecules in the system.

Note: The Progress as reported in the Job Explorer is that of individual dynamics runs, rather than the complete Solvation Free Energy run. After each equilibration or production run, this progress is reset to 0.

Tip: Each contribution in the free energy of solvation calculation is independent. Providing that you have the appropriate licenses and CPUs available these can be run simultaneously.

As before, on completion the report, chart and study table documents are returned. The report document includes the Electrostatic contribution.

Open the report document **PA_nOct.txt** and scroll down to the section containing the solvation free energy data.

The Electrostatic contribution for propionic acid in octanol is about -29.4 kcal/mol, close to the Ideal contribution, and close to the electrostatic energy of an optimized molecule. The sum of the Ideal and the Electrostatic contribution is about -3.9 kcal/mol, indicating that about 3.9 kcal/mol is stored in the electrostatic interaction between propionic acid and n-octanol.

Note: The free energy values quoted in this tutorial are taken from a much longer run, available in the Examples folder. As the simulations in this tutorial are much shorter, your results may be different.

Before proceeding with the final contribution, save all open documents and clear the work space.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

The van der Waals contribution is the most difficult to determine since the free energy derivative is non-linear. This means you need to have sufficient number of coupling parameter steps to capture the curvature. You can use the same number of equilibration and production steps as for the Electrostatic contribution, but increase the number of coupling parameter steps.

Open the same input structure document as used in the previous step, **PA_nOct.xsd**.

On the Forcite Solvation Free Energy dialog, for the **Contribution** select **van der Waals**. For the number of Coupling parameter **Steps**, specify **10** and close the dialog.

Click **Run** to start the calculation and close the dialog.

This creates a new folder, **PA_nOct Forcite FreeEnergy (3)**, in the Project Explorer. Since you have used twice as many steps as for the Electrostatic contribution, this run takes about twice as long.

On completion, open the resulting chart document.

Open the chart document **PA_nOct FreeEnergy.xcd**.

Note how the free energy as a function of the coupling parameter is non-monotonous. After an initial dip the free energy becomes positive, indicating the cost to create a cavity in the octanol solvent. Once a cavity is created, the attractive dispersion interaction with the solvent dominates, and the free energy turns negative. The final value ought to be negative, and about -2.8 kcal/mol.

Open the text document **PA_nOct.txt** and confirm that the van der Waals contribution to the solvation free energy is about -3 kcal/mol.

You have obtained all contributions to the solvation free energy.

The total sum is:

$$25.5 - 29.4 - 2.8 = -6.7 \text{ kcal/mol}$$

Tip: You can run all contributions in a single calculation by selecting **All** for Contribution. The calculation provided in the Examples folder was run this way. Such a calculation returns all the graphs in a single chart document and a single study table with separate data sheets for each contribution.

Finally, to calculate $\log P$ for propionic acid, you could repeat a calculation using water as solvent, instead of octanol. Use the experimental hydration free energy of propionic acid of -6.36 kcal/mol ([Wolfenden, 1981](#)). Since this value is slightly less negative than the calculated value for octanol, you can predict that propionic acid is soluble in octanol, and expect $\log P$ to be positive.

$\log P$ is obtained by the equation:

$$\log P = 0.434 \frac{A_{\text{water}} - A_{\text{octanol}}}{RT}$$

Where:

0.434 corresponds to ${}^{10}\log e$.

R is the gas constant ($1.987 \cdot 10^{-3}$ kcal/mol/K).

T the temperature in the simulation (298 K).

A_x is the solvation free energy in solvent x.

Substituting the above data gives $\log P = 0.25$, in excellent agreement with the experimental value of 0.246 ([Vitas-M Lab](#)).

Select **File | Save Project** from the menu bar.

This is the end of the tutorial.

References

Wolfenden, R.; Andersson, L.; Cullis, P. M.; Southgate, C. C. B., "Affinities of amino acid side chains for solvent water", *Biochemistry*, **20**(4), 849–855 (1981).

Log P data obtained from Vitas-M Lab (ID: STL168039), <https://vitasmlab.biz/findedsstk/?stk=STL168039>.

Calculating the melting temperature of a metal using the coexistence method

Purpose: Introduces the use of Forcite and an embedded atom method forcefield to calculate the melting point of a metal using the coexistence method.

Modules: Forcite Plus, Amorphous Cell

Time: 

Prerequisites: Visualizer Tutorial

Background

Determination of the melting temperature of a material is of interest in a range of materials applications.

The most basic method for determining the melting point of a material is to simply heat a unit cell of solid until it melts. Practically this means running an NVT or NPT ensemble dynamics simulation while increasing the thermostat temperature over the course of the run, in a way mimicking a real experiment. However, due to the small time scales available in molecular dynamics, the rate of heating is very high. This, coupled with the small system size results in superheating, so provides only an upper bound to the melting temperature. In a similar way a liquid may also be cooled until it crystallizes, giving hysteresis bounds between which the melting temperature may be found.

A slightly more sophisticated procedure is the coexistence method, where a solid-liquid interface cell is constructed at a temperature near the predicted melting temperature. The main calculation in this approach is typically performed in the NVE or NPH ensemble. If the temperature of the system as a whole lies below the melting temperature, some region of the cell will crystallize, generating latent heat and raising the temperature. Likewise if the temperature is too high, some of the cell will melt, cooling the system. In this way a molecular dynamics calculation run for long enough will equilibrate to the melting temperature.

The paper "Precise calculation of melting curves by molecular dynamics" ([Karavaev, 2016](#)) provides a good overview of the different methods available to determine melting points.

In addition to evaluating the melting point, the coexistence method may also be used to obtain relevant properties such as solid-liquid interface stiffness or energy, which may be used as parameters in more coarse-grained approaches such as phase field models.

Introduction

This tutorial shows you how to calculate the melting temperature of fcc copper using the coexistence method. You will use a modified and simplified version of the method described in ([Asadi, 2015](#)).

This tutorial covers:

- [Getting started](#)
- [Creating the forcefield](#)
- [Equilibrating the crystal](#)
- [Equilibrating the liquid](#)
- [Building the coexistence cell](#)
- [Establishing the melting temperature](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio

Open the **New Project** dialog and enter **CoexistenceMelt** as the project name, click the **OK** button.

The new project is created with *CoexistenceMelt* listed in the Project Explorer.

2. Creating the forcefield

You will first need a suitable forcefield, several EAM forcefields are included in Materials Studio. However, you may wish to use a different forcefield, either because you believe it to be more accurate for your problem or because you need to work with an element not included in the standard Materials Studio forcefields. EAM forcefields are commonly published in a tabulated representation in one of several standard formats and Materials Studio includes a script to convert these into the .off format. Two example files containing tabulated EAM data are also provided, you will use one of these in this tutorial.

Click the **Import** button  and navigate to the **Examples\Scripting** folder. Make sure that **All Files (*.*)** is selected and double-click on **ConvertEAMtoOFF.pl**.

Click **Import** again and double-click on **CuNi_Example.eam.alloy.txt**.

In the Project Explorer, double-click on **ConvertEAMtoOFF.pl**. Change the input filename (around line 35) to **CuNi_Example.eam.alloy** and press **CTRL+S**.

On the Scripting toolbar, click the **Debug** button.

Tip: You could add the EAM conversion script to the User Menu commands and make the input filename an argument. Refer to the Executing scripts from the User menu tutorial for more information.

The script should now run and create a forcefield file called **CuNi_Example.eam.alloy.off**. Open and inspect the forcefield.

Open the **CuNi_Example.eam.alloy.off** forcefield and select the **Interactions** tab. Open the **Show interaction** dropdown list.

An EAM forcefield consists of three types of interactions: Electron Density, Embedding Function, and EAM Pair Potential.

The electron density function for a pair of atoms i and j describes the contribution of atom j to the electron density experienced by i . Summed over all neighbors of i , this gives the total electron density ρ , which forms the input to the embedding function. You will create a plot of the embedding function for copper.

Set **Show interaction** to **Embedding Function**. Select the row for the **Cu** forcefield type.

At the top of the Interactions tab, click **Extract To**.

A study table is created with two columns containing the embedding energy for a range of densities.

In the study table select columns **A** and **B**. Click the **Quick Plot** button  on the Study Table Viewer toolbar.

A plot shows the energy stored in a copper atom when it is embedded in a field of given electron density. The embedding energy is 0 at zero density and becomes more negative as the density increases. At a certain density, the embedding energy becomes less favorable.

Set **Show interaction** to **EAM Pair Potential**. Select the row for the combination of the **Cu** and **Cu** forcefield types. At the top of the Interactions tab click **Extract To**.

In the study table select columns **A** and **B** and click the **Quick Plot** button .

The EAM Pair Potential is largely repulsive and prevents atoms from collapsing under the embedding energy.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

3. Equilibrating the crystal

The next step is to import the fcc Cu structure.

Click **Import**, navigate to the **Structures\metals\pure-metals** folder and double-click on **Cu.xsd**. Select **File | Save As...** and rename the file **Cu_Solid**.

To run realistic molecular dynamics simulations many more than the 4 atoms of the unit cell are required.

Select **Build | Symmetry | Supercell** to open the Supercell dialog. Set the **Supercell range** to **10** in all three directions, click **Create Supercell**, and close the dialog.

You will use this structure as the basis for the solid region of the coexistence calculation. First, run a short calculation using the NVT ensemble to reduce stress before starting the NPT run. Since this is an initial equilibration run, you will use a Velocity Scale thermostat which is able to very rapidly correct the kinetic energy.

Forcite Plus: Calculating the melting temperature of a metal using the coexistence method

Click the **Forcite** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Forcite | Calculation** from the menu bar.

Set the **Task to Dynamics** and click **More...** to open the Forcite Dynamics dialog. Set the **Ensemble** to **NVT**, the **Temperature** to **1200 K**, and the **Frame output every** to **500**. On the **Thermostat** tab, select **Velocity Scale** as the **Thermostat** and close the dialog.

On the **Energy** tab select **Browse...** from the **Forcefield** dropdown list, then choose **CuNi_Example.eam.alloy.off** in the Choose Forcefield dialog.

You do not need to set the cutoff distance when working with an EAM tabulated forcefield. Forcite will always use the full range of the tabulation when working with EAM.

Note: This is not the case for van der Waals tabulated potentials. These use the usual van der Waals cutoff distance which can be set on the Forcite Non-Bond Options dialog.

Click **Run** and close the dialog.

When the NVT run starts a new folder, **Cu_Solid Forcite Dynamics**, is created. The results of the NVT dynamics calculation are stored in this folder when the job is complete.

Next, run an NPT dynamics calculation from the final frame of the trajectory. This ensures that the lattice parameter has the correct equilibrium value for the current forcefield, this could be slightly different from the experimental value. The Andersen barostat allows only isotropic changes in the cell - this is suitable as the cell should remain cubic. The Velocity Scale thermostat can change the dynamics of the atoms in an unphysical way, which could influence the result, so it is advisable to use the NHL thermostat instead. This has a much weaker perturbation effect on the system, so it is preferred for production runs.

Ensure that **Cu_Solid Forcite Dynamics\Cu_Solid.xsd** is the active document and open the Forcite Calculation dialog, click **More...** on the Setup tab.

Set the **Ensemble** to **NPT**, the **Total simulation time** to **25 ps**, and the **Pressure** to **0.000101325 GPa**.

On the **Thermostat** tab, set the **Thermostat** to **NHL** and set the **Q ratio** to **1**.

On the **Barostat** tab, set the **Barostat** to **Andersen**. Close the dialog.

Click **Run** and close the dialog.

A new folder, **Cu_Solid Forcite Dynamics**, will be created in the existing **Cu_Solid Forcite Dynamics** folder. While this calculation is running, you can start preparing the liquid cell. While the calculation is running, you should save the project.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

4. Equilibrating the liquid

You now need to establish the density of liquid copper at a temperature above the melting temperature. The experimentally determined density of liquid copper at the melting point is 8.02 g/cm^3 . However, the interatomic potential used here may result in a different value.

Forcite Plus: Calculating the melting temperature of a metal using the coexistence method

You will create an initial liquid geometry using the Amorphous Cell module and equilibrate this using molecular dynamics. This will be used later to construct the coexistence cell.

To create a unit cell of liquid using the Amorphous Cell module, start with an atomistic document containing a single Cu atom.

Select the project root and create a new **3D Atomistic Document**, rename it **Cu_Atom**.

Sketch a single Cu atom. Save and close the document.

You will now use the Amorphous Cell module to create an initial liquid geometry. Since the aim is just to create an initial configuration in a disordered state, the default forcefield, Universal, can be used.

Select **Modules | Amorphous Cell | Calculation** from the menu bar to open the Amorphous Cell Calculation dialog.

In the **Composition** table, click in the **Molecule** column and select **Cu_Atom.xsd** from the dropdown list. Set the **Loading** to **4000** and the **Density** to **8.02**.

Click the **Options...** button to open the Amorphous Cell Options dialog. Uncheck the **Optimize geometry** checkbox and close the dialog.

In the Project Explorer click on the tree root, then click the **Run** button to start the construction. Close the dialog.

A new folder, **Cu_Atom AC Construct**, is created in the Project Explorer.

Once the Amorphous Cell job is finished, copy the single frame output trajectory to a new atomistic document.

Make **Cu_Atom AC Construct\Cu_Atom.xtd** as the active document. Select **Edit | Select All** followed by **Edit | Copy** from the menu bar.

Create a new 3D Atomistic document in the project root, right-click in this document and select **Edit | Paste** from the menu bar.

Rename the document to **Cu_Liquid** and save.

You will now establish the equilibrium density at 1500 K. You will repeat the steps used earlier for the solid, this time using the higher temperature.

Open the Forcite Dynamics Calculation dialog. Set the **Ensemble** to **NVT**, the **Total simulation time** to **5 ps**, and the **Temperature** to **1500 K**.

On the **Thermostat** tab, select **Velocity Scale** as the **Thermostat**. Close the dialog.

Click **Run** on the Forcite Calculation dialog.

A new folder, **Cu_Liquid Forcite Dynamics**, is created and populated with the results of the NVT calculation. Wait for this to finish before continuing with an NPT dynamics simulation.

Since this system is a liquid, which can fit into a cell of any shape, you can require the simulation cell to remain cubic. Therefore, the Andersen barostat remains suitable.

Forcite Plus: Calculating the melting temperature of a metal using the coexistence method

Ensure that **Cu_Liquid Forcite Dynamics\Cu_Liquid.xsd** is the active document.

Open the Forcite Dynamics dialog, set the **Ensemble** to **NPT** and the **Total simulation time** to **25 ps**. On the **Thermostat** tab, set the **Thermostat** to **NHL**. Close the dialog.

Click the **Run** button to start the calculation and close the dialog.

Like before, a new folder, **Cu_Liquid Forcite Dynamics**, will be created in the existing **Cu_Liquid Forcite Dynamics** folder. You should now wait for all running calculations to finish. Once they are complete, you will take the value of the density from the liquid NPT calculation text report.

Open **Cu_Liquid Forcite Dynamics\Cu_Liquid Forcite Dynamics\Cu_Liquid.txt**. At the bottom of this file, in the **---- Dynamics summary ----** section, find the average density.

Make a note of this number for later.

Save the project.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

5. Building the coexistence cell

Now you will use the Amorphous Cell Packing task to build our coexistence cell. Copy the final trajectory of the solid NPT calculation into the root directory so you can work there.

Double-click on **Cu_Solid Forcite Dynamics\Cu_Solid Forcite Dynamics\Cu_Solid.xsd** on the Project Explorer, to bring the equilibrated solid Cu structure into focus.

Right-click in the 3D viewer and select **Copy**.

Create a new 3D Atomistic document in the project root, right-click in this document and select **Paste**. Rename this document **Cu_Build**.

Close **Cu_Solid Forcite Dynamics\Cu_Solid Forcite Dynamics\Cu_Solid.xsd**.

You should now have a copy of the equilibrated solid structure, **Cu_Build.xsd**, in focus.

You will constrain these atoms not to move in a dynamics simulation in preparation for later, and extend the cell to include a vacuum region.

Select **Edit | Select All**. Select **Modify | Constraints** to open the Edit Constraints dialog. Check the **Fix Cartesian position** checkbox and close the dialog.

To maintain the integrity of our interface if atoms have drifted across periodic boundaries during the dynamics calculations, hide all but the original cell contents.

Right-click in the 3D viewer and choose **Display Style** to open the Display Style dialog. On the **Lattice** tab, change the **Display Style** to **Original** then close the dialog.

Right-click in the 3D viewer and select **Lattice Parameters** to open the Lattice Parameters dialog. On the **Advanced** tab, uncheck the **Keep fractional coordinates fixed during changes to the lattice** checkbox. On the **Parameters** tab, double the c value and close the dialog.

You now have an atomistic document which contains the solid in one half and a vacuum region on the other.

Press the up arrow twice to rotate the structure.

Select **Tools | Atom Volumes & Surfaces** to open the Atom Volumes & Surfaces dialog. Leave all the settings at their defaults and click **Create**. Wait for this process to finish and then close the dialog.

This should now have created an isosurface separating the solid and vacuum regions. The Amorphous Cell Packing task will fill in an enclosed isosurface. The isosurface you just created now encloses the solid, so you need to reverse it so it encloses the vacuum before proceeding.

Open the Display Style dialog, on the **Isosurface** tab check the **High values inside** checkbox. Close the dialog.

Now the vacuum region can be filled.

Open the Amorphous Cell Calculation dialog. Set the **Task to Packing** and the **Density** to the value calculated earlier. This value should be around **7.7**.

In the **Composition** table, **Cu_Atom.xsd** should still be present. Click the **More...** button to open the Amorphous Cell Packing dialog. Check the **Pack in isosurface enclosed volume** checkbox and close the dialog.

Click the **Options...** button to open the Amorphous Cell Options dialog and ensure that the **Optimize geometry** checkbox is still unchecked. Close the dialog.

Ensure the **Cu_Build.xsd** structure is in focus, then click **Run** to start the construction. Close the dialog.

A new folder **Cu_Build AC Packing** is created in the Project Explorer and the output of the packing job is stored here when the simulation is complete.

Now copy the single frame output trajectory to a new atomistic document.

Bring the document **Cu_Build AC Packing\Cu_Build.xtd** into focus.

Select **Edit | Select All** followed by **Edit | Copy** from the menu bar.

Create a new 3D Atomistic document in the project root, right-click in this document and select **Paste**. Select the isosurface and press **DELETE**.

Rename the document to **Cu_Melt**.

6. Establishing the melting temperature

Note: At this stage you could check the constraints are in place by selecting [Color by Constraint](#) on the Display Style dialog.

Now run a short NVT calculation to minimize stress in the liquid.

Select **Cu_Melt.xsd** as the active document and open the Forcite Calculation dialog.

Open the Forcite Dynamics dialog and set the **Ensemble** to **NVT**, the **Total simulation time** to **5 ps**, and the **Temperature** to **1500 K**. Change **Frame output every** to **250**. On the **Thermostat** tab, select **Velocity Scale** for **Thermostat**. Close the dialog.

Click the **Run** button to start the calculation.

This creates a folder named **Cu_Melt Forcite Dynamics**. Wait until this run is finished.

At this stage you would usually run a series of calculations in the NPT ensemble, at a range of temperatures around the estimated melting point. The extent to which the cell melts or freezes during the calculation gives us an indication of how close the ensemble temperature is to the melting temperature. For this potential 1200 K was found to be closest to the melting temperature.

From the final trajectory of this NPT run you will run an NPH calculation which should equilibrate to the melting temperature.

To save time you will perform only one NPT calculation at 1200 K. First, remove the constraints that were added earlier.

Open **Cu_Melt Forcite Dynamics\Cu_Melt.xsd** as the active document.

Select **Edit | Select All** to select all atoms then select **Modify | Constraints** to open the Edit Constraints dialog. Uncheck the **Fix Cartesian position** checkbox and close the dialog.

Now you will run the NPT calculation. The crystal and the liquid should each have the correct density for the applied pressure, but there is now an interfacial region between them which could have a different density, so the c cell parameter must be allowed to adjust for this. However, the a and b cell parameters act differently (they are determined by the lattice constant of the crystal), so a barostat that allows the cell parameters to vary independently is required, such as the Parrinello barostat.

Open the Forcite Dynamics dialog.

Set the **Ensemble** to **NPT**, the **Total simulation time** to **25 ps**, and the **Temperature** to **1200 K**.

On the **Thermostat** tab, set the **Thermostat** to **NHL**.

On the **Barostat** tab, set the **Barostat** to **Parrinello**. Close the dialog.

Click the **Run** button to start the calculation.

This run may take a little longer than previous calculations.

Select **File | Save Project** followed by **Window | Close All** from the menu bar.

Now you have a cell prepared near the melting temperature and the main calculation in the NPH ensemble can be run.

Open **Cu_Melt Force Dynamics\Cu_Melt Force Dynamics\Cu_Melt.xsd** as the active document.

Open the Forcite Dynamics dialog.

Set the **Ensemble** to **NPH** and the **Total simulation time** to **50 ps**. Close the dialog.

Click the **Run** button to start the calculation and close the dialog.

Note: It may seem counterintuitive that *Temperature* field is available for an NPH ensemble calculation. However, this input temperature determines the Q-factor of several barostats.

The NPH calculation for this potential equilibrates to around 1179 K.

While the steps detailed should provide a decent estimate for the melting temperature of a material, you notice that the value obtained for copper is quite different from experimentally obtained values (1358 K). There are a few things to keep in mind if you use this method for research:

- This method effectively calculates the melting temperature of the potential. As such, a potential which was never intended to describe the melting point of a material, or a potential which is poorly fitted, may result in a melting temperature quite different from the experimental value.
- Depending on the potential used, runtime parameters such as the cutoff distance may play a role.
- In this simulation the Cu(1 0 0) surface is used. However, other surfaces such as (1 1 1) may behave differently.

There may be finite size effects which influence the accuracy of the result.

As this is a tutorial, to keep runtime low a small cell is used.

In a real calculation you should ensure your simulation is converged with respect to cell length and interface area and that your system is sufficiently large that size effects are negligible. These considerations are detailed more thoroughly in the reference materials.

Select **File | Save Project** from the menu bar.

This is the end of the tutorial.

References

Asadi, E.; Zaeem, M. A.; Nouranian, S.; Baskes, M. I., "Two-phase solid–liquid coexistence of Ni, Cu, and Al by molecular dynamics simulations using the modified embedded-atom method", *Acta Mat.*, **86**, 169-181 (2015). <http://dx.doi.org/10.1016/j.actamat.2014.12.010>.

Karavaev, A. V.; Dremov, V. V.; Pravishkina, T. A., "Precise calculation of melting curves by molecular dynamics", *Comp. Mat. Sci.*, **124**, 335-343, (2016). <http://dx.doi.org/10.1016/j.commatsci.2016.08.014>.

Chapter 12: GULP tutorials

The following tutorial illustrates how to utilize GULP's capabilities.

- [Calculating the properties of diamond](#)
- [Forcefield fitting with GULP: SnO₂ library derivation](#)

Calculating the properties of diamond

Purpose: Introduces the GULP module for calculating the properties of ionic materials and molecular solids.

Modules: Materials Visualizer, GULP

Time: 

Prerequisites: Using the crystal builder Visualizer Tutorial

Introduction

Typically, classical simulations techniques in Materials Studio have concentrated on simulating condensed phases of liquids or soft materials and molecular structures. GULP provides tools that allow the simulation of ionic materials, metals, and molecular solids, previously the domain of computationally expensive quantum mechanics calculations. GULP includes 2D surface and molecular calculations as well as traditional 3D crystal structures.

This tutorial takes you through a simple calculation of the mechanical properties of diamond using GULP. You then create a surface of diamond and calculate the surface energy.

This tutorial covers:

- [Getting started](#)
- [To optimize and predict mechanical properties](#)
- [To calculate the surface energy of the unreconstructed \(111\) surface of diamond](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **diamond** as the project name, click the **OK** button.

The new project is created with *diamond* listed in the Project Explorer. Load the crystal structure of the system to study. In this tutorial, you work with diamond.

Click the **Import** button  on the toolbar to open the Import Document dialog. Navigate to **Examples\Documents\3D Model** and double-click on **C.xsd**.

This structure has a lattice parameter of 3.567 Å, close to the experimentally measured, low temperature value of 3.556 Å. During this tutorial you can:

- verify that cell optimization with the Brenner potential produces a lattice parameter in good agreement with the experimental value.
- calculate the tensor of elastic coefficients for this structure.
- calculate the energy of the (111) surface of diamond.

2. To optimize and predict mechanical properties

Begin with the structure optimization. This calculation is very quick as the cell is very small and the structure you loaded was previously optimized.

Click **GULP**



on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the GULP Calculation dialog with several task options available. You need to carry out a geometry optimization.

Change the **Task** to **Geometry Optimization**.

GULP has many different forcefield libraries that use a variety of techniques from two-body interactions to many-body interactions. As you are working with diamond, use the [Brenner](#) potential for the calculations. The Brenner potential is a bond order potential you can apply to systems containing carbon, hydrogen, and oxygen. It has seen much use in simulating structures such as diamond and carbon nanotubes.

From the **Forcefield** dropdown list, select **Brenner** and click **View....**

The forcefield libraries are stored as text files and you can view them to see information such as references and charges.

Close the **GULP Forcefield Library: Brenner** view.

You can obtain a variety of properties from GULP energy calculations.

Select the **Properties** tab.

There are several properties available. These are all very quick to calculate on a small system like the diamond unit cell, so you can leave them all selected.

However, calculating lattice properties here generates elastic coefficients in an orientation that is different from the conventional orientation of the cubic crystal. This is a consequence of using a primitive cell in the calculation, and of specifying the structure in the GULP input file using cell parameters rather than cell vectors. Later, you can run a separate calculation to generate mechanical properties in a conventional representation, so for this Geometry Optimization calculation turn off calculation of lattice properties.

Clear selection of **Lattice properties** on the **Properties** tab.

Click **Run** to start the job.

When the job has completed a new folder, called C GULP GeomOpt, contains the following files:

- **C.xsd** is the optimized structure. Because the frequency calculation also generates phonon properties, this display includes the reciprocal lattice and Brillouin zone and path.
- **C.xtd** contains frames showing the structure after each optimization step. In this case optimization is very short, with 2-3 frames at most.
- **C.gin** is a text document containing the GULP input file.
- **C.gout** is a text document containing the GULP output.

The optimized structure displays in the primitive cell with 2 atoms in each cell. Comparing the results of the subsequent calculations with existing scientific literature is easier if you convert the structure to conventional cell.

Make the optimized structure C.xsd the current document. From the menu bar, select **Build | Symmetry | Conventional Cell**.

Now you can inspect the lattice parameters of the optimized cell.

From the menu bar, select **Build | Symmetry | Lattice Parameters**.

The lattice parameter is approximately 3.566 Å, in good agreement with the experimental value of 3.556 Å. Indicating that the Brenner potential accurately describes the geometry of the ground state of sp³-hybridized carbon.

Now change the symmetry of the diamond structure to P1.

From the menu bar, select **Build | Symmetry | Make P1**.

Many simulations require conversion of a high symmetry crystal structure to P1 symmetry. For example, during a molecular dynamics simulation the atoms move away from their equilibrium positions, and their positions no longer satisfy the symmetry constraints of the higher symmetry space group. The use of P1 symmetry in this tutorial allows generation of elastic constants for the same orientation as in the Brenner *et al.* ([2002](#)) paper.

On the **Setup** tab, for the **Task** select **Energy**.

Select the **Properties** tab and clear selection of all properties except for **Lattice properties**.

This makes it easier to see the results of elastic properties calculations in the output file.

Click **Run** to start the job.

When the job completes, a new set of output files appears in the C_GULP_Energy subfolder in the C_GULP_GeomOpt folder. You can now compare the calculated elastic coefficients to the previously reported ones.

Open **C.gout**. Press **CTRL + F** and find **Elastic Constant**.

Compare the C11, C12, and C44 values with those published by Brenner *et al.* ([2002](#)). To convert elastic coefficients from GPa to Mbar, divide the value in GPa by 100.

	Brenner (in Mbar)	GULP (in Mbar)
C11	10.7	10.75
C12	1.0	1.25
C44	6.8	7.21

3. To calculate the surface energy of the unreconstructed (111) surface of diamond

You can calculate the surface energy using the following equation:

$$\Delta U_{SE} = \frac{U_{surf} - U_{bulk}}{A}$$

GULP: Calculating the properties of diamond

Where:

U_{surf} is the energy of the surface

U_{bulk} is the energy of the bulk system

A is the surface area

You already have the energy of the bulk diamond from your previous calculation, but you need to normalize this by the number of atoms in the cell.

In the **C.gout** output file from the last calculation, search for **Total Lattice Energy** and write down the value in eV.

This energy value is close to -58.958 eV for the 8-atom cell of diamond. As you have a different number of atoms in the surface calculation, you need to scale the bulk energy to match.

Now you can build the (111) surface of diamond.

Change focus to the **C.xsd** document in the **C GULP Energy** subfolder. In the **Properties Explorer**, change the **Filter to Symmetry System** and note the **NumberOfAtoms**.

This structure contains 8 atoms in its symmetry system.

From the menu bar, select **Build | Surfaces | Cleave Surface** to open the Cleave Surface dialog. Change the **Cleave plane** to **1 1 1** and the **Fractional Thickness** to **8.0**. Click **Cleave** and close the dialog.

This creates a new structure, **C (1 1 1).xsd**. This is an ideally terminated surface; in more realistic scenarios you might investigate various known reconstructions that reduce the energy required to create a surface. It is also instructive to introduce hydrogen termination of the dangling bonds on the surface. However, this tutorial demonstrates only how to use straightforward GULP surface calculations.

On the **GULP Calculation** dialog, on the **Setup** tab change the **Task to Surface Calculations**. Click **More...** to open the **GULP Surface Calculations** dialog.

Use the **GULP Surface Calculations** dialog to define the surface region to use in the surface energy calculation. GULP optimizes atomic positions in the surface region while keeping the rest of the atoms (and the lattice parameters) fixed. The final output file includes the values of surface energies that correspond to both relaxed and unrelaxed surface geometries. You can also investigate convergence of the surface energy as a function of the number of surface layers.

Next, calculate the surface energy using 1, 2, or 3 surface layers.

Make sure that the surface layers selector shows 1 to 1. Click **Select** on the **GULP Surface Calculations** dialog.

This selects the top layer of atoms.

Click **Add** to add the selected atoms to the **SurfaceAtoms** set.

The set becomes visible in the 3D viewer. You need to find out how many atoms are in this set.

in the **Properties Explorer**, change the **Filter to Set** and note the value of the **NumItems** property.

The set contains eight atoms, the same as in the previous calculation of the bulk diamond.

Check **Calculate surface energy** and enter the bulk energy value produced in the previous calculation, in eV.

Since the number of atoms is the same, the value is about -58.958 eV.

Click Run.

When the calculation finishes, you can examine the output files in the C (1 1 1) GULP Surface subfolder.

Open **C (1 1 1).xtd** and click **Play**  on the **Animation** toolbar.

The atoms in the surface layer change their positions slightly.

In the **Properties Explorer**, change the **Filter** to **Lattice 2D**. Click **Step Forward** on the **Animation** toolbar to examine the individual frames.

The main piece of information you need is the calculated surface energy.

Open **C (1 1 1).gout** and search for **Surface energy**.

The file includes two entries, first for unrelaxed geometry, then for the optimized structure of the surface layer. The values are about 5.95 J/m² and 5.07 J/m², respectively. You can see that surface relaxation changes the energy significantly.

You can now repeat this exercise using wider surface areas.

Make **C GULP Energy\C (1 1 1).xsd** the active document. On the **GULP Surface Calculations** dialog, change the surface layers selector to show 1 to 2 and click **Select**.

This selects the two top layers of atoms.

Click Add to add the selected atoms to the **SurfaceAtoms** set.

This set now contains twice as many atoms as in the previous calculation, so adjust the bulk energy accordingly (-117.916 eV).

Run the calculation again.

When the calculation finishes, extract again the surface energy values from the output file in the C (1 1 1) GULP Surface (2) subfolder. The unrelaxed surface energy is the same as before, since you started with the same geometries. The relaxation effect is smaller now, and relaxed surface energy is about 5.36 J/m².

You can repeat this exercise with surface layers 1 to 3 included (remember to scale the bulk energy accordingly). The relaxed surface energy hardly changes when you add the third layer. This is expected since interatomic interactions are sufficiently short ranged in this system, and surface relaxation of an additional layer far from the terminated surface has little effect on the energy.

There are numerous examples of calculations of the surface energy of diamond in the literature using more accurate quantum-mechanical approaches. For example, a density functional theory, DFT, calculation using the popular PBE exchange-correlation functional produces surface energy of 5.66 J/m² according to Yin et al. (2015). Effects of relaxation were also studied in DFT calculations, for example, by De La Pierre et al. (2014) who used a more accurate B3LYP functional. They found that relaxation reduces the (111) surface energy by about 1.6 J/m² in qualitative agreement with the result of this investigation.

GULP: Calculating the properties of diamond

You can repeat this exercise to calculate the surface energies of other surfaces, such as (100) and (110). According to De La Pierre et al. ([2014](#)), the surface energy of the unreconstructed (100) surface is the least affected by atomic relaxation.

This is the end of the tutorial.

References

- D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, S.B. Sinnott, *J. Phys.: Condens. Matter* **14** (2002) 783.
- W.-J Yin, Y.-P. Chen, Y.-E. Xie, L.-M. Liu, S.B. Zhang, *Phys. Chem. Chem. Phys.* **17** (2015) 14083.
- M. De La Pierre, M. Bruno, C. Manfredotti, F. Nestola, M. Prencipe, C. Manfredotti, *Molecular Physics* **112** (2014) 1030.

Forcefield fitting with GULP: SnO₂ library derivation

Purpose: Explains how to use the Forcefield fitting task in GULP to obtain new potential parameters or to refine the existing ones.

Modules: Materials Visualizer, GULP

Time:  

Prerequisites: None

Introduction

The current libraries in GULP do not have parameters to describe the SnO₂ bulk structure. Therefore, to be able to model this material and to calculate its different properties with GULP, new forcefield parameters have to be derived. The Forcefield fitting task in GULP can be used to obtain those. The bulk modulus, some elastic constants and the experimental structure of SnO₂, have been used as observables in the forcefield fitting procedure.

This tutorial covers:

- [Getting started](#)
- [To define the forcefield types and functional forms](#)
- [To define the observables used in the fitting](#)
- [Fitting procedure](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ff_library** as the project name, click the **OK** button.

The new project is created with **ff_library** listed in the Project Explorer. You will load the crystal structure of the system you will be studying later.

2. To define the forcefield types and functional forms

The first step when performing a forcefield fitting task is to define the forcefield types and functional forms that describe the different interactions in the system. For the case under consideration, you need to define Buckingham parameters for the O-O, Sn-O and Sn-Sn two body terms.

When creating a new library you can proceed in two different ways, you can create a new library file (**.lib**) from scratch or you can modify an existing one. In this tutorial you will create a new library from scratch for the SnO₂ case. A library is just a text document, so you must open a text document.

Click the **New** button  on the toolbar and select **Text Document** from the dropdown list.

Rename the new text file to **SnO2.lib**.

GULP: Forcefield fitting with GULP: SnO₂ library derivation

You will be prompted that changing the extension may make the file unusable.

Click the **Yes** button to change the file extension.

Click the **GULP** button  on the **Modules** toolbar and choose **Calculation** from the dropdown list.

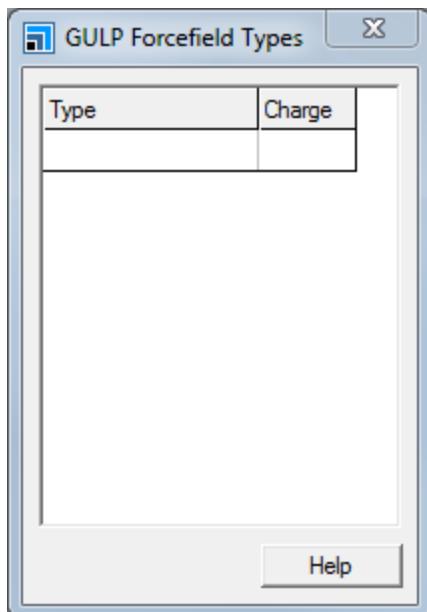
This opens the GULP Calculation dialog.

Change the **Task to Fit Forcefield**. Select **Browse...** from the **Forcefield** dropdown list to open the Choose GULP Forcefield dialog, then choose **SnO₂.lib** from the dropdown list. Change the **Charges** to **Forcefield assigned** and click the **More...** button.

This opens the GULP Fit Forcefield dialog, before entering the potentials parameters, the atom types should be defined.

Click the **Types...** button.

This opens the GULP Forcefield Types dialog which lists atom types and charge definitions.

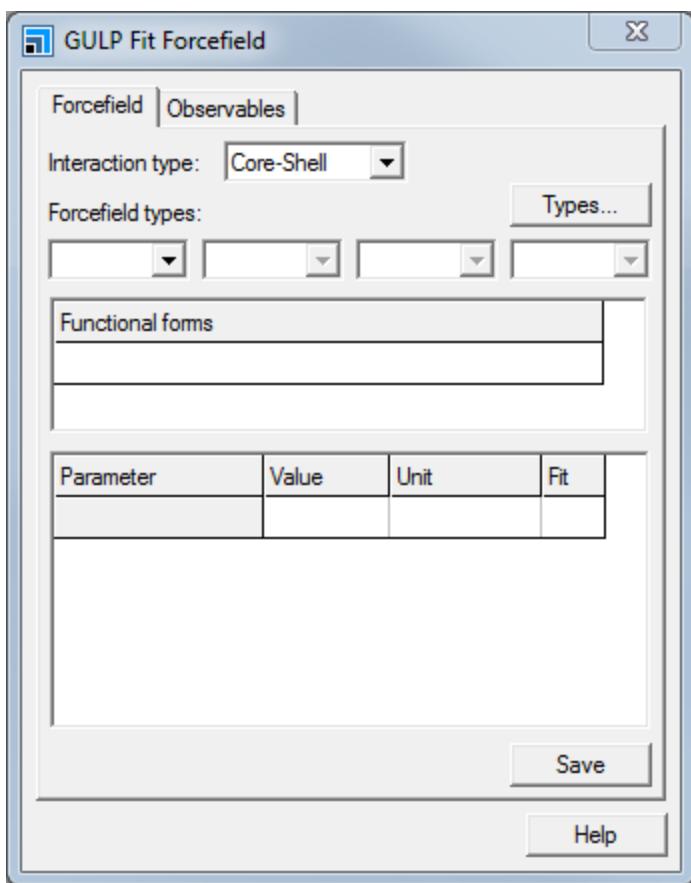


GULP Forcefield Types dialog

You are going to add two new atom types, Sn core and O core, with appropriate charges.

In the **Type** box enter **O core** and in the **Charge** box enter **-1.025**. On the next line, enter **Sn core** and **2.050**. Close the **GULP Forcefield Types** dialog.

You can now define the potential parameters on the GULP Fit Forcefield dialog.



GULP Fit Forcefield dialog, Forcefield tab

You need to define the functional form for each combination of potentials, O core - O core, Sn core - Sn core, and Sn core - O core.

Change the **Interaction type** to **Two-body**. In the **Forcefield types** section select **O core** as the first forcefield type and **O core** also for the second. In the **Functional forms** section, select **Buckingham (buck)** from the dropdown list.

Repeat this for the **O core - Sn core** and **Sn core - Sn core** combinations.

Next, you need to enter the following parameters for each case (these initial values are taken from *Bandura et al. J. Phys. Chem. B 2006, 110, 8386-8397*):

Potential Pair	A (eV)	rho (Å)	C (eV*Å ⁶)	rmax (Å)
O core - O core	5000	0.273	48.7	15.0
O core - Sn core	100000	0.169	16.0	15.0
Sn core - Sn core	1000000	0.205	6.3	15.0

Change the **Forcefield types** back to **O core** and **O core**. Choose the **Buckingham(buck)** functional form. Scroll down the **Parameter** box and enter the values for the parameters as listed above. Repeat this for **O core - Sn core** and **Sn core - Sn core**.

Initially you will only fit the A parameters for the three two-body terms. You will then use the obtained A parameters to fit the rho parameters, and finally those to fit the C ones. You need to indicate that the A parameters are the ones you want to fit.

For each pair potential, in the **Fit** column check the corresponding box for the Buckingham **A parameter**.

Click the **Save** button.

A new .lib file (SnO₂_2.lib) with all the defined atom types and parameters is created, containing:

```
species
Sn core 2.05
O core -1.025

buck 1
Sn core Sn core 1000000.0000000000 0.2050000000 6.3000000000 &
0.0000000000 15.0000000000 1 0 0
Sn core O core 100000.0000000000 0.1690000000 16.0000000000 &
0.0000000000 15.0000000000 1 0 0
O core O core 5000.0000000000 0.2730000000 48.7000000000 0.0000000000 &
15.0000000000 1 0 0
```

Close the **GULP Fit Forcefield** dialog.

3. To define the observables used in the fitting

To obtain the Buckingham parameters for the SnO₂ library, the following observables have been used in the fitting:

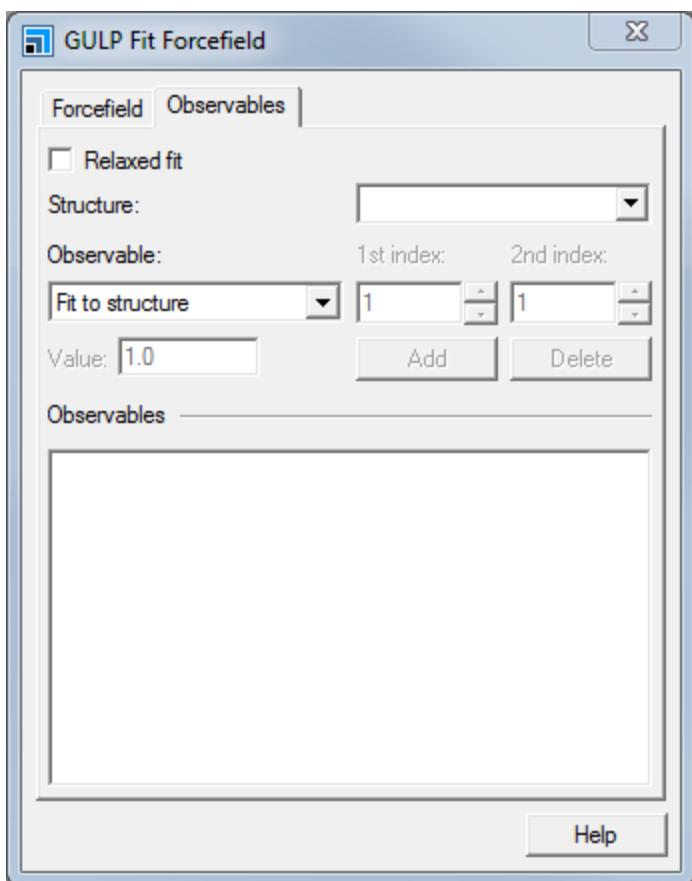
1. Experimental SnO₂ structure
2. Experimental bulk modulus: 212.3 GPa
3. Experimental elastic constants: C₁₁ = 261.7, C₃₃ = 449.6, C₄₄ = 103.1, and C₆₆ = 207.4 GPa.

Before defining all the above observables in the GULP Fit Forcefield dialog, you need to open the SnO₂ structure.

Click the **Import** button  on the toolbar to open the Import Document dialog. Navigate to the **Structures\metal-oxides** folder and double-click on **SnO₂.xsd**.

Once you have imported the structure, you can proceed to define all the observables in the dialog.

On the **GULP Calculation** dialog, check that the **Forcefield** is \SnO₂_2. Open the **GULP Fit Forcefield** dialog and select the **Observables** tab.



GULP Fit Forcefield dialog, Observables tab

You will perform a relaxed fitting to obtain the SnO₂ library. The relaxed fit option fits to structural displacements on relaxation rather than to the derivatives. This also means any observables are fitted to the optimized rather than experimental structure.

Check the **Relaxed fit** checkbox. Select **SnO2.xsd** from the **Structure** dropdown list. To define the experimental structure as observable select **Fit to structure** from the **Observable** dropdown list.

As you want to fit to the structure, you need to add it to the observables.

Click the **Add** button.

The SnO₂ structure will appear in the Observables list on the GULP Fit Forcefield dialog. Now you will add the other observables that you want to fit to.

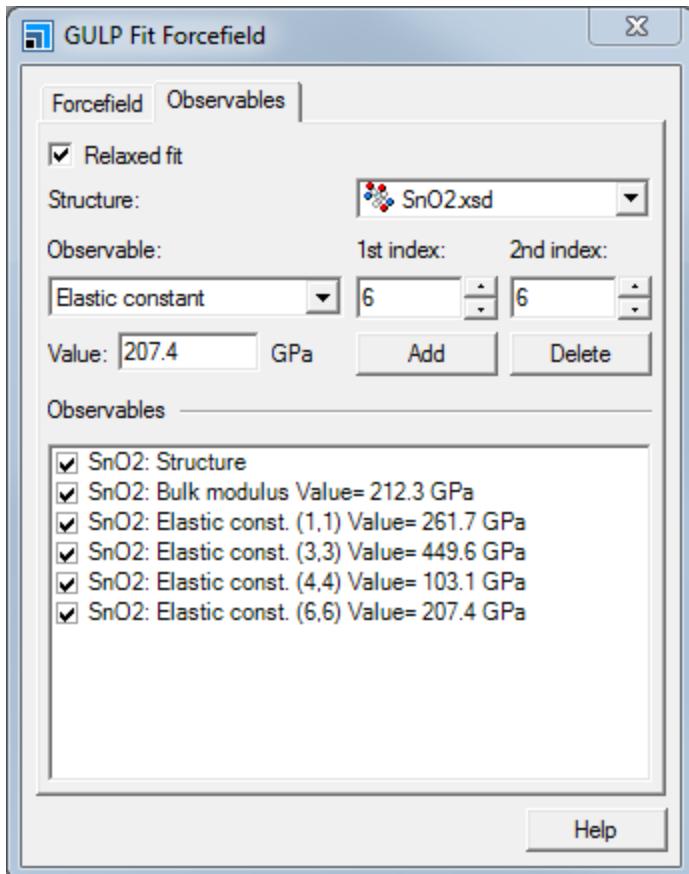
Change the **Observable** to **Bulk modulus**. Set the **Value** to **212.3** and click the **Add** button.

Change the **Observable** to **Elastic constant**. Ensure that the **1st Index** is set to **1** and the **2nd Index** is set to **1**. Set the **Value** to **261.7**. Click the **Add** button. Repeat this for:

1st Index = 3, 2nd Index = 3 and Value = 449.6

1st Index = 4, 2nd Index = 4 and Value = 103.1

1st Index = 6, 2nd Index = 6 and Value = 207.4.



GULP Fit Forcefield dialog Observables tab with values set as required

Close the **GULP Fit Forcefield** dialog and leave the GULP Calculation dialog open.

4. Fitting procedure

Now that the functional forms and observables have been defined, you can run the fitting calculation.

Click the **Run** button on the **GULP Calculation** dialog.

When the calculation is finished, the results of the fitting can be found in the **.gout** file. The new library is returned in the **.lib** file.

Open the GULP output file, **SnO₂_2.gout**.

Tip: The contents of your output file may vary from this example.

In the **.gout** calculation you will find the new A parameters and also the value of the sum of squares, which gives an indication about the quality of the fitting, for example:

**** Fit completed successfully ****

```
Final sum of squares =      4.302300
Final gradient norm  =      0.000286
Final values of parameters :
```

Parameter No.	Parameter Original	Parameter Final	Parameter Type	Species
1	1000000.000000	404423.175101	Buckingham A	
2	100000.000000	88619.438577	Buckingham A	
3	5000.000000	4053.048025	Buckingham A	

Final values of numerical parameter gradients :

Parameter No.	Parameter Gradient	Parameter Type	Species
1	-0.000013	Buckingham A	
2	-0.000182	Buckingham A	
3	-0.000220	Buckingham A	

Final values of residuals :

Observable no.	Type	observable	calculated	residual	Error(%)
1	Bulk modulus	212.30000	211.95855	0.11659	-0.161
2	Elastic Const	261.70000	268.06136	0.40467	2.431
3	Elastic Const	449.60000	448.42642	0.01377	-0.261
4	Elastic Const	103.10000	97.62695	0.29954	-5.308
5	Elastic Const	207.40000	203.19004	0.17724	-2.030
6	Structure	4.73727	4.68035	3.24018	-1.202
7	Structure	3.18638	3.18995	0.01269	0.112
8	Structure	0.30700	0.30506	0.03762	-0.632

Comparison of initial and final observables :

Observable no.	Type	Observable	Initial	Final
1	Bulk modulus	212.30000	198.30781	211.95855
2	Elastic Const	261.70000	255.18258	268.06136
3	Elastic Const	449.60000	457.46019	448.42642
4	Elastic Const	103.10000	97.16571	97.62695
5	Elastic Const	207.40000	188.18899	203.19004
6	Structure	4.73727	4.76579	4.68035
7	Structure	3.18638	3.27295	3.18995
8	Structure	0.30700	0.30498	0.30506

The .lib document will also be updated with the optimized value of A.

[Open SnO₂_2 GULP Fit\SnO₂_2.lib](#)

The value for A has changed from 5000 to 4053.048.

As stated above, you will use the results obtained here for the A parameters to fit the rho parameters, and then again to obtain the C parameters. To this end, you need to modify the .lib file used in the

GULP: Forcefield fitting with GULP: SnO₂ library derivation

calculation, you should define the parameters obtained here as new values for the calculation and indicate which parameters you want to fit.

Open the **GULP Calculation** dialog. Select **Browse...** from the **Forcefield** dropdown list to open the **Choose GULP Forcefield** dialog. Select the **SnO₂_2.lib** document in the **SnO₂_2 GULP Fit** folder.

The new forcefield document is imported.

Open the **GULP Fit Forcefield** dialog and check that the **Forcefield types** are **O core** and **O core**. Scroll down to the fitted parameters.

The value for A has been updated to 4053.

Note: The value for your forcefield may not be exactly the same as this example due to minor differences in calculations, this is expected.

Check the **Fit** checkbox for the **rho** parameter. Repeat this for the **O core - Sn core** and **Sn core - Sn core** pair potentials. Click the **Save** button.

A new forcefield, **SnO₂_2 GULP Fit\SnO₂.lib**, is created.

On the **GULP Calculation** dialog, change the **Forcefield** to **SnO₂_2 GULP Fit\SnO₂.lib** and click the **Run** button.

Once the calculation is complete, you need to fit for C.

Repeat the last few steps, opening the newly optimized forcefield and fitting for C.

The final library obtained for SnO₂ after fitting A, rho and C, is:

```
species
O core -1.025
Sn core 2.05

keyword
buck 1
O core O core 4053.0480000000 0.2729750000 43.4236690000 0.0000000000 & 15.0000000000 0
0 0
O core Sn core 88619.4390000000 0.1689920000 16.2778010000 & 0.0000000000 15.0000000000
0 0 0
Sn core Sn core 404423.1800000000 0.2049250000 39.3054100000 & 0.0000000000
15.0000000000 0 0 0
```

This is the end of the tutorial.

Chapter 13: Kinetix tutorials

The following tutorials illustrate how to utilize Kinetix's capabilities.

- [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#)
- [Multi-site modeling of CO oxidation on a Pt\(1 1 1\) surface](#)

Simple modeling of CO oxidation on a Pt(1 1 1) surface

Purpose: Introduces the Kinetix module for setting up a simple kinetic Monte Carlo simulation.

Modules: Materials Visualizer, Kinetix

Time: 

Prerequisites: None

Background

Kinetic Monte Carlo (kMC) simulation, in the Kinetix module, is a method that studies the kinetics at a surface. It is characterized by atomic scale spatial resolution and time scale comparable to laboratory kinetic experiments. It can simulate systems over long times (about nine orders of magnitude longer than molecular dynamics) because it only simulates the reactions of the atoms and molecules in the system. Kinetix module uses the CARLOS program (<http://www.win.tue.nl/~johanl/projects/nCarlos>) developed at Eindhoven Technical University to carry out the simulation.

The precise positions of atoms and molecules and their velocities are not included in Kinetix simulations. The configuration of a system is assumed to be near a particular minimum of its potential energy surface. A consequence is that the exact time that reactions occur and which reactions occur is not determined. Instead probability distributions for these times and reactions are generated.

Introduction

A complete kMC simulation needs a complex specification, with many different reactions specified, each of which requiring detailed knowledge of reaction probabilities.

In this tutorial you will set up the processes involved in a simple oxidation/reduction (ORR or redox) reaction, specifically CO oxidation on a Pt(1 1 1) surface, using a simplified set of processes to model the reactions. This is similar to the model described by [Ziff et al., 1986](#) for the oxidation of CO on a Pt(100) lattice, referred to as the ZGB model.

The minimum set of processes consists of: CO adsorption, dissociative O₂ adsorption, CO₂ formation, and CO₂ desorption. The last two processes can be combined to give:

- CO(gas) → CO(ads)
- O₂(gas) → 2O(ads)
- CO(ads) + O(ads) → CO₂(gas)

Although more complete modeling of the reactions would involve other processes such as diffusion and O₂ desorption this tutorial will be restricted to just these three processes. Later in the tutorial further processes will be added to make the simulation more realistic.

Kinetix uses two document types specific to this type of simulation. A Processes document contains the specifications of the lattice and species involved in a simulation and the reactions and other processes that can occur during a simulation. A Configuration document contains the description of the specific configuration(s) of species on the simulation grid. The simulation acts on the configuration document using the details in the processes document to determine how the configuration should evolve over time.

This tutorial covers:

- [Getting started](#)
- [Specifying the processes](#)
- [Creating an initial configuration](#)
- [Running a Kinetix simulation](#)
- [Analyzing the results of a Kinetix simulation](#)
- [Adding further processes](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ORR_simple** as the project name, click the **OK** button.

The new project is created with *ORR_simple* listed in the Project Explorer. You will create a basic processes document describing the simulation lattice and the species that will be involved in the simulation.

Click the **Kinetix** button  on the **Modules** toolbar and select **Process Builder** from the dropdown list to open the Kinetix Process Builder dialog.

This can be used to specify the geometry of the lattice on which the simulation will be performed. You will be working with a hexagonal lattice and because you will be using only one lattice site per cell, you should set the symmetry to the maximum possible. The lattice dimension corresponds to the distance between the metal atoms in a Pt crystal, or more specifically in the (1 1 1) surface cleaved from such a crystal.

Enter **Hexagonal ZGB model** in the **Description** text box. Set the **Type** for the lattice to **Hexagonal**, the **Symmetry** to **p 6 m m**, and the **Length** to **2.77 Å**. Click the **Create** button and close the dialog.

This will create a new Processes document which you will use to specify the species and the processes involved in the simulation.

In the **Project Explorer**, right-click on **KinetixProcesses.xkp** and select **Rename** from the shortcut menu. Change the name to **ZGBProcesses.xkp**.

You will now specify the species that will be used in the simulation. Note that there is always a definition corresponding to a vacancy (a lack of any species at a specific site). By default this has the symbol **V**.

Select the **Species** tab, enter **CO** in the first empty cell in the **Name** column and press **TAB**. Enter **O** in the next row and press **TAB**.

The default properties (radius, charge, and color) of the species will suffice for this tutorial, although they can be changed later if desired.

2. Specifying the processes

Kinetix does not take the gas phase into account so the exact processes [above](#) cannot be used. A Kinetix simulation models the changes at a particular site or sites in a configuration, accounting for the species

populating the site(s) before and after the process. The absence of any species at a site is described as a vacancy, indicated by the symbol V. The ORR processes can be represented as:

- $V \rightarrow CO$
- $2V \rightarrow 2O$
- $CO + O \rightarrow 2V$

This description does not consider CO_2 as it is implicit in the last process. Because the model combines the CO_2 formation and its immediate desorption it is not explicit.

For each process you will define the reaction and sites involved, together with the details of the rates of the reactions. Reaction rates can be specified explicitly or using an Arrhenius expression. In this tutorial you will specify the reaction rates explicitly.

First specify the CO adsorption process.

Select the **Processes** tab of **ZGBProcesses**. Ensure that the **process of type** is set to **Adsorption** and click the **Add** button.

A new process, named *NewProcess* will be added to the list and the *Process Details* tab provides further options.

Enter **COAds** as the **Identifier** and **CO adsorption** as the **Description**.

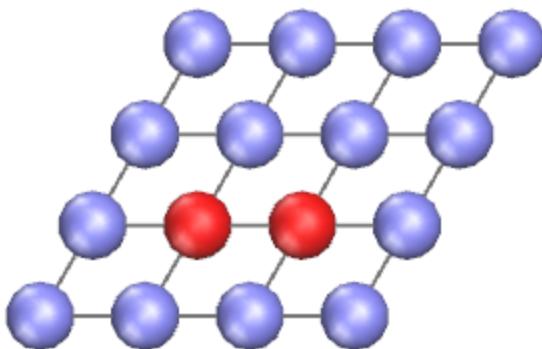
Change the **Specification type** to **Rates** and set the **Rate coefficient** to **0.55**. On the **Process Sites** tab select **CO** from the **Adsorbate(s)** dropdown list.

Next you will specify the O_2 adsorption process. This is different from the CO adsorption process, it is a dissociative process where the O_2 molecule creates two separate O species when it is adsorbed.

On the **Processes** tab click the **Add** button to create a new process.

On the **Process Details** tab enter **O2Ads** as the **Identifier** and **O_2 adsorption** as the **Description**. Change the **Specification type** to **Rates** and set the **Rate coefficient** to **0.15**.

On the **Process Sites** tab check the **Dissociative adsorption** checkbox. Select the **Site View** tab to review the site set up:



Site view showing dissociative adsorption process

This is a view of the sites used in the specification of the current process, and the role that each site plays in the process. The red color indicates that the specification is incomplete or incorrect for that site. In the

current situation this is because you have not yet specified the species involved in this adsorption process.

On the **Process Sites** tab select **O** from both the **Adsorbate(s)** dropdown lists.

On the *Site View* tab the colors of the sites will change from red to white when the adsorbate is specified.

Right-click in the **Site View** and select **Site View Colors** from the shortcut menu to open the Kinetix Site View Colors dialog. Review the coloring of the sites and close the dialog.

Lastly you will specify the CO₂ formation process. This uses a different type of process and a different method of specifying the process rate to indicate that the formation and desorption should happen immediately when a given pattern occurs. An alternative way of considering this is as a process with an infinitely large rate coefficient.

On the **Processes** tab select **Desorption** as the **process of type** and click the **Add** button. On the **Process Details** tab enter **CO2Des** as the **Identifier** and **CO2 formation and desorption** as the **Description**. Change the **Specification type** to **Immediate**.

On the **Process Sites** tab check the **Associative desorption** checkbox and select **CO** and **O** from the **Species** dropdown lists.

You have now specified the processes to be used in the first simulation, you should check the processes are appropriate before proceeding.

On the **Site View** tab click the arrow buttons for the **Process index** to scroll through the processes defined.

Check that none of the processes are shown as invalid, indicated by red sites. Check that the **Multiplicity** reported is correct. This should be **1** for **COAds**, **3** for **O2Ads**, and **6** for **CO2Des**.

For each process review the **Process Details** and **Process Sites** tabs, checking the details for each process.

Before you continue, save the project.

Select **File | Save Project** from the menu bar.

3. Creating an initial configuration

In addition to these processes you also need an initial configuration for the simulation. A configuration is the way in which the adsorbates are distributed over the sites. The occupation of every site is necessary for a complete specification of a configuration.

You want to start with an empty surface where all sites are vacant. You can define such a configuration with the Configuration Builder.

Click the **Kinetix** button  on the **Modules** toolbar and select **Configuration Builder** from the dropdown list to open the Kinetix Configuration Builder dialog.

This allows you to specify the size of the simulation. A larger simulation will reduce the statistical noise in the results, at the expense of extra computation time. A large simulation is not easy to visualize (and will

be slow), so it is desirable to specify a smaller range of the total simulation to display. The portion of the simulation displayed can be manipulated to review the results and check that they are representative of the whole simulation.

Change the **Configuration size** to **64 × 64**. and ensure that the **Type of configuration** is set to **Constant**. In the **Species to fill** section select **V** from the **Adsorption sites** dropdown list. Click the **Create** button and close the dialog.

A new document called **KinetixConfiguration.xkc** will be created.

Rename the newly created configuration document to **ZGB.xkc**. Select **File | Save Project** from the menu bar.

4. Running a Kinetix simulation

You are now ready to carry out a simulation.

Click the **Kinetix** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Kinetix | Calculation** from the menu bar.

This opens the Kinetix Calculation dialog where a number of different simulation tasks are available. These provide control over the length of the simulation and how parameters such as temperature, pressure, and potential vary with time. Simple *Rate coefficients* have been specified as the reaction rates for each of the processes rather than an *Arrhenius* expression, so there is no dependency on temperature, pressure, or potential. In this situation you should use the *Constant conditions* task.

Ensure that **ZGB.xkc** is the active document. On the Setup tab of the Kinetix Calculation dialog select **Constant conditions** from the **Task** dropdown list. Click the **More...** button to open the Kinetix Constant Conditions dialog.

For this simulation the only parameters on the *Kinetix Constant Conditions* dialog of interest are the *Simulation time* and *Sampling interval*. The rate coefficients specified mean that the default values for these parameters are satisfactory for the current simulation.

Close the **Kinetix Constant Conditions** dialog.

On the Setup tab choose **ZGBProcesses.xkp** from the **Processes** dropdown list.

Inspect the contents of the other tabs on the **Kinetix Calculation** dialog, all the default values for the settings are appropriate for a simple initial investigation.

The **Processes** tab lists the processes that are defined in the selected processes document, and allows you to decide which to use. It can be useful to repeat simulations using different processes, for example an initial simulation with adsorption, diffusion and desorption processes to generate a realistic starting configuration for a second simulation which might omit the adsorption processes to model temperature programmed desorption.

The **Job Control** tab controls details about where and how the job will be run. The **More...** button opens the Kinetix Job Control Options dialog which allows you to control features such as updates from the server while the calculation proceeds.

The frequency with which results are generated are controlled by the *Sampling interval* and *Configuration output every* options on the task details dialogs. Two types of raw results are created -

one containing summaries of the concentrations, process rates and so on, and another which contains periodic snapshots of the actual configuration. The frequency of each is individually controlled. These outputs are used for analysis and the configurations can be displayed directly. They can also be used to *Restart* a simulation if, for example, you find that the initial simulation was not long enough.

Click the **Run** button and close the dialog.

A new folder, entitled **ZGB Kinetix ConstCond**, opens in the Project Explorer. The calculation should take less than a minute to complete. Six documents are generated in the new folder, as follows:

- **ZGB - calculation** - the state file containing a copy of the current application state.
- **ZGBProcesses.xkp** - a copy of the original processes document.
- **ZGB.kin** - the input for the CARLOS program.
- **ZGB.kout** - the main text output from the CARLOS program, giving an overview of the input and the simulation performance. There are other output files containing more detailed results that are hidden within the Project Explorer which are accessed by the Analysis functionality.
- **ZGB.xkc** - the configuration at the end of the simulation.
- **ZGBTraj.xkc** - a multi-frame document containing snapshots of the configuration at points during the simulation, as requested by the parameters on the Output tab of the Kinetix Calculation dialog.

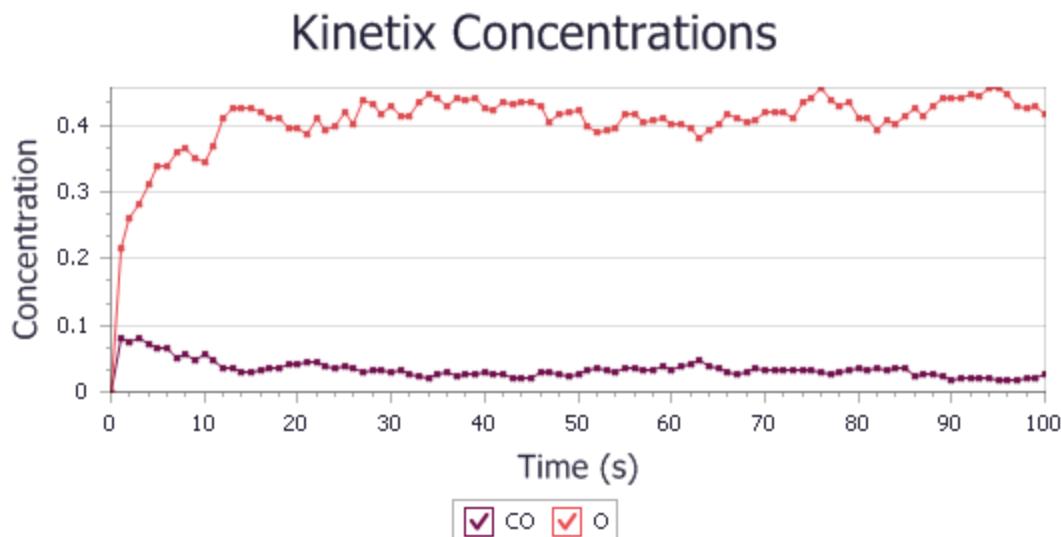
5. Analyzing the results of a Kinetix simulation

Next you will generate charts of how the average concentrations and reaction rates evolve with time.

In the Project Explorer, open **ZGB.kout** from the results folder. Click the **Kinetix** button  on the **Modules** toolbar and select **Analysis** to open the Kinetix Analysis dialog.

Select **Concentrations** and check the checkboxes for the **CO** and **O Species**. Click the **View** button.

A chart document is displayed showing the average concentration of each species as a function of simulation time. (The simulation is a Monte Carlo process involving random selections, so your results may not be identical to these.)

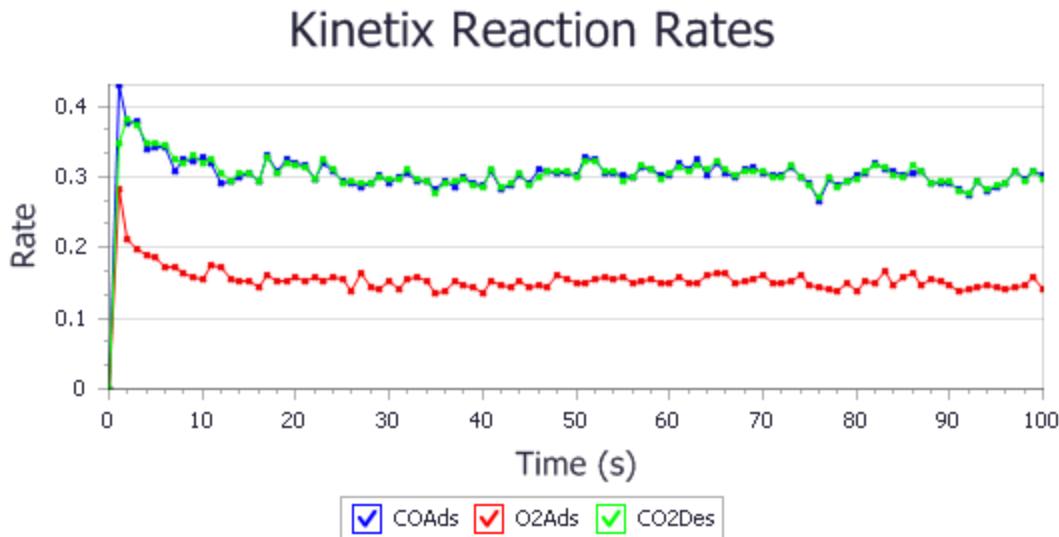


Average concentrations of species during the simulation

Kinetix: Simple modeling of CO oxidation on a Pt(1 1 1) surface

In the Kinetix Analysis dialog select **Rates** and check the checkboxes for the **COAds**, **O2Ads**, and **CO2Des Reactions**. Click the **View** button.

A chart document is displayed showing the average reaction rates in reactions per unit cell per second for each process as a function of simulation time.



Average reaction rates of processes during the simulation

These charts show that the concentration of O quickly increases to about 0.4, and that of CO settles down to a low value, so that an approximate steady state is soon reached. These reaction rates for the COAds and CO2Des processes are approximately equal and that of the O2Ads is approximately half of the others, as would be expected to maintain the steady state.

It is now instructive to see how the configuration evolves with time.

In the Project Explorer, open **ZGBTraj.xkc** from the results folder. Click the **Play** button  on the Configuration Viewer to show an animation of the trajectory.

Click the **Stop** button .

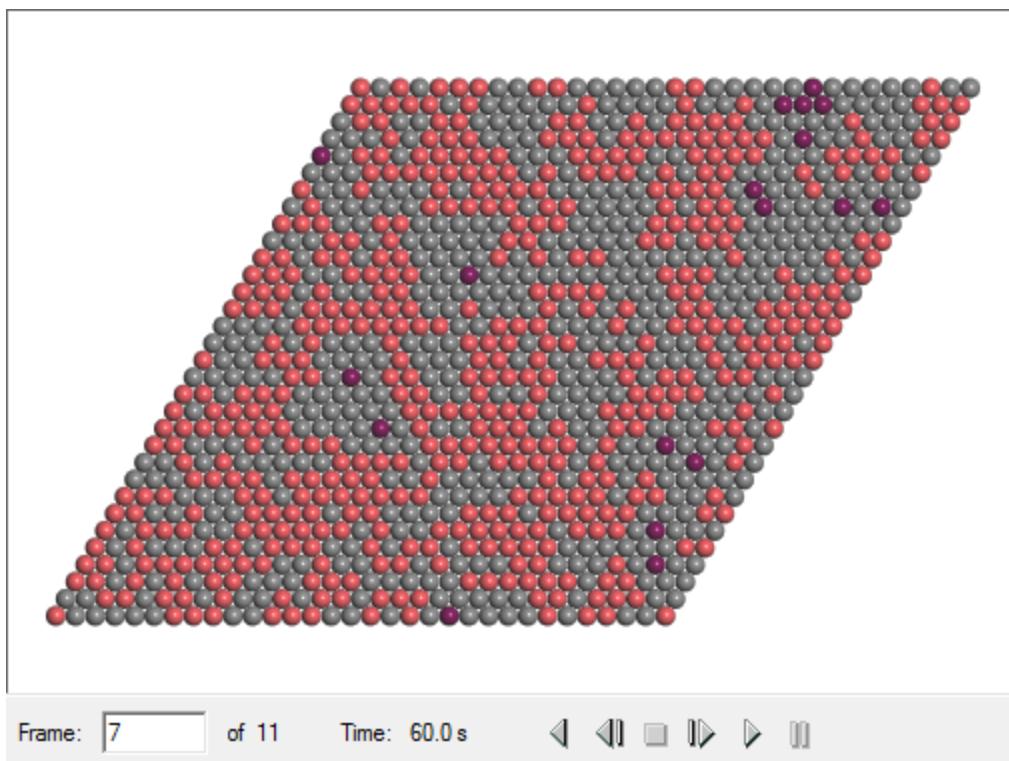
Altering the display of the configuration document can be useful in the review and interpretation of results.

Right-click in **ZGBTraj.xkc** and select **Display Style** from the shortcut menu to open the Kinetix Configuration Display Style.

On the **Options** tab change the **Background color** to **white**. On the **Style** tab change both the **Radius scale** and the **Vacancy scale** values to **1.4** then close the dialog.

In the Configuration View enter **7** as the **Frame** and press **TAB**.

Your ZGBTraj .xkc view should look like this:



Configuration during the simulation

Inspection of the configuration shows that none of the CO species are adjacent to O species. This is as expected because the CO2Des process is specified to occur immediately that such a pair occurs.

The species in the configuration view are colored according to the colors originally defined in the ZGBProcesses.xkp document, but they can be altered if desired.

Right-click in **ZGBTraj.xkc** and select **Properties** from the shortcut menu to open the Kinetix Configuration Properties dialog showing the species used and their colors. Change the **Color** of one of the species and close the dialog.

Now save the project and close the open documents.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

6. Adding further processes

Although the simulation so far has the necessary processes for adsorption of CO and O₂ and desorption of CO₂, it does not properly represent the full set of processes involved in the reactions. In particular those for diffusion of CO and O species. Diffusion is generally a much faster process than adsorption or desorption. Care must be taken in selecting the parameters to avoid spending too much of the calculation time on diffusion.

The desorption of CO or O₂, the converse of the adsorption processes, has also been omitted. Adsorption rate coefficients depend only weakly on temperature, but desorption rate coefficients have a strong dependence on temperature.

You will first add a process to describe diffusion of CO.

Open the original **ZGBProcesses.xkp** document and select the **Processes** tab. Choose **Diffusion** for the new process type and click the **Add** button.

On the **Process Details** tab enter **CODiff** as the **Identifier** and **CO diffusion** as the **Description**. Change the **Specification type** to **Rates** and the **Rate coefficient** to **25**.

On the **Process Sites** tab choose **CO** for the **Species**.

The diffusion process assumes that a species moves from one site to another that was previously vacant, leaving the original site vacant.

You will now add a similar process to describe diffusion of O.

On the **Processes** tab add another **Diffusion** process.

On the **Process Details** tab enter **ODiff** as the **Identifier** and **O diffusion** as the **Description**. Change the **Specification type** to **Rates** and the **Rate coefficient** to **15**.

On the **Process Sites** tab choose **O** for the **Species**.

By choosing rate coefficients of 25 and 15, these processes are much faster than the adsorption of CO and oxygen. However the CO₂ formation is currently described by an immediate process, so will occur whenever a CO species is at a site adjacent to one occupied by an O species. The CO₂ formation should occur with a rate coefficient intermediate between those of the adsorption processes and those of the diffusion processes.

On the **Processes** tab select the **CO2Des** process. On **Process Details** tab change the **Specification type** to **Rates** and enter a **Rate coefficient** of **5**.

You now need to add the processes for desorption of CO and O₂ as follows:

Process type	Identifier	Description	Specification type	Rate coefficient	Associative desorption	Species
Desorption	CODes	CO desorption	Rates	0.001	No	CO
Desorption	O2Des	O ₂ desorption	Rates	0.001	Yes	O O

Add two new processes specified according to the table above.

This will be the final form of the processes document for this tutorial. Before continuing you should save the project.

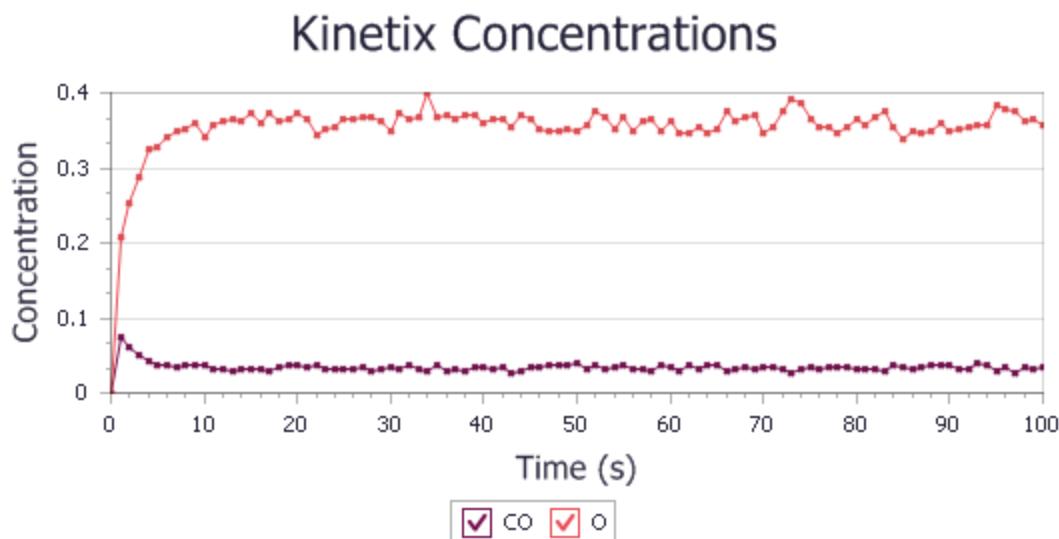
Select **File | Save Project** from the menu bar.

You will now rerun the simulation and compare some of the results with the previous run.

Make **ZGB.xkc** the active document. Open the **Kinetix Calculation** dialog and ensure that the **Constant conditions** task is selected. Click the **Run** button and close the dialog.

A new folder, named ZGB_Kinetix_ConstCond (2), is added to the Project Explorer. When the job is complete the same set of documents will be created as for the previous run.

In the Project Explorer, open **ZGB.kout** from the new results folder. Open the **Kinetix Analysis** dialog and set up a **Concentrations** analysis of the **CO** and **O** species. Click the **View** button.



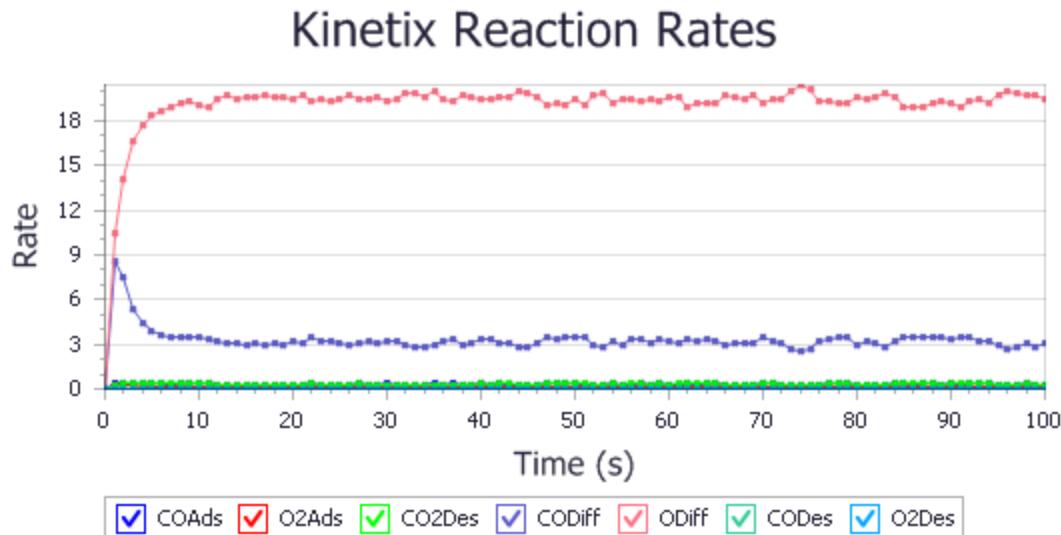
Average concentrations of species during the simulation including diffusion

Comparison with the equivalent plot from the first run shows that the steady state concentration of O is lower than previously, and that the concentration of CO has increased.

Using the Kinetix Analysis dialog perform a **Rates** analysis for all of the **Reactions**. Click the **View** button.

The chart produced from this will immediately show that the simulation is dominated by the two diffusion processes. Although CO diffusion was specified with a higher rate coefficient than that for O diffusion, the O diffusion dominates the Rates chart because of the greater average concentration of O. You will now generate another Rates chart without the diffusion processes.

On the Kinetix Analysis dialog uncheck the **CODiff** and **ODiff** checkboxes. Click the **View** button and close the dialog.



Average reaction rates of processes during the simulation including diffusion

Comparison of this *Rates* chart with that from the first run shows that the rates of the three main processes of interest (COAds, O2Ads, and CO2Des) have all increased slightly, although they show the same relative values.

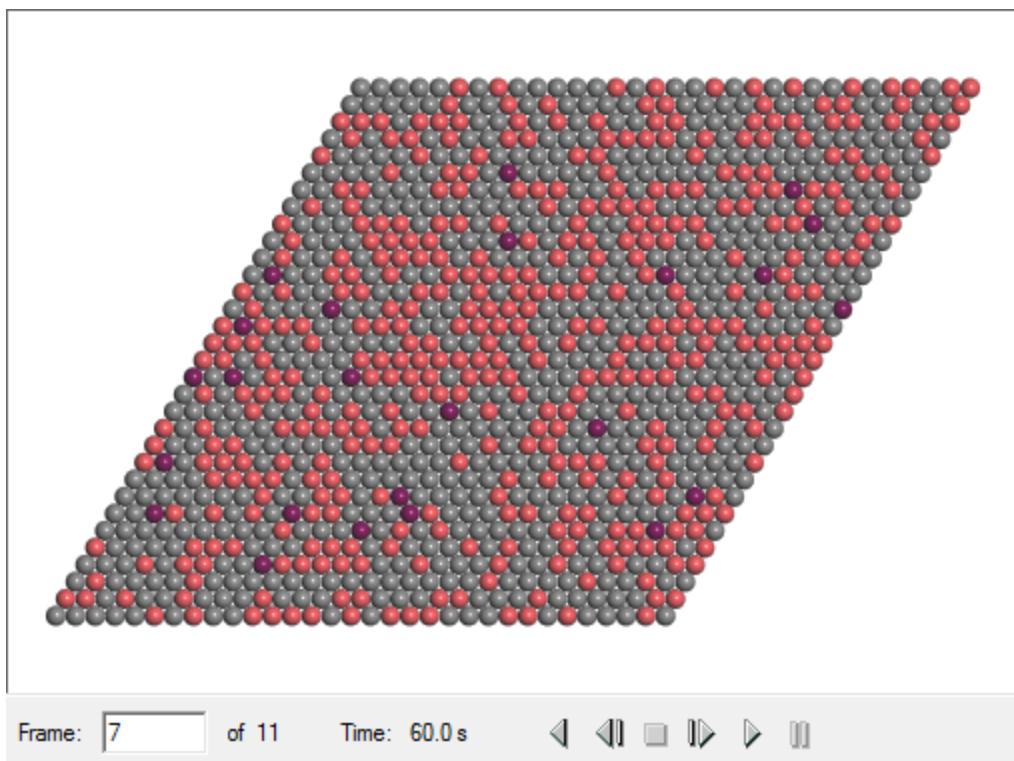
As expected, because of the very low rate coefficients specified for these processes, the CODEs and O2Des processes have negligible contributions.

You should now inspect the new configuration evolution.

In the Project Explorer, open **ZGBTraj.xkc** from the new results folder. Modify the appearance in the same way that you did for the previous configuration document, and use the **animation controls** to step through the frames. **Stop** the animation.

In the Configuration View enter **7** as the **Frame** and press **TAB**.

Your new ZGBTraj.xkc view should look approximately like:



Configuration during the simulation including diffusion

The inclusion of the diffusion processes have allowed the CO and O species to move around the configuration, and the change of the CO2Des process to use a rate coefficient of 5 means that it is possible for CO species to exist in lattice sites adjacent to O species.

Although the second version of this simulation is more realistic than the initial simple run, due to the inclusion of the diffusion and desorption processes, there is still scope for improvements to the model. These improvements are discussed in the [Multi-site modeling of CO oxidation on a Pt\(1 1 1\) surface](#) tutorial.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

R.M. Ziff, E. Gulari, Y. Barshad, "Kinetic Phase Transitions in an Irreversible Surface-Reaction Model", *Phys. Rev. Lett.*, **56**, 2553-2556 (1986)

Multi-site modeling of CO oxidation on a Pt(1 1 1) surface

Purpose: Introduces Kinetix simulations on lattices with multiple sites.

Modules: Materials Visualizer, Kinetix

Time: 

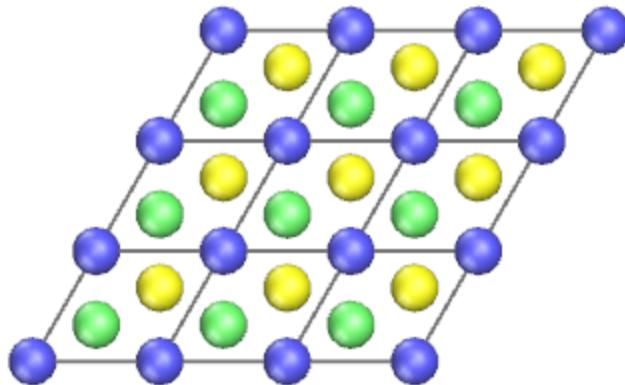
Prerequisites: [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#)

Background

The systems modeled by kinetic Monte Carlo (kMC) simulations, using the Kinetix module, can be described with varying degrees of sophistication.

The [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#) tutorial created a model similar to the that described by [Ziff et al., 1986](#) but adapted for the Pt(1 1 1) surface. This uses a single site per lattice cell with all the adsorbates on the same lattice site. The first simulation incorporated processes just for the adsorption of CO and O₂ and desorption of CO₂. Subsequently further processes were added to simulate diffusion and desorption of CO and O₂. The addition of these latter processes changed the dynamics of the system, resulting in different concentrations in the final coverage.

However even the modified simulation in that tutorial is an over-simplification of the system. In most reaction systems the adsorbates do not all sit at the same type of site. In the system being modeled CO prefers to adsorb onto top sites but the oxygen atoms are found at the hollow sites. In a hexagonal lattice such as this, there are two hollow sites, the fcc site at position (1/3, 1/3) and the hcp site at position (2/3, 2/3). These two hollow sites are not equivalent. The oxygen atoms prefer the fcc sites, but at high coverages they can also be found at the hcp sites.



Lattice showing top sites (blue) and hollow sites (fcc green, hcp yellow)

The difference between the hollow sites is modeled by specifying different processes acting at each of the types of site, each with different reaction rates for otherwise similar processes.

In the previous tutorial the rate coefficients were arbitrary to illustrate the types of processes that might be involved in a simple mode, and how they can interact. To run a realistic simulation it is necessary to use realistic rate coefficients. Determining these is often the most difficult part of setting up a realistic kinetic Monte Carlo simulation. In practice you can obtain the rate coefficients from either calculated or

experimental data or, in some cases, they can be estimated from similar systems for which data is available.

Introduction

Because you will be using a more complex lattice than in the earlier tutorial it is necessary to define more processes to model all the possible reactions. In addition the specification of the individual processes will be more complex.

For example, the distance between adjacent sites in the new lattice will be only 1.6 Å. This is too small for adjacent sites to both be occupied so you will need to add specifications to ensure that this cannot happen.

The rate of a particular process can be dependent on the species occupying neighboring sites. This can be modeled in the form of lateral interactions which will be introduced here.

This tutorial covers:

- [Getting started](#)
- [Creating the processes document](#)
- [Adding the adsorption processes](#)
- [Adding the desorption processes](#)
- [Adding the diffusion processes](#)
- [Reviewing the processes document](#)
- [Running the simulation](#)
- [Analyzing the results](#)
- [Adding lateral interactions](#)
- [Using lateral interactions and running the simulation](#)
- [Analyzing the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ORR_MultiSite** as the project name, click the **OK** button.

The new project is created with *ORR_MultiSite* listed in the Project Explorer.

2. Creating the processes document

You will create a basic processes document describing the simulation lattice and the species that will be involved in the simulation.

Click the **Kinetix** button  on the **Modules** toolbar and select **Process Builder** from the dropdown list.

As in the previous tutorial, you will be working with a hexagonal lattice. However because you will be using more than one lattice site per cell you will need to think carefully about the symmetry. Inspection of the lattice diagram above, and in particular the different nature of the fcc and the hcp hollow sites, shows that the desired symmetry specification is p 3.

Enter **Hexagonal ZGB model** as the **Description**. Select **Hexagonal** from the **Type** dropdown list and **p 3** from the **Symmetry** dropdown list. Set the **Length** to **2.77 Å**. Click the **Create** button and close the dialog.

This will create a new processes document called **KinetixProcesses.xkp**.

Rename the new document **ZGBMultiSite.xkp**.

The Processes document was created with a single lattice site, the top site at position (0,0) in the cell. You should now add the specification of the hollow sites.

On the **General** tab click the **Add Site...** button to open the Kinetix Add Sites dialog. Change the **Site type** to **Hollow**. Click the **Add** button and close the dialog.

In the processes document, two new sites are added to the *Sites* table on the *General* tab at (0.333, 0.333) and (0.667, 0.667).

You will now specify the species that will be used in the simulation, and specify radii for them. These radii will be used in the generation of minimum cutoff distances when creating interactions, and are also used in the display of simulations resulting from this document.

On the **Species** tab enter **CO** as the **Name** in the first empty row. Change the **Radius** to **1.3**.

Add a second species, named **O** with a **Radius of 1.3**.

The other default properties (charge and color) of the species will suffice for this tutorial, although they can be changed later if desired.

3. Adding the adsorption processes

The adsorption processes used here will be superficially similar to those in the previous tutorial. However hollow sites will make the specification more complicated. In addition you must ensure that adsorption does not occur adjacent to occupied sites.

The rate coefficient for adsorption of CO can be calculated from ([Jansen, 2003](#), [Jansen, 2012](#)):

$$k_{ads}^{(CO)} = \frac{P_{CO} A_{site} \sigma}{\sqrt{2\pi m_{CO} k_B T}}$$

Where:

P_{CO} is the pressure of CO

A_{site} is the area of a single site

σ is the sticking coefficient

m_{CO} is the mass of CO

k_B is the Boltzmann constant

T is the temperature

For a temperature of 1200 K, a CO pressure of 1 atm, and a sticking coefficient of 1.0 the rate coefficient for the CO adsorption is $9.68 \times 10^7 \text{ s}^{-1}$.

For oxygen adsorption a similar expression is used with a pressure of 0.5 atm. An additional factor of 3 is used in the denominator to account for the number of different possible orientations of the O₂ molecule. Thus a rate coefficient of $1.49 \times 10^7 \text{ s}^{-1}$ for the oxygen adsorption is obtained.

First specify the CO adsorption process.

Select the **Processes** tab of the processes document. Ensure that **process of type** is set to **Adsorption** and click the **Add** button.

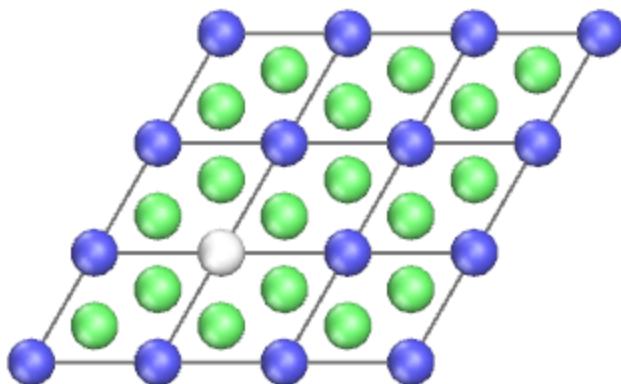
A new process, named *NewProcess* is added to the list on the *Processes* and the *Process Details* tab provides further options.

On the **Process Details** tab enter **COAds** as the **Identifier** and **CO adsorption** as the **Description**. Change the **Specification type** to **Rates** and set the **Rate coefficient** to **9.68e7 s⁻¹**.

On the **Process Sites** tab select **CO** from the **Adsorbate(s)** dropdown list.

You now need to specify the blocking sites, that is those sites at which the presence of a species will prevent the adsorption from occurring.

Select the **Site View** tab:



Site view showing adsorption process before blocking sites added

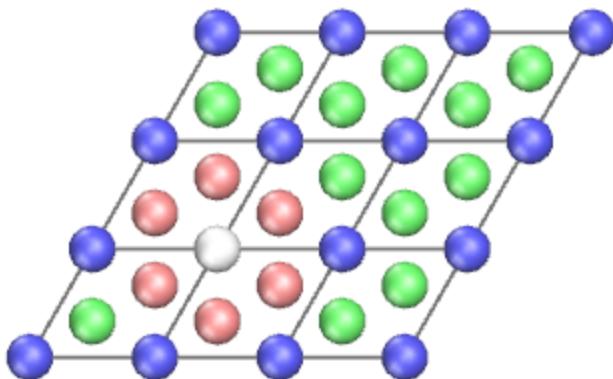
The white site represents the site where the adsorption will occur. The 6 neighboring sites should be defined as "blocking". This is achieved by specifying that the process is enabled only if these sites are vacant.

On the **Process Sites** tab select **V** from the **with enabling species** dropdown list in the **Site environment** section.

In the **Site View**, hold down **CTRL** and select each of the 6 sites surrounding the one colored white.

On the **Process Sites** tab click the **Add selected sites** button.

Six sites will be added to the list in the *Site environment* section, with a *Nearest distance* of 1.599 Å. This is the distance to the nearest active site in the current process. In the *Site View* these sites are now colored pink, to indicate their new role as contributing to the site environment requirements for the process. The *Site View* now looks like this:

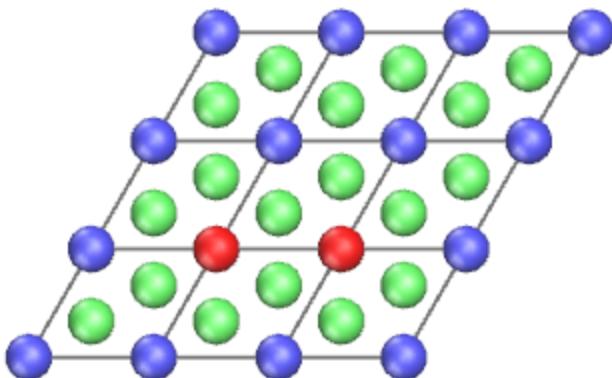


Site view showing adsorption process after blocking sites added.

Next you will specify the O₂ adsorption process. There are two possible sites for the adsorption so you will need to specify a separate process for each site.

On the **Processes** tab click the **Add** button. On the **Process Details** tab enter **O2Adsf** as the **Identifier** and **O2 adsorption onto fcc site** as the **Description**. Change the **Specification type** to **Rates** and set the **Rate coefficient** to **1.49e7 s⁻¹**.

On the **Process Sites** tab check the **Dissociative adsorption** checkbox and select the **Site View** tab:



Site view showing dissociative adsorption process before any corrections

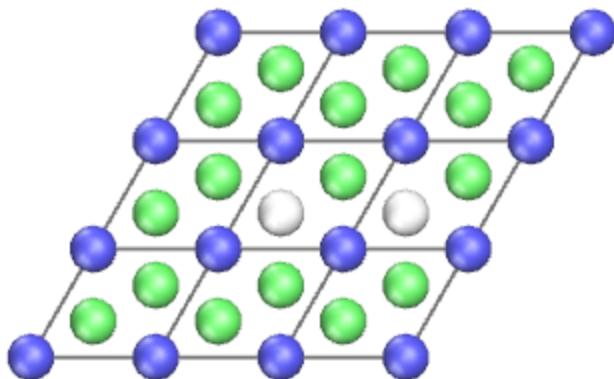
The active sites, shown in red, are not in the fcc hollow sites. The red color indicates that the species for these sites have not been set.

On the **Site View** tab select one of the fcc hollow sites.

On the **Process Sites** tab click the **+** button for one of the **Adsorption site(s)**. Select **O** from the corresponding **Adsorbate(s)** dropdown list.

Repeat this procedure for the other fcc site and the second **Adsorption site**, also populating it with **O**.

The **Site View** should now look like this:



Site view showing dissociative adsorption process on fcc sites

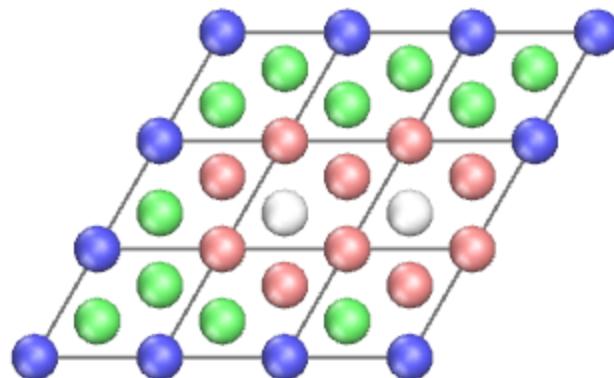
This process has a *Multiplicity* of 3 as there are three different orientations determined from the symmetry defined for the lattice. This is the reason for the extra factor of 3 in the calculation of the rate coefficient for the oxygen adsorption processes.

To complete the specification of this process, you need to add the blocking sites. There will be 10 surrounding two adsorption sites.

On the **Site View** select the 10 sites surrounding the two white sites occupied by O species.

On the **Process Sites** tab click the **Add selected sites** button to populate these sites with vacancies.

Ten sites will be added to the *Site environment* list, each with a *Nearest distance* of 1.599 Å. The *Site View* should now look like this:



Site view showing dissociative adsorption process on fcc sites after blocking sites added

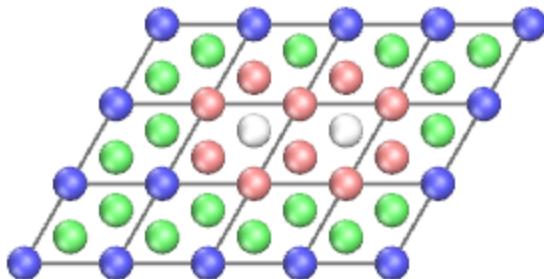
Tip: If you make any mistakes during the specification of processes, you can either *Undo* the last change(s) to the document, or you can *Delete* the process concerned and enter a new one.

The third adsorption process that you will need to add is that for O₂ onto the hcp sites. There will be one extra step here because one of the necessary blocking sites is not currently shown in the *Site View*.

Right-click in the **Site View** and select **Display Style** from the shortcut menu to open the Kinetix Site View Display dialog. Change the **U Max** value to 2.

Repeat the procedures used for the **O2Adsf** process to create a similar process **O2Adsh** using the hcp hollow sites. Use the same value (**1.49e7 s⁻¹**) for the **Rate coefficient**.

The *Site View* should now look like this:



Site view showing dissociative adsorption process on hcp sites after blocking sites added

On the **Kinetix Site View Display** dialog change the **U Max** back to 1 and close the dialog.

Notice that although one of the blocking sites lies outside the display range specified for the *Site View* it is still shown. This is so that you always see the important sites relating to the current process regardless of the display parameters.

Before continuing you should save the project.

Select **File | Save Project** from the menu bar.

If you wish, you can compare your document at this stage with a version (**ZGBMultiSite Stage 1.xkp**) provided in the Examples library.

Select **File | Import...** from the menu bar to open the Import File dialog. Choose **Kinetix Files** from the file types dropdown list for the **File name**. Navigate to **Examples/Kinetix/Processes** and select **ZGBMultiSite Stage1.xkp**. Click the **Open** button.

4. Adding the desorption processes

As with the adsorption processes, there will be more desorption processes than in the previous tutorial. There will need to be two versions of the CO₂ formation desorption process, one using oxygen from the fcc hollow site and the other using oxygen from the hcp hollow site. Similarly there will be two processes for desorption of oxygen.

Desorption processes are simpler to specify than the equivalent adsorption processes, because there is no need to specify any blocking sites.

For these desorption processes you will give the rate coefficients by specifying the *Prefactor* and *Activation energy* for an *Arrhenius expression*.

The rate coefficient for CO desorption has been obtained from temperature-programmed desorption spectra ([van Bavel et al., 2003](#)). Experimental measurements indicate that the prefactor used for the CO desorption on Pt(111) should be $1.0 \times 10^{13} \text{ s}^{-1}$, for many processes the observed value is close to this.

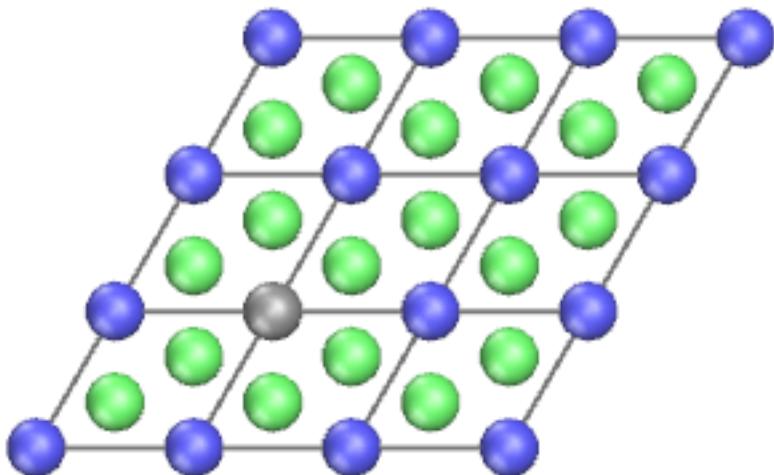
For oxygen desorption the results from kMC simulations correlate with experimental temperature-programmed desorption spectra ([Jansen et al., 2005](#)). However, this only provides parameters for desorption from the fcc sites - due to the experimental conditions all the oxygen atoms were located at fcc sites. To get usable parameters for oxygen desorption from hcp sites the activation energy is modified by the difference in adsorption energy of atomic oxygen between fcc and hcp sites, as calculated by [Offermans et al.](#).

The activation energies for the CO_2 formation have been calculated by [Yakovkin and Petrova](#).

First you will specify the CO desorption process, the reverse of the CO adsorption process.

Add a new **Desorption** process with **CODes** as the **Identifier** and **CO desorption** as the **Description**. Change the **Prefactor** to **1.0e13 s⁻¹** and the **Activation energy** to **33.2 kcal/mol**.

Set up the process sites and species so that the Site View is displayed as below, ensuring that the top site has been selected in the Site View and that **CO** has been chosen as the **Species** on the Process Sites tab.

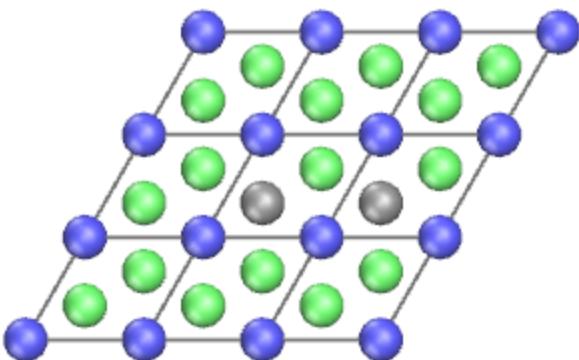


[Site view showing CO desorption process from a top site](#)

Next you will specify the process for O_2 desorption from fcc sites, the reverse of the O_2 adsorption onto fcc sites.

Add a new **Desorption** process with **O2Desf** as the **Identifier** and **O2 desorption with fcc site oxygen** as the **Description**. Change the **Prefactor** to **7.2e18 s⁻¹** and the **Activation energy** to **61.8 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that the fcc sites are chosen and that **O** is chosen as the species for these sites.

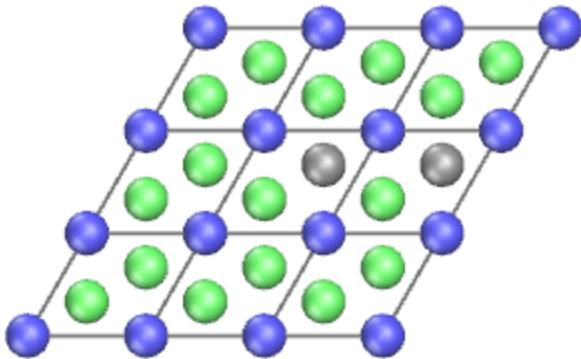


Site view showing associative desorption process from fcc sites

Next you will specify the process for O₂ desorption from hcp sites, the reverse of the O₂ adsorption onto hcp sites.

Add a new **Desorption** process and enter **O2Desh** as the **Identifier** and **O2 desorption with hcp site oxygen** as the **Description**. Change the **Prefactor** to **7.2e18 s⁻¹** and the **Activation energy** to **45.1 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that the hcp sites are chosen and that **O** is chosen as the species for these sites.

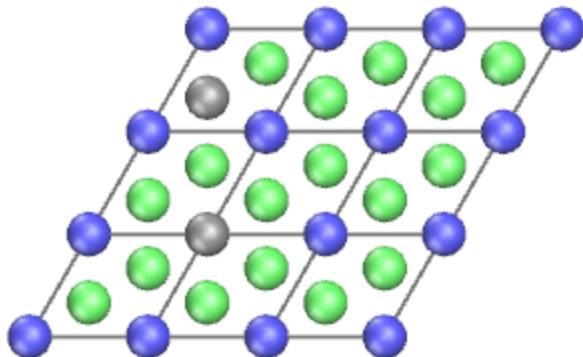


Site view showing associative desorption process from hcp sites

Now you will specify two versions of a process for CO₂ formation and desorption. First you will use oxygen from an fcc site. Note that the site used for the O is not the fcc site adjacent to the top site used for the CO. This is because of the distances concerned, and the decision that species cannot be present on adjacent sites (by use of the blocking sites in the adsorption processes, and later on in the diffusion processes).

Add a new **Desorption** process and enter **CO2Desf** as the **Identifier** and **CO2 desorption with fcc site oxygen** as the **Description**. Change the **Prefactor** to **1.0e13 s⁻¹** and the **Activation energy** to **51.9 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that **CO** is specified for the top site and **O** for the fcc site.

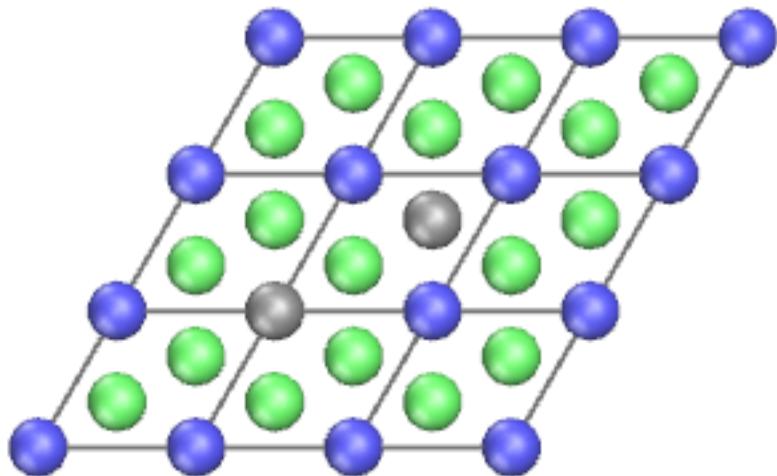


Site view showing associative desorption process from top and fcc sites

Finally, for the desorption processes, you will add a process for CO₂ formation and desorption using oxygen from an hcp site.

Add a new **Desorption** process and enter **CO2Desh** as the **Identifier** and **CO2 desorption with hcp site oxygen** as the **Description**. Change the **Prefactor** to **1.0e13 s⁻¹** and the **Activation energy** to **26.5 kcal/mol**.

On the **Process Sites** tab check the **Associative desorption** checkbox. Set up the process sites and species so that the Site View is displayed as below, ensuring that **CO** is specified for the top site and **O** for the hcp site.



Site view showing associative desorption process from top and hcp sites

You have now added all the desorption processes. Before continuing you should save the project.

Select **File | Save Project** from the menu bar.

If you wish, you can compare your document at this stage with a version (**ZGBMultisite Stage 2 .xkp**) provided in the Examples library.

5. Adding the diffusion processes

There are more diffusion processes than in the previous tutorial. CO can diffuse from a top site to an adjacent top site, as before. But this system has three-fold symmetry (rather than six-fold) to allow for the different treatment of the fcc and hcp sites. So you must specify two versions of the CO diffusion process so that it has the correct multiplicity.

Because, following diffusion, a previously vacant site becomes occupied, blocking sites around the destination should be added. However, to simplify the calculation you can take advantage of the vacancies in all sites adjacent to the source.

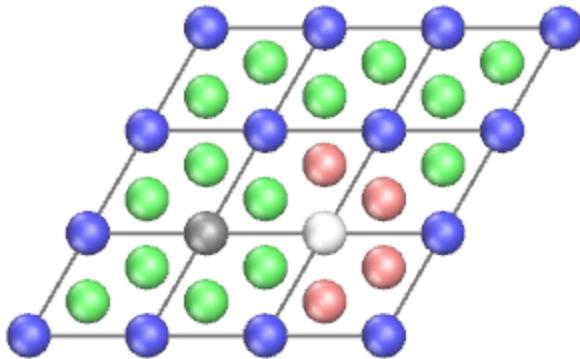
Diffusion is generally much faster than adsorption or desorption. This can mean that using realistic rate coefficients for diffusion would lead to almost all the simulation time being spent on diffusion which is inefficient and unnecessary. The role of diffusion in almost all reaction systems is to equilibrate the adlayer, this can also be accomplished using smaller rate coefficients than those observed by experiment. A pragmatic approach is to start with small rate coefficients for diffusion and increase them over a number of short simulations. The results will change as long as diffusion is not fast enough to equilibrate the adlayer. When the results become constant it is no longer necessary to increase the diffusion rate coefficient as this indicates that the adlayer is at equilibrium.

For CO diffusion the rate coefficient can be small; the same order of magnitude as for the desorption process. In this case it is desirable to use the same activation energy for the diffusion process as the equivalent desorption process. Thus the two rate coefficients will have the same ratio irrespective of simulation temperature.

For oxygen diffusion the process is much faster than the equivalent desorption. This is modeled as a process without a transition state, so for diffusion from fcc to hcp sites there is a significant activation energy while for the inverse diffusion from hcp to fcc sites the activation energy is effectively zero.

Add a new process of type **Diffusion**. Specify **CODiff** for the **Identifier** and **CO diffusion** for the **Description**. Change the **Prefactor** to **2.0e13 s⁻¹**, and the **Activation energy** to **33.2 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that the species for the source site is **CO**.

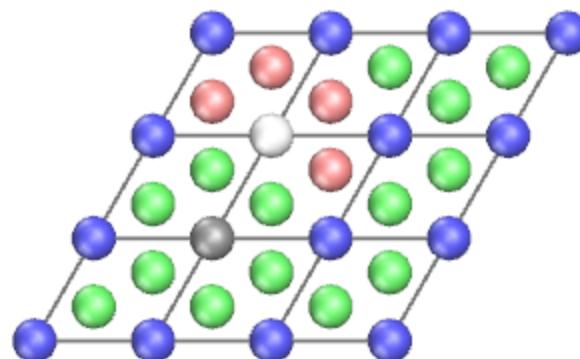


Site view showing the first CO diffusion process between top sites

The **Multiplicity** of the diffusion process you have just added is 3, this confirms that you will need a second version of it as there are six possible equivalent CO diffusion processes. You will now add the second version of the CO diffusion process using the same specification parameters for different sites. The identifier can be the same as the previous one, so that the statistics for the two processes will be merged in the simulation results.

Add a new process of type **Diffusion**. Specify **CODiff** for the **Identifier** and **CO diffusion** for the **Description**. Change the **Prefactor** to **2.0e13 s⁻¹**, and the **Activation energy** to **33.2 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that **CO** is chosen for the species, and that the pair of sites used is 60 or 180 degrees different from the pair used in the previous process.

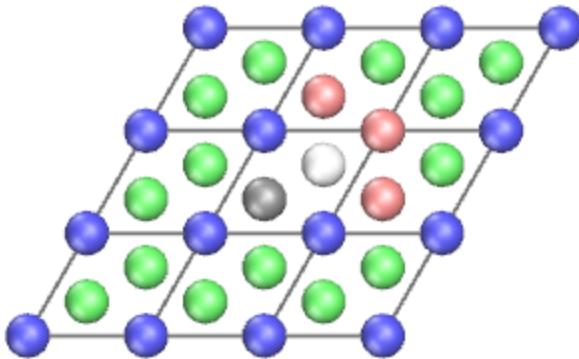


Site view showing the second CO diffusion process between top sites

You will now add processes for the diffusion of oxygen in both directions between the fcc and hcp sites. These processes, with their symmetry equivalents, allow diffusion of oxygen throughout the lattice. First specify the diffusion from the fcc site to the hcp site.

Add a new process of type **Diffusion**. Specify **ODiff_fh** for the **Identifier** and **Oxygen diffusion from fcc to hcp sites** for the **Description**. Change the **Prefactor** to **1.0e11 s⁻¹** and the **Activation energy** to **8.37 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that **O** is chosen for the species, and that you have the source and destination sites the correct way round, as indicated on the site view.



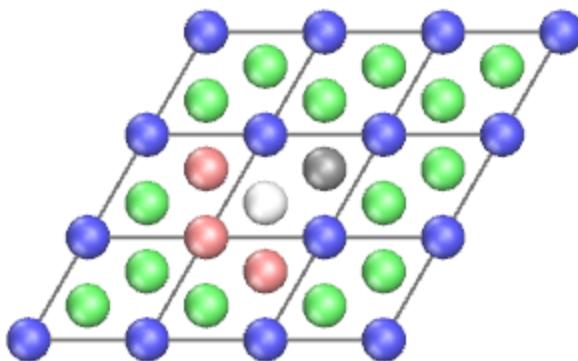
Site view showing O diffusion from fcc to hcp sites

You will now add the reverse process. You will use a different identifier and different process rates from the previous one.

Add a new process of type **Diffusion**. Specify **ODiff_hf** for the **Identifier** and **Oxygen diffusion from hcp to fcc sites** for the **Description**. Change the **Prefactor** to **1.0e11 s⁻¹**, and the **Activation energy** to **0.001 kcal/mol**.

Specify the process sites and species, including **blocking sites** in the **Site environment** section, so that the site view shows as below. Ensure that **O** is chosen for the species, and that you have the source and destination sites the correct way round, as indicated on the site view.

The activation energy for this process should be zero to reflect the lack of transition state, but the underlying server calculation requires that the value should be positive, so an arbitrarily low value of 0.001 is used.



Site view showing O diffusion from hcp to fcc sites

You have now added all the necessary diffusion processes. Before continuing you should save the project.

Click the **Save Project** button .

If you wish, you can compare your document at this stage with a pre-saved version of it in the file *ZGBMultiSite Stage 3.xkp* in the Examples library provided with Materials Studio.

6. Reviewing the processes document

At this point it is worth checking the processes you have entered.

Select the **Processes** tab, twelve processes should be listed:

Use	Index	Identifier	Type	Spec
<input checked="" type="checkbox"/>	1	COAds	Adsorption	Rates
<input checked="" type="checkbox"/>	2	O2Adsf	Adsorption	Rates
<input checked="" type="checkbox"/>	3	O2Adsh	Adsorption	Rates
<input checked="" type="checkbox"/>	4	CODes	Desorption	Arhenius
<input checked="" type="checkbox"/>	5	O2Desf	Desorption	Arhenius
<input checked="" type="checkbox"/>	6	O2Desh	Desorption	Arhenius
<input checked="" type="checkbox"/>	7	CO2Desf	Desorption	Arhenius
<input checked="" type="checkbox"/>	8	CO2Desh	Desorption	Arhenius
<input checked="" type="checkbox"/>	9	CODiff	Diffusion	Arhenius
<input checked="" type="checkbox"/>	10	CODiff	Diffusion	Arhenius
<input checked="" type="checkbox"/>	11	ODiff_fh	Diffusion	Arhenius
<input checked="" type="checkbox"/>	12	ODiff_hf	Diffusion	Arhenius

Processes for the ZGB multi-site simulation

On the **Site View** tab click the arrow buttons for the **Process index** to scroll through the processes defined.

Check that none of the processes are shown as invalid, as would be shown by sites colored red in the **Site View**. Check that the **Multiplicity** seems as expected for each process. Errors in the multiplicity can occur either because the wrong sites have been specified, or the wrong species combination for an associative or dissociative process.

Scroll through the processes with both the **Process Details** and the **Process Sites** tabs showing, checking the details for each process.

7. Running the simulation

Before running the simulation, you will need a new configuration document. The one that you generated in the previous tutorial will not suffice because there are now three sites per lattice cell compared to a single one before.

Click the **Kinetix** button  on the **Modules** toolbar and select **Configuration Builder** from the dropdown list.

Change the **Configuration size** to **64 × 64**. Ensure that the **Type of configuration** is set to **Constant** and select **V** from the **Adsorption sites** dropdown list. Click the **Create** button and close the dialog.

A new document, **KinetixConfiguration.xkc** will be created. Note that this has a different appearance from that in the previous tutorial due to the multiplicity of sites per lattice cell.

Rename the newly created configuration document to **ZGBMultiSite.xkc** and **save** the project.

Click the **Kinetix** button  on the **Modules** toolbar and select **Calculation** from the dropdown list or choose **Modules | Kinetix | Calculation** from the menu bar.

In this tutorial, you have not specified explicit rate coefficients (except for the adsorption processes). Using the Arrhenius expression the rate coefficients are highly dependent on the temperature. Hence you need to specify the desired temperature for the simulation. A variable temperature can be specified using the *Temperature programmed* task, but for this tutorial you will use a constant temperature.

Compared with the previous tutorial, the rate coefficients are extremely high. This means that the default values for the *Simulation time* and *Sampling interval* are no longer appropriate. Instead the simulation will happen very much faster than this, at a nanosecond time-scale. You can find this experimentally by running simulations with even shorter simulation times and sampling intervals, gradually increasing the sampling interval until a statistically meaningful number of reactions occur in each sampling interval.

Ensure that **ZGBMultiSite.xkc** is the active document, and that the **Constant conditions** task is chosen. Click the **More...** button to open the Kinetix Constant Conditions dialog.

Set the **Temperature** to **1200** K. Set the **Simulation time** to **1.0e-7** s and the **Sampling interval** to **1.0e-9** s and close dialog.

On the **Setup** tab select **ZGBMultiSite.xkp** from the **Processes** dropdown list.

Click the **Run** button and close the dialog.

A new folder, entitled **ZGBMultiSite Kinetix ConstCond** opens in the Project Explorer. When the job is complete the same set of documents should be created as seen in the previous tutorial.

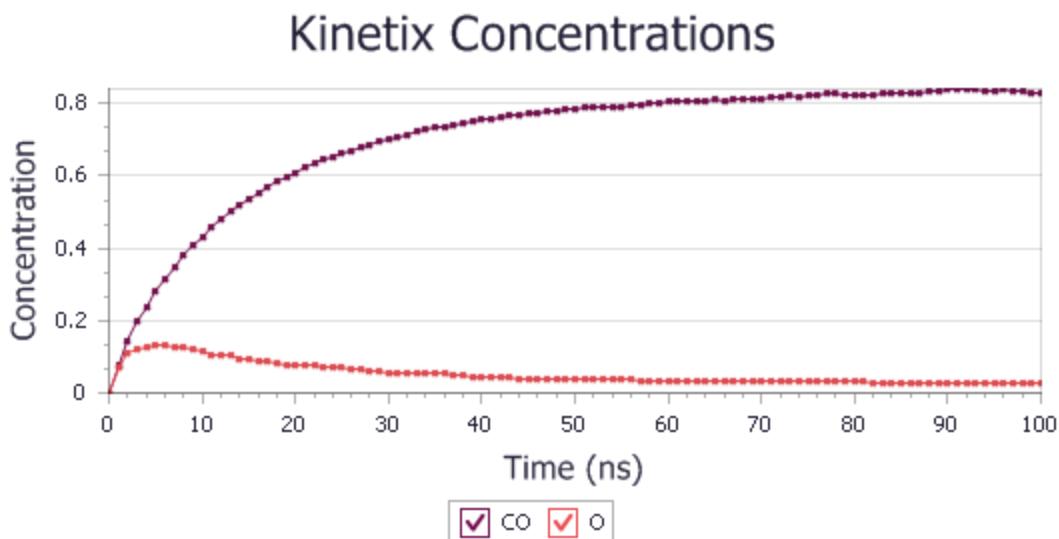
8. Analyzing the results

In the Project Explorer, open **ZGBMultiSite.kout** from the new results folder.

Click the **Kinetix** button  on the **Modules** toolbar and select **Analysis** from the dropdown list to open the Kinetix Analysis dialog.

Select **Concentrations** and check the **CO** and **O Species** checkboxes. Click the **View** button.

This will generate a chart similar to this:



Average concentrations of species during the simulation

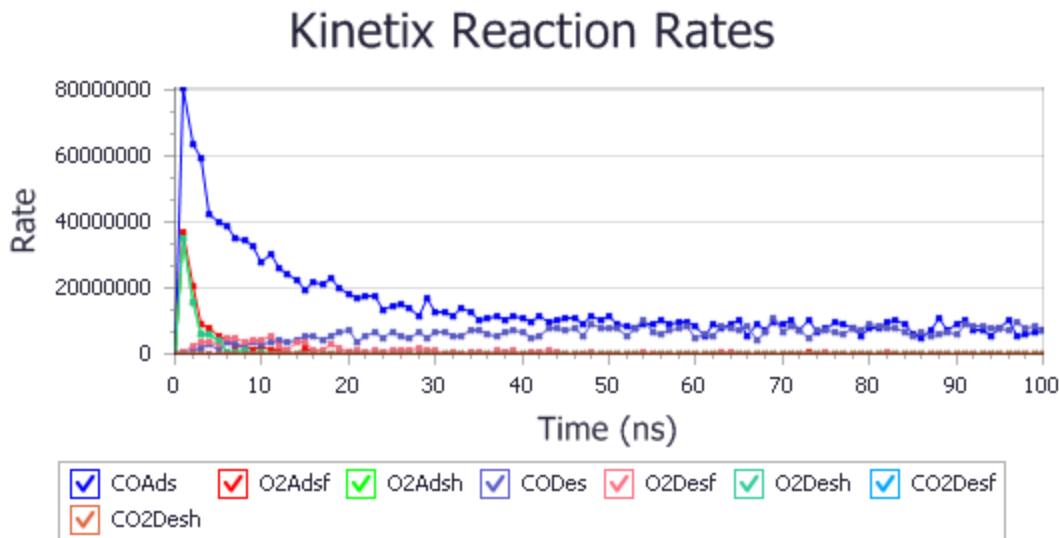
On the Kinetix Analysis dialog select **Rates** and check all the **Reactions** checkboxes. Click the **View** button.

The chart produced from this will immediately show that the simulation is dominated by the two diffusion processes. You will now generate another Rates chart without the diffusion processes.

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On the Kinetix Analysis dialog uncheck the **CODiff**, **ODiff_fh**, and **ODiff_hf** checkboxes. Click the **View** button. and close the dialog

This will generate a chart similar to this:



Average reaction rates of processes during the simulation

You should now inspect the new configuration evolution.

In the Project Explorer, open **ZGBMultiSiteTraj.xkc** from the new results folder. Use the **animation controls** to step through the frames. **Stop** the animation.

The chart documents and the configuration trajectory document are linked by point selection in the chart. As you step through the frames in the configuration trajectory the equivalent time point will be selected on one of the graphs in the each of the open charts. Conversely if a point is selected in one of the charts the configuration trajectory will change to show the frame nearest to the time of the chosen point.

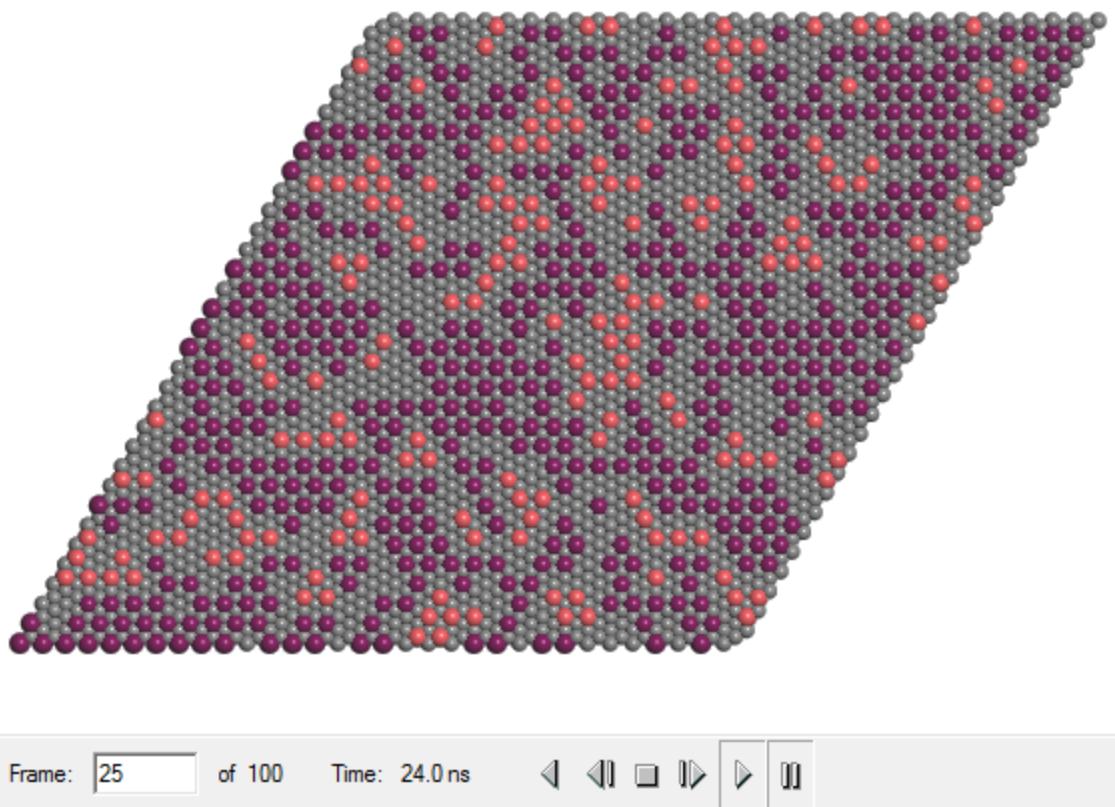
You should be able to confirm the correct use of the blocking sites. Each of the CO or O species should be completely surrounded by vacancies. You can now alter the display to give more emphasis to these species.

Right-click in **ZGBMultiSiteTraj.xkc** and select **Display Style** from the shortcut menu to open the Kinetix Configuration Display Style dialog.

On the **Options** tab change the **Background color** to **white**. On the **Style** tab change the **Radius scale** to **1.3**.

Close the dialog.

Your new **ZGBMultiSiteTraj .xkc** view should look approximately like:



Configuration during the simulation

This example shows the initialization phase of the simulation. You can click the buttons on the Configuration Viewer toolbar to step through the frames; towards the end of the calculation the site occupancies represent steady state conditions. The model used for the simulation in this tutorial is more sophisticated than that used in the [Simple modeling of CO oxidation on a Pt\(1 1 1\) surface](#) tutorial. Consideration is given to multiple sites and their different roles in the reactions. The reaction rates are specified using an Arrhenius expression, providing temperature dependence. However, another level of sophistication can be added to help make the model more realistic - lateral interactions.

9. Adding lateral interactions

Lateral interactions model the effect on a process (in modifying the activation energy) of species on nearby sites.

In Kinetix lateral interactions are described by specifying the change in the activation energy of a process for a combination of involved species and their neighbors. These are incorporated into the final descriptions of the processes when the input file is created for the server calculation.

Interactions are symmetric with respect to the species concerned. So the change in activation energy of a process involving species A when B is adjacent is the same for a similar process involving species B when A is adjacent.

Values for the lateral interactions between the oxygen atoms on fcc sites have been obtained from density-functional theory calculations ([Jansen et al., 2005](#)). It is assumed that the interactions for hcp sites have the same values. Values for the interactions between CO molecules have been taken from fits of kMC simulations to temperature-programmed desorption experiments of CO/Rh(100) ([Jansen, 2004](#)). Values for interactions between CO and oxygen and between oxygen atoms at different hollow sites have all been estimated, based on the distance between the sites and values of lateral interactions for other systems at similar distances.

You will need to add three sets of lateral interactions, for different combinations of the two species involved in an interaction. First you will add the interactions for the *CO-CO* combination.

On the **Interactions** tab of the original **ZGBMultiSite.xkp** select **CO** from each of the **Interactions** dropdown lists and specify a **cutoff** of **3.5 Å**. Click the **Add** button.

A new interaction will be added to the list in this tab, with the details listed on the *Interaction Details* tab. All possible combinations of sites between the minimum and maximum cutoff distances are listed. Some of these are irrelevant because, for example, CO can exist only on the top sites (with site index 1).

Many of the interaction details listed are related to each other by the symmetry defined for the lattice. Although these relationships are not shown in the list, they are honored when the lists are modified, such as by deletion of a detail item or modification of the interaction value.

You should remove the irrelevant interaction details from the list for this process, and specify the desired interaction value for the remaining details.

On the **Interaction Details** tab, select a row with **2** or **3** as the site index (the third component of the site description) for either **Site for CO** column. Press **DELETE**.

Repeat this to remove all interactions apart from those between top sites, so all remaining interactions should have site index 1 for both sites.

Note: The *Interactions Details* tab does not support selection of multiple rows.

There should be six items remaining in the *Interaction Details* list.

Click in one of the **Interaction** cells and change the value to **6.69**. The two symmetry-related interaction rows will be updated automatically.

Repeat this procedure until all **Interaction** values are **6.69**.

Next you will add lateral interactions between *CO* and *O*. Here you will make use of the fact that *CO* can only exist on the top site, while *O* can exist only on hollow and fcc sites.

On the **Interactions** tab select **O** for the second interacting species and click the **Add** button.

On the **Interaction Details** tab select a row with site index **1** for the **Site for O** column and press **DELETE**.

Repeat this until all remaining **Site for O** have an index of 2 or 3.

Delete all the interactions where the **Site for CO** has an index of 2 or 3.

Change all the **Interaction** values to **2.39**.

There should also be six items remaining in the *Interaction Details* list for this interaction.

Next you will add lateral interactions between *O* and *O*. This is more complicated in that there will be two sets of interactions at different distances, hence with different interaction values.

On the **Interactions** tab select **O** for both the species and click the **Add** button.

On the **Interaction Details** tab delete all rows with a **Site for O** index of **1**.

There will be six interaction items between fcc sites (with a site index of 2), and six interaction items between hcp sites (with a site index of 3). These will all show a distance of 2.77 Å. Similarly there will be six interaction items between an fcc site and an hcp site, showing a distance of 3.199 Å.

Change the **Interaction** value to **6.21** for all those interaction items showing a distance of 2.77 Å.

Change the **Interaction** value to **2.39** for all those interaction items showing a distance of 3.199 Å.

The Interaction Details tab should look like:

	Site for O	Site for O	Distance	Interaction
	(0, 0 / 2)	(-1, -1 / 3)	3.199	2.39
	(0, 0 / 2)	(-1, 1 / 3)	3.199	2.39
	(0, 0 / 2)	(1, -1 / 3)	3.199	2.39
	(0, 0 / 3)	(-1, 1 / 2)	3.199	2.39
	(0, 0 / 3)	(1, -1 / 2)	3.199	2.39
	(0, 0 / 3)	(1, 1 / 2)	3.199	2.39
	(0, 0 / 3)	(-1, 0 / 3)	2.770	6.21
	(0, 0 / 3)	(-1, 1 / 3)	2.770	6.21
	(0, 0 / 3)	(0, -1 / 3)	2.770	6.21
	(0, 0 / 3)	(0, 1 / 3)	2.770	6.21
	(0, 0 / 3)	(1, -1 / 3)	2.770	6.21
	(0, 0 / 3)	(1, 0 / 3)	2.770	6.21

Process Details Process Sites **Interaction Details**

Interaction details tab

Before continuing you should save the project.

Select **File | Save Project** from the menu bar.

If you wish, you can compare your document at this stage with a pre-saved version of it in the file *ZGBMultiSite Stage 4.xkp* in the Examples library provided with Materials Studio.

10. Using lateral interactions and running the simulation

By default, any interactions that have been defined will be used to conditionally modify the activation energy for any process that uses an Arrhenius expression for the rate specification. In the simulation run earlier in this tutorial there were no interactions defined, so there were no such modifications.

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For each such process, the extent to which the lateral interactions modify the activation energy is governed by the *Brønsted-Polanyi factor*, denoted by α . When the process is first created α is set to a value dependent on the type of the process. These default values are correct for your purposes, but you should check that they have not been accidentally altered.

On the **Process Details** tab check the details for each of the processes. For each **Desorption** process the **Use interactions** checkbox should be **checked** and the **Brønsted-Polanyi factor** should be **1.0**.

For each **Diffusion** process the **Use interactions** checkbox should be **checked** and the **Brønsted-Polanyi factor** should be **0.5**.

You can now run another simulation, and compare the results with the previous one which did not use lateral interactions.

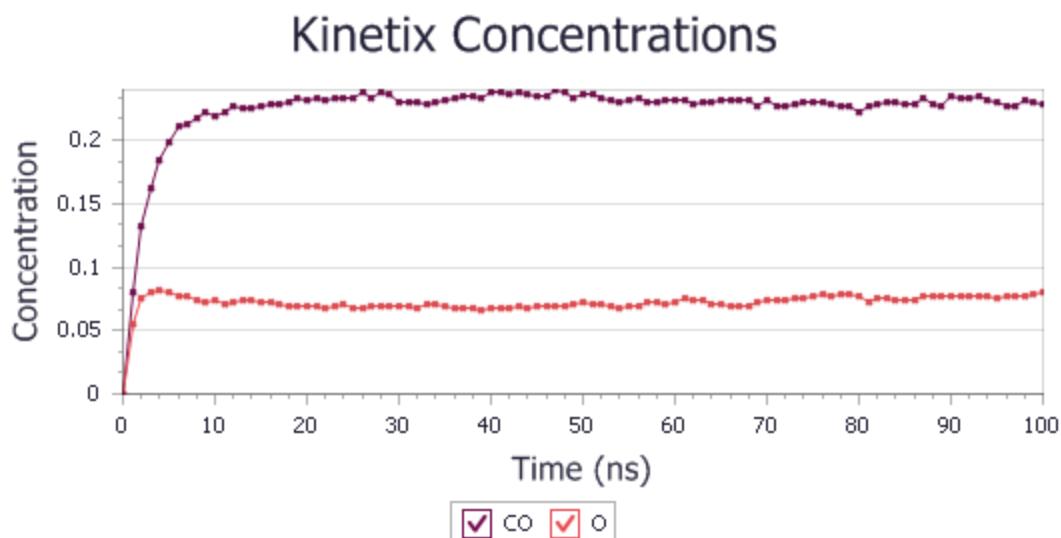
Open the **Kinetix Calculation** dialog. Ensure that the original **ZGBMultiSite.xkc** is the active document, and that the **Constant conditions** task is selected. On the **Job Control** tab uncheck the **Automatic** checkbox and set the **Job description** to **ZGB MultiSite With Interactions**.

Click the **Run** button and close the dialog.

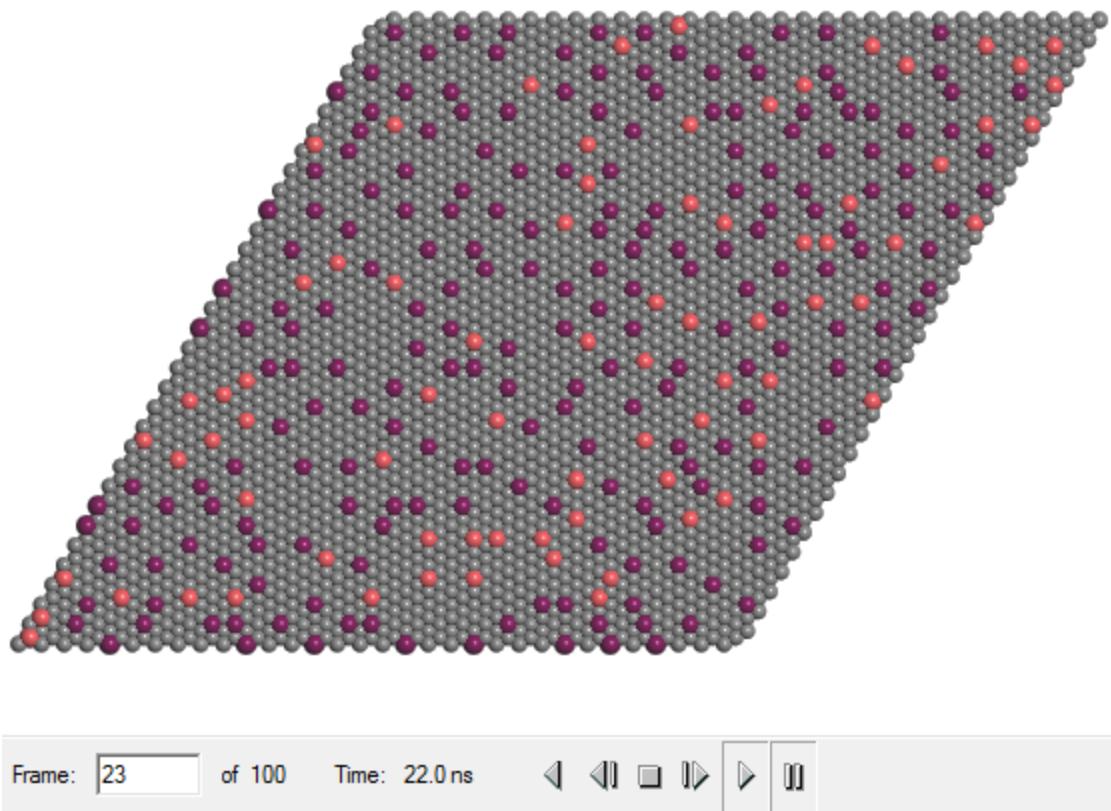
11. Analyzing the results

You should generate a chart of **Concentrations**, and also make the same changes to the display style of **ZGBMultiSite With InteractionsTraj.xkc** that you made for the earlier simulation.

These should look similar to the following:



Average concentrations during simulation with interactions



Configuration during simulation with interactions

You can now compare these results with those generated before you added the lateral interactions. You should be able to see immediately that the concentration of CO stabilizes at a value of about 0.23, much lower than previously, and that the oxygen concentration also stabilizes to about 0.06 whereas in the earlier simulation it dropped to about 0.03.

At this point you might like to export the trajectory in the form of an .avi file to play in a presentation. This is the end of the tutorial.

References

- A.P.J. Jansen, "An introduction to Monte Carlo Simulations of Surface Reactions", <https://arxiv.org/abs/cond-mat/0303028> (2003).
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- A.P.J. Jansen and W.K. Offermans, "Lateral interactions in O/Pt(111): Density Functional Theory and kinetic Monte Carlo", in the *Proceedings of the International Conference on Computational Science and Its Applications (ICCSA-2005)*, (Springer, Berlin, 2005), pp. 1020-1029.
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- W.K. Offermans, A.P.J. Jansen, and R.A. van Santen, "Ammonia activation on platinum{111}; A density-functional theory study", *Surf. Sci.*, **600**, 1714-1734 (2006).
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I.N. Yakovkin and N.V. Petrova, "Microscopic model of CO oxidation on Pt(111)", *Surf. Sci.*, **600**, 2600-2607 (2006).

R.M. Ziff, E. Gulari, Y. Barshad, "Kinetic Phase Transitions in an Irreversible Surface-Reaction Model", *Phys. Rev. Lett.*, **56**, 2553-2556 (1986)

Chapter 14: Mesocite tutorials

The following tutorials illustrate how to utilize Mesocite's capabilities.

- [Coarse-grained molecular dynamics of a lipid bilayer](#)
- [Effects of surfactant on a lipid bilayer using DPD](#)
- [Effect of shearing on an oil droplet](#)
- [Calculating input parameters for a DPD simulation](#)
- [Generating a MS Martini 3 Forcefield and Bead Topology](#) on page 504
- [Polymer Coarse Graining with Martini 3 Tools](#) on page 516
- [Preparation of a Granular Material](#) on page 528
- [Building Mesoscale Amorphous Cell Using Mesocite Builder](#) on page 536

Coarse-grained molecular dynamics of a lipid bilayer

Purpose: Demonstrates how to set up and simulate a lipid bilayer using the mesoscale modeling tools

Modules: Materials Visualizer, Mesocite

Time: 

Prerequisites: Building mesoscale molecules Visualizer Tutorial

Background

Coarse-grained molecular dynamics enables the simulation of longer time and larger length scales than is available to atomistic molecular dynamics. This is achieved by representing groups of several atoms as a single unit or bead. A forcefield is parameterized for the interaction between each type of bead in the system. In general, coarse-grained forcefields have to be parameterized for each system to be studied. However, [Marrink et al.](#) have generated a coarse-grained forcefield, MARTINI, which is parameterized for a wide range of organic moieties, focusing on simulations of biomolecular materials such as lipids.

Dipalmitoylphosphatidylcholine (DPPC) is a phospholipid and the major constituent of pulmonary surfactant. It is also used for research purposes in the study of liposomes, lipid bilayers, and models of biological membranes.

Materials Studio includes a slightly modified version of the MARTINI forcefield, MS Martini, which can be used to run coarse-grained molecular dynamics simulations of bead structures.

Introduction

In this tutorial, you will use Mesocite to run a coarse-grained molecular dynamics simulation of a lipid bilayer using the MS Martini forcefield. You will use the mesostructure building tools to build an initial starting structure and perform some equilibration of the bilayer.

This tutorial covers:

- [Getting started](#)
- [To create lipid and solvent molecules](#)
- [To apply the forcefield types and modify the forcefield](#)
- [To build the bilayer](#)
- [To optimize and equilibrate the structure](#)
- [To simulate the bilayer and analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CG_bilayer** as the project name, click the **OK** button.

The new project is created with *CG_bilayer* listed in the Project Explorer.

You can access the mesostructure building tools through the Build menu or using the Mesostructure toolbar. To use the toolbar make sure it is visible.

Select **View | Toolbars** from the menu bar and ensure the **Mesostructure** toolbar is enabled.

2. To create the lipid and solvent molecules

The first step is to define the bead types to be used in building molecules for lipid and solvent. You will use the same representation as used by Marrink et al. where 1 bead represents approximately four heavy atoms with an average mass of 72 g/mol and an effective radius of 2.35 Å.

Click the **Bead Types** button  on the Mesostructure toolbar to open the Bead Types dialog. Click the **Defaults...** button to open the Bead Type Defaults dialog.

Set the **Mass** to **72** and the **Radius** to **2.35** and close the Bead Type Defaults dialog.

On the **Bead Types** dialog, define the following new bead types: **C**, **GL**, **NC**, **PO**, and **W**. Close the dialog.

With the defined bead types you can build the initial bead representations of the lipid and solvent.

Click the **Mesomolecule** button  on the Mesostructure toolbar to open the Build Mesomolecule dialog.

To build the lipid molecule in its characteristic conformation it is convenient to build the molecule in three steps. Start with the phosphate and choline head groups.

Define a repeat unit of **1** unit of **PO** and **1** unit of **NC**. Click the **Build** button.

Next add two glycerol beads to the phosphate group.

Delete the existing repeat unit definition and define a new repeat unit of **1** unit of **GL**. Select the **PO** bead in the structure and check the **Add to branch points** checkbox. Click the **More...** button to open the *Mesomolecule Branches* dialog and verify that **Branch from selected beads** is checked and the **Number of branches to attach** is set to **2**.

Close the dialog and click the **Build** button.

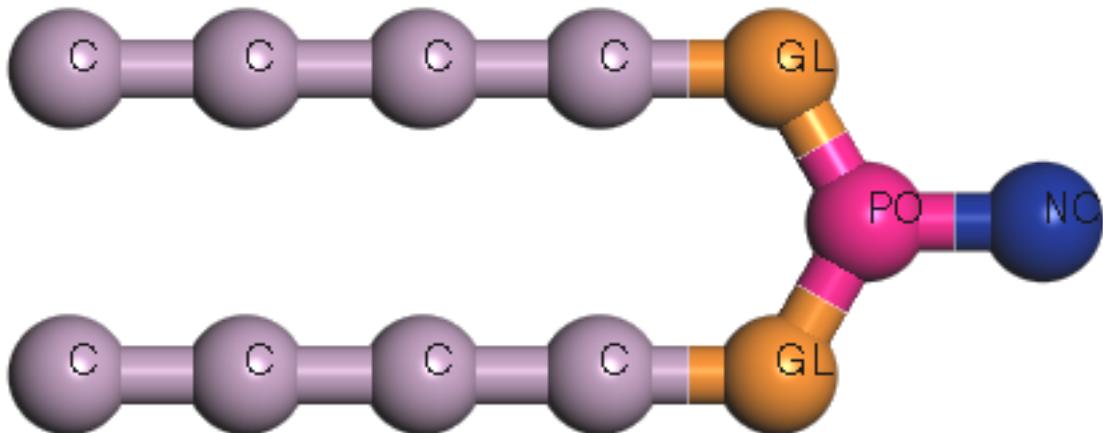
Tip: Use the *Label* dialog to apply *BeadTypeName* labels to your document.

Finally add the carbon tails to both glycerol beads. You will add four tails and delete the two that are not needed in order to generate a suitable starting geometry for the structure.

Delete the existing repeat unit definition and define a new repeat unit of **4** units of **C**. Select the two **GL** beads in the structure and click the **Build** button.

In the resulting structure delete the two branches that point out in the direction of the head group.

You should have a mesomolecule that looks the same as the image below.



Initial bead structure of the lipid in ball and stick display style, with the beads labeled by their BeadTypeName

Save the document and **close** the view. In the Project Explorer, **rename** the document to **DPPC.xsd**.

Finally build a solvent molecule. This will be a single bead of type W, representing four water molecules.

Delete the existing repeat unit definition and define a new repeat unit of **1** unit of **W**. Click the **Build** button and close the dialog.

Save and close the new document, then **rename** it to **solvent.xsd**.

3. To apply the forcefield types and modify the forcefield

You will use the MS Martini forcefield to perform all of the calculations in this tutorial. MS Martini is based on the MARTINI forcefield developed by Marrink et al. and has been parameterized to study lipid bilayers and other organic moieties. The basic forcefield uses an equilibrium bond distance of 4.7 Å and an equilibrium angle of 180° for all the forcefield types. For bonds that are non-linear (for example cis-unsaturated bonds) Marrink et al. have used a modified angle of 120° and they use this non-linear cis bond angle to represent the GL-PO-GL bond angle. This non-linear cis bond angle is not included in MS Martini by default and you will need to make a small modification to the provided forcefield to allow for its use.

As you are going to modify the existing MS Martini, you need to import it into the project.

Select **Modules | Mesocite | Forcefield Manager** from the menu bar to open the Mesocite Forcefield Manager. Select **MS Martini** and click the **>>** button to open the forcefield. Close the dialog.

Save and close the document, **rename** it to **MS Martini CIS.off**.

First you will define the forcefield types on the beads. These are the types listed in the MARTINI paper parameterizing the DPPC lipid.

BeadTypeName	MS Martini Forcefield Type	Charge
C	C1	0
GL	Na	0
PO	Qa	-1.0
NC	Q0	1.0
W	P4	0

As there are no bead typing rules in Mesocite, you need to manually assign forcefield types to the beads. You can do this using the Properties Explorer, or using the Mesocite dialog. In the following you will use the Mesocite dialog.

Select **Modules | Mesocite | Calculation** from the menu bar.

This opens the *Mesocite Calculation* dialog. The Setup tab is used to define the task, the Energy tab defines the forcefield and non-bond terms, and the Job Control tab is used to specify the calculation settings. As you will customize the forcefield, you should select the imported version of Martini rather than the standard version.

Select the **Energy** tab and select **Browse...** from the **Forcefield** dropdown list. On the Choose Forcefield dialog select **MS Martini CIS.off**.

Click the **More...** button for the **Forcefield** to open the Mesocite Preparation Options dialog.

The Mesocite Preparation Options dialog displays a list of all the forcefield types in the current forcefield. You can now assign selected types to selected beads in the lipid and solvent structures.

Open the **DPPC.xsd** document. In the 3D Viewer hold down **ALT** and **double-click** on any **C** bead.

All the beads of BeadTypeName C are selected.

Select **C1** in the list of forcefield types and click the **Assign** button. Repeat this for the **GL**, **PO**, and **NC** bead types, assigning the forcefield types in the table [above](#).

Two bead types, NC and PO, also have charges assigned. You need to assign the charges using the Properties Explorer or the Charges dialog.

Select the **PO** bead and, in the **Properties Explorer**, set the **Charge** to **-1**. Repeat this for the **NC** bead setting the **Charge** to **1**. Save and close the document.

Finally you need to specify the forcefield type of the solvent bead to be high polarity (P4).

Open the **solvent.xsd** document. Select **P4** on the Mesocite Preparation Options dialog, click the **Assign** button and close the dialog. Save and close the document.

Now you will modify the forcefield by adding an explicit bond angle term for the GL-PO-GL bond angle, which corresponds to the angle between forcefield types Na-Qa-Na.

Open the forcefield document **MS Martini CIS.off** and select the **Interactions** tab. Choose **Angle Bend** from the **Show interaction** dropdown list. In the empty row, set both **Fi** and **Fk** to **Na**, and set **Fj** to **Qa**. Change the **Functional Form** to **Cosine Harmonic**.

For the GL-PO-GL bond angle, Marrink et al. used an equilibrium bond angle, or T0, of 120° and a force constant of 10.8 kcal/mol (45 kJ/mol).

Set **T0** to **120** and **K0** to **10.8**. Save and close the forcefield document.

You are now ready to use the Mesostructure Template builder to build the mesomolecules into a bulk structure.

4. To build the bilayer

In this part of the tutorial, you will build the bulk structure containing the bilayer and the water using the Mesostructure builder. You will build a box which is $64 \times 64 \times 100 \text{ \AA}$. Into this box, you will add a slab former to pack with the DPPC lipid.

To calculate the depth of the slab you will use the experimental area per lipid, which is about 65 \AA^2 , and the fact that in Martini 1 solvent bead represents four water molecules ([Marrink et al.](#)). First determine the volume of a bead, using the density and molar weight of water.

Water has a density of 1 g/cm^3 and molar weight of 18 g/mol . Hence the volume of 1 water molecule is $18/N_{\text{av}} \text{ cm}^3$, or $18/N_{\text{av}} 10^{24} \text{ \AA}^3 = 29.9 \text{ \AA}^3$, where $N_{\text{av}} = 6.02 \times 10^{23}$ is Avogadro's number. As there are four water molecules per bead, the volume of a bead is $4 \times 29.9 = 119.6 \text{ \AA}^3$.

Now determine the number of lipid beads using the experimental area per lipid.

The total area of the slab is $64 \times 64 = 4096 \text{ \AA}^2$. As the area per lipid is 65 \AA^2 there are $4096/65 = 63$ lipids on either side of the bilayer, or $2 \times 63 = 126$ in total. Each lipid contains 12 beads, therefore the slab contains $126 \times 12 = 1512$ lipid beads.

Using the number of beads and their volume, you can calculate the depth of the slab.

There are 1512 lipid beads with a volume of 119.6 \AA^3 per bead, so the total volume is $1512 \times 119.6 = 180835 \text{ \AA}^3$. Since the area is 4096 \AA^2 , the depth must be $180835/4096 = 44 \text{ \AA}$.

Now you can build the template, starting with a system former.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. Change both the **X** and **Y Extents** to **64** and the **Z Extent** to **100**. In the **Filler** text box, enter **solvent**. Click the **Build** button.

A new template document is created containing a single blue system former. Add a slab of depth 44 \AA to the template.

Change the **Former type** to **Slab**. Change the **Depth** to **44** and the **Orientation** to **Along Z**.

You will need to use the surface packing to pack the lipid heads onto both surfaces.

Check the **Enable surface packing** checkbox and enter **lipid** in the **Filler** text box. Click the **Add** button and close the dialog. **Save** the document.

Now that you have built the template, you need to fill it with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog.

You need to specify the components that you want to associate with the fillers.

Click in the **Mesoscale Molecule** column for the **solvent** filler and select **solvent.xsd**. For the **lipid** filler select the **DPPC** structure.

Confirm that the target **Density** is set to **1 g/cm³**.

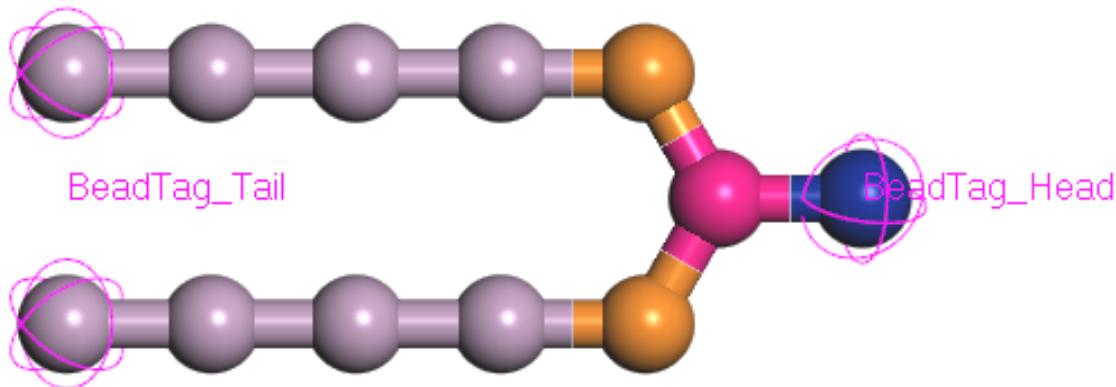
On the **Options** tab, **uncheck** the **Randomize conformations** checkbox.

Before building the mesostructure, you need to define the head and tail beads on the lipids so that the lipid heads stick to the surface of the slab former.

Click the **More...** button to open the Bead Packing Options dialog. Change focus to the lipid structure in **DPPC.xsd**.

Select the **NC** head bead and click the **Create bead Head set from selection** button. Select both terminating tail beads, change the **Bead tag to Tail** and click the **Create bead Tail set from selection** button. Close the dialog.

The labeled DPPC bead structure is shown below.



Prepared DPPC lipid structure

You can now build the mesostructure.

Make the template the active document. On the **Build Mesostructure** dialog, click the **Build** button and close the dialog.

A 3D Atomistic Structure document is returned containing the solvent and lipid molecules packed in different former areas of the template.

In the Project Explorer, **rename** the document to **bilayer.xsd**.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

You have now prepared the initial structure. The next stage is to equilibrate the structure and perform a production run.

5. To optimize and equilibrate the structure

The structures generated by the Mesostructure Builder are very rough and will have overlapping beads. Therefore, before trying to run some dynamics on this structure, you should optimize the geometry first to remove close contacts and any initial stresses in the system.

The optimization is best carried out in three steps:

1. Optimize the intermolecular interactions, keeping the internal conformation and the cell rigid
2. Optimize all molecular interactions in a fixed cell
3. Optimize the cell and all other degrees of freedom

This reduces the chance that bead overlap is resolved by introducing unrealistic bond lengths or angles.

Open the **Mesocite Calculation** dialog, on the **Setup** tab change the **Task** to **Geometry Optimization** and click the **More...** button to open the Mesocite Geometry Optimization dialog. Check the **Keep motion groups rigid** checkbox.

By keeping motion groups rigid, the distance between all atoms in a motion group is fixed during the optimization. To keep all molecules rigid, define motion groups for each molecule.

Open **bilayer.xsd**, click the **More...** to open the Motion Groups dialog. Click the **Assign automatically** button and close the dialog.

Now you can perform an initial geometry optimization.

On the **Mesocite Calculation** dialog, click the **Run** button.

The optimization may take a few minutes to complete. You can look at the live update charts to see the energy profile.

Open **bilayer Energies.xcd**.

You should see a very high initial energy which drops rapidly. This is due to the overlaps from the initial model build process, which are gradually removed by the optimizer.

Once you have completed this initial optimization, the next stage is to run another minimization, this time without constraining the motion groups.

Open **bilayer Mesocite GeomOpt\bilayer.xsd**.

On the **Mesocite Geometry Optimization** dialog and **uncheck** the **Keep motion groups rigid** checkbox.

Click the **Run** button.

Finally optimize the cell parameters as well.

Open **bilayer Mesocite GeomOpt\bilayer Mesocite GeomOpt\bilayer.xsd**. On the **Mesocite Geometry Optimization** dialog check the **Optimize cell** checkbox. Close the dialog.

Click the **Run** button.

To reduce the folder nesting, save the resulting structure to the root folder of the project.

Open **bilayer Mesocite GeomOpt\bilayer Mesocite GeomOpt\bilayer Mesocite GeomOpt\bilayer.xsd**. On the **File** menu choose **Save As....** Enter **bilayer_opt** as **File name**, navigate to the **Documents** folder, and click **Save**.

You can delete the motion groups from the structure as they are no longer needed, then clear the workspace before proceeding with the next step.

Press and hold **ALT** and double-click on a motion group in **bilayer_opt.xsd** to select all motion groups. Press **DELETE**.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**. Reopen **bilayer_opt.xsd**.

Now continue with the dynamics run.

On the **Setup** tab change the **Task** to **Dynamics** and click the **More...** button to open the Mesocite Dynamics dialog. Set the **Time step** to **40 fs** and change the **Ensemble** to **NPT**.

The time step of 40 fs is the time step used by Marrink et al. in their parameterization of the MARTINI forcefield. The NPT ensemble is used to equilibrate the pressure and temperature in the system. You will initially use the Velocity scaling thermostat to equilibrate the temperature in the system and the Andersen barostat to relax the residual stress. Velocity scaling is a very approximate thermostat and is only useful for quickly bringing the system closer to equilibrium.

Select the **Thermostat** tab and set the **Thermostat** to **Velocity Scale**. On the **Barostat** tab set the **Barostat** to **Andersen** and close the dialog.

Click the **Run** button on the Mesocite Calculation dialog.

The structure should now be suitable to carry out a production run and analyze the results.

6. To simulate the bilayer and analyze the results

The final production run will be a long NPT dynamics with the Nose thermostat and Andersen barostat.

Make **bilayer_opt.xtd** in the **bilayer_opt Mesocite Dynamics** folder the active document.

Open the Mesocite Dynamics dialog and select the **Thermostat** tab, set the **Thermostat** to **Nose**. On the **Dynamics** tab set the **Frame output every** to **250** steps and close the dialog.

Tip: In a real calculation you would run a much longer production run, monitoring the density plot to assess when it is converged.

You can restart the calculation so that the velocities on the atoms from the previous simulation are used as starting velocities for this simulation. As you have already performed some equilibration of the velocities, restarting enables you to re-use those velocities.

On the **Mesocite Calculation** dialog, check the **Restart** checkbox and click the **Run** button. On the warning dialog click the **Yes** button. Close the **Mesocite Calculation** dialog.

This calculation will take several minutes to complete. When the calculation completes, you can change focus to the trajectory and perform some analysis.

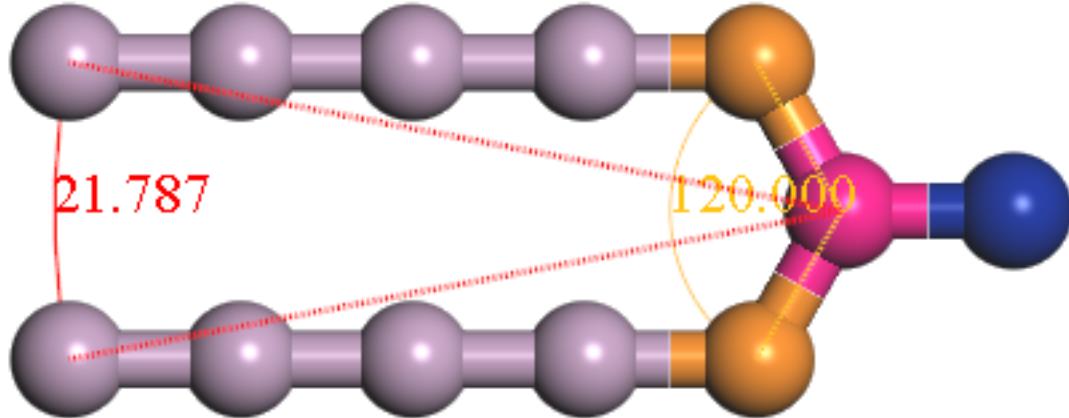
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

You are now ready to perform some analysis on the structure.

For this analysis, you will look at the difference in the angle distribution between the GL-PO-GL bond angle and the C-PO-C angle. Initially, you will edit the DPPC molecule and add GL-PO-GL and C-PO-C angle monitors. You will perform a pattern match against the trajectory to find all the GL-PO-GL and C-PO-C angles and then analyze the angle distributions.

Open the trajectory document in the **bilayer_opt Mesocite Restart** folder and the initial DPPC structure.

Make **DPPC.xsd** the active document. Define two bond angles as illustrated below. Select the **GL-PO-GL** bond angle.



The two bond angles that can be used in the analysis

Now you can use the pattern matching tools to create two sets of these bond angles on the trajectory.

Select **Edit | Find Patterns** from the menu bar to open the Find Patterns dialog. Select **DPPC.xsd** as the **Pattern document** ensuring that the GL-PO-GL angle is still selected. Change the **Match** property to **BeadTypeName**. Make **bilayer_opt.xtd** the active document and click the **Find** button.

Angle monitors are created on all the GL-PO-GL bond angles in the system and they are all selected. You can create a set of these so that you can select them later and use the set in the analysis.

Click the **New Sets...** button to open the Define New Set dialog. Enter the name **GLPOGLAngles** and click the **OK** button. In **bilayer_opt.xtd**, deselect the angles.

You can now use the Find Patterns tool to find the C-PO-C angle that you defined and create a set for those angles.

Change back to **DPPC.xsd** and select the **C-PO-C angle**. Make **bilayer_opt.xtd** the active document and, on the **Find Patterns** dialog, click the **Find** button.

Click the **New Sets...** button to open the Define New Set dialog and enter the name **CPOCAngles**. Click the **OK** button and close the **Find Patterns** dialog. Click anywhere in **bilayer_opt.xtd** to deselect the angles.

You have created two sets containing the two different angles. Now you can analyze their distribution.

Select **Modules | Mesocite | Analysis** from the menu bar to open the Mesocite Analysis dialog.

There are many different types of analysis that you can perform on a trajectory. For this example, you will perform an Angle distribution analysis.

In the **Analysis** section, select **Angle distribution**. Select **GLPOGLAngles** from the **Sets** dropdown list and click the **Analyze** button.

Select **CPOCAngles** from the **Sets** dropdown list and click the **Analyze** button.

You should see two different charts. The restricted GL-PO-GL angle has a peak centered around 100° and for the C-PO-C angles there is a broader peak spread between 10° and 80°. This shows the flexibility of the tails in comparison to the constrained head angle.

This is the end of the tutorial.

References

S.J. Marrink, H.J. Risselada, S. Yefimov, D.P. Tieleman, A.H. de Vries., "The MARTINI forcefield: coarse grained model for biomolecular simulations.", J. Phys. Chem. B, 111:7812-7824, 2007.

Effects of surfactant on a lipid bilayer using DPD

Purpose: Demonstrates how to set up and simulate a lipid bilayer using the mesoscale modeling tools

Modules: Materials Visualizer, Mesocite

Time: 

Prerequisites: Building bulk mesostructures Visualizer Tutorial

Background

The DPD method is designed to allow hydrodynamic behavior in fluids to be captured. In addition, the use of a soft potential allows much larger time steps than are traditionally available in either classical atomistic calculations or coarse-grained molecular dynamics.

The ability to study long time scales and to include hydrodynamic behavior makes DPD the perfect tool for studying lipid and surfactant systems. In this tutorial, based on a paper by [Groot and Rabone](#), you will simulate the effect of adding surfactant to a lipid membrane.

Introduction

In this tutorial, you will use Mesocite to run several mesoscale dynamics simulation of different lipid bilayers using the DPD method. You will use the mesostructure building tools to build an initial starting structure and perform some equilibration of the bilayers. You will then perform a production run and use the analysis tools to examine the structure of the bilayer.

This tutorial covers:

- [Getting started](#)
- [To create the input structure](#)
- [To equilibrate the structures](#)
- [To perform a production run](#)
- [To analyze the results](#)

Note: Completion of this tutorial entails running a DPD calculation. Depending on the configuration of your computer server, this calculation could take a considerable amount of time.

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DPD_lipid** as the project name, click the **OK** button.

The new project is created with *DPD_lipid* listed in the Project Explorer.

2. To create the input structures

The first step is to build mesomolecule models of water, lipid, and surfactant molecules. Groot and Rabone used a coarse graining approach where one bead represents three molecules of water (W). As the volume of a water molecule at room temperature is about 30 \AA^3 , they defined the volume of a bead to be $(3 \times 30) = 90 \text{ \AA}^3$. At the standard density of 3 beads per unit volume, this translates to a fundamental length unit of $(3 \times 90)^{1/3} = 6.46 \text{ \AA}$. Likewise, given that the mass of a water molecule is 18 amu, the mass of a bead is $(3 \times 18) = 54 \text{ amu}$. You will use these mass and length units based on water in this tutorial. The length unit will also serve as the diameter of a bead, corresponding to a radius of $6.46/2 = 3.23 \text{ \AA}$.

In the coarse graining approach of Groot and Rabone, one bead also maps on three carbon atoms (C), or 1.5 ethylene oxide groups (E). These have slightly different densities and molecular weights. Whilst you could have beads with different masses in the DPD calculation, there has been little validation on the effect of this. Therefore, you will use same mass for all beads in this tutorial. As the C and E beads are used in both the lipid and surfactant molecules, you will differentiate between them using CL and EL for the lipids, and CS and ES for the surfactants. This is not essential for the calculation but does add clarity to the visualization of the bilayer.

Select **Build | Build Mesostructure | Bead Types** from the menu bar to open the Bead Types dialog. Click the **Defaults...** button to open the Bead Type Defaults dialog. Set the **Mass** to **54** and the **Radius** to **3.23**. Close the Bead Type Defaults dialog.

Define the following new bead types: **CL**, **CS**, **EL**, **ES**, **H**, and **W** and close the Bead Types dialog.

Note: The bead radius is used in the mesomolecule builder to determine the bond length. Otherwise it is used only for visualization and has no effect on the calculation. The bead mass, on the other hand, is used in the DPD simulation.

Now you have defined the bead types, you can create the structures.

Select **Build | Build Mesostructure | Mesomolecule** from the menu bar to open the Build Mesomolecule dialog. Build a mesomolecule of **1** unit of **W** and rename the new document to **water.xsd**.

Build a mesomolecule of **4** units of **ES** and **4** units of **CS**. Rename the document **surfactant.xsd**.

Build a mesomolecule of **2** units of **H** and **1** unit of **EL**.

In the resulting structure, select the **EL** bead. Define a sequence of **5** units of **CL**. Check the **Add to branch points** checkbox and click the **Build** button. Rename the document **lipid.xsd**. Close the dialog and click anywhere in the 3D Viewer to deselect any items.

It is convenient at this point to define forcefield types on the three molecules. This avoids having to type individually all the bulk structures that you are going to build later. You can assign forcefield types using the Properties Explorer or the Type facility of the Create DPD Forcefield dialog. In this tutorial you will use the Type functionality.

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Select **Mesocite | Forcefield Manager** from the menu bar to open the Mesocite Forcefield Manager dialog. Click the **DPD...** button to open the Create DPD Forcefield dialog. Ensure that **lipid.xsd** is the active document and click the **Type** button. Repeat this for the documents **surfactant.xsd** and **water.xsd**. Close the Mesocite Forcefield Manager dialog.

Later in this tutorial you will use the other controls on the Mesocite Forcefield Manager dialog, you can ignore these for now.

Tip: You can use the Label dialog to verify the forcefield types, by applying a label for the **ForcefieldType** property of a bead.

Now you have built the components, you need to construct the cell containing these mesomolecules. You will build several cells containing varying concentrations of lipid and surfactant but keeping a fixed volume of water. You can use the Mesostructure template tools to pack the membrane molecules into a slab which will then force the bilayer to form. In this tutorial you will build a slab of 30 Å in a box of 90 × 90 × 90 Å, such that the solvent occupies 70% of the volume, and the membrane 30%.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. Change all the **Extent (X Y Z)** values to **90**. In the **Filler** text box, enter **solvent** and click the **Build** button.

To build the slab for the membrane you will add a slab former to the template, positioned in the middle of the box with a normal along the x direction.

On the **Build Mesostructure Template** dialog, change the **Former type** to **Slab**. Set the **Depth** to **30.0** and enter **membrane** in the **Filler** text box. Click the **Add** button and close the dialog.

Now that you have built the template, you need to fill it with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog. Make sure that the template is in focus.

You need to specify the components that you want to use as the fillers - you will fill the 'solvent' with water and 'membrane' with lipid and surfactant.

Click in the **Mesoscale Molecule** column for the **solvent** filler and select **water.xsd**. Repeat this for the **membrane** filler, selecting **lipid.xsd** and **surfactant.xsd**.

For the **membrane** filler, set the **Relative Amount of lipid** to **50** and **surfactant** to **50**.

This will build a box with 70% volume fraction of water beads and 30% volume fraction of 50/50 mixture of lipid and surfactant. Due to the differing number of beads in the lipid and surfactant molecules, this will not give you a molar ratio of 50:50.

Before building the box, you need to specify the target density. By setting the density to that of water (1 g/cm³) the resulting structure has a reduced density of 3 beads per cubic length scale. This follows from the mass scale of 53 amu and the length scale of 6.46 Å. A reduced density of 3 is the value most commonly used in DPD, and was also used in the study by Groot and Rabone.

On the Components tab, make sure the **Density** is set to **1 g/cm³**. Click the **Build** button. Rename the document **W70_L50_S50.xsd**.

As you will be repeating this for several runs, you should build several cells at concentrations ranging from 100% lipid to 100% surfactant.

Ensure that the template is the active document. Modify the **Relative Amount to lipid 20** and **surfactant 80**. Click the **Build** button. Rename the document **W70_L20_S80**.

Make the template the active document and modify the **Relative Amount to lipid 0** and **surfactant 100**. Click the **Build** button. Rename the document **W70_S100**.

Make the template the active document and modify the **Relative Amount to lipid 100** and **surfactant 0**. Click the **Build** button. Rename the document **W70_L100**. Close the dialog.

You have now built the initial structures. The next stage is to equilibrate the structures.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To equilibrate the structures

In this section of the tutorial, you will begin to equilibrate the structures by performing geometry optimization. The first step is to set up the forcefield. Since you have assigned forcefield types on the molecules, these should already be set on the structures built from them.

Open **W70_L50_S50.xsd**. Select **Modules | Mesocite | Forcefield Manager** from the menu bar and click the **DPD...** button to open the Create DPD Forcefield dialog.

You should see a matrix of forcefield types corresponding to those in the document. The values are currently displayed in physical units (based on kcal/mol and Å) whereas DPD work, including that of Groot and Rabone, has usually been carried out using reduced units. Mesocite DPD allows you to set up the calculation using either physical or reduced units (in which case the conversion to physical units will be performed automatically). You will use reduced units here.

Change the **Units** to **Reduced** and click the **More...** button to open the Mesocite DPD Units dialog.

You need to enter the Length and the Mass scales to be used for the unit conversion. As discussed earlier in the coarse graining method of Groot and Rabone, one length unit corresponds to 6.46 Å and one mass unit to the mass of a bead, 54 amu.

Change the **Length scale** to **6.46** and the **Mass scale** to **54**. Close the dialog.

It can be shown that the DPD repulsion parameters a_{ij} can be related to the Flory-Huggins Chi parameter χ as follows:

$$a_{AB}(\rho = 3) = 25 + 3.50\chi$$

where the a_{ij} are in reduced units.

Tip: There are various ways of estimating χ . You can derive it from Solubility Parameters, as calculated by Synthia or from Cohesive Energy Density calculations using Forcite Plus, COMPASS, and Amorphous Cell. There are various tables of χ values for polymers derived from experimental work. Alternatively, you can use the Blends module to get a first estimate of the value of χ . In many cases, you might use a mixture of these techniques based on what you have derived or have used in the past and fit them to reproduce a known mesoscale structure.

In this tutorial, you will use the "set1" values of a_{ij} as used by Groot.

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	CL	CS	EL	ES	H	W
CL	78					
CS	78	78				
EL	86.7	86.7	78			
ES	86.7	86.7	78	78		
H	104	104	79.3	79.3	78	
W	104	104	79.3	79.3	79.3	78

The diagonal elements used by Groot and Rabone are chosen such that a monomer bead fluid has the compressibility of water. This value scales with the number of water molecules represented by a bead (Groot and Rabone, 2001). The default value in Mesocite (25) is based on the case where a bead represents one water molecule ([Groot and Warren, 1997](#)). Since in the present case a bead represents 3 water molecules, the diagonal terms are about three times higher than the default.

On the **Create DPD Forcefield** dialog edit the matrix and set the **Repulsions** to the values shown in the table above. Click the **Create** button and close the dialog.

Tip: You can expand the dialog to see the whole matrix by dragging one of its corners.

When you click the Create button, a new Forcefield document is created and listed as **W70_L50_S50.off** in the project explorer. The values in the forcefield document are written in physical units and the forcefield is automatically set on the Energy tab of the Mesocite Calculation dialog.

Tip: As the interactions are stored in a forcefield document, you can add other interactions to the calculation such as bond angle terms to control rigidity of the bonds. You can also edit the Description of the forcefield to annotate it with references, updates, and so on.

You can change the name of the forcefield document so that it is not specific to a particular structure. As these are generated from set1 in the Groot and Rabone paper, you can indicate that in the name.

Rename the forcefield document **GrootRaboneSet1.off**.

When you change the name of the forcefield, this is updated on the Energy tab of the Mesocite Calculation dialog.

Select **Modules | Mesocite | Calculation** to open the Mesocite Calculation dialog and select the **Energy** tab.

You should see that the Forcefield is set to **\GrootRaboneSet1**. As DPD uses very short soft interactions, you can also decrease your calculation time by changing the van der Waals nonbond cutoff distance. Again, you should set this to the length scale that you used earlier. If you leave this at the default value, the calculation time will increase but without benefit.

Make **W70_L50_S50.xsd** the active document.

Click the **More...** button for the **Summation method** section to open the Mesocite Non-Bond Options dialog. Set the **Cutoff distance** to **6.46** and the **Spline width** to **0**. Close the dialog.

Note: It is important that you have the right 3D periodic structure in focus when you change the cutoff distance, since Mesocite has separate settings for periodic and nonperiodic structures.

Before starting the DPD calculation, you should optimize the structure.

Select the **Setup** tab on the **Mesocite Calculation** dialog and change the **Task to Geometry Optimization**. Click the **Run** button.

Note: You should always pre-optimize structures in this way. Although you may not obtain a perfectly optimized structure, the geometry optimization will remove discrepancies between the structure and the forcefield. In particular, the Mesostructure Builder has to estimate an initial connector length, and this may not be a good match for the spring parameters defined by the forcefield.

When the calculation is complete, you should see that the energy has dropped significantly indicating an improvement in the initial geometry.

Repeat the Geometry Optimization calculation on the other three structures.

When all the calculations are complete, tidy up the project.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To perform a production run

Now that you have performed some initial geometry optimization, you can run the DPD dynamics calculation and analyze the mean-squared displacement (MSD) of the water beads.

Ensure that the optimized **W70_L50_S50.xsd** is the active document.

On the **Mesocite Calculation** dialog, change the **Task to DPD** and click the **More...** button.

You will run 50,000 steps of DPD dynamics with a frame output every 2000 steps.

On the Mesocite DPD dialog change the **Number of steps** to **50000** and the **Frame output every** to **2000** steps. Close the dialog.

Note: Although you can change the temperature in Mesocite DPD, the repulsion matrix used by Groot and Rabone was parameterized for room temperature. In general, changing the temperature will in principle also require the repulsion matrix to be changed.

You are now ready to run the calculation.

With the optimized structure in focus click the **Run** button on the **Mesocite Calculation** dialog.

This calculation is quite long and will take some time to complete.

Repeat the DPD calculation on the other three optimized structures.

When all the calculations are complete, you can move onto the next step to perform the MSD analysis and compare the effect of adding surfactant to the lipid membrane on the diffusion of water.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

5. To analyze the results

The first part of the analysis is a visual inspection of the results. This will be easier if you change the visibility of the water beads. As you need them later in the analysis, you can create a set of the water beads.

Change focus to one of the trajectories. Hold down **ALT** and double-click on one of the water beads. Select **Edit | Edit Sets** from the menu bar to open the Edit Sets dialog. Click the **New...** button to open the Define New Set dialog.

Enter the name **water** and uncheck the **Show set** checkbox. Click the **OK** button.

Repeat this for all the trajectories and close the dialog.

You can now access the set of water beads in the analysis without having them visible.

Right-click in the 3D atomistic document and select **Display Style** to open the Display Style dialog. On the **Bead** tab, change the **Display style** to **None**.

Repeat this for all the trajectories and close the dialog.

Apart from a visual inspection, you can also view the concentration profiles of the water molecules in the x-direction. You can use this to identify holes in the layer.

Select **Modules | Mesocite | Analysis** to open the Mesocite Analysis dialog. Select **Concentration profile**.

You can specify the frame range, specific beads, and the direction. If you don't choose a direction, you will automatically get the profiles in the X, Y, and Z axis. You will examine the concentration profile in the x-direction for the water beads from frame 6 to the end of the trajectory.

Click the **Trajectory ...** button to open the **Trajectory Specification** dialog. Enter **6-END** and close the dialog. Select **water** from the **Sets** dropdown list and check the **Specified direction** checkbox. Click the **Analyze** button.

Repeat this for all trajectories, resetting the **Trajectory Specification** to **6-END** for each.

For each trajectory a study table and a chart is generated, containing the raw concentration data and a plot of concentration as a function of distance respectively.

You should see that as you increase the percentage of surfactant, the lipid bilayer becomes less stable. This results in the water beads moving through the bilayer. For the 100% lipid system, there are no holes in the bilayer and the water cannot penetrate from one side to the other. However, at 100% surfactant, the relative concentration of the water beads is high where the layer should be - indicating there are holes in the layer.

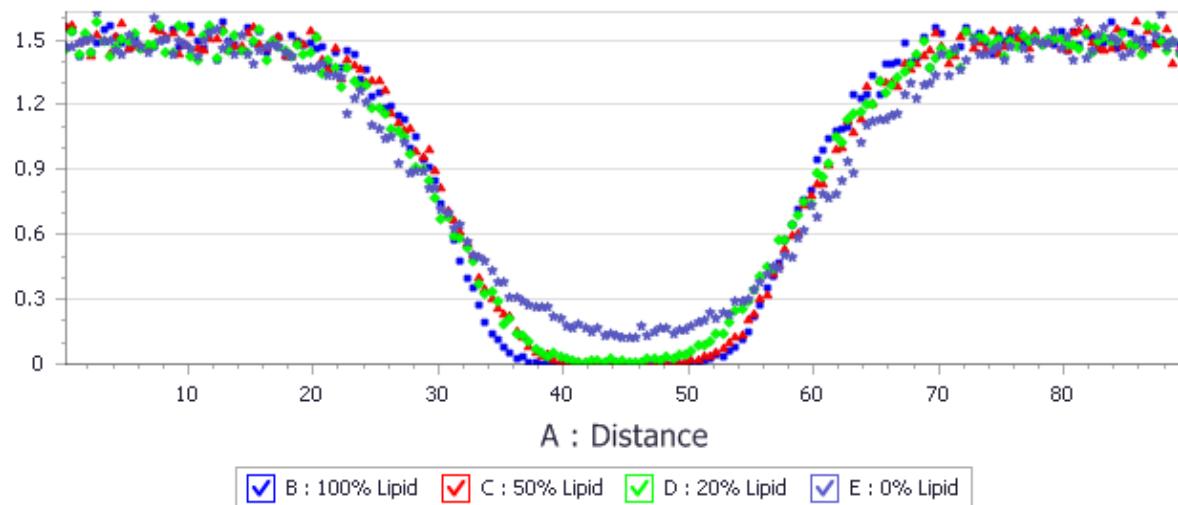


Chart containing the overlaid concentration profiles

Note: You can generate the above chart by copying and pasting data from the generated study tables into a new study table and using the Plot Graph functionality.

You can look at the mean-squared displacement of the water beads. You can calculate the overall mean square displacement and anisotropic components. You want to compare the MSD of the water beads in the XX direction.

Select **Modules | Mesocite | Analysis** and select **Mean square displacement**. Select **water** from the **Sets** dropdown list and check the **Include anisotropic components** checkbox. Click the **Analyze** button.

Repeat this for all trajectories.

The slope of the chart indicates the speed of the diffusion of the water beads with a steeper slope meaning fast diffusion. Examine the xx component of the diffusivity.

Right-click on the project root and select **New | Study Table Document** from the shortcut menu. Rename the new document **MSD_XX_comparison.std**.

In the **W70_L100 Mesocite MSD.std** study table select the **xx component** tab and select both columns. Click the **Copy** button  . In **MSD_XX_comparison.std** select the first two columns and click the **Paste** button .

Right-click in the **MSD** column header and select **Properties** from the shortcut menu to open the Column Properties dialog. Amend the **Description** to **100% lipid**.

The xx components of the MSD for the other trajectories can be added to this.

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For **W70_L50_S50 Mesocite MSD.std** choose the **xx component** tab and select and **Copy** only column **B**. Select column **C** in **MSD_XX_comparison.std** and **paste** the data, rename the column **50% lipid**.

Repeat this for **W70_L20_S80 Mesocite MSD.std** and **W70_S100 Mesocite MSD.std**, pasting into columns **D** and **E** of the new study table and amending the column names accordingly.

Now the columns in the comparison study table can be used to plot the XX MSD components for each combination of lipid, water, and surfactant.

Select all the columns in **MSD_XX_comparison.std** and click the **Quick Plot** button .

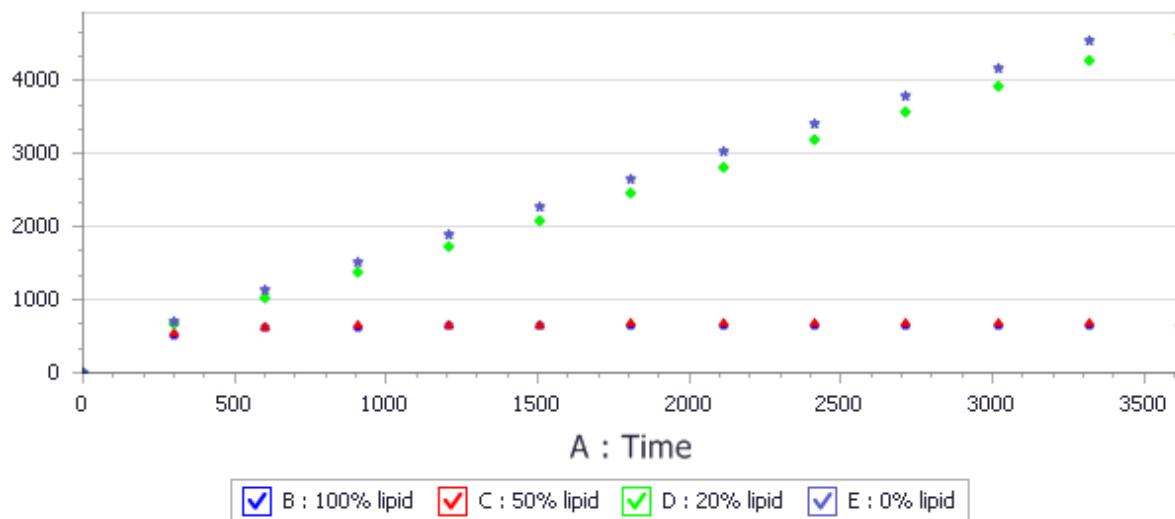


Chart containing the overlaid xx components of the diffusivity of the water beads

Again, as you increase the percentage of surfactant, the diffusivity increases. In the original paper, the membrane started to break down around 80% lipid content. The exact result that you get may vary from that above because the simulation runs are short. If you run the calculation for longer, the diffusivity will tend to increase as the bilayer absorbs water.

This is the end of the tutorial.

References

R.D. Groot and K.L. Rabone, "Mesoscopic Simulation of Cell Membrane Damage, Morphology Change, and Rupture by Nonionic Surfactants", *Biophysical Journal*, 2001, **81**, 725-736.

R.D. Groot and P.B. Warren, "Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation", *J. Chem. Phys.*, 1997, **111**, 107.

Effect of shearing on an oil droplet

Purpose: Demonstrates the use of shearing in DPD and the effect on morphology of an oil droplet in water

Modules: Materials Visualizer, Mesocite

Time:  

Prerequisites: Building bulk mesostructures Visualizer Tutorial

Background

Production of new materials often involves the use of processing conditions to affect the properties of the final product. A dispersion of oil in water forms a droplet with a distribution of sizes which can be controlled by shearing the system. DPD provides the capability to simulate shearing at a mesoscale level and visualize the effect of shear on a system.

This tutorial is inspired by some early work done on DPD, studying shearing effects on oil droplets, carried out by [Clark et al.](#) and [Jones et al.](#)

Introduction

In this tutorial, you will use Mesocite to run a DPD shearing calculation on an oil-water droplet. You will specify the initial conditions using the mesostructure builder, run an equilibration DPD calculation, and then perform a shear calculation and visualize the results.

This tutorial covers:

- [Getting started](#)
- [To create the input structure](#)
- [To equilibrate the structures](#)
- [To perform a shearing run](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DPD_shear** as the project name, click the **OK** button.

The new project is created with *DPD_shear* listed in the Project Explorer.

2. To create the input structures

The first step is to build mesomolecule models of water and oil. When working with DPD, you can either spend time accurately parameterizing the system by using molecular dynamics or other methods, use data from published simulations, or use your chemical intuition to derive the parameters and tune the parameters to a known system. As there have been several studies of oil/water systems, you will use parameters from a previous publication.

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The inputs to the Mesocite DPD simulation require the parameterization of the contents of a bead. For this simulation, you will use the default parameters of bead mass of 100 amu. As a water molecule has a mass of 18 amu, this means that one bead represents about 5 molecules of water. As the mass of a CH₂ oil group is 14 amu, each oil bead represents a chain of approximately 7 CH₂ groups.

Select **Build | Build Mesostructure | Bead Types** from the menu bar to open the Bead Types dialog.

Define the following new bead types: **Oil** and **Water**, close the Bead Types dialog.

Note: The bead radius is only used for visualization and has no effect on the calculation. However, the bead mass is used in the DPD simulation.

Note: Whilst you could have beads with different masses in the DPD calculation, there has been little validation on the effect of this. Therefore, you are advised to use the same mass for all beads.

Now you have defined the bead types, you can create the structures.

Select **Build | Build Mesostructure | Mesomolecule** from the menu bar to open the Build Mesomolecule dialog. Build a mesomolecule of **1** unit of **Water** and rename the new document to **water.xsd**.

Build a mesomolecule of **1** unit of **Oil** and rename the document **oil.xsd**. Close the **Build Mesomolecule** dialog.

Before continuing, you can set the forcefield type for the beads. The forcefield type is preserved when mesostructures are built, so defining this now will save time later. You can use the Properties Explorer to assign a forcefield type by selecting the bead and editing the ForcefieldType property. Alternatively, you can use the Type button which will set the forcefield type to the same value as the BeadTypeName. This is accessed from the Forcefield Manager for Mesocite.

Select **Modules | Mesocite | Forcefield Manager** from the menu bar to open the Mesocite Forcefield Manager. Click the **DPD...** button.

This opens the Create DPD Forcefield which enables you to create DPD specific forcefields by entering the repulsive interaction parameter in either physical or reduced units. It also enables you to assign forcefield types.

With **oil.xsd** in focus, click the **Type** button. Change focus to **water.xsd** and click the **Type** button.

Close the **Mesocite Forcefield Manager** dialog.

You can ignore the Repulsions that are displayed in the Create DPD Forcefield dialog at the moment. You will set these correctly in the next section.

Now you have built the components, you need to construct the cell containing these mesomolecules. You will build a mesostructure template which contains an oil droplet. In this example, you will use default values to build a box of 100 × 100 × 100 Å and place a droplet former of radius 20 Å.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. In the **Filler** text box, enter **water** and click the **Build** button.

This creates a new mesoscale document named **Mesostructure_Template.msd**. You can either start this calculation from random starting conditions or you can define a droplet former. In this case, you will define a droplet former.

On the **Build Mesostructure Template** dialog, change the **Former type** to **Droplet**. Set the **Radius** to **20.0** and enter **oil** in the **Filler** text box. Click the **Add** button and close the dialog.

Now that you have built the template, you need to fill it with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the **Build Mesostructure** dialog. Make sure that **Mesostructure Template.msd** is in focus.

You need to specify the components that you want to use as the fillers - you will fill the 'water' filler with water and 'oil' filler with oil

Click in the **Mesoscale Molecule** column for the **water** filler and select **water.xsd**. Repeat this for the **oil** filler, selecting **oil.xsd**.

You can also control the density, the conformations of the mesoscale molecules, and the surface packing capabilities. In this example, you will leave these at their default values.

Click the **Build** button and close the dialog. Rename the new document **Water_Oil_20rad.xsd**.

You have now built the initial structure. The next stage is to equilibrate the structure.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

3. To equilibrate the structures

The first step before equilibration is to create a DPD forcefield. You can choose whether to set up the DPD calculation in Physical or Reduced units. As most papers still refer to reduced units for the repulsive interactions, you will use reduced units.

Open the **Mesocite Forcefield Manager** dialog and click the **DPD...** button.

There are a variety of papers which quote interaction parameters ranging from 30 to 80 between the oil and water beads. As it is known that oil and water are very repulsive, you will use a value of 50.

Open **Water_Oil_20rad.xsd**. On the Create DPD Forcefield dialog, change the **Units** to **Reduced**. Set the value for the **Oil-Water** cell in the **Repulsions** grid to **50**.

Click the **Create** button and close the **Mesocite Forcefield Manager** dialog.

A forcefield document named **Water_Oil_20rad.off** is created. This will be used in the DPD calculation and is set as the current forcefield in the Mesocite Calculation dialog.

Note: If you are modifying the bead parameters such as the bead mass from their defaults, you should also set the Length and Mass scale before creating the forcefield. However, as you are using default parameters you do not need to change any of the settings.

Usually when dealing with output from the Mesostructure Builder, you are advised to perform a short geometry optimization before continuing with the DPD run. This is performed to equilibrate bond lengths in the system but, as you have no bonds between the particles, you can just run a DPD calculation.

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Select **Modules | Mesocite | Calculation** from the menu bar. Select **DPD** from the **Task** dropdown list and click the **More...** button to open the Mesocite DPD dialog.

You should increase the number of steps so that you can see how stable the droplet is.

On the Mesocite DPD dialog change the **Number of steps** to **10000** and the **Frame output every** to **1000** steps. Close the **Mesocite DPD** dialog.

As the potential used in DPD is a soft harmonic potential which has finite range, you can also decrease your calculation time by changing the van der Waals non-bond cutoff distance. Again, you should set this to the value of the Length scale. If you leave this at the default value, the calculation time will increase but without benefit.

Make **Water_Oil_20rad.xsd** the active document.

Select the **Energy** tab and click the **More...** button for the **Summation method** section to open the Mesocite Non-Bond Options dialog.

Set the **Cutoff distance** to **8.0 Å** and the **Spline width** to **0 Å**. Close the dialog.

On the Energy tab, you should also see that the Forcefield is set to \Water_Oil_20rad.

You are now ready to perform a DPD equilibration run.

On the Mesocite Calculation dialog, click the **Run** button and close the dialog.

The calculation will take several minutes to complete. When the calculation is complete, you can animate the trajectory to see how the particles are moving in the box. You should set the Lattice Display Style to In-Cell to keep the beads in the cell.

Change focus to **Water_Oil_20rad.xtd**. Right-click and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Lattice** tab change the **Style** to **In-Cell**.

Hold down **ALT** and **double-click** on one of the **Water** beads. On the **Bead** tab of the Display Style dialog select **None**. Close the dialog.

You should also set the animation options for the trajectory so that the atom positions are updated and the animation stops at the last frame.

Click the **Animation Mode** button and select **Stop At End**. Click the **Animation Mode** button and select **Options** to open the Animation Options dialog.

Check the **Recalculate atom visibility every frame** checkbox and close the dialog. Click the **Play** button.

You should see the gray oil droplet beads move around in the solvent. You can also use an isosurface to visualize the bead positions.

Select **Modules | Mesocite | Analysis** from the menu bar to open the Mesocite Analysis dialog. Select the **Density field** option.

There are several options for creating density fields, including defining density fields for a set of beads, and the field resolution. However, you will use the default values.

Hold down **ALT** and **double-click** one of the **Oil** beads.

Click the **Analyze** button and close the dialog.

A new trajectory named **Water_Oil_20rad Mesocite Density Field.xtd** is created. This contains one density field and its respective isosurface. You can visualize the density field by animating the trajectory. Before animating, you should change the display options so that the isosurface is rendered.

Right-click in **Water_Oil_20rad Mesocite Density Field.xtd** and select **Display Options** from the shortcut menu. Uncheck the **Fast render on move** checkbox and close the dialog. On the Animation toolbar, click the **Play** button.

The animation should play and you should see the oil droplet moving around the box.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To perform a shearing run

The equilibration run demonstrated that the initial interaction parameters gave a reasonable interaction between the oil and solvent as the oil remained in a droplet through the simulation. Now you will use the shearing functionality to put a shear force on the structure. You will restart the calculation but not append the trajectory.

Ensure that the trajectory **Water_Oil_20rad.xtd** is the active document.

Open the **Mesocite Calculation** dialog and check the **Restart** checkbox on the **Setup** tab.

You will run another 10,000 steps but this time with shearing switched on.

Click the **More...** button to open the Mesocite DPD dialog. Check the **Enable shearing** checkbox and set the **Shear rate** to **0.1** reduced units. Close the dialog.

You have limited control over the direction of the shearing. For this calculation, it is not so important as you are just shearing a droplet so you can leave it at the default value.

You are now ready to run the calculation.

Click the **Run** button and click the **Yes** button on the warning dialog. Close the **Mesocite Calculation** dialog.

The calculation will take several minutes to complete. When completed, you can perform the same visual analysis as you did previously.

Hold down **ALT** and **double-click** on one of the **Oil** beads.

In the **Mesocite Analysis** dialog, check the **Exclude analyzed objects in output** checkbox and click the **Analyze** button. Close the dialog.

You should see that, under the initial shear, the oil droplet stretches but does not break. You could repeat the calculation with a higher shear rate, for example 0.30 using Reduced units, and you should see the oil droplet breaks.

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Note: The shearing in DPD physically shears the cell by deforming and re-setting the cell parameters. If you choose to write out the frame more frequently, you will see the cell deforming. In this example, if you write out the frame every 250 steps, you will see a deformation.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Clark, A. T.; Lal, M.; Ruddock, J. N.; Warren, P. B.; "Mesoscopic Simulation of Drops in Gravitational and Shear Fields." *Langmuir*, **16**, 6342-6350, (2000)

Jones, J. L.; Lal, M.; Ruddock, J. N.; Spenley, N. A.; "Dynamics of a drop at a liquid/solid interface in simple shear fields : A mesoscopic simulation study.", *Faraday Discussions*, **112**, 129-142 (1999).

Calculating input parameters for a DPD simulation

Purpose: Illustrates how to obtain input parameters for a DPD simulation of a real system.

Modules: Materials Visualizer, Mesocite

Time:  

Prerequisites: Building mesoscale molecules, Building bulk mesostructures Visualizer Tutorials

Background

One of the strengths of the DPD task in Mesocite is that hydrodynamic simulations can be performed on systems in which the chemical nature of the species is included. The chemistry of the system is imparted by the molecular architecture and the bead-bead repulsions. This tutorial explores the steps to calculate the bead-bead repulsions, and run a Mesocite DPD calculation in Materials Studio.

Note: This tutorial covers calculating DPD input parameters using solubility parameters. There are alternative methods available to obtain DPD input parameters which are not covered.

Introduction

The goal of this tutorial is to determine DPD input parameters for a system containing a mixture of SEBS and polypropylene (PP). SEBS is a triblock copolymer with polystyrene extremes and a copolymer of ethylene and butylene in the interior. The blocks are incompatible and phase separation is known to occur. The phase diagram of SEBS in polypropylene shows a variety of phases as a function of composition. You will consider the situation where the length of the individual blocks in SEBS is variable, and polypropylene has an average molecular weight of 20 000 amu.

This tutorial covers:

- [Getting started](#)
- [To determine the number of beads in each chain](#)
- [To calculate Flory-Huggins parameters for binary mixtures](#)
- [To convert Flory-Huggins parameters into DPD inputs](#)
- [Creating the input structure](#)
- [To simulate SEBS in PP matrix](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DPD_input** as the project name, click the **OK** button.

The new project is created with *DPD_input* listed in the Project Explorer.

2. To determine the number of beads in each chain

The number of beads in each chain depends on the model resolution. In principle the resolution can be chosen independent of the physical system being studied, and the polymer model be adjusted to match the chosen resolution. Here you will choose the resolution such that the polymers are reasonably described by a simple bead-spring model.

The mean-square end-to-end distance (MSD) of a bead-spring model scales linearly with the number of beads. The MSD of a real bulk polymer also scales linearly with the number of monomers, but only after a certain number of monomers, due to correlation. This number is given by the characteristic ratio, C_∞ . The characteristic ratio is a measure of the stiffness of a chain and can be obtained experimentally.

Tip: The characteristic ratio (at 298 K) can be calculated for many polymers using the Synthia module in Materials Studio.

The characteristic ratio can be used to determine the number of beads in each chain: If one bead represents, on average, C_∞ monomers, the MSD scaling of the bead-spring model matches that of the real chain. With M_m the mass of the monomer and M_p the mass of the real chain, the number of beads in the polymer is thus given by:

$$n_{DPD} = \frac{M_p}{M_m C_\infty}$$

The characteristic ratio of polypropylene is 6.7 ([Brandrup and Immergut, 1989](#)). The mass of a propylene monomer is 42 amu. Hence the mass of one propylene bead is $6.7 \times 42 = 281.4$ amu, and the polypropylene chain in this tutorial contains $20\,000 / 281.4 \approx 71$ beads.

Note: The characteristic ratio is the minimum number of monomers per bead to ensure that the MSD of the bead-spring model scales linearly. You could increase this further, for example to model very long chains. By increasing the bead mass, less beads are required to model a chain of a given length. Typically the bead mass is chosen such that the chain length in DPD does not exceed 100 beads.

You could derive bead masses from the characteristic ratios for the other species in the same way, but it is more common in DPD to fix the masses of all beads to be the same. In this tutorial you will fix the bead mass to be 281.4 amu, and consequently one bead represents 6.7 monomers of propylene, or $42/104 \times 6.7 = 2.7$ monomers of styrene.

Note: To accurately model the stiffness of polystyrene at this resolution would require angular interactions, which are ignored in this tutorial.

The choice of chain lengths in SEBS is quite arbitrary. In this tutorial you will use 10 beads in the styrene blocks and 20 in the central ethylene/butylene segment. Hence an SEBS chain has a molecular weight of $(10+20+10) \times 281.4 \approx 11\,000$ amu, about half that of PP.

3. To calculate Flory-Huggins parameters for binary mixtures

To parameterize a DPD bead-spring model you need to set up the interactions between all different species. You can identify three chemically distinct chemical units in this simulation: polystyrene (PS), polypropylene (PP), and the random copolymer of ethylene and butylene that makes up the central portion of the SEBS molecule (EB). Therefore you must obtain interaction parameters for each pair of these: PS-PP, PS-EB, and PP-EB.

The DPD interaction parameters are usually obtained in two steps: first the Flory-Huggins interaction parameters are determined, which are then converted to DPD parameters. There are various ways to obtain Flory-Huggins interaction parameters. Here you will calculate them from the solubility parameters δ_i :

$$\chi_{ij} = \frac{\nu}{RT} (\delta_i - \delta_j)^2$$

Where:

R is the gas constant

T the absolute temperature

ν is the volume per mole beads

The solubility parameter can be measured experimentally and are given in the table below:

Species	Solubility parameter (J/cm ³) ^{1/2}
PS	19.52
PP	16.06
EB	16.49

Tip: Solubility parameters can be calculated for many monomers using the Synthia module in Materials Studio.

The molar volume of polypropylene at 298 K is 49.0 cm³ per mole monomers. Since one bead represents 6.7 propylene monomers, the reference volume ν is $6.7 \times 49.0 = 328.3 \text{ cm}^3/\text{mol}$.

Note: Since the reference volume scales with the number of monomers per bead, the product of chain length and interaction parameter, χN , is invariant under coarse-graining.

Using the solubility parameters given above, and $\nu/RT = 0.133 \text{ cm}^3/\text{J}$, the following Flory-Huggins parameters are obtained:

Species	PS	PP	EB
PS	0	1.59	1.22
PP	1.59	0	0.02
EB	1.22	0.02	0

4. To convert Flory-Huggins parameters into DPD inputs

Groot and Warren ([1997](#)) performed a series of DPD calculations on binary mixtures with a variety of repulsion parameters, a . They then computed Flory-Huggins parameters and found a linear relationship between χ and a . This relationship can be used to obtain input parameters for a pair of species with a known χ value.

The relationships that Groot and Warren obtained are for densities, in reduced units, of 3 and 5. As lower densities are more efficient you will use $\rho = 3$, for which the relationship is (in reduced units):

$$a_{ij}(\rho = 3) = 25 + 3.50\chi_{ij}$$

The first term is the self repulsion of beads. This value was chosen by Groot and Warren such that a pure DPD fluid has a compressibility similar to that of liquid water.

Using the above expression the following repulsion parameters are obtained for the DPD calculation:

Species	PS	PP	EB
PS	25.0	30.6	29.3
PP	30.6	25.0	25.1
EB	29.3	25.1	25.0

To ensure that the physical density corresponds to the reduced density of 3, for which the correlation was derived, the length scale must be set. As derived above, the bead volume is 328.3 cm^3 per mole beads, or 545 \AA^3 for one bead. Hence 3 beads occupy a volume of $3 \times 545 = 1635 \text{ \AA}^3$, corresponding to a cube with edge $1635^{1/3} = 11.8 \text{ \AA}$. This value must be chosen as length scale to match both the required physical and reduced density. Half the length scale (5.9 \AA) may be used as the bead radius for display purposes.

Note: Both physical and reduced units can be used as input to Mesocite. When using reduced units, Mesocite will automatically convert the values to physical units using the mass, length and energy scales specified.

5. To create the input structure

The first step is to define the bead types with which to build mesomolecule models of SEBS and polypropylene molecules.

Select **Build | Build Mesostructure | Bead Types** from the menu bar to open the Bead Types dialog. Click the **Defaults...** button to open the Bead Type Defaults dialog. Set the **Mass** to **281.4** and the **Radius** to **5.9**. Close the Bead Type Defaults dialog.

Define the following new bead types: **PP**, **PS** and **EB** and close the Bead Types dialog.

This defines three bead types, PP, PS, and EB, with the same mass and radius.

Note: The bead radius is used in the mesomolecule builder to determine the bond length. Otherwise it is used only for visualization and has no effect on the calculation. The bead mass, on the other hand, is used in the DPD simulation.

Now you have defined the bead types, you can create the mesomolecule structures.

Select **Build | Build Mesostructure | Mesomolecule** from the menu bar to open the Build Mesomolecule dialog. Build a mesomolecule of **71** units of **PP** and rename the new document to **PP.xsd**.

Build another mesomolecule containing **10** units of **PS**, **20** units of **EB**, and another **10** units of **PS**. Rename the document **SEBS.xsd**.

Close the dialog.

Tip: Mesostructure tools are also accessible from the Mesostructure toolbar.

Now you have built the components, you need to construct the cell containing these mesomolecules. The construction is a two-step process: first you create a template containing one or more formers; then you fill the formers with the molecules, or a mixture thereof. In this case you use a simple template containing just one system former of size $100 \times 100 \times 100 \text{ \AA}$.

Select **Build | Build Mesostructure | Mesostructure Template** from the menu bar to open the Build Mesostructure Template dialog. Ensure all the **Extent (X Y Z)** values are set to **100.0**. In the **Filler** text box, enter **SEBS_PP** and click the **Build** button. Close the template dialog.

A new template document is created **Mesostructure_Template.msd**, containing a system former displayed as a blue box. The next task is to fill the box with mesomolecules.

Select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog. Make sure that the template is in focus.

The dialog shows the **SEBS_PP** filler you defined earlier, and you can select the mesomolecules to be associated with this filler. In this case you will use a mixture of SEBS and polypropylene with the same mass of both components.

Click in the **Mesoscale Molecule** column for the **SEBS_PP** filler, selecting **PP.xsd** and **SEBS.xsd**.

Ensure that the **Relative Amount** is set to **1.0** for both components.

Note: The relative amount for a given type of molecule refers to the *mass* contained in molecules of this type, not to the *number* of those molecules in the system. Since in this case PP is about twice the mass of SEBS, there will be about half as many PP molecules than SEBS molecules in the structure.

Before building the mixture of polystyrene and SEBS, you need to specify the target density, either in reduced units (with the appropriate reduced unit scales set), or directly in physical units. Here you will set the density directly in g/cm³. The molecular weight of PP is 42 amu and molar volume is 49.0 cm³/mol. Hence the density is 42/49 = 0.857 g/cm³.

On the Components tab set the **Density** to **0.857 g/cm³**. Click the **Build** button and close the dialog. Rename the document **SEBS_PP.xsd**.

Note: Alternatively you can set the density to 3 in reduced units, after specifying the Length scale (11.78 Å) and mass scale (281.4 amu) on the Reduced Units dialog.

You have now built the initial structure. The next stage is to simulate SEBS/PP matrix.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

6. To simulate SEBS in PP matrix

Now that you have determined all of the input parameters, you can perform a simulation.

Open **SEBS_PP.xsd**. Select **Modules | Mesocite | Forcefield Manager** from the menu bar and click the **DPD...** button to open the Create DPD Forcefield dialog.

As no force field types are assigned to the beads the Repulsions matrix is empty.

Click **Type** to assign forcefield types to beads in the active document.

You should see a matrix of forcefield types corresponding to those in the document. The values are currently displayed in physical units (based on kcal/mol and Å) whereas in DPD work, including that of Groot and Warren, has usually been carried out using reduced units. Mesocite DPD allows you to set up the calculation using either physical or reduced units (in which case the conversion to physical units will be performed automatically). You will use reduced units here.

Mesocite: Calculating input parameters for a DPD simulation

Tip: When constructing multiple structures (for example, different concentrations of the polymers) you can avoid retying the beads by assigning force field types directly on the input molecules before building the structures.

Change the **Units** to **Reduced** and click the **More...** button to open the Mesocite DPD Units dialog.

You need to enter the Length and Mass scales to be used for the unit conversion, as discussed earlier.

Change the **Length scale** to **11.8** and the **Mass scale** to **281.4**. Close the dialog.

You now need to enter the forcefield parameters for this simulation.

Species	EB	PP	PS
EB	25.0	25.1	29.3
PP	25.1	25.0	30.6
PS	29.3	30.6	25.0

On the **Create DPD Forcefield** dialog edit the matrix and set the **Repulsions** to the values shown in the table above. Click the **Create** button and close the dialogs.

When you click the Create button, a new Forcefield document is created and listed as **SEBS_PP.off** in the Project Explorer. The values in the forcefield document are written in physical units and the forcefield is automatically set on the Energy tab of the Mesocite Calculation dialog.

Tip: As the interactions are stored in a forcefield document, you can add other interactions to the calculation such as bond angle terms to control rigidity of the bonds. You can also edit the Description of the forcefield to annotate it with references, updates, and so on.

You can change the name of the forcefield document so that it is not specific to a particular structure. When you change the name of the forcefield, this is updated on the Energy tab of the Mesocite Calculation dialog.

Click the **Mesocite** button  on the **Modules** toolbar, then select **Calculation** from the dropdown list and select the **Energy** tab.

You should see the custom forcefield **\SEBS_PP** selected in the Forcefield chooser.

As DPD uses very short soft interactions, you can decrease your calculation time by changing the van der Waals nonbond cutoff distance. You should set this to the length scale that you used earlier. If you leave this at the default value, the calculation time will increase but without benefit since the interaction beyond the length scale is zero.

Make **SEBS_PP.xsd** the active document.

Click the **More...** button for the **Summation method** section to open the Mesocite Non-Bond Options dialog. Set the **Cutoff distance** to **11.8** and the **Spline width** to **0**. Close the dialog.

Note: It is important that you have the right 3D periodic structure in focus when you change the cutoff distance, since Mesocite has separate settings for periodic and nonperiodic structures.

Finally you can run the DPD simulation. You can leave all simulation parameters at their default value, but to save time you will reduce the length of the run.

Select the **Setup** tab and set the **Task** to **DPD**. Click the **More...** button next to the task to open the Mesocite DPD dialog. Set the **Number of Steps** to **1000** and change **Frame output every** to **100** steps. Close the Mesocite DPD dialog.

Click the **Run** button and close the Mesocite Calculation dialog.

Since this tutorial is concerned with the parameterization of the DPD simulation, it is not necessary to analyze the output of the job. If you do choose to analyze the results, you should begin to see the two polymers separating. However, a much longer calculation would be required to see the full effect. By changing the composition of the block copolymer different phases may be obtained.

Tip: You can restart calculations by checking the **Restart** checkbox on the **Setup** tab.

Select **File | Save Project** from the menu bar followed by **Window | Close All**.

This is the end of the tutorial.

References

- Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd Edition, John Wiley & Sons Inc: New York (1989).
Groot R. D.; Warren, P. B. "Dissipative Particle Dynamics: Bridging the gap between atomistic and mesoscopic simulation", *J. Chem. Phys.*, **107**, 4423-4435 (1997).

Generating a MS Martini 3 Forcefield and Bead Topology

Purpose: Demonstrates how to customize the MS Martini 3 Forcefield and use it to generate a bead topology file for molecules.

Modules: Materials Visualizer, Mesocite

Time: 

Prerequisites:

Background

Materials Studio includes a modified version of the Martini 3 forcefield (see, [Souza, 2021](#)), MS Martini 3. For a more detailed description of Martini forcefield versions and the new types and interactions in Martini 3 including the MS Martini 3 forcefield, see the MS Martini 3 section in the Forcefields in Mesocite theory topic in the Mesocite section of the Materials Studio online help.

The Martini 3 publication provides a group of forcefield types for non-bonded interactions, with each type corresponding to a group of atoms in the underlying atomic structure (see, [Souza, 2021](#)). In addition, it also gives parameters for valence interactions (bond stretch, angle bend, torsion) for some specific molecules.

You can create system-specific Martini 3 forcefield files using the Materials Studio scripts available in **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools** menu:

1. The **Create Bead Mapping** script generates the bead model corresponding to the input atomistic document using the assigned motion groups.
2. The **MS Martini 3 Forcefield Generator** script extracts the Martini 3 forcefield parameters for the non-bonded interactions as well as creating valence interactions for the mesoscale model.
3. The **MS Martini 3 Merge Forcefield Files** script merges two custom Martini 3 forcefield files and adds cross terms between the forcefield types in each file for the non-bonded interactions.
4. The **MS Martini 3 Coarse Grainer** script uses *mapping templates* to generate the bead model corresponding to the input atomistic document. You can add more details with custom mapping templates. For example, motion groups for bead mapping, and distance, angle, and torsion measurements for customization of forcefield parameters. In addition, this script creates the system-specific forcefield file containing the customized parameters including the valence interactions.

Introduction

In this tutorial, you build a mesoscale dilinoleylphosphatidylcholine (DLiPC, DLPC) lipid structure using the **Create Bead Mapping** script, and generate a reduced MS Martini 3 forcefield file for that molecule using the **MS Martini 3 Forcefield Generator** script. These scripts configure the bead model for use in Mesocite simulations and create a customized MS Martini 3 forcefield for the model. The forcefield file includes specialized valence interactions for the given molecules and structures. Using the **MS Martini 3 Merge Forcefield Files** script, you combine two custom Martini 3 forcefield files, one for the lipid and one for the water. Then you use the combined Martini 3 forcefield to perform Mesocite simulations of a bilayer lipid model with water.

This tutorial covers:

- [Getting started](#)
- [To select the server to run Materials Studio scripts](#)
- [Generating a bead-based configuration \(optional\)](#)
- [Preparing the bead-based configuration](#)
- [Generation of MS Martini 3 forcefield and topology file for DLPC](#)
- [Building the bilayer membrane with the DLPC lipid](#)
- [Simulation of the bilayer DLPC membrane](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Martini3-Bilayer** as the project name, click **OK**.

The new project is created with *Martini3-Bilayer* listed in the Project Explorer.

2. To select the server to run Materials Studio scripts

Before preparing the structures, select the server where you want to run the Materials Studio scripts.

Note: You cannot run Materials Studio scripts on a server whose gateway uses the secure authentication level.

The MS Martini 3 scripts at **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools** run on a Materials Studio server. The *Gateway location* for the scripts can be your local machine ([My Computer](#)) or an appropriate server and queue.

From the menu bar, select **Tools | Materials Studio Scripts | Script Job...**to open the Script Job Control dialog. Choose the **Gateway location** and the **Queue**, if appropriate. Close the dialog.

To generate output folders for the scripting jobs with shorter names, specify the format.

From the **Tools** menu, select **Options....** On the **Jobs** tab, change the **Job folder Format** to **%n %t** and click **OK**.

3. Generating a bead-based configuration (optional)

This step is optional. You can follow these steps to prepare the bead-based configuration starting from an all-atom DLPC configuration. Alternatively, to start directly from a bead-based DLPC model, continue from [Preparing the bead-based configuration](#).

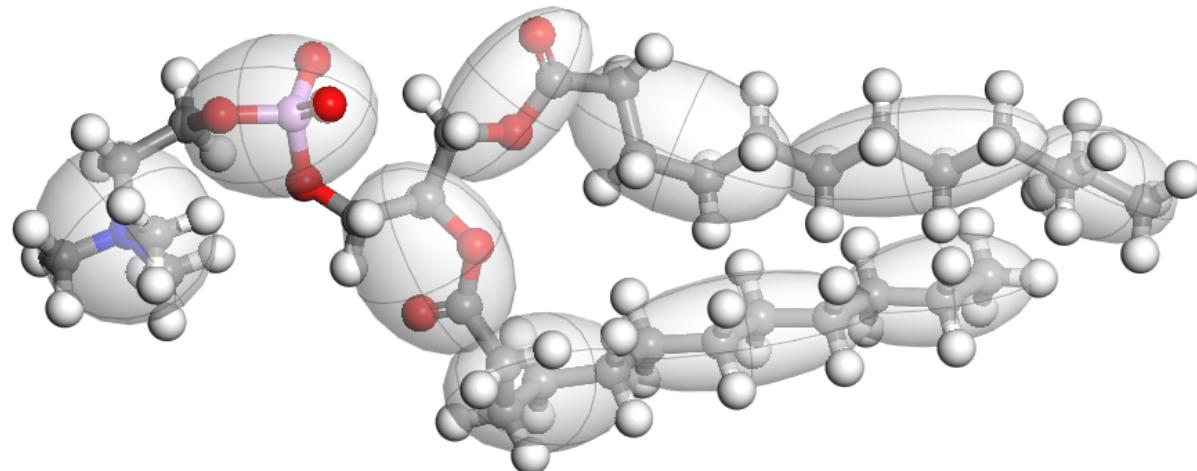
In the Project Explorer, right-click **Martini3-Bilayer** and select **New | Folder**. Change the new folder's name to **DLPC CG**.

With the new folder selected, right-click and choose **Import....** Open the **Examples\Scripting\Martini3 Tools** directory, select **DLPC.xsd**, and click **Open**.

This imports an all-atom structure of the DLPC lipid molecule, as in the image below. This model has some pre-created motion groups, each of which corresponds to a group of atoms to convert to a single bead.

Generating a MS Martini 3 Forcefield and Bead Topology

Tip: When you prepare your own structures, use the *Motion Groups* dialog to add motion groups to the structure.

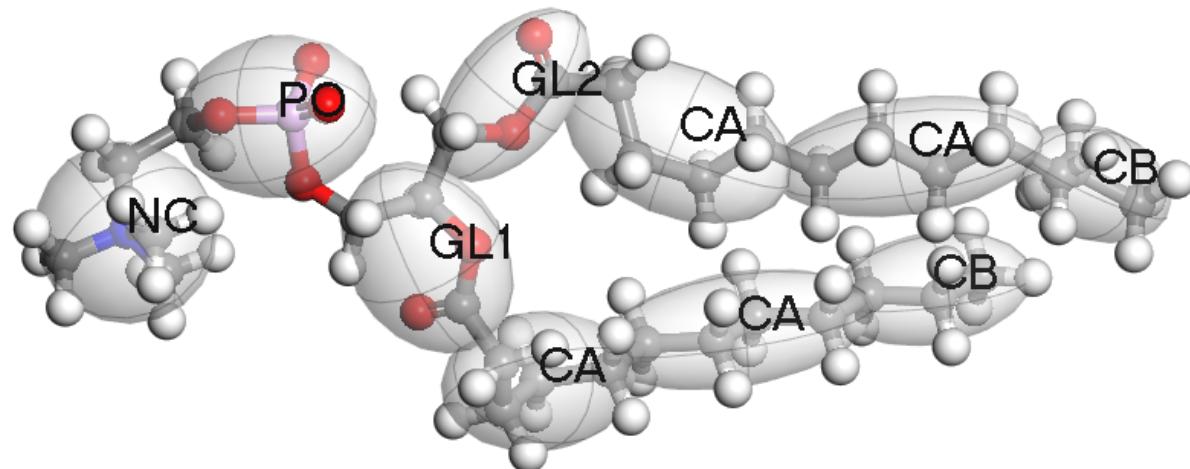


The **DLPC.xsd** file showing the DLPC molecule in ball and stick display style with motion groups defining each atom group.

Open the **Properties Explorer** and filter by **Motion Group**. Select each motion group in the active **DLPC.xsd** document and edit its **Name** property.

Left to right, the top chain motion group names are: **NC**, **PO**, **GL1**, **GL2**, **CA**, **CA**, **CB**.

Left to right, the bottom chain (connected to **GL1**) motion group names are: **CA**, **CA**, and **CB**.



The **DLPC.xsd** file showing the DLPC molecule in ball and stick display style with labels showing the names of motion groups.

With **DLPC.xsd** as the active document, select **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools | Create Bead Mapping** from the menu bar and run.

The script generates a **DLPC_CBM** folder containing:

- A copy of the input DLPC.xsd 3D Atomistic document
- A copy of the CreateBeadMapping.pl script
- CreateBeadMapping.pl.out - a text output file reporting the actions of the script
- DLPC-CG_Bead_Map.std - a study table including the mapping template for the molecule
- DLPC-CG.xsd - a bead-based configuration of DLPC molecule

Note: There is a difference between the DLPC-CG_Bead_Map.std output document and the DLPC-CG_Bead_Typing.std file that you can generate using the Coarse Grainer.

The DLPC-CG_Bead_Map.std study table generated by the Create_Bead_Mapping script includes one mapping template for each molecule or subunit in the input atomistic document. This mapping template is a model of the molecule or subunit containing motion groups. Each of these motion groups defines a group of atoms that map onto a bead. The script copies the motion groups to the mapping template along with the molecule. You can add additional details to the mapping templates, such as additional motion groups for bead mapping, or distance, angle, and torsion measurements to control forcefield valence parameters. Then you can use the study table as input for the **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools | MS Martini 3 Coarse Grainer** tool.

For more details on how to use the **MS Martini 3 Coarse Grainer** script, see the Polymer Coarse Graining with Martini 3 Tools and Mesocite tutorial.

4. Preparing the bead-based configuration

Create a new folder to store the bead-based configuration preparation structures.

In the Project Explorer, right-click **Martini3-Bilayer** and select **New | Folder**. Change the new folder name to **Martini3_DLPC**.

If you generated your own bead-based configuration in the last section, copy it to the new folder.

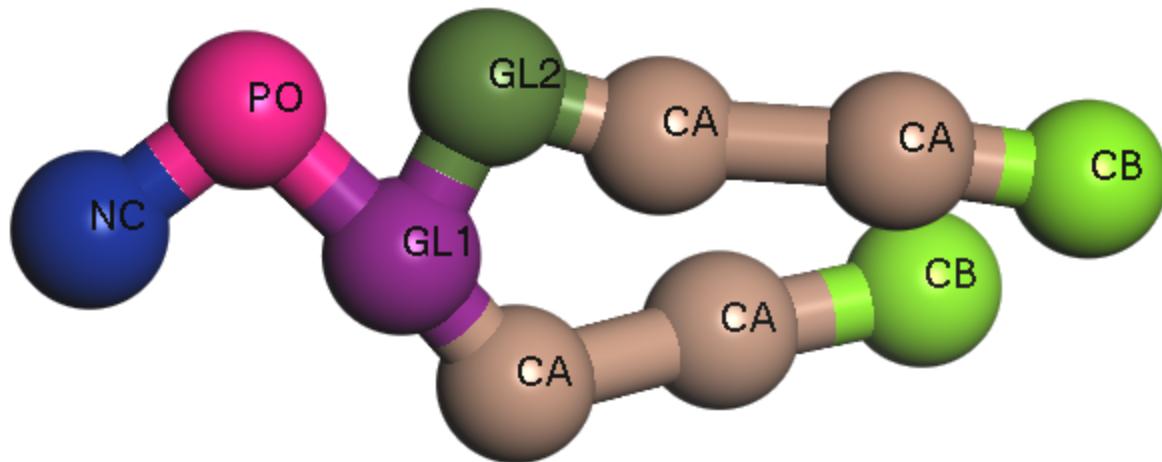
Copy the generated **DLPC-CG.xsd** file from the **DLPC CBM** folder to the new folder.

If you did not generate your own bead-based configuration, use the bead-based DLPC configuration in the Examples folder.

With the new folder selected, right-click and choose **Import....** Navigate to the **Examples\Scripting\Martini3 Tools** folder, select **DLPC-CG.xsd**, and click **Open**.

The beads of the imported DLPC-CG.xsd file have been given types. These are not Martini 3 forcefield types. The masses and radii have been given default values.

Martini 3 contains parameters for non-bonded interactions, and also for valence interactions for certain molecules, such as phospholipids, proteins, small molecules, and ionic molecules. To generate a MS Martini 3 forcefield for the DLPC molecule including valence interactions, you must provide a Martini 3 forcefield type for each bead.



The `DLPC-CG.xsd` file showing the DLPC molecule with ball and stick display style.

Note: This image shows the names of the beads and repeat units. You can add these to your structure using the *Label* dialog.

Before you assign forcefield types to the beads in the DLPC lipid structure, label the beads so that you can identify them by their type.

Right-click in the 3D Atomistic document and select **Label**. From the **Object type** list, select **Bead**, and from the **Properties**, choose **BeadTypeName**. Click **Apply**.

The table below provides a suitable Martini 3 forcefield type and electric charge for each bead type. (See [Souza, 2021](#) for more information about the Martini 3 forcefield type system.)

Bead Type	Martini 3 Forcefield Type	Charge
NC	Q1	1.0
PO	Q5	-1.0
GL1	SN4a	0.0
GL2	N4a	0.0
CA	C1	0.0
CB	C1	0.0

Next, you need to assign the Martini 3 forcefield types to each bead.

Open the **Properties Explorer** and filter by **Bead**. Select each bead in the document and enter its **ForcefieldType** according to the *Martini 3 Forcefield Type* column in the table above.

In the **Properties Explorer**, enter **1** and **-1** for the **Charge** property of the **NC** and **PO** beads, respectively.

On the Label dialog, click **Remove All** and close the dialog. **Save** the document.

5. Generation of MS Martini 3 forcefield and bead topology file for DLPC

Now you can generate the forcefield for the bead-based DLPC configuration.

With **DLPC-CG.xsd** as the active document, select **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools | MS Martini 3 Forcefield Generator** from the menu bar and run.

This script uses the Martini 3 forcefield type for each bead provided in the *ForcefieldType* parameter and the bead type name. Using these, it creates a **DLPC-CG.off** MS Martini 3 forcefield file specialized for the DLPC molecule.

The script also creates a copy of the **DLPC-CG.xsd** file with the forcefield type of each bead defined as the bead type name.

By default, the script generates bond stretch, angle bend, and torsion parameters for *all bead combinations* in the structure. You might need to use values other than the defaults. For more information, see Souza *et al.* [1].

Open the generated **DLPC-CG.off** file.

Select the **Interactions** tab of the Forcefield Viewer. From the **Show interaction** list, choose **Angle Bend**. Change the equilibrium angle (**T0**) of each sequence listed as follows:

Fi	Fj	Fk	Angle (T0)
CA	CA	CB	180
CA	CA	GL1	180
CA	CA	GL2	180
CA	GL1	PO	139.1
GL2	GL1	PO	108

Note: Fi and Fk might swap places in your .off file. Such cases are equivalent to the non-swapped case and do not affect the definition of the angle bend.

Press **Delete** to remove the other rows not listed above.

From the **Show interaction** list, choose **Bond Stretch** and change the **R0** bond distance to:

- **3.12** for GL1, GL2
- **4.2** for GL1, PO
- **4.0** for NC, PO

Press **Delete** to remove the other rows except for the X,X default bond stretch interaction.

From the **Show interaction** list, choose **Torsion**, and press **Delete** to remove all rows.

Save and close the forcefield file.

Before you build your bilayer, tidy the Materials Studio workspace and save the project.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

6. Building the bilayer membrane with the DLPC lipid

To build the bilayer lipid membrane, you must first determine the simulation box dimensions. To calculate the box lengths, you use the experimental area of each lipid; about 65 \AA^2 . Use the Martini 3 regular bead size that is equivalent to four water molecules. Water has a density of 1 g/cm^3 and a molar mass of 18 g/mol . So four water molecules occupy a volume of 119.6 \AA^3 (for details of this calculation, see the [Coarse-Grained molecular dynamics of a lipid bilayer](#) tutorial).

For a total area of $64 \times 64 = 4096 \text{ \AA}^2$ and an average area for each lipid of 65 \AA^2 , you can have about 63 lipids in each half of the bilayer. DLPC has 9 regular beads and 1 small bead. As an approximation, you can take the lipid as having 10 regular beads. In this case, the bilayer lipids have $2 \times 63 \times 10 = 1260$ beads. As each regular size bead occupies 119.6 \AA^3 volume, the bilayer in total occupies a volume of $150,696 \text{ \AA}^3$. Since the area is $64 \times 64 = 4096 \text{ \AA}^2$, you require a bilayer thickness of $150,696/4096$, or about 37 \AA .

Now you can build the template of the simulation box with the dimensions $64 \times 64 \times 80$. While the bilayer membrane has the 37 \AA thickness, water occupies the remaining 43 \AA thickness of the simulation box.

Prepare a folder to store the bilayer files in this project.

In the **Martini3-Bilayer** project root, create a new folder called **Bilayer-DLPC**. Copy the **DLPC-CG.xsd** and **DLPC-CG.off** files from the **Martini3 DLPC\DLPCCG MSM3FG** folder to the new folder.

Use the mesostructure builder to prepare a template for the membrane structure.

From the menu bar, select **Build | Build Mesostructure | Mesostructure Template** to open the Build Mesostructure Template dialog. On the **Add Formers** tab, choose **System** as the **Former type** and enter **64, 64, and 80** as the **X, Y, and Z** lengths. Enter **W** as the **Filler** and click **Build**.

This generates the template in a file named **Mesostructure_Template.msd** in the **Bilayer-DLPC** folder.

From the **Former type** list, select **Slab**, and enter **37** for **Depth**. Select **Along Z** for **Orientation**. Select **Enable surface packing**, choose **Both** for **Packing surface**, and enter **DLPC** as the **Filler**. Click **Add** and close the dialog.

You need to add water to the project, so that you can use it as the solvent filler structure.

From the menu bar, select **Build | Build Mesostructure | Bead Types** to open the Bead Types dialog. Scroll to the end of the list and add a new bead type, **W**, with mass **72 amu** and radius **4.7 \AA**. Close the dialog.

From the menu bar, select **Build | Build Mesostructure | Mesomolecule** to open the Build Mesomolecule dialog. For the **Component Name**, select **W**. For **Number**, enter **1** and click **Build**. Close the dialog.

This generates a **Mesomolecule.xsd** file with one W bead inside.

In the Properties Explorer, choose **Bead** as the **Filter** and select the **W** bead in **Mesomolecule.xsd**. In the Properties Explorer, enter **W** as the **ForcefieldType** of the bead. Rename the file to **W.xsd** and **Save**.

Next, add the W and DLPC bead structures to the template.

Ensure that **Mesostructure Template.msd** is the active file and select **Build | Build Mesostructure | Mesostructure** from the menu bar to open the Build Mesostructure dialog.

For the **W** filler, select **W.xsd** as the **Mesoscale Molecule**.

For the **DLPC** filler, select **Bilayer-DLPC\DLPC-CG.xsd** as the **Mesoscale Molecule**.

Keep the default **Relative Amount** and **Fraction** values and make sure that the **Density** is 1.0 g/cm^3 .

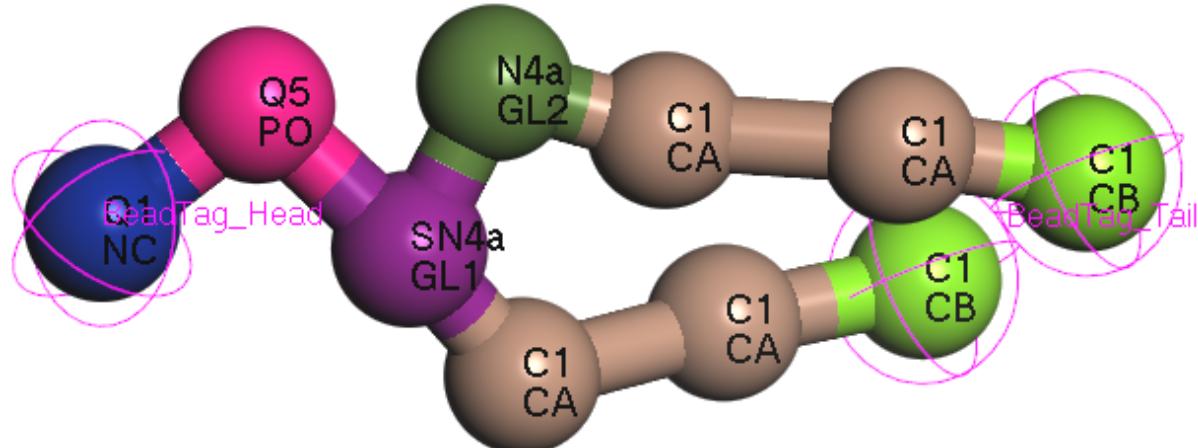
On the **Options** tab, clear selection of **Randomize conformations** and click **More...** to open the Bead Packing Options dialog.

You can use this dialog to define the head and tail beads of the DLPC molecule. The Mesostructure Builder uses these definitions to align the heads of lipid molecules in the bilayer to the Slab surface on both sides of the slab and the tails to the lipid molecules on the other side of the bilayer.

Open **DLPC-CG.xsd** and select the **NC** bead. On the Bead Packing Options dialog, from the **Bead tag** list, select **Head** and click **Create**. Select both the terminal **CB** beads in DLPC. From the **Bead tag** list, select **Tail**, and click **Create**. Close the dialog.

Click anywhere in the structure document to clear the selection of the beads.

The DLPC molecule now has head and tail sets tagged and labeled.



The **DLPC-CG.xsd** file showing the DLPC molecule in ball and stick display style with labels for the Name and ForcefieldType of beads, and the repeat unit. The **BeadTag_Head** for the NC bead and the **BeadTag_Tail** for both CB beads indicate the head and tail sets.

Open the **Mesostructure Template.msd** file and, on the **Build Mesostructure** dialog, click **Build** and close the dialog. Rename the resulting **Mesostructure Template Packed.xsd** file to **DLPC membrane.xsd**.

The generated membrane structure contains DLPC-CG and W solvent molecules. However, the **DLPC-CG.off** forcefield file does not include W bead interactions and cross terms between the W bead and the beads in the DLPC molecule.

You can use the MS Martini 3 Merge Forcefield Files script to add these interactions to your forcefield. Before using the script, you need to generate a MS Martini 3 forcefield file for the **w.xsd** structure.

Generating a MS Martini 3 Forcefield and Bead Topology

Select **W.xsd** and run the **MS Martini 3 Forcefield Generator** again.

This generates a **w.off** forcefield file containing only W bead self-interactions.

Now you can build the combined MS Martini 3 forcefield file and add the missing cross interactions.

Open **Bilayer-DLPC\W MSM3FG\DLPC-CG.off** and select **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools | MS Martini 3 Merge Forcefield Files** from the menu bar to open the MS Martini 3 Merge Forcefield Files dialog. For the **Forcefield_File_to_Merge** parameter, enter **W.off** and click **OK**.

This generates a new output folder named **DLPCCG MSM3MFF**. This contains **DLPC-CG MERGED.off**, a merged forcefield file with all types and interactions from both files as well as nonbond cross terms.

You now can run Mesocite calculations on the **DLPC membrane.xsd** structure, using the **DLPC-CG MERGED.off**.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

7. Simulation of the bilayer DLPC membrane

First, create a folder to store the simulation files.

In the project root, create a new folder and name it **Bilayer-DLPC-MD**. Copy the **DLPC membrane.xsd** and **DLPC-CG MERGED.off** files from **Bilayer-DLPC\W MSM3FG\DLPCCG MSM3MFF** into the new folder.

Open **Bilayer-DLPC-MD\DLPC membrane.xsd**.

The Mesostructure Builder approximately aligns the bilayer molecules. However, you need to optimize the structure before running dynamics simulations. You can optimize the structure incrementally; first refining the atom positions, then adding cell optimization, and finally optimizing the motion groups as well.

First, optimize the geometry with fixed motion groups and no cell optimization.

From the menu bar, select **Modules | Mesocite | Calculation** to open the Mesocite Calculation dialog.

On the **Setup** tab, from the **Task** list, select **Geometry Optimization**. Click **More...** to open the Mesocite Geometry Optimization dialog.

Clear selection of **Optimize cell** and select **Keep motion groups rigid**. Click **More...** and, in the Motion Groups dialog, click **Assign automatically**.

This assigns motion groups to each molecule.

Close the Motion Groups and Mesocite Geometry Optimization dialogs.

On the Mesocite Calculation dialog, select the **Energy** tab. From the **Forcefield** list, select **Browse...** and choose the **DLPC-CG MERGED.off** file in the **Bilayer-DLPC-MD** folder.

Click **Run**.

This creates a new output folder containing a new DLPC_membrane.xsd file and output charts.

Next, optimize the geometry with fixed motion groups and allowing optimization of the unit cell.

Create a new folder in the **Bilayer-DLPC-MD** folder and name it **OPT1**. Copy the **DLPC membrane.xsd** output file from the previous optimization to the new folder. Rename the file to **DLPC OPT1.xsd** and make this file the active document.

Open the Mesocite Geometry Optimization dialog and select **Optimize cell**.

Click **Run** on the Mesocite Calculation dialog.

This creates another new output folder containing a further-optimized DLPC_OPT1.xsd file and output charts.

Finally, optimize the geometry of the structure, including the unit cell and motion groups.

Create a new folder in the **Bilayer-DLPC-MD** folder and name it **OPT2**. Copy the **DLPC OPT1.xsd** output file from the previous optimization to the new folder. Rename the file to **DLPC OPT2.xsd** and make this file the active document.

On the Geometry Optimization dialog, clear selection of **Keep motion groups rigid**. Close the dialog.

Select and delete the motion groups in the structure.

In **DLPC OPT2.xsd**, hold down **ALT**, and double-click one of the motion groups. Press **Delete**.

On the Mesocite Calculation dialog, click **Run**.

The DLPC membrane is now ready for you to run dynamic simulations.

Generating a MS Martini 3 Forcefield and Bead Topology

Create a new folder in the **Bilayer-DLPC-MD** folder and name it **MD**. Copy the **DLPC OPT2.xsd** output file from the previous optimization to the new folder. Rename the file to **DLPC MD.xsd** and make this file the active document.

On the Mesocite Calculation dialog, from the **Task** list, select **Dynamics** and click **More...** to open the Mesocite Dynamics dialog.

On the **Dynamics** tab, specify:

Field	Value	Unit
Ensemble	NPT	
Initial velocities	Random	
Temperature	298	K
Pressure	1.013e-4	GPa
Time step	20	fs
Total simulation time	10000	ps
Frame output every	1000	steps

On the **Thermostat** tab, from the **Thermostat** list, select **Nose**, and keep the default **Q ratio** value of **1.0**. On the **Barostat** tab, from the **Barostat** list, select **Parrinello**, and keep the default **Cell time constant** of **10 ps**. Close the dialog.

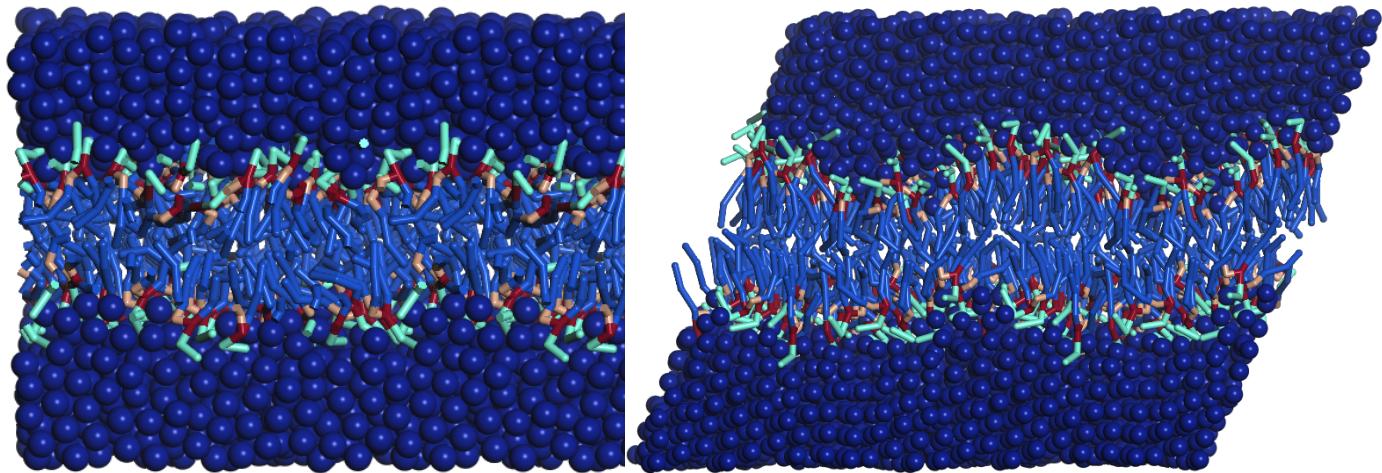
Note: The duration of the dynamics simulation depends on your hardware, job settings, and other processes running on the Materials Studio server. You can choose the simulation server, queue, and other settings on the *Job Control* tab of the Mesocite Calculation dialog. For example, specify *Run in parallel on* to control the number of cores to use before running the simulation.

Click **Run** to start the molecular dynamics simulation.

The dynamics proceeds with no constraints except those defined in the Martini 3 parameterization. The dynamics simulation builds up an aligned lipid bilayer membrane.

When the simulation completes, open **DLPC MD.xsd** in the output folder and visualize the lipid bilayer configuration.

Typically, none of the water beads can enter or pass through the lipid membrane and the membrane molecules stays aligned while binding at NC-PO bead heads. The CA-CA-CB chains can move in alignment with the DLPC molecules at the other side of the bilayer - shown in the right-hand image below. Compare this with the initial configuration of the membrane after the optimization steps - shown in the left-hand image below.



Images of the initial and final steps of the **DLPC MD.xtd** file for the dynamics simulation at left and right, respectively. The water bead display style uses CPK with 0.5 and the DLPC molecule beads display as balls and sticks with 0.7 values. The colors of the bead types differ in these images.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

Tip: To return to the longer output folder names, from the *Tools* menu, select *Options....* On the *Jobs* tab, change the *Job folder Format* to **%N %M %T** and click **OK**.

This is the end of the tutorial.

References

1. Souza, P.C.T. et al., "Martini 3: a general purpose forcefield for coarse-grained molecular dynamics", *Nature Methods* volume 18, pages 382–388 (2021).

Polymer Coarse Graining with Martini 3 Tools

Purpose: Demonstrates how to generate templates for bead mapping, use templates with the *MS Martini 3 Coarse Grainer*, and customize the MS Martini 3 forcefield for a given polymer structure.

Modules: Materials Visualizer, Mesocite, Amorphous Cell

Time: 

Prerequisites: Using the polymer builder, [Packing molecules into existing structures](#)

Background

Materials Studio includes a modified version of the Martini 3 forcefield (see, [Souza, 2021](#)), MS Martini 3. For a more detailed description of Martini forcefield versions and the new types and interactions in Martini 3 including the MS Martini 3 forcefield, see the MS Martini 3 section in the Forcefields in Mesocite theory topic in the Mesocite section of the Materials Studio online help.

The Martini forcefields and MS Martini 3 contain only non-bond interactions for the mesoscale forcefield types. For bonded structures, you must add the valence terms for all Martini forcefields according to the molecules and their chemical interactions.

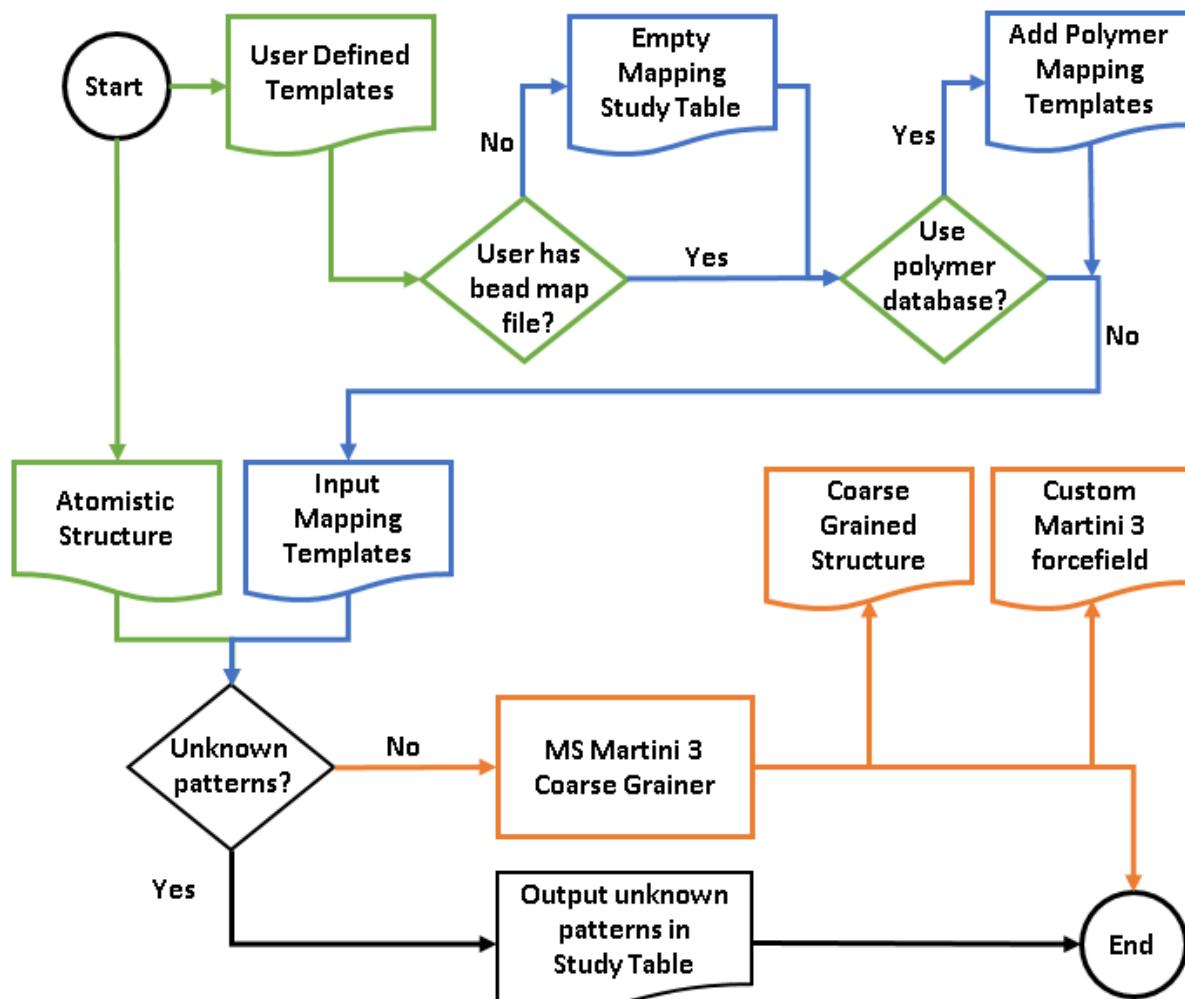
You can automate bead mapping and forcefield typing using template patterns in the form of a study table document. This document might be either a list of user-defined custom templates or generated using the prepared templates. Once the structure has beads assigned, you can apply forcefield types, allowing you to generate a system-specific forcefield from the MS Martini 3 forcefield. You can then add customized valence terms to this forcefield.

Note: This tutorial uses the MS Martini 3 scripts provided in the **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools** folder of your Materials Studio installation. You can follow the Polymer Coarse Graining with Martini 3 Protocols tutorial to achieve the same results; using Pipeline Pilot protocols to generate the coarse grain model and custom MS Martini 3 forcefield.

The *Tools / Materials Studio Scripts / Coarse Graining* menu provides several scripts to generate coarse grain model and custom MS Martini 3 forcefield files.

1. The *Create Bead Mapping* script attempts to generate mapping templates for the given atomistic structure based on the Materials Studio 3D Atomistic structure. You can specify additional details, such as motion groups for bead mapping, distance, and angle and torsion measurements for customization of forcefield parameters.
2. The *MS Martini 3 Coarse Grainer* script uses the mapping templates to generate the bead model corresponding to the input atomistic document. In addition, it creates the system-specific forcefield file containing the customized parameters including the bonded interactions.

The coarse graining process used by the *MS Martini 3 Coarse Grainer* script is:



The flowchart of the *MS Martini 3 Coarse Grainer* script.

Green indicates user inputs.

Blue indicates an internal workflow.

Black indicates where the coarse grain process has insufficient templates.

Orange indicates coarse grain processes with the outputs.

The internal database of mappings used to generate mapping templates includes selected polymers, lipids, and amino acids as defined by [Souza](#) and [Alessandri](#).

Introduction

In this tutorial, you generate a mesoscale polybenzamide (PB) structure using Martini 3 bead definitions and a customized MS Martini 3 forcefield starting from an atomistic structure. To customize the forcefield file, you generate templates with system-specific interactions defined for the input structures.

This tutorial covers:

- [Getting started](#)
- [To generate an amorphous cell with polybenzamide](#)
- [To generate the bead mapping for polybenzamide](#)
- [To generate the bead structure of an amorphous polybenzamide cell](#)
- [To run geometry optimization and dynamics using Mesocite](#)
- [To analyze the density of amorphous polybenzamide at the mesoscale](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project called *CGpolymer*.

Open the New Project dialog and enter **CGpolymer** as the name, click **OK**.

A new project is created with *CGpolymer* listed in the Project Explorer.

To generate output folders for the scripting jobs with shorter names, specify the format.

From the **Tools** menu, select **Options....** On the **Jobs** tab, change the **Job folder Format** to **%n %t** and click **OK**.

2. To generate an amorphous cell with polybenzamide

In this section, you build an atomistic structure of a polybenzamide molecule and then build an amorphous polybenzamide using the Amorphous Cell module.

First, build an atomistic structure of a polybenzamide molecule.

From the menu bar, select **Build | Build Polymers | Homopolymer**. On the Homopolymer dialog, select the **Polymerize** tab. For the **Library**, select **amides** and for the **Repeat unit**, select **benzamide**. Use the default settings of **Isotactic**, **10** for **Chain length**, and **1** for **Number of chains**.

Click **Build** and close the dialog.

The build generates a 3D Atomistic document, named **Polybenzamide.xsd**, in the Project folder. The structure includes 10 repeat units of benzamide. The repeat units at both ends have additional hydrogens.

Next, build an amorphous polybenzamide using the Amorphous Cell module.

From the menu bar, select **Modules | Amorphous Cell | Calculation**. On the **Setup** tab, select **Construction**, and verify that **Density** is **1.0** and **Output** is **1 frame**.

You must ensure that the amorphous cell construction avoids ring spearing.

Click **Options** and ensure selection of **Check ring spearing** and close the dialog.

For the composition **Molecules**, select **Polybenzamide.xsd**, and increase the **Loading** to **30**.

Select the **Energy** tab and, from the **Forcefield** list, select **COMPASSIII**. Verify that **Charges** use **Forcefield assigned** values.

On the **Job Control** tab, select a server.

Click **Run**.

This construction takes some time to generate and optimize the amorphous cell containing polybenzamide.

When the job completes, select **Polybenzamide.xtd**. Press **CTRL+A** to select the entire structure and **CTRL+C** to copy the selection.

Select the project root in the **Project Explorer**, create a new 3D Atomistic file, and press **CTRL+V** to paste the selected structure into the new file. Rename the file to **PolybenzamideCell.xsd**. Save all the documents.

3. To generate the bead mapping for polybenzamide

In this section, you build the templates for bead mapping and forcefield typing of benzamide. You use these templates in a study table to customize the MS Martini 3 forcefield and generate a coarse grain model for polybenzamide.

Note: You cannot run Materials Studio scripts on a server whose gateway uses the secure authentication level.

The MS Martini 3 scripts provided in **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools** run on a Materials Studio server. The *Gateway location* for the scripts can be your local machine ([My Computer](#)) or an appropriate server and queue of your choice.

Make sure that the active document is **Polybenzamide.xsd** and from the menu bar, select **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools | Create Bead Mapping**.

Unlike *MS Martini 3 Coarse Grainer*, the *Create Bead Mapping* script does not have an input dialog and automatically operates on the *ActiveDocument*.

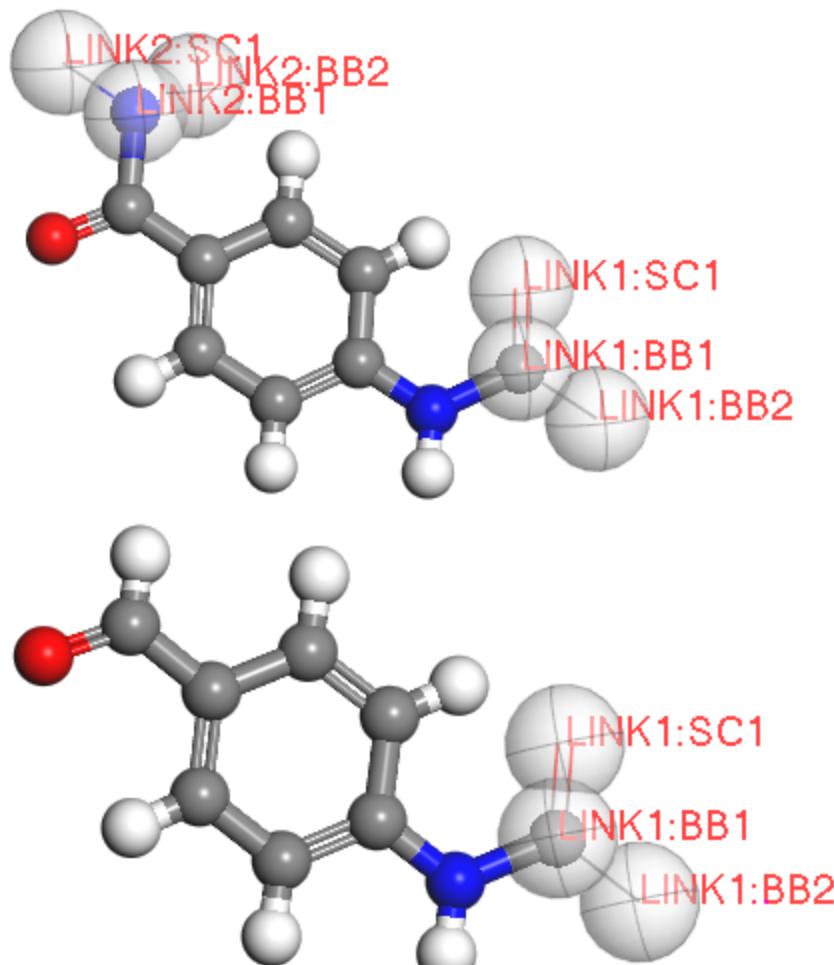
This processes the atomistic document and generates a template study table.

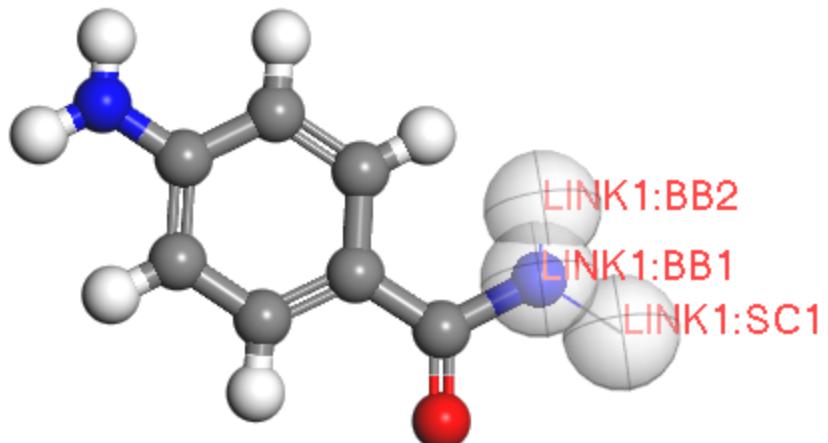
	A	B	C	D	
	Structure	Fragment Type	Fragment SMILES	Fragment Formula	
1		BENZAMID subunit	Nc1ccc(C(=O)cc	C7H6N1O1	
2		BENZAMID subunit	Nc1ccc(C(=O)cc	C7H5N1O1	
3		BENZAMID subunit	Nc1ccc(C(=O)cc	C7H6N1O1	
4					

The output study table with template structures in the Structure column.

The *Create Bead Mapping* script also generates the output of the MaterialsScript function call. By default, the function prints out the processed subblocks of the structure and how the subblocks are added to the template study table.

Double-click the structure in each row in the table to open the structure files.





The structures from each row of the Polybenzamide Bead Map.std file.

Tip: To highlight the labels, right-click, and select *Label*, select *Motion Group*, and choose *Name* as the property value to display. Select red as the color and click *Apply*.

Open the benzamide subunit template structure with the two motion groups, LINK1 and LINK2, highlighted with red labels in the first image above.

These structures act as templates to guide the coarse-graining process. The first structure represents an internal fragment of the polymer chain, while the second and third represent the beginning and ending fragments.

Motion groups with names starting with "LINK" represent neighboring atoms of the fragment. The fragment formula does not include these.

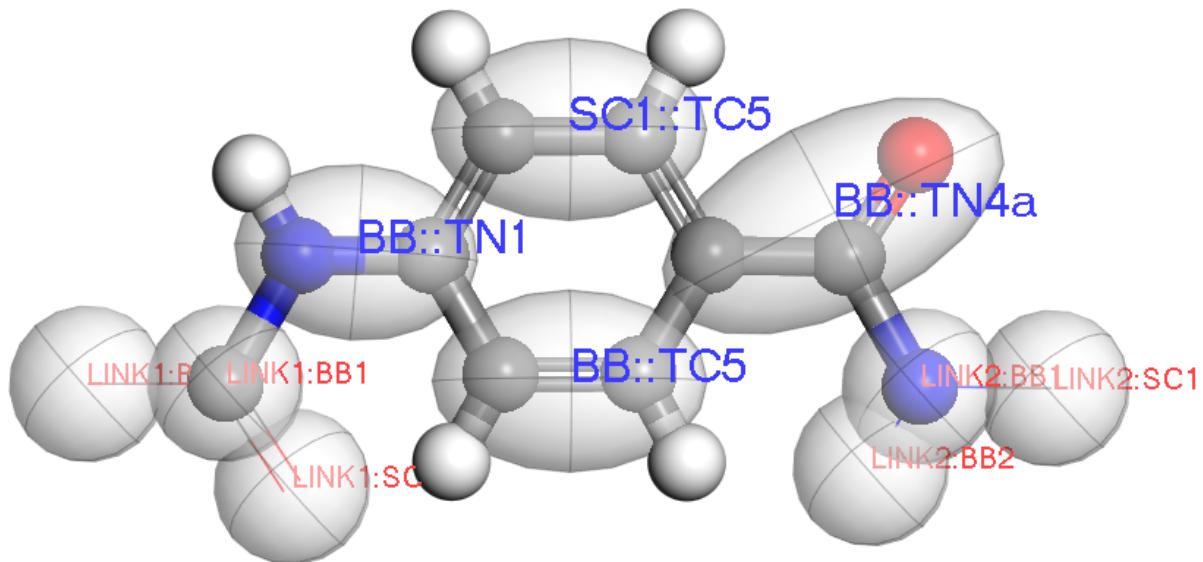
Any other motion group found in the template transforms into a bead in the final coarse-grained structure. You need to add these by hand.

The connecting atoms and *LINK motion groups* do not have any effect on the pattern used during matching and do not contribute to the *Fragment SMILES* and *Fragment Formula* columns in the study table.

Select and then right-click a carbon atom in the ring to view the pattern in the template. Select the **benzamide** repeat unit. Compare the **ChemicalFormula** of the selection in the Properties Explorer and the **Fragment Formula** in the study table.

From the menu bar, select **Modify | Motion Groups** to open the Motion Groups dialog. Select each atom group and click **Create** to add motion groups with blue labels as shown in the image below. Then, close the Motion Groups dialog.

Tip: How you assign motion groups and measurements has a significant impact on achieving a correct coarse grain model and customization of the Martini 3 forcefield. You can use the provided prepared study table, Examples\Scripting\Martini3 Tools\Polybenzamide Bead Map.std, to continue with this tutorial section. This allows you to learn how to generate study table templates for the customization of Martini 3 forcefields. You can also use the prepared study table to continue with the subsequent sections of the tutorial.



In the **Properties Explorer**, select the **Motion Group** filter.

Select each motion group in the template structure and use the Properties Explorer to specify the **Name** properties as shown in the image above.

Hold down **CTRL** and select the motion groups that you added, right-click in the template structure and select **Label**. On the **Label** dialog, select **Motion Group** as the **Object type**, select blue as the **Color**. From the **Properties** list, select **Name**. Click **Apply** and close the dialog.

Compare your template with the image above.

The *MS Martini 3 Coarse Grainer* uses these motion groups with their *Name* values to map atoms to beads and assign the Martini 3 forcefield types. The *Name* field includes a string with a : delimiter. The scripting function processes the string as an array where each substring between : is a property of the field, ordered as follows:

1. *Type of bead assignment*: Backbone (BB), side-chain (SC).

Here, SC1, SC2, etc., indicates the side-chain order starting from BB. Linked BB beads can also have an order number starting from linked BB such as BB1, BB2. The LINK motion groups are virtual beads to use in linking only for representation and not actual atom-to-bead mappings.

2. *Name of the bead*: You can leave the name field empty; as in this example of the tutorial. The function assigns unique bead names if this field is empty. If you provide a name, you must specify unique names for each bead in each template.
3. *Martini 3 forcefield type*: The forcefield type to assign to this bead. The forcefield typing in this tutorial follows the Martini 3 small molecules assignment from [Alessandri, 2021](#).
4. *Charge of the bead*: This is optional. The default is 0.
5. *Mass of the bead*: This is optional. Specify a value to use other than that assigned by the default Martini 3 scheme that uses forcefield types to determine masses; such as Regular, Small (S), and Tiny (T). Any mass value given in templates overwrites the default values.

Note: In the image above, the top motion group assignment specifies side-chain 1 (SC1) connected to the backbone (BB) even though the structure does not have a side-chain as a branch. This ensures the uniqueness of the beads. You must indicate each branched bead, such as in a ring structure, with SC starting from 1 until the branch ends or closes back to the backbone (BB).

Here, SC1 branches from BB and closes back to BB, resulting in the ring structure.

The scripting function uses all motion groups assigned with blue labels as patterns to match in the given document during the automatic coarse grain process. The scripting function does not use motion groups with labels starting with LINK. Those motion groups are virtual sites, used only to add custom topology Martini 3 forcefield parameters.

To add custom topology forcefield parameters and Martini 3 forcefield constraints such as 'hinging' ring structures, include additional forcefield parameters in the templates. Without the definition of torsion terms for the ring section of the molecule, the connected four beads can fold during optimization and dynamics. To prevent this, you need to add torsion terms.

To add these terms, select **Measure/Change** from the toolbar and select **Torsion**. Select the **BB::TN4a**, **BB::TC5**, **SC1::TC5**, and **BB::TN1** motion groups in order.

Tip: On adding measurements, only select motion groups. Do not add measurements between atoms, as the mapping only considers motion groups.

This generates a torsion measurement between those motion groups.

From the toolbar, select **Measure/Change** and select **Angle**. Create angle measurements between **LINK2:BB1**, **BB::TN4a**, and **BB::TC5**, and between **BB::TC5**, **BB::TN1**, and **LINK1:BB1**.

These angle bending additions define the zig-zag behavior of polybenzamide chains.

The protocol converts these measurements to torsion or angle bend forcefield terms. You can optionally specify the numerical parameters of each term by using the Name string of the measurement. The name can consist of two values as follows, separated by a colon:

1. *Equilibrium value*: The bond distance, angle, or torsion angle of the constraint.
2. *Force constant*: The value to replace the default forcefield constant for the bond stretch, angle bend, or torsion.

You can omit either value, in which case Materials Studio uses a default.

Select the torsion measurement and change the **Name** to **180.0:20.0**.

Press **ALT** and double-click an angle measurement, change the **Name** to **120.0**:

While the angle and torsion measurements modify the forcefield parameters, the distance measurements modify the forcefield parameter, and define bonds between beads if they are not already connected.

From the toolbar, select **Measure/Change** and select **Distance**. Select the **BB::TC5** and **SC1::TC5** motion groups.

This creates an additional bead connector, required by the torsion interaction defined above; each torsion must have 4 connected beads.

Add distance measurements between each of the following pairs of motion groups:

- BB::TN1 and SC1::TC5
- BB::TN1 and BB::TC5
- BB::TN1 and LINK1:BB1
- BB::TN4a and SC1::TC5
- BB::TN4a and BB::TC5
- BB::TN4a and LINK2:BB1

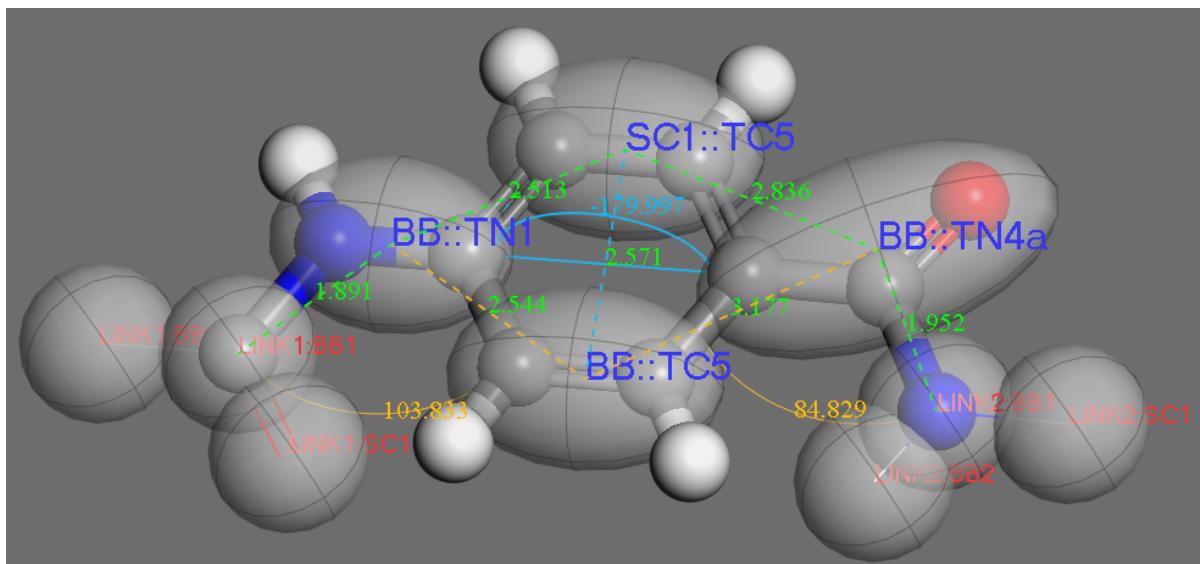
Press **ALT** and double-click one of the distance measurements.

This selects all the distance measurements in the file.

Change the **Name** field to **3.65**: in the Properties Explorer.

This adds bond stretch terms for all beads with a distance 3.65 Å and the default bonding force constant.

Compare your template with the template image shown below.



Close the template and save the structure file.

You must now prepare the other two benzamide templates in the first and last rows in the same way by adding motion groups and measurements.

To reduce the assignment and typing work, you can copy your prepared template into the structure files in the first and last rows of the study table, and then modify them.

Select the structure files in the first and last rows of the study table in the first column and delete them.

Select the template structure that you already prepared, right-click, and select **Copy**.

Select the cell in the first row and first column, right-click, and select **Paste**.

Also paste the prepared template structure in the cell in the last row and first column.

Now, the study table includes the same structure files in each row. You need to edit the motion groups and measurements for the templates in these rows to define the templates for terminating the bead mappings of the molecule with **BB::TN1** and **BB::TN4a**.

In this tutorial example, benzamide does not have a different bead mapping for the terminating bead. However, the terminating bead mappings, their forcefield typing, and customization might be different for other molecules. When the terminating beads are different, use these templates to customize the bead mapping and the addition of specialized forcefield typing through measurements.

Open the structure file in the first row of the study table and modify the **BB::TN1** motion group and its measurements as follows:

1. Select the motion groups with **LINK1** labels and their assigned atoms, and then press **DELETE**.
 2. On the **Sketch** toolbar, click  **Adjust Hydrogen**.
 3. Select the **BB::TN1** motion group and press **DELETE**.
 4. Select the same atoms but including the new hydrogen atom and recreate the **BB::TN1** motion group.
- From the menu bar, select **Modify | Motion Groups** and click **Create**.
5. Assign **BB::TN1** as the **Name** label of the motion group.
 6. Recreate the distance and torsion measurements for the **BB::TN1** motion group, using the *Name* labels as below:
 - A distance measurement between **BB::TN1** and **SC1::TC5**, with the *Name* label **3.65**:
 - A distance measurement between **BB::TN1** and **BB::TC5**, with the *Name* label **3.65**:
 - A torsion measurement between **BB::TN1**, **SC1::TC5**, **BB::TC5**, and **BB::TN4a**, with the *Name* label **180.0:20.0**.

Open the structure file in the last row of the study table and repeat the steps 1 to 6 above but for the **LINK2** motion groups. Instead of naming the new motion group **BB::TN1**, use the **BB::TN4a** motion group name again. Assign the following measurements to **BB::TN4a**:

- A distance measurement between **BB::TN4a** and **SC1::TC5**, with the *Name* label **3.65**:
- A distance measurement between **BB::TN4a** and **BB::TC5**, with the *Name* label **3.65**:
- A torsion measurement between **BB::TN1**, **SC1::TC5**, **BB::TC5**, and **BB::TN4a**, with the *Name* label **180.0:20.0**.

Save all structures and study table and select **Window | Close All**.

4. To generate the bead structure of an amorphous polybenzamide cell

You now use the MS Martini 3 Coarse Grainer script to convert the amorphous cell to a bead structure, and generate the custom MS Martini 3 forcefield for this structure.

Open **PolybenzamideCell.xsd** and make it the active document for coarse graining. Make sure that the **Polybenzamide Bead Map.std** file is in the same folder.

From the **Tools | Materials Studio Scripts | Coarse Graining | MS Martini 3 Tools** menu, select **MS Martini 3 Coarse Grainer** to open the MS Martini 3 Coarse Grainer dialog.

For the **Bead_Map_Table**, enter **Polybenzamide Bead Map**. Clear selection of the **Polymers_Mappings**, **Lipids_Mappings**, and **Aminoacids_Mappings** parameters.

These options turn off the internal template databases and use only the template study table file that you provide in the **Bead_Map_Table** parameter.

Click **OK**.

The scripting function runs in several minutes, to generate both the CG model and the custom Martini 3 forcefield for the given amorphous cell. Once the script run completes, the subfolder in the Materials Studio project contains the **PolybenzamideCell-CG.xsd** and **PolybenzamideCell-CG.off** files for the CG model and custom Martini 3 forcefield.

5. To run geometry optimization and dynamics using Mesocite

From the menu bar, select **Modules | Mesocite | Calculation**. Open **PolybenzamideCell-CG.xsd** to make it the active document.

On the **Setup** tab of the Mesocite Calculation dialog, for the **Task**, select **Geometry Optimization**.

On the **Energy** tab, for the **Forcefield**, select **Browse....** On the **Choose Forcefield** dialog, select the **PolybenzamideCell-CG.off** file from the project folder.

The atoms map to beads according to the geometry centers of the selected motion groups. So, the bead distances and the new generated cell are not in a relaxed state; they are under stress. You require several geometry optimizations to relax the initial structure as follows:

On the **Setup** tab of the Mesocite Calculation dialog, click **More....** For the **Quality** select **Medium**, for **External Pressure** specify **0.0**, and select **Optimize cell**. Click **Run**.

Select the generated **PolybenzamideCell-CG.xsd** output file. On the Mesocite Geometry Optimization dialog, clear **Optimize cell**. Close the Mesocite Geometry Optimization dialog and click **Run**.

As the system is not at an equilibrium state at room temperature and zero pressure, when this geometry optimization completes you require several dynamics steps to further relax and heat the structure before running production simulations.

Note: If a dialog saying "Do you wish to merge the energy parameters from the original run?" opens during these steps, click **Yes**, and continue.

Open the output **PolybenzamideCell-CG.xsd**. On the **Setup** tab of the Mesocite Calculation dialog, for the **Task** select **Dynamics**, and click **More....** On the **Dynamics** tab of the Mesocite Dynamics dialog, for the **Ensemble** select **NVT**, for the **Time step** specify **1.0 fs**, and increase the **Total simulation time** to **100 ps**. On the **Thermostat** tab, verify that the **Thermostat** is **Velocity Scale**. Click **Run** on the Mesocite Calculation dialog.

Ensure that the active view is on the output **PolybenzamideCell-CG.xtd** in the sub-folder. On the Mesocite Calculation dialog, click **Restart**. On the **Dynamics** tab of the Mesocite Dynamics dialog, for the **Ensemble** select **NPT**, increase the **Total simulation time** to **1000**. On the **Thermostat** tab, select the **Thermostat** as **NHL**, and for the **Decay constant** specify **4.0 ps**. On the **Barostat** tab, select the **Barostat** as **Andersen**, and leave the default **Cell time constant** as **10.0 ps**. Click **Run**.

After the dynamics run completes, open the output **PolybenzamideCell-CG.xtd**. On the Mesocite Calculation dialog, ensure that **Restart** is checked. On the **Dynamics** tab of the Mesocite Dynamics dialog, for the **Time step** select **5.0 fs**. On the **Thermostat** tab, for the **Decay constant** specify **10.0 ps**. Click **Run** on the Mesocite Calculation dialog.

After these initial relaxation steps, select the final generated **PolybenzamideCell-CG.xtd** and ensure that **Restart** is checked on the Mesocite Calculation dialog. On the **Dynamics** tab of the Mesocite Dynamics dialog, for the **Ensemble**, select **NPT**. Increase the **Time step** to **10 fs** and the **Total simulation time** to **10000**.

Click **Run** on the Mesocite Calculation dialog.

6. To analyze the density of amorphous polybenzamide at the mesoscale

In this section, you compare the density of amorphous polybenzamide analyzing the results of the mesoscale structure using the customized MS Martini 3 forcefield in Mesocite.

Open the **PolybenzamideCell-CG Density.xcd** file containing the results for the CG model of the polybenzamide amorphous cell.

The density of the CG model is about 1.2 g/cm^3 .

Forcite calculations with the COMPASSIII forcefield also provide about 1.2 g/cm^3 density for the same amorphous polybenzamide structure.

This is the end of the tutorial.

Tip: To return to the longer output folder names, from the *Tools* menu, select *Options....* On the *Jobs* tab, change the *Job folder Format* to **%N %M %T** and click **OK**.

References

1. Souza, P. C. T.; *et al.*, “Martini 3: a general purpose forcefield for coarse-grained molecular dynamics”, *Nature Methods*, **18**, 382-388 (2021).
2. Alessandri, R.; Barnoud, J.; Gertsen, A. S.; Patmanidis, I.; de Vries, A. H.; Souza, P. C. T.; Marrink, S. J. “Martini 3 Coarse-Grained Force Field: Small Molecules”, *Adv. Theory Simulations*, **5**, 2100391 (2021).

Preparation of a Granular Material

Purpose: Demonstrates the use of the Granular Dynamics task in Mesocite

Modules: Materials Visualizer, Mesocite

Time: 

Prerequisites: Building mesoscale molecules

Background

The manufacturing process of lithium-ion batteries includes a step for the creation and mixing of an electrode slurry, containing particles of Active Material (AM) and carbon-binder domain (CBD). The AM phase is typically a transition metal oxide at the cathode end and a graphite powder at the anode. The CBD phase contains carbon black and a polymer binder such as poly(vinylidene fluoride).

The CBD phase is initially in solution. During the manufacturing process the solvent is evaporated, reducing the size of the particles. Once dried, the material undergoes a mechanical compression (calendering) to reduce it to its final thickness. The micro-structure of the calendered electrode material is important for predicting electrode properties, such as porosity, which ultimately determine battery performance.

This tutorial is based on an article by Lombardo et al. ([Lombardo, 2021](#)), which demonstrates how to model this process. You build a slurry solution, and subject this to an isotropic compression. The sample then dries under anisotropic compression. Finally, you simulate the calendering process, and determine some structural properties of the electrode material.

Introduction

In this tutorial, you use Mesocite to run a Granular Dynamics calculation on a model slurry.

This tutorial covers:

- [Getting started](#)
- [Creating the initial structure](#)
- [Equilibrating the system](#)
- [Removing the solvent](#)
- [Simulating the calendering process](#)
- [Analyzing the final material](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Granular** as the project name and click the **OK** button.

The new project is created with *Granular* listed in the Project Explorer.

2. Creating the initial structure

In this tutorial, you use a number of prepared scripts from the Examples/Scripting/Granular Dynamics folder. These invoke Mesocite through its scripting interface, rather than through the Materials Studio client.

Import the **CreateGranularModel.pl** script from the Examples/Scripting/Granular Dynamics folder.

You can use this script to construct a simulation cell containing a mixture of:

- Active Material (AM) particles with a distribution of sizes.
- Carbon-binder domain (CBD) particles, consisting of small solid particles bound by a liquid (solvent) material.

Open the script and inspect the parameters.

The script's parameters include:

- LengthXY: width of the simulation cell in the x and y directions (μm).
- LengthZ: height of the simulation cell in the z direction (μm).
- Density_CBD_liq: density of the liquid component of the CBD particles ($\text{pg}/\mu\text{m}^3$).
- Density_CBD: density of CBD particles ($\text{pg}/\mu\text{m}^3$).

Note: The CBD particles are nanoporous, so this is lower than the density of compacted CBD material.

- Density_AM: density of the AM particles ($\text{pg}/\mu\text{m}^3$).
- Mass_dry: the total mass of dry material, including the AM and the solid part of the CBD particles (pg).
- Fraction_dry: the fraction of dry material relative to the total mass (dimensionless).
- Fraction_CBD: fraction of the dry mass that is CBD (dimensionless).
- Diameter_CBD: diameter of the CBD particles (μm).
- Diameter_AM: diameters of the AM particles (μm).
- Composition_AM: distribution of sizes of AM particles (number fractions).

In this tutorial, you create a rectangular simulation box with a square cross-section of $40\ \mu\text{m} \times 40\ \mu\text{m}$ and height $400\ \mu\text{m}$. A box of this size contains around 5000 particles, typical for a granular dynamics simulation.

Change **LengthXY** to **40** and **LengthZ** to **400**. Leave the other parameters unchanged from their default values and save the script. On the **Scripting** toolbar, click **Debug** .

While the script runs, this creates several bead definition documents involved in the simulation, and a bead model called **CBD(4729)_AM(153).xsd**. When the script completes, you can continue to work with the bead model, but Materials Studio does not save the intermediate documents.

Next, create a forcefield for the simulation. The forcefield provides interactions in addition to the granular interactions.

Import the Examples/Scripting/Granular Dynamics/CreateGranularForcefield.pl script.

You can use this script to create a forcefield containing shifted Lennard-Jones potentials, represented as a tabulated van der Waals interaction. The shifted Lennard-Jones potential is characterized by three parameters: an energy (epsilon), a distance (sigma); and a cutoff distance (rc). It is identical to the usual Lennard-Jones form, except that a linear term makes the energy and force exactly zero at a distance of rc.

Open the script and observe the parameters.

The script's parameters include:

- Epsilon_AM: used to calculate the energy parameter of the interaction between AM particles, according to $\text{epsilon} = \text{Epsilon_AM} \times d$ where d is the particle diameter ($\text{pg } \mu\text{m}/\mu\text{s}^2$).
- Sigma_AM: used to calculate the distance parameter of the interaction between AM particles, according to $\text{sigma} = \text{Sigma_AM} \times d$ where d is the particle diameter (dimensionless).
- Cutoff_AM: used to calculate the distance beyond which to ignore the interaction between AM particles, according to $\text{rc} = \text{Cutoff_AM} \times d$ where d is the particle diameter (dimensionless).
- DiameterCorrection: the constant factor used to modify the particle diameters before calculating the shifted Lennard-Jones parameters. This allows you to use a slightly different diameter for the granular dynamics interaction (dimensionless).
- Name_CBD: name of the bead type identifying the CBD particles.
- Epsilon_CBD: used to calculate the energy parameter of the interaction between CBD particles, according to $\text{epsilon} = \text{Epsilon_cb} \times d$ where d is the CBD diameter in the model (either wet or dry) ($\text{pg } \mu\text{m}/\mu\text{s}^2$).
- Sigma_CBD: used to calculate the distance parameter of the interaction between CBD particles, according to $\text{sigma} = \text{Sigma_CBD} \times d$ where d is the CBD dry diameter (dimensionless).
- Cutoff_CBD: distance beyond which to ignore interaction between CBD particles (μm).
- Diameter_CBD_dry: diameter of dry CBD particles (μm).

On line 33, check that the filename is **CBD(4729) AM(153).xsd**. Click **Debug** .

This creates a forcefield for the bead model.

3. Equilibrating the system

Next, carry out a geometry optimization to remove overlaps between particles.

Import the **Examples/Scripting/Granular Dynamics/Minimization.pl** script into the root folder.

On line 25 and 26, make sure that the script uses the **CBD(4729) AM(153)** files with the **.xsd** and **.off** extensions, respectively.

The geometry optimization only takes a few seconds, so you can run it in debug mode.

On the **Scripting** toolbar, click **Debug** .

From the generated energies chart, you can see that the total enthalpy has reduced significantly. The system is now suitable for a granular dynamics simulation. Before proceeding save the project.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

Now, import the script for the granular dynamics simulation under compression.

Create a new folder called **Compression**.

Save a copy of the minimized structure **CBD(4729) AM(153).xsd** and the forcefield **CBD(4729) AM (153).off** into this folder.

Tip: You can make a copy of a document by holding the CTRL key and, in the Project Explorer, dragging the file to the destination folder. Make sure that you save the document first.

Import the **Examples/Scripting/Granular Dynamics/Compression.pl** script into this folder and make sure that, on lines 30 and 31, the script uses the **CBD(4729) AM(153)** files with the **.xsd** and **.off** extensions, respectively. Ensure that the value assigned to **PressureTarget** is **1.0**.

The compression script can consume more resources than before, so you might want to run it on a Materials Studio server rather than your computer.

Click the arrow for **Run on Server**  and select **Script Job...** to open the Script Job Control dialog. Select a suitable **Gateway location** and close the dialog.

Click **Run on Server**  to start the compression simulation.

This script compresses the cell until the pressure is equal to one atmosphere. It runs a series of constant volume simulations.

Note: The Job Explorer reports the progress of each individual compression step. After each step, the progress returns to 0.

Wait for the job to complete and then open **Compression/Compression Script/CBD(4729) AM(153)_Compression.xtd**. Click **Play**  on the **Animation** toolbar.

You can see that the script has reduced the size of the cell.

Open **Compression/Compression Script/CBD(4729) AM(153).std**. Select the first two columns and click **Quick Plot** .

The chart generated shows how the pressure increases to atmospheric during compression of the system.

Note: The final pressure might slightly exceed the target pressure as it is recorded at the end of the final compression cycle.

4. Removing the solvent

In this stage, you can model the drying process by changing the size of the CBD particles to represent the effect of removing solvent from them.

In the root folder, create a new folder called **Drying**.

Save a copy of **Compression/Compression Script/CBD(4729) AM(153).xsd** into the new folder.

From the menu bar, select **Build | Build Mesostructure | Bead Types** to open the Bead Type dialog.

Create a new bead type called **CBD_d** with **Mass 4.71e11 g/mol** and **Radius 6.5e3 Å**. Close the dialog.

In **Drying/CBD(4729) AM(153).xsd**, press and hold ALT, then double-click a CBD particle.

This selects all CBD particles.

Tip: If the Properties Explorer is not open, from the menu bar, select *View / Explorers / Properties Explorer*.

In the **Properties Explorer**, change the **BeadTypeName** and the **ForcefieldType** to **CBD_d**.

You can see that the CBD particles are much smaller than before, indicating the reduction in volume when evaporating the solvent from it.

Note: You can simulate the drying process more realistically by introducing bead types with fractional solvent content, and then running a series of drying simulations.

Because you have removed the liquid, the particles become much harder, with much larger Epsilon values.

Import **Examples/Scripting/Granular Dynamics/CreateGranularForcefield.pl** into the **Drying** folder.

Change line 41 to:

```
Name_CBD => 'CBD_d' ;
```

Change the following parameters to these values:

- Epsilon_AM: 400
- Sigma_AM: 0.93
- Cutoff_AM: 1.2
- Epsilon_CBD: 800

Save the script file, and then click **Debug** .

This creates a new version of the forcefield with a reduced size for the CBD particle, representing removal of the solvent.

Rename the output forcefield to **CBD(4729) AM(153)_dry.off**.

Save a copy of **Minimization.pl** in the **Drying** folder. On line 26, change the forcefield (\$off) to **CBD(4729) AM(153)_dry.off**.

Before running the minimization, add the drying script to the same folder.

Import **Examples/Scripting/Granular Dynamics/Drying.pl** into the same output folder. Ensure that the value assigned to **PressureTarget** on line 35 is **1.0**. Change **NumberOfSteps** to **1000** and **TrajectoryFrequency** to **100**. Before the closing round braces for the \$mesociteSettings list, add:

```
TimeStep => 1e5
```

Save the script.

This script compresses the material anisotropically until the pressure reaches 1 atm.

With **Minimization.pl** in focus, click **Run on Server**  to start the geometry optimization.

When it finishes, open **Drying/Minimization Script/Drying.pl** and click **Run on Server** .

When the job completes, inspect the configuration and pressure evolution.

Open **Drying/Minimization Script/Drying Script/CBD(4729) AM(153)_Drying.xtd** and click **Play**  on the **Animation** toolbar.

You can see that the cell size has reduced in the Z-direction.

Open the **CBD(4729) AM(153).std** study table in the same folder, select the first two columns, and click **Quick Plot** .

You can see how the Z-pressure increases during compression of the system.

5. Simulating the calendering process

Finally, simulate the calendering process. In this manufacturing step, the material passes through two adjacent rollers (calenders) to reduce its porosity and improve the particles contacts; this enhances the energy density of the battery. You can simulate the unidirectional compression using two granular walls perpendicular to the z-direction. The top wall makes an oscillatory motion during the dynamics, while the bottom wall remains static.

Create a new folder called **Calendering**.

Save copies of the **Drying/Minimization Script/Drying Script/CBD(4729) AM(153).xsd** and **CBD(4729) AM(153)_dry.off** files into this folder.

Ensure that **Calendering/CBD(4729) AM(153).xsd** is the active document. Select **Build | Symmetry | Redefine Lattice** to open the Redefine Lattice dialog. Ensure that the settings are **A = 1 0 0, B = 0 1 0, and C = 0 0 1**, and then click **Redefine**. Close the dialog.

This causes all particles to move inside the unit cell.

Import the script **Examples/Scripting/Granular Dynamics/Calendering.pl** into the Calendering folder.

Change the **NumberOfSteps** to **10000**, **TrajectoryFrequency** to **100**, and **GranularWallPeriod** to **1**.

Before the closing round braces for the \$mesociteSettings list, add:

```
TimeStep => 1e5
```

Save the script.

Preparation of a Granular Material

This script forces the material to compress under the effect of an external wall.

Click **Run on Server**  and wait for the job to complete.

On completion, inspect the evolution of the granular structure.

Open **Calendering/Calendering Script/CBD(4729) AM(153).xtd** and click **Play** .

You can see that the particle domain has reduced further in the Z-direction.

6. Analyzing the final material

Open the file **Calendering/Calendering Script/CBD(4729) AM(153).xsd**.

This is the final state of the material after processing and you can now perform further analysis on the structure.

You can calculate the radial distribution function of the AM particles.

Open the **Mesocite Analysis** dialog and select **Radial distribution function**. Change **Cutoff** to **100000** and **Interval** to **500**. Make sure that the structure document is active, then press **CTRL+A**.

This selects the entire structure.

Click **Analyze**.

The radial distribution function has a sharp peak around 1.3 µm corresponding to CBD contact.

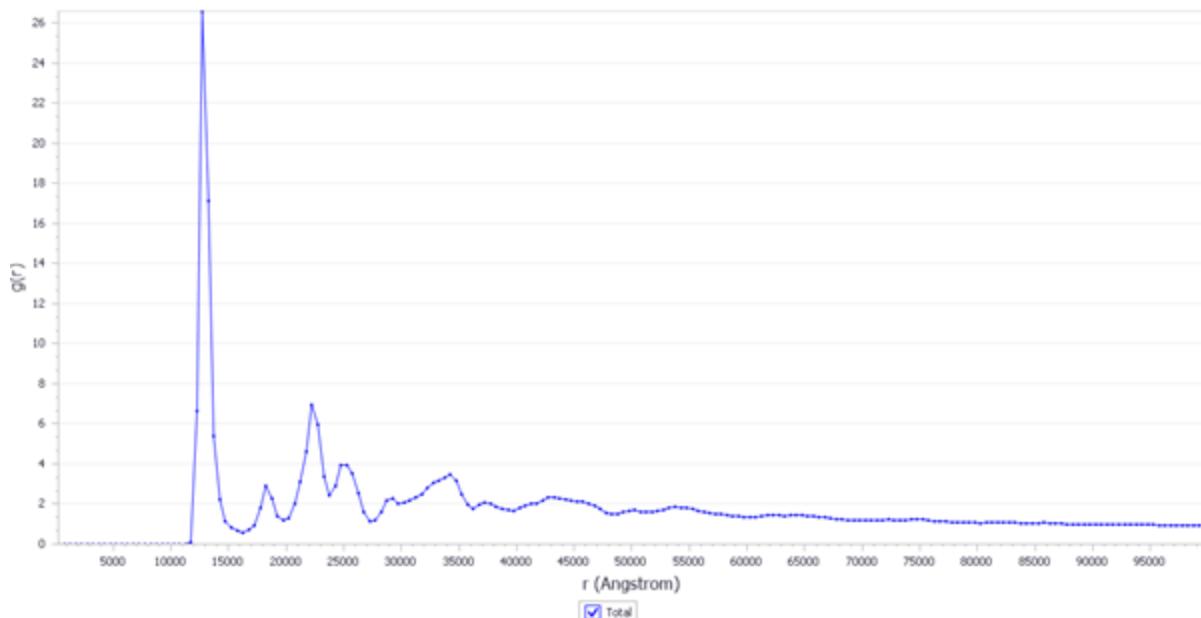
In the structure document, hold down **CTRL** and **ALT**, then double-click a CBD particle.

This clears the selection of the CBD particles, while keeping the others selected.

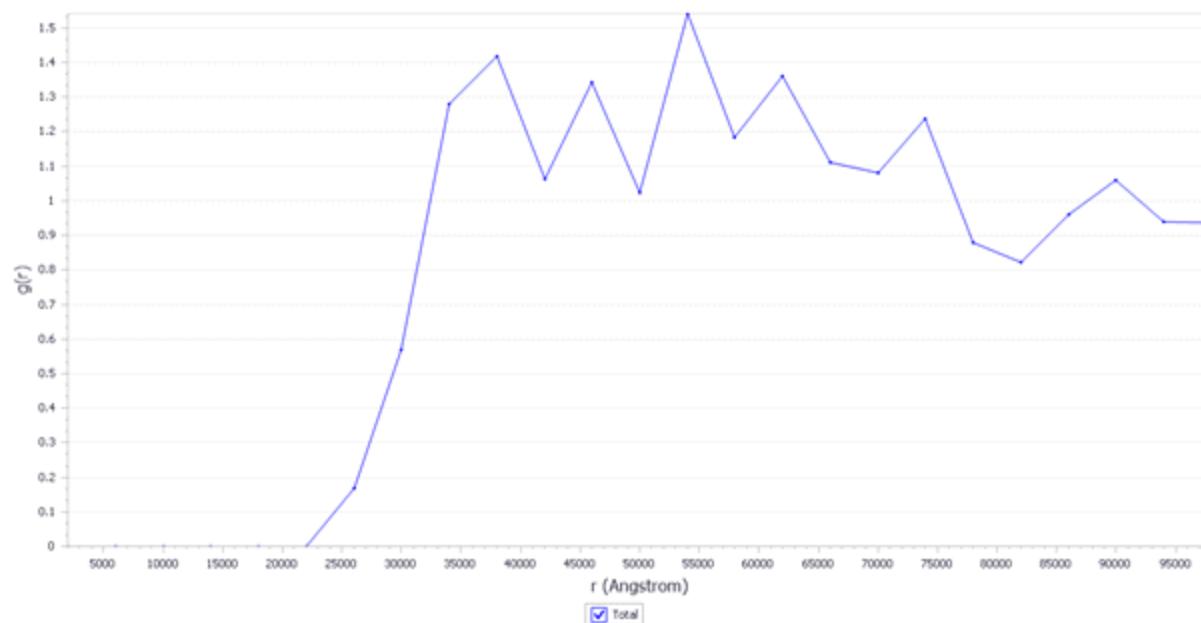
Change **Interval** to **4000** and click **Analyze**.

Now, the radial distribution function shows a smooth transition from 0 to 1 at around 3 µm (30,000 Å), the average distance between AM particles.

Mesocite Analysis - RDF (selection)



Mesocite Analysis - RDF (selection)



The study by Lombardo et al. progresses to a more complex calculation, modeling different positions in the electrode layer with different drying rates. The finding is that the distribution of CBD particles is not homogeneous.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Lombardo, A. C. Ngandjong, A. Belhcen, A. A. Franco, "Carbon-Binder Migration: A Three-Dimensional Drying Model for Lithium-ion Battery Electrodes", *Energy Storage Materials*, 2021, **43**, 337–347.

Building Mesoscale Amorphous Cell Using Mesocite Builder

Purpose: Demonstrates how to use the Mesocite Builder to build a mesoscale amorphous cell using bead-based mesomolecules.

Modules: Materials Visualizer, Mesocite, Forcite

Time: 

Prerequisites:

Introduction

Building and equilibrating large-scale amorphous cells with polymers needs considerable computation time and resources. Using bead-based molecules instead reduces the time to construct the mesoscale amorphous cells. This alternative approach reduces the computation time significantly as there are fewer particles in the simulation cells. With fewer light atoms, such as hydrogens, you can increase the timestep of the dynamics runs from 1 fs to 2 fs in this tutorial.

This tutorial demonstrates how to build a mesoscale amorphous cell of polyethylene using Mesocite Builder and equilibrate the cell with Mesocite. First, you construct a bead-based representation of polyethylene using Mesocite Builder. Then, you equilibrate the simulation cell with Mesocite, and calculate the radius of gyration of polyethylene in the mesoscale amorphous cell.

This tutorial covers:

- [Getting started](#)
- [Creating polyethylene mesomolecule](#)
- [Assigning forcefield types at mesomolecule](#)
- [Creating mesoscale amorphous cell of polyethylene](#)
- [Equilibrating mesoscale amorphous cell](#)
- [Analyzing the radius of gyration of the mesoscale polyethylene](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

If Materials Studio is not already open, double-click on the **Materials Studio** icon  on your desktop to start the program or, alternatively, select **BIOVIA | Materials Studio 2025** from the list of programs on the Windows **Start** menu.

Open the New Project dialog, enter **MesoPolymerAC** as the name and click the **OK** button.

The new project is created with *MesoPolymerAC* listed in the Project Explorer.

You can access the mesostructure building tools through the Build menu or using the Mesostructure toolbar. To use the toolbar, make sure that it is visible.

From the menu bar, select **View | Toolbars** and ensure the **Mesostructure** toolbar is enabled.

To generate output folders for the jobs with shorter names, specify the format.

From the **Tools** menu, select **Options....** On the **Jobs** tab, change the **Job folder Format** to **%n %m %t** and click **OK**.

2. Creating polyethylene mesomolecule

In this section, you build a bead structure of a polyethylene molecule with 20 monomers.

Before building the mesoscale polyethylene molecule, you need to define the bead types of each bead in the polyethylene mesomolecule in the project. This tutorial uses a united atom type of model in the coarse grain of polyethylene, removing only hydrogens. So you can define the CH₂ and CH₃ groups as beads.

Click **Bead Types**  on the Mesostructure toolbar to open the Bead Types dialog. Click **Defaults...** to open the Bead Type Defaults dialog.

Set the **Mass** to **14** and the **Radius** to **0.8** and close the Bead Type Defaults dialog.

On the **Bead Types** dialog, define the following new bead types: **CH2** and **CH3**. For the **Mass** of **CH3** specify **15**. Close the dialog.

Create a folder where you can store your mesoscale polyethylene structure.

Create a new folder called **MesoPE**.

Next, build a mesoscale structure of a polyethylene molecule with 20 monomers consisting two beads with the molecule made up of CH₂ chain and CH₃ end beads.

Click **Mesomolecule**  on the Mesostructure toolbar to open the Build Mesomolecule dialog.

Select **CH3** for the first row **Component Name** and keep **Number** as **1** as the initial bead of the chain.

Select **CH2** for the second row **Component Name**. Enter **38** as the **Number** of chain beads.

Select **CH3** for the third row **Component Name** and keep **Number** at **1** as the last bead of the chain.

By default, the mesomolecule builder generates a linear mesomolecule. In a linear mesomolecule, you can only define a torsion between consequent beads where the torsion angle is 180 degrees and you cannot rotate a torsion. The Mesocite Builder constructs amorphous cells using angle manipulations of the torsions available for mesomolecules. As linear torsions in a structure are fixed, you cannot use these torsions in a Mesocite Builder construction.

You can prevent linear torsions in the mesomolecule.

Select **Randomize conformation**, click **Build**, and close the dialog.

This generates the **Mesomolecule.xsd** file in the **MesoPE** folder.

Select the file and rename it to **PE.xsd**.

3. Assigning forcefield types at mesomolecule

Mesocite Builder uses Mesocite energy calculations, this requires selection of a forcefield and assignment of forcefield types to the beads of the mesomolecules.

To demonstrate the construction of an amorphous cell in Mesocite Builder, this tutorial uses pcff forcefield parameters for polyethylene without hydrogen.

Note: You can use other forcefields available in Mesocite. You can also create a custom MS Martini 3 forcefield for mesomolecules. For example, see the Polymer Coarse Graining with Martini 3 Tools tutorial.

From the menu bar, select **Modules | Forceite | Forcefield Manager** to open the Forceite Forcefield Manager. Select **pcff** from the **Standard Forcefields** and click **>>**. Close the dialog.

This imports the **pcff.off** forcefield file into the project.

From the menu bar, select **File | Save Project** followed by **Window | Close All**.

To determine the forcefield types of the CH₂ and CH₃ beads, you can use the forcefield typing feature of Forceite for the atomistic counterpart of the polyethylene molecule.

Create a folder where you can store your 3D atomistic polyethylene structure.

Create a new folder called **AtomPE** in the root of the project.

Next, build an atomistic polyethylene molecule.

From the menu bar, select **Build | Build Polymers | Homopolymer**.

On the Homopolymer dialog, select the **Polymerize** tab. For the **Library**, select **olefins** and for the **Repeat unit**, select **ethylene**. For the **Tacticity**, select **Isotactic**. Specify **20** for **Chain length**, and **1** for **Number of chains**.

Click **Build** and close the dialog.

The build generates a 3D Atomistic document, named **Polyethylene.xsd**, in the **AtomPE** folder.

Make sure that **Polyethylene.xsd** is the active document.

Select **Modules | Forceite | Calculation** from the menu bar to open the Forceite Calculation dialog,

Select the **Energy** tab, from the **Forcefield** list, select **pcff**. Click **More...** to open the Forceite Preparation Options dialog.

In the **Forcefield types** section, clear selection of **Calculate automatically**, and click **Calculate**. Close the dialog and the Forceite Calculation dialog.

Next, examine the assigned pcff forcefield types for at the backbone and terminating atoms of the polymer.

Right-click in **Polyethylene.xsd** and select **Label**. Choose **ForcefieldType** as the property value to display and click **Apply**. Close the dialog.

Examine the structure to see the **c2** and **c3** forcefield types assigned to backbone and end of chain atoms, respectively.

Next, assign the same forcefield types to mesoscale polyethylene molecule .

Double-click the **PE.xsd** file in the **MesoPE** folder.

Press and hold **ALT**, double-click one of the end green beads to select both terminal beads.

In the **Property Explorer**, make sure that the **Filter** is **Bead**. For the **ForcefieldType** field, enter **c3**.

Press and hold **ALT**, double-click one of the pink chain beads to select them all.

In the **Property Explorer**, assign **c2** for the **ForcefieldType** field. Save the document.

Note: The CH₂ and CH₃ beads in this model represent charge-neutral groups. When modeling a group of atoms with a net charge, assign charges to the beads using the *Property Explorer* before using the mesomolecule at Mesocite Builder.

From the menu bar, select **File | Save Project** followed by **Window | Close All**.

4. Creating mesoscale amorphous cell of polyethylene

Next, build an amorphous cell of mesoscale polyethylene that has beads assigned with the forcefield types.

From the menu bar, select **Modules | Mesocite | Builder**.

On the **Setup** tab, select **Construction**. For the **Density**, specify **0.95**, and ensure that the **Output** is **1** frame.

Click **Options...**, ensure selection of **Optimize geometry**, and close the Mesocite Builder Options dialog.

For the **Composition**, select **PE.xsd** from the **MesoPE** folder, and increase the **Loading** to **20**.

Select the **Energy** tab, from the **Forcefield** list, select **Browse....** Select **pcff.off** on the Choose Forcefield dialog.

On the **Job Control** tab, select a server.

Click the project root so that the job stores the output files at the top level of the project. Click **Run** and close the dialog.

When the job completes, the constructed amorphous cell file PE.xtd displays in the results folder PE M C.

5. Equilibrating mesoscale amorphous cell

When you select the *Optimize cell* option, Mesocite Builder also optimizes the constructed amorphous cells in each frame. Before you continue with the analysis of the amorphous polyethylene, equilibrate the amorphous cell at a specific temperature and pressure. In this tutorial, use room temperature and zero pressure for equilibrating the mesostructure.

Make sure that **PE.xtd** is the active document.

From the menu bar, select **Modules | Mesocite | Calculation**. On the **Setup** tab, for the **Task** select **Dynamics**, and click **More....**

On the **Dynamics** tab of the Mesocite Dynamics dialog, for the **Ensemble** select **NVT**, for the **Time step** specify **1.0 fs**, and increase the **Total simulation time** to **100 ps**. On the **Thermostat** tab, for the **Thermostat** select **Velocity Scale**.

Select the **Energy** tab and make sure **pcff.off** is selected as the **Forcefield**.

On the **Job Control** tab of the Mesocite Calculation dialog, select a server.

Click **Run**.

This initial dynamics run, with 1 fs timestep, equilibrates the structure at the room temperature.

Next, you further equilibrate the resulting structure also at zero pressure.

After the dynamics run completes, open the output **PE.xtd** in the subfolder **PE M D**.

On the **Setup** tab of the Mesocite Calculation dialog, select **Restart**.

On the **Dynamics** tab of the Mesocite Dynamics dialog, for the **Ensemble** select **NPT**, increase the **Total simulation time** to **5000**. On the **Thermostat** tab, for the **Thermostat** select **NHL**, and for the **Decay constant** specify **4.0 ps**. On the **Barostat** tab, for the **Barostat** select **Andersen**, and leave the default **Cell time constant** as **10.0 ps**.

Click **Run**.

Note: If a dialog saying "Do you wish to merge the energy parameters from the original run?" opens when you start the job, click **Yes**, and continue.

The resulting cell is now equilibrated both at room temperature and zero pressure.

In the next and final dynamics step, increase the timestep to 2 fs and run a longer time scale simulation, ready to analyze the resulting trajectory in the next section.

Open the output **PE.xtd** from the previous dynamics run in the subfolder **PE M R**.

On the **Dynamics** tab of the Mesocite Dynamics dialog, increase the **Time step** to **2.0 fs**, and for the **Total simulation time** specify **5000** again.

On the **Thermostat** tab, ensure that **Decay constant** is **4.0 ps**.

Click **Run** and close the dialog.

Note: If the dynamics run fails due to large energy deviations or beads moving large distances, reduce the timestep to 1 fs and run the simulation again. Then, repeat the dynamics run with a timestep to 2 fs by restarting the calculation from the *PE.xtd* results document generated with the shorter timestep.

The example coarse grained model in this tutorial only differs from the atom-based polyethylene by the missing hydrogens. Such a model is generally referred to as a united atom model. Depending on the forcefield parameterization of the coarse grained models, you can increase the timestep of the dynamics. Here, you increased the timestep to 2 fs from 1 fs, by removing hydrogens from the structure. The increased timestep and reduced number of particles in the cell help to accelerate this simulation. To further increase the timestep up to 20 fs, you can use the MS Martini 3 forcefield to model mesostructures.

6. Analyzing the radius of gyration of the mesoscale polyethylene

Finally, analyze the radius of gyration of mesoscale polyethylene created with Mesocite Builder and equilibrated using the steps in previous sections.

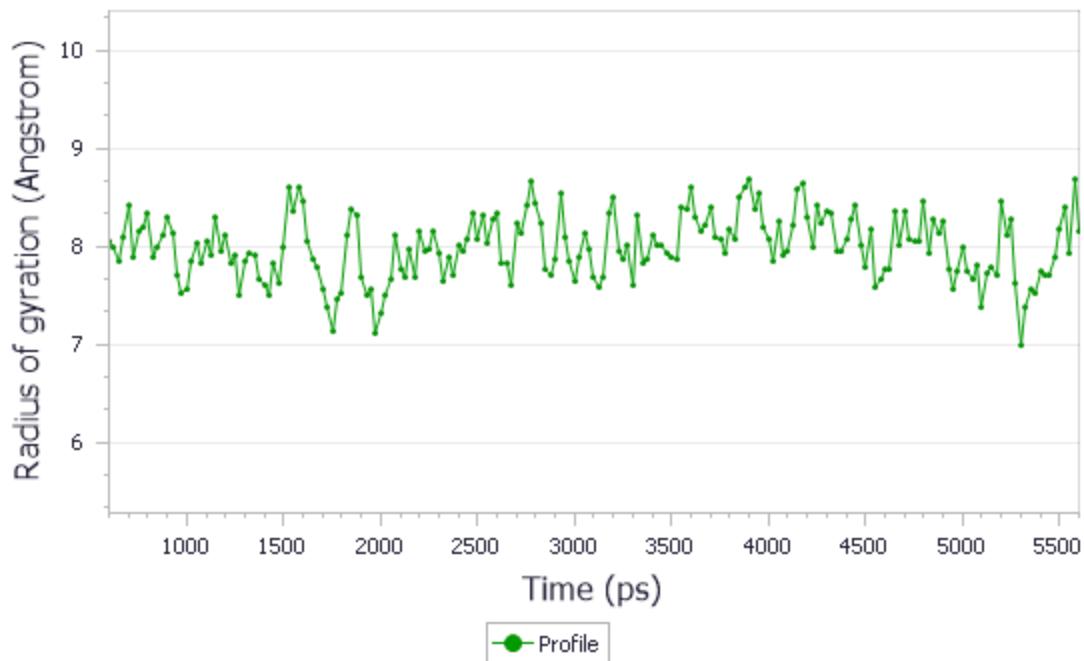
Open the output **PE.xtd** from the final equilibration step in the lowest subfolder **PE M R** to make it the active document.

From the menu bar, select **Modules | Mesocite | Analysis**.

From the list of analyses, select **Radius of gyration evolution**. Click **Analyze** and close the dialog.

The analysis produces a chart containing the evolution of the radius of gyration, similar to this.

Mesocite Analysis - Radius of gyration evolution



Compare your results with the radius of gyration value of about 8 for atomistic polyethylene chains with 20 monomers, calculated by Forcite using pcff for polyethylene chains without hydrogens.

For further analysis, you can build an amorphous cell using the atom-based Polyethylene.xsd in **AtomPE** folder with the Amorphous Cell module. Use pcff and equilibrate the constructed amorphous cells using the NPT ensemble for 20 ns. Calculate the radius of gyration using Forcite Analysis and compare your results with those from the Mesocite Builder system using the coarse model.

Select **File | Save Project** from the menu bar.

This is the end of the tutorial.

Chapter 15: MesoDyn tutorials

The following tutorials illustrate how to utilize MesoDyn's capabilities.

- [Running a simple MesoDyn simulation](#)
- [Obtaining input parameters for MesoDyn](#)
- [Using explicit charges and salt solutions](#)
- [Using pseudodynamics](#)

Running a simple MesoDyn simulation

Purpose: To introduce the MesoDyn calculation panel, launch a short simulation to the server and look at the results graphically. Also to look at restarting a simulation and shearing.

Modules: Materials Visualizer, MesoDyn

Time: 

Prerequisites:

Background

The large size and slow dynamics of mesoscale structures makes quantum mechanics or molecular modeling with atomistic detail prohibitively expensive. These structures are critical to the properties of materials and therefore methods have been developed to elucidate mesophase behavior. At such length scales, fast atomic degrees of freedom contribute only to effective potentials. MesoDyn uses such an approach. The Materials Studio implementation permits the user to perform simulations on Linux or Windows servers, while system setup and post simulation analysis can be done from the desktop PC.

Introduction

This tutorial uses most of the default values on the MesoDyn Calculation dialog to run a short simulation of phase separation of a symmetric diblock copolymer melt system. The default starting point is a homogeneous mixture. Repulsive interactions between the two blocks of the polymer will drive the system closer to its equilibrium state, which is a lamellar phase separated structure. The results are visualized using 2D and 3D graphics. Restarting a simulation and subjecting the system to a shearing force are also demonstrated.

This tutorial covers:

- [Getting started](#)
- [To set up a MesoDyn calculation](#)
- [To control the job settings and run the job](#)
- [To examine the results](#)
- [To restart the simulation with shear](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

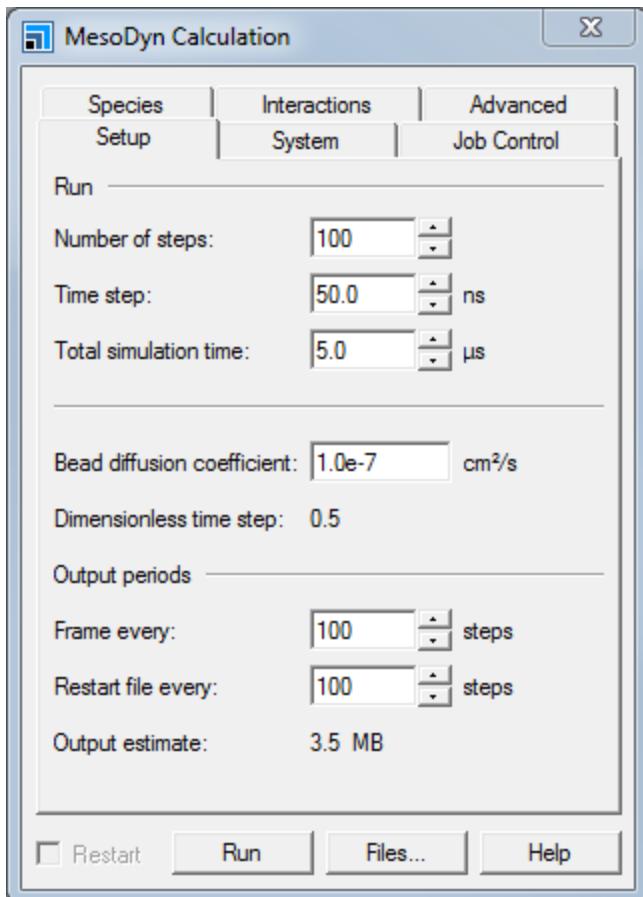
Open the **New Project** dialog and enter **MD_simple** as the project name, click the **OK** button.

The new project is created with *MD_simple* listed in the Project Explorer.

2. To set up a MesoDyn calculation

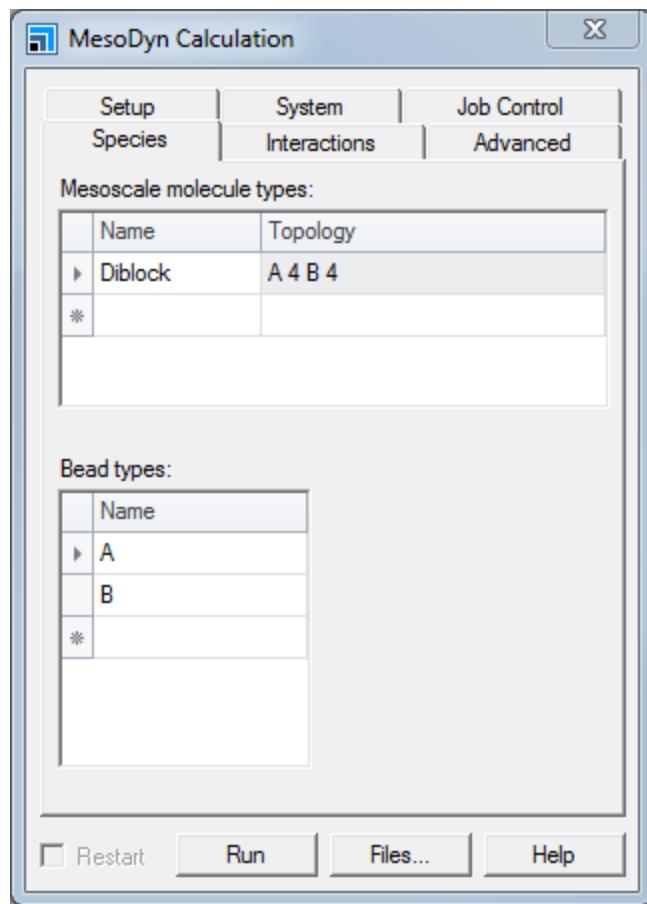
The first step is to open the MesoDyn Calculation dialog.

Click the MesoDyn button  on the **Modules** toolbar and select **Calculation** to open the MesoDyn Calculation dialog.



MesoDyn Calculation dialog, Setup tab

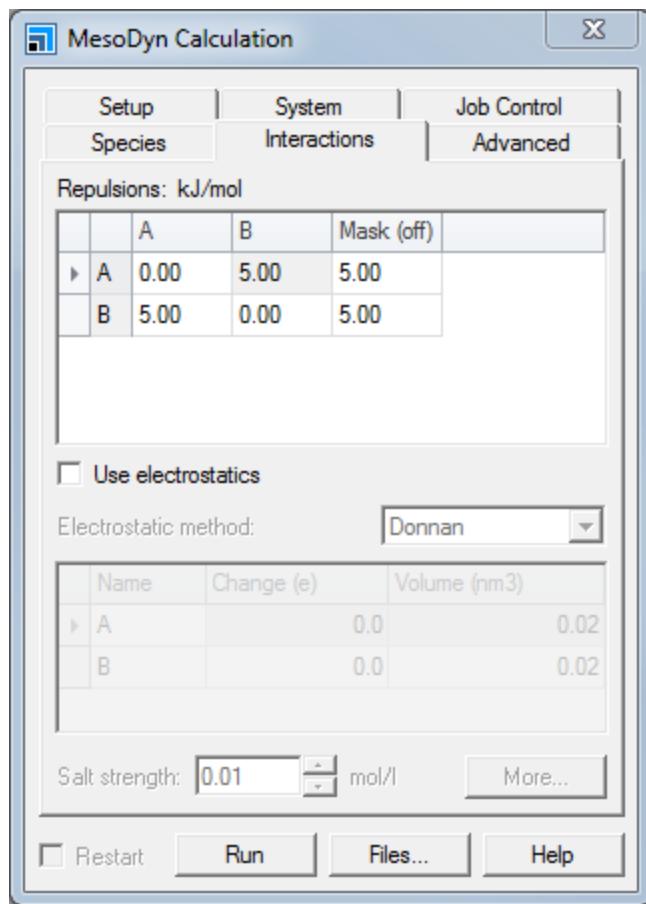
Select the **Species** tab and ensure that the default diblock copolymer consisting of bead types **A** and **B**, with topology **A 4 B 4** are defined in the Bead types and Mesoscale molecule types grids.



MesoDyn Calculation dialog, Species tab

The *Species* tab allows you to set the parameters that define bead types and molecular topology. Although the default diblock copolymer system used in this tutorial does not require modification of the default parameters on this tab, this is where you would define the *Mesoscale molecule types* and *Bead types* in other calculations.

Select the **Interactions** tab.



MesoDyn Calculation dialog, Interactions tab

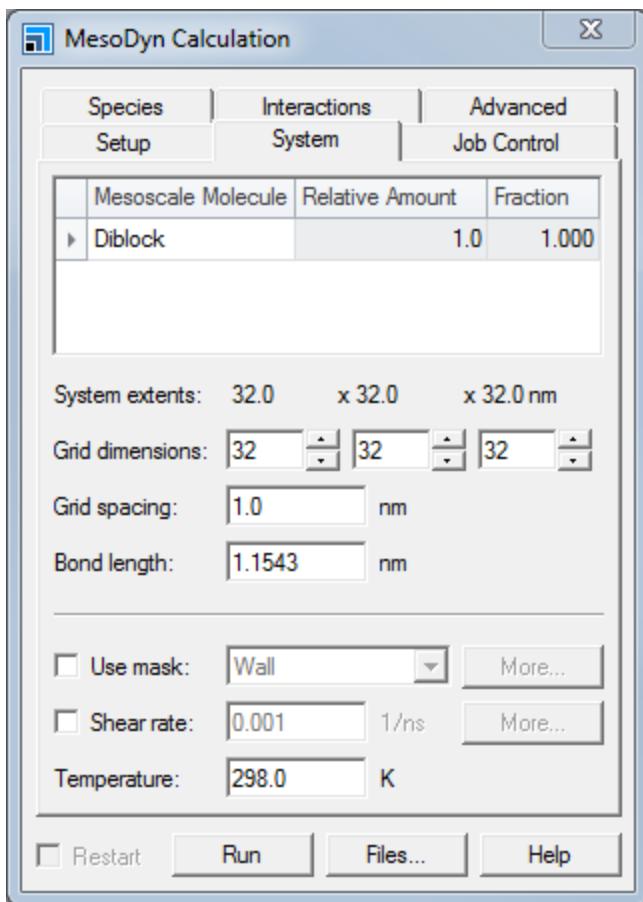
The repulsion of the beads is specified in the *Repulsions* panel. The values of the off-diagonal terms are greater than zero and this will tend to cause phase separation. The matrix of interactions is symmetric, so any changes made below the diagonal are reflected above the diagonal.

This tutorial does not involve the electrostatics functionality, so leave the option unchecked. Likewise, salt strength controls are not used.

Note: Values appear for bead-mask interactions even though the *Use Mask* control on the System tab is not checked. Mask status (**on** or **off**) is indicated in the *Mask* cell heading of the *Repulsions* panel.

For this tutorial, the default values are appropriate.

Select the **System** tab.



MesoDyn Calculation dialog, System tab

The **System** tab specifies the concentrations of individual molecules, cell size, and other external variables.

There is only one molecule in the system, so the composition cannot be changed. To shorten the length of the calculation, reduce the grid dimensions to 16×16×16.

Change the **Grid dimensions** value from 32 to **16** in all three dimensions.

Note: The bond length parameter, which defines the Gaussian chain, is fixed at 1.15 times the grid spacing. This ensures the isotropy of all grid restricted operators. The bond length is therefore approximately the same size as the lattice on which the density profiles will be reported.

Select the **Setup** tab.

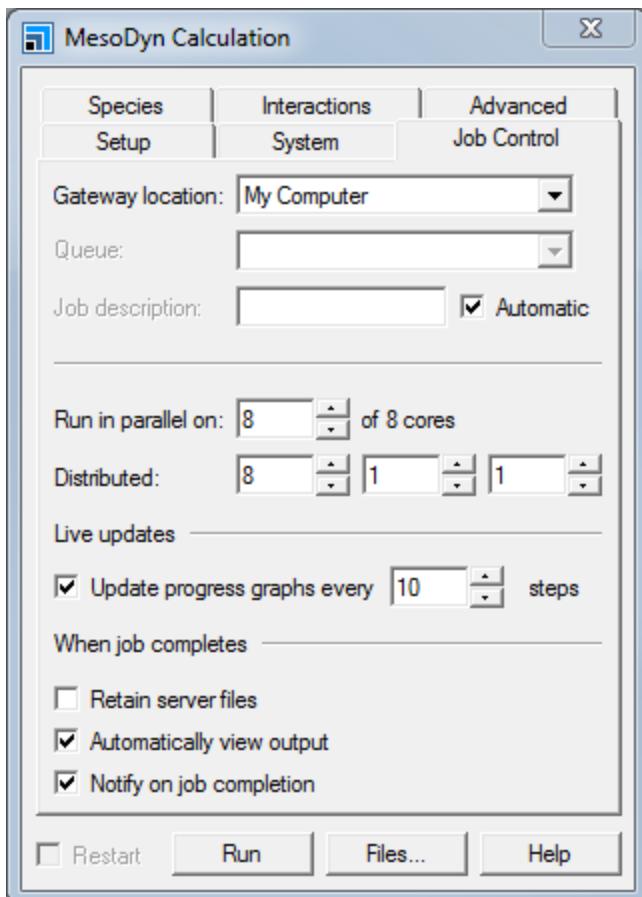
A lengthy simulation is not required for this tutorial, so the simulation will be configured to run for only 500 time steps of the default 50 ns each.

Change the **Number of steps** to **500**. Set the **Frame every** to **100** steps (five frames will be generated) and set the **Restart file every** to **500**.

Check the **Output estimate** and make sure the output files are not too large (compare with your available disk space).

3. To control the job settings and run the job

Select the Job Control tab.



MesoDyn Calculation dialog, Job Control tab

From this tab you can choose the gateway location where the calculation will run, which queue (if any) to submit the job to, and parallel simulation topology, as well as set various options such as the job description, live update settings, and what happens when the job completes. For now, simply change the update frequency and number of processors, if necessary.

Change the **Update progress graphs every** to **50** steps. Ensure that **Run in parallel on** is set to **1** processor.

Note: As you will later restart the run using shear, the processor topology must be supported by the shear protocol. Shear requires an N processor job to be distributed as $1 \times N \times 1$. If you want to use multiple processors in this tutorial you therefore have to ensure the topology is in this format. It is not possible to restart a run originally distributed as $N \times 1 \times 1$ by a run with shear, if $N > 1$.

Specify a name for the calculation.

Uncheck the **Automatic** checkbox and enter **MD_simpletut_run** as the **Job description**. Click the **Run** button.

The Job Explorer is displayed, indicating the status of the calculation. The run should take less than ten minutes on a standard PC.

Two chart viewers will open, displaying the files `FreeEnergy.xcd` and `OrderParameters.xcd`. These are the live documents that are updated regularly while the calculation is running. They display the free energy evolution and order parameters of the system, respectively. These can be useful visual aids to indicate the progress of your calculation, for example you can observe the free energy decreasing and the order parameters increasing during the run, indicating that phase separation is taking place.

4. To examine the results

A number of files have been saved in the `MD_simpletut_run MesoDyn Dynamics` folder. The `MD_simpletut_run.mtd` file contains the density and potential fields - the concentration of that species throughout the box at the relevant instants of the simulation. Double-clicking this file in the Project Explorer displays the simulation cell with a colored-dot representation of the fields.

Make the `MD_simpletut_run.mtd` file the active document.

By default only the density fields are displayed. The display shows each species (bead) in a single color, at all points in the cell where the concentration of that bead is greater than the field's mean value; so that if a species A ranges from 0 to 1 in its concentration, it will be displayed as a series of dots at each point in the cell where the concentration of A is greater than 0.5.

Select one of the beads for further examination.

Click the **Volumetric Selection** button  on the **Volume Visualization** toolbar to open the Volumetric Selection dialog. Uncheck the **B Density** checkbox and select the **A Density** field so that it is highlighted in blue.

The background of the icon and name turns dark blue and the frame of the cell turns yellow, indicating selection.

Right-click in `MD_simpletut_run MesoDyn Dynamics\MD_simpletut_run.mtd` and select **Display Style** from the shortcut menu to open the Display Style dialog.

Controls on the *Field* tab toggle the color of dots between a custom color and a range determined by the field value. The Color Maps tool on the Volume Visualization toolbar allows you to change the color spectrum used to indicate the field, select the range of field values that should be colored, specify any exclusions from the spectrum, and crop/clamp options for field points outside the indicated range.

On the **Field** tab click the **Color by field values** radio button.

The default display style is 32 colors in a blue to red spectrum (blue for low density, red for high). The range of densities is from 0 to 1. Points with densities below 0.5 are not displayed.

Click the **Color Maps** button  on the **Volume Visualization** toolbar to open the Color Maps dialog. Display the entire spectrum by clicking and dragging in the **Color range chooser**.

Hoving the cursor over the chooser indicates the density corresponding to each color and whether it is excluded. Excluded densities (that is, colors) are also indicated by horizontal gray lines through the corresponding colors. Clicking on any band toggles between excluded and included.

The default field display is low quality, dot size = 1. Increasing the quality increases the number of dots used to represent the field. Altering the dot size has a predictable effect on the image. You can display

the cell without the field visible by selecting the *Empty* radio button. The cell can be made invisible by unchecking the *Show box* checkbox. The entire field, including cell and dots, can be made invisible by unchecking the *Visible* checkbox.

The dot display of the field can be replaced by a 3D volume rendering of the fields by selecting the *Volume* radio button. This option is rather memory intensive and should be utilized with some caution.

Try some of these options for yourself.

The cell can be viewed with periodic replicas visible, using the *Display range* controls of the *Field* tab. The displayed range can be incremented in any of the three Cartesian directions (both positive and negative directions are permitted) and by non-integer amounts.

The other files created in the simulation are also of considerable interest.

- `FreeEnergy.xcd` shows the evolution of free energy during the simulation, which reaches equilibration asymptotically.
- `OrderParameters.xcd` shows the instantaneous value of the order parameter for each species (bead type) in the system.
- `MD_simpletut_run.MesoDyn_par` is a text version of the input parameters. This file may be edited and read back in to the *MesoDyn Calculation* dialog using the *Files* button.
- `MD_simpletut_run.MesoDyn_out` reports the completion status of the simulation and the numerics of the integration.

Slices and isosurfaces provide useful 2D and 3D representations of the phase morphology. These can be generated for any field in the system and color-coded in the same manner as fields themselves. Both options are available on the *Volume Visualization* toolbar.

First, create a 3D isosurface linking points with the same concentration of type A beads.

With no field selected, click the **Create Isosurface** button  on the Volume Visualization toolbar to open the Choose Fields To Isosurface dialog. Select the **A Density** field and click the **OK** button.

This creates a surface linking all the points in the cell that have the same density of type A beads. Use the Display Style dialog to control the coloring of this surface.

On the **Display Style** dialog select the **Isosurface** tab.

Custom coloring, using the color control, is the default. Coloring the surface by the potential energy experienced by the A beads along the surface is more useful here.

Select **A Potential** from the **Mapped field** dropdown list.

The coloring method automatically changes to *Color by mapped field*. Now the surface is color mapped by the potential energy of the A beads along this surface.

Select the surface and press **DELETE** to remove it.

It is also interesting to examine the system using 2D slices.

With no field selected, click the **Create Slices** arrow  on the Volume Visualization toolbar and select **Best Fit**.

This opens the Choose Fields to Slice dialog, select **A Density** and click the **OK** button.

MesoDyn: Running a simple MesoDyn simulation

The density of A beads in a slice through the system is displayed. You can use the Display Style dialog and *Color Maps* tools to manipulate the color mapping.

Select the **Slice** and press **DELETE** to remove it.

Choose one of the bead types on the **Volumetric Selection** dialog. Click the **Field Distribution** button  on the **Volume Visualization** toolbar.

A graph of the selected field's values is displayed.

Note: If the *Field Distribution* button is pressed while no field is selected in the Volumetric Selection dialog, a new dialog is displayed and you are prompted to select a field. You can select multiple fields, if desired.

Make the trajectory the active document and uncheck the checkboxes for all the density fields on the Volumetric Selection dialog. Check one of the potential fields.

A field is displayed which shows the potential felt by the selected species at each point in the box. You can use the *Field* tab in the Display Style dialog, and the Color Maps tool to control the appearance of the field.

Close any dialogs that remain open.

The MesoDyn Analysis dialog allows you to plot enthalpy, entropy, free energy, compressibility, order parameter and electrostatics as an evolution or an average. Parts of the run, for example equilibration stages, can be excluded from the graphing and averaging. The order parameter plot can be chosen for one or more of the species present. In this tutorial the two curves should be the same, since there are two components of equal density in the system.

Select **Modules | MesoDyn | Analysis** from the menu bar to open the MesoDyn Analysis dialog.

Select **Thermodynamics** and click the **View** button. Repeat this for each analysis type.

Select **Window | Close All** from the menu bar, followed by **File | Save Project**.

5. To restart the simulation with shear

In the Project Explorer, double-click on the **MD_simpletut_run MesoDyn Dynamics/MD_simpletut_run - Calculation** file.

This opens MesoDyn Calculation dialog. Note that the *Restart* checkbox is inactive. This function becomes active when an output file is the current document.

In the Project Explorer, double-click on **MD_simpletut_run.MesoDyn_out**.

Now the *Restart* checkbox is active.

Check the **Restart** checkbox on the MesoDyn Calculation dialog.

Several of the parameters on the MesoDyn Calculation dialog are now inactive. These are variables that cannot be altered in a restarted run.

Select the **Species** tab.

The bead definitions and molecular architecture of the system are fixed for the entire simulation, and the controls are grayed out, prohibiting modifications.

Select the **Interactions** tab.

Modifications to the repulsions are allowed, however leave all the settings on this tab as they are for this tutorial. Note that charges can be added to some of the beads at this stage, by checking *Use electrostatics* and selecting **Donnan** from the *Electrostatic method* dropdown list.

Select the **System** tab.

Most of the controls on this tab are inactive in *Restart* mode. A mask cannot be introduced in the middle of a run, however, if one had been defined at the start, it could be modified now. Temperature and shear options can be modified at this time.

Check the **Shear rate** checkbox, and input a rate of **0.001** 1/ns.

Select the **Setup** tab.

The value of *Number of steps* indicates how many steps (of length *Time step*) should be run beginning from the current configuration. Thus this number can be left unmodified or even decreased.

Leave the **Number of steps** set to **500**. Set **Frame every** to **100** steps. Set **Restart file every** to **500** steps.

Check that the estimated results folder is not too large (compare with your available disk space).

Click the **Restart** button. Wait for the restarted job to finish before continuing.

Output files are listed in the Project Explorer under the folder *MD_simpletut_run MesoDyn Dynamics/MD_simpletut_run MesoDyn Dynamics*. These files are much the same as those generated in the earlier run, however, the effect of the shear should be apparent. Note, for example, the initial decrease in order parameter as the shearing acts to mix the system.

The mesoscale trajectory document, *MD_simpletut_run.mtd*, contains structural information which, when compared with the results of the previous calculation, indicate the effect of the shear. Very clear lamellar order has developed under shear.

Complete the analysis by creating an isosurface of the A density field, to confirm the apparent lamellar structure.

Open the **Choose Fields To Isosurface** dialog, select **A Density**, and click the **OK** button.

This creates a surface linking the points where the A field falls to around half its maximum density. This is a reasonable approximation to the dividing surface in the system, and demonstrates clear lamellar order.

You can delete the files generated during this tutorial.

This is the end of the tutorial.

Obtaining input parameters for MesoDyn

Purpose: To demonstrate the necessary steps to obtain input parameters for a MesoDyn calculation of a real system.

Modules: Materials Visualizer, MesoDyn

Time: 

Prerequisites: None

Background

The strength of MesoDyn is that full simulations are performed on systems in which the chemical nature of the species is included. The chemistry of the system is imparted through the molecular architecture and the bead-bead repulsions. This tutorial explores the steps required to perform these calculations in the Materials Studio environment. It should be noted that there are other ways to determine these parameters, some involving other simulation tools, others involving experimental data. Finally, it is recognized that alternative methods of parameterizing the simulation are not necessarily inferior in their predictive power.

Introduction

The goal of this tutorial is to determine MesoDyn input parameters for a system of a binary mixture of SEBS in polypropylene. SEBS is a triblock copolymer with polystyrene extremes and a copolymer of ethylene and butylene in the interior. The blocks are incompatible and phase separation is known to occur. The phase diagram of SEBS in polypropylene shows a variety of phases as a function of composition. The length of the individual blocks in SEBS varies from sample to sample, and you will assume block lengths at your convenience. The polypropylene in question has a molecular weight distribution centered around $M_p = 20000$, and this value will be taken as the polymer weight. Time will not permit simulation of all the input parameters, so some will be provided.

This tutorial covers:

- [Calculating Flory-Huggins parameters for binary mixtures](#)
- [Converting Flory-Huggins parameters into MesoDyn inputs](#)
- [To simulate SEBS in a polypropylene matrix](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Calculating Flory-Huggins parameters for binary mixtures

There are three chemically distinct chemical units in this simulation: polystyrene, polypropylene, and the random copolymer of ethylene and butylene that makes up the central portion of the SEBS molecule. The Flory-Huggins interaction parameters must be obtained for each pair of these, that is PS-PP, PS-EB, PP-EB (where PS is polystyrene, PP is polypropylene, and EB is a random copolymer of ethylene and butylene).

The solubility parameters can be obtained experimentally, by using quantitative structure property relationship (QSPR) methods (such as those available in the Synthia module), or from atomistic simulations.

Solubility parameters for the various components of the system, generated using QSPR methods with Synthia, are given in the table below:

Species	van Krevelen Solubility Parameter (J/cm ³) ^{1/2}
PS	19.52
PP	16.06
PE	16.80
PB	16.34
EB	16.49

The solubility parameters can be used to derive Flory-Huggins interaction values using:

$$\chi = \frac{V_{ref}(\delta_i - \delta_j)^2}{RT}$$

Where V_{ref} is a reference volume, taken to be the molar volume of one of the monomers (actually the mean volume of the two monomers).

The chain lengths are determined from the degrees of polymerization and the characteristic ratios of the polymers. According to the [Polymer Handbook](#), polypropylene has a characteristic ratio of 6.7. The following characteristic ratios are used in this tutorial:

Species	C _n
PS	9.9
PP	6.7
EB	7.32

The following molar volumes at 298 K, from Synthia, are used:

Species	Molar Volume (cm ³ /mol)
PS	96.98
PP	49.04
EB	48.89

These parameters are given for the homopolymers in [Bicerano's Prediction of Polymer Properties](#), and for the copolymer they are obtained using Quantitative Structure Property Relationships (QSPR), using the Synthia module.

Using the above data (and taking arithmetic means of the molar volumes as the input to the equation for the FH parameter) you can obtain a table of Flory-Huggins parameters for pairs of species in the system:

Species	PS	PP	EB
PS	0	0.35	0.270
PP	0.35	0	0.004
EB	0.270	0.004	0

Converting these parameters into MesoDyn input is covered in the [next section](#).

The expression for the MesoDyn chain length (N_{Meso}) is:

$$N_{meso} = \frac{M_p}{M_m C_n}$$

Where:

M_p is the polymer molecular weight

M_m is the monomer weight

C_n is the characteristic ratio

Hence you should use a chain for PP of $20000/(42 \times 6.7) \sim 71$.

This is just about as long a chain as you should use routinely. However, if this calculation results in a chain of more than 100 MesoDyn beads, all is not lost. You can rescale the parameters, by increasing the interaction parameter by the same factor that you reduce the chain length (so that $\chi \times N$ remains constant).

The chain lengths in the SEBS are arbitrary. Choose 10 beads in the styrene blocks and 20 in the central ethylene/butylene segment. Again if the chain lengths are known experimentally, characteristic ratios (from experimental, QSPR, or RIS/RMMC calculations) should be used to determine N_{Meso} .

2. Converting Flory-Huggins parameters into MesoDyn inputs

The MesoDyn input parameter is related to the Flory-Huggins parameter through:

$$\nu^{-1} \epsilon_{IJ} = \chi_{IJ} RT$$

where $\nu^{-1} E_{IJ}$ is the input parameter.

Using the above expression you obtain the following table of MesoDyn input repulsions for pairs of species in the system (in kJ/mol):

Species	PS	PP	EB
PS	0.0	0.867	0.669
PP	0.867	0.0	0.010
EB	0.669	0.010	0.0

3. To simulate SEBS in a polypropylene matrix

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MD_input** as the project name, click the **OK** button.

The new project is created with *MD_input* listed in the Project Explorer.

Select **Modules | MesoDyn | Calculation** from the menu bar to open the MesoDyn Calculation dialog. Select the **Species** tab.

Each chemical species present and the connectivity of the molecules are specified on the *Species* tab.

In the **Bead types** text box enter: **PS** as A, **PP** as B, and **EB** as C. In the **Mesoscale molecules types** text box enter: **Polypropylene - PP 71** and **SEBS - PS 10 EB 20 PS 10**.

An interaction parameter must be input for each pair of species. This is accomplished on the *Interactions* tab.

On the **Interactions** tab enter the MesoDyn repulsions parameters as follows:

Species	PS (A)	PP (B)	EB (C)
PS (A)	0.00	0.867	0.669
PP (B)	0.867	0.00	0.010
EB (C)	0.669	0.010	0.00

Check the input parameters carefully before launching the simulation.

On the **System** tab ensure that the **Grid dimensions** are **16×16×16**. Ensure that the **Relative Amount** is set to **1** (the default) for both molecules. Set the **Temperature** to **298 K**.

On the **Setup** tab set the **Number of Steps** to **500**, save a **Frame every 50** steps, and set the **Restart file** to be created after **500** steps.

Note: These runs are much shorter than typical simulations. Run lengths in thousands of time steps are still considered quite short. It is prudent to check the hardware demands of the calculation before launching a full production run. The equilibration of the system can be inferred from the evolution of the free energy.

On the **Job Control** tab choose the server on which you will run the simulation. Uncheck the **Automatic** checkbox and enter **SEBS+PP** as the **Job description**. Set the live updates to **Update progress graphs every 50** steps.

Note: Generally you would turn off live updates for a full simulation, since there is a non-negligible overhead associated with this step.

Click the **Run** button.

When the run completes you may analyze the results using the usual tools. When you have finished, you can remove all the files created by this tutorial.

This is the end of the tutorial.

References

Bicerano. J. *Prediction of Polymer Properties*, 2nd Edition, Marcel Dekker: New York (1996).

Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd Edition, John Wiley & Sons Inc.: New York (1989).

Using explicit charges and salt solutions

Purpose: To introduce the MesoDyn electrostatics using the Donnan approximation.

Modules: Materials Visualizer, MesoDyn

Time: 

Prerequisites: [Running a simple MesoDyn simulation](#)

Background

MesoDyn in Materials Studio allows you the explicit use of charges with the Donnan approximation. This tutorial demonstrates how to input charges and run a simulation with electrostatics, and compare the results with a similar result using uncharged systems.

Introduction

The lack of direct inclusion of electrostatics in MesoDyn has often been considered a major limitation of the method. Full implementation of Poisson-Boltzmann charges requires some account of the long-ranged potentials, which would significantly reduce computational efficiency. As a first the ideas of Donnan are used, these ignore the long-ranged interaction by assuming perfect screening. With this approximation in place real charges can be assigned to the beads and the effect of charges on phase behavior can be simulated.

This tutorial covers:

- [Getting started](#)
- [To compare charged and non-charged systems](#)
- [To vary other parameters](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Charges can be used in MesoDyn by checking the checkbox on the *Interactions* tab, and assigning charges to each species. Under the limitations of the Donnan theory, the charged particles are assumed to reside in a salt solution. The strength of the salt solution can be specified on the *Interactions* tab.

It must also be determined whether the input interaction parameters should be changed so that they no longer include electrostatic interactions. In general if a bead has a net charge (even in a strongly polar system most beads will average to neutral) its interactions should include all contributions. However, if two species are to be treated as charged, then it is realistic to calculate χ in the absence of electrostatics.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MD_salt** as the project name, click the **OK** button.

The new project is created with **MD_salt** listed in the Project Explorer.

2. To compare charged and non-charged systems

For this tutorial you will perform two calculations on the same system, one with and one without charges.

Click the MesoDyn button  on the **Modules** toolbar and select **Calculation** to open the MesoDyn Calculation dialog. Change the **Number of steps** to **400**.

Next, indicate that the terminal groups of the diblock are different species.

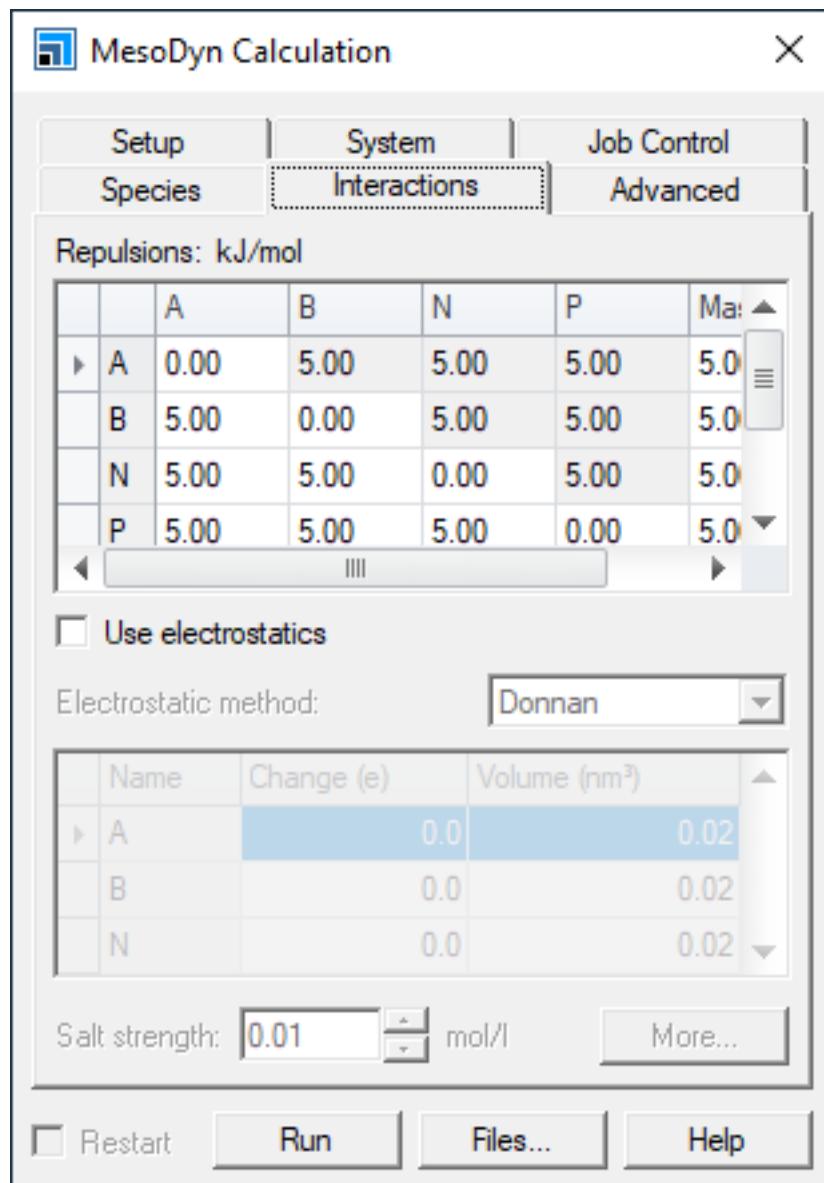
Select the **Species** tab and replace the A 4 B 4 topology with **P 1 A 3 B 3 N 1**.

A message prompts you to add the unknown beads to the **Bead types** table. Click the **Yes** button for both the P and N beads.

The interactions of P and A, and B and N, must be identical so the system behaves like a true diblock.

Select the **Interactions** tab.

The first calculation will use no charges.



MesoDyn Calculation dialog - Interactions tab with A, B, P and N beads defined

Complete the **Repulsions** grid as follows:

	A	B	P	N
A	0.0	5.0	0.0	5.0
B	5.0	0.0	5.0	0.0
P	0.0	5.0	0.0	5.0
N	5.0	0.0	5.0	0.0

On the **Job Control** tab uncheck the **Automatic** checkbox and enter **no_electrostatics** as the **Job description**. Click the **Run** button.

When the job is complete you will run the same system again, but this time including a charge on the terminal beads of the diblock.

On the **Interactions** tab check the **Use electrostatics** checkbox and ensure that **Donnan** is selected as the **Electrostatic method**. Assign a **Charge** of **0.5** to bead **P**, and **-0.5** to bead **N**.

On the **Job Control** tab, change the **Job description** to **with_electrostatics** and click the **Run** button.

Wait for the job to complete. The job takes significantly longer when charges are specified.

When the job is completed, compare the structures side by side. It is useful to color the P and A fields green, and the B and N fields red.

Click the **Volumetric Selection** button  on the **Volume Visualization** toolbar to open the Volumetric Selection dialog. Select the **A Density** field so that it is highlighted in blue on the dialog.

Right-click in **no_electrostatics MesoDyn Dynamics\no_electrostatics.mtd** and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Field tab** change the color of the **A Density** field to **green**. On the **Volumetric Selection** dialog select the **P Density** field and change its color to **green** also.

Repeat these steps for the **B** and **N** density fields, changing their color to **red**.

Repeat this procedure to similarly color the density fields in **with_electrostatics MesoDyn Dynamic/with_electrostatics.mtd**.

The comparison of this view for the case with and without electrostatics may not be entirely convincing. A more dramatic effect is noted in the order parameters and free energy graphs.

In the **Project Explorer**, locate the MesoDyn results folders for these two calculations. Each folder should contain two graphs called **FreeEnergy .xcd** and **OrderParameters .xcd**. Double-click on the chart documents in the Project Explorer.

Comparing the **OrderParameter** graphs from the two simulations clearly shows that the non-charged system is more strongly segregated.

The obvious conclusion is that the oppositely charged end-groups are interpenetrating the lamellae leading to a more diffuse phase boundary and potentially a more complex morphology.

3. To vary other parameters

If numerical stability problems occur when using charges, techniques similar to those used in pseudo-dynamics may be tried:

Time step - Reducing the time step is often the best way to increase the numerical stability of a calculation. The **Time step** parameter is found on the **Setup** tab.

Compressibility - The compressibility, which more accurately would be described as the incompressibility of the fluid, may be altered to improve numerical stability. The **Compressibility** parameter is found on the **Advanced** tab.

Solver tolerance - It may be necessary to use a value for solver tolerance that is lower than the specified default value. In general, a value leading to 5-20 iterations per time step should be used. The *Solver tolerance* parameter is found on the *Advanced* tab.

Max. iterations - Increasing the maximum number of iterations may improve numerical stability but should be used as a last resort. The *Max. iterations* parameter is found on the *Advanced* tab.

Max. line searches - Similarly the number of line searches should only be increased if all else fails. The *Max. line searches* parameter is found on the *Advanced* tab.

Noise parameter - A lower value implies more noise. Increasing the noise, by decreasing this value, may allow the system to escape from numerical traps. The *Noise* parameter is found on the *Advanced* tab.

Salt strength - For charged systems the salt strength is used to screen the charges, and must be large for the Donnan approximation to be valid. Increasing the value from the default may aid numerical stability. The *Salt strength* parameter is found on the *Interactions* tab.

You can delete the files generated during this tutorial.

This is the end of the tutorial.

Using pseudodynamics

Purpose: To introduce the use of using the potential-field only solve space. To highlight best operating practices for successful implementation.

Modules: Materials Visualizer, MesoDyn

Time: 

Prerequisites: None

Background

The significant computational demands of MesoDyn create a pressing need for shortcuts. The heart of the dynamics algorithm is the update of the potential fields at given time step, followed by a corresponding update of density fields at the next half time step. The updating of one field as a result of the other's new value is the rate determining step of the simulation.

Fraaije's group examined the possibility of updating only the potential fields and creating density fields solely upon user-request ([Maurits, 1998](#)). The algorithm was proved to give results identical to the full algorithm but with a 10-fold increase in the number of time steps that could be performed in the same amount of CPU time. It was, however, noted that the system became less stable numerically, leading to a necessary reduction in dynamics time step of around 50%. Nevertheless a 5-fold reduction in CPU requirements is most welcome.

Introduction

This tutorial demonstrates setting up a simulation with the fast pseudo-dynamics option selected, and the consequent changes that are made to other input options in order to best guarantee numerical stability and results accuracy. You will view results in the form of 2D and 3D graphics

This tutorial covers:

- [Getting started](#)
- [To set up a MesoDyn calculation with fast pseudo-dynamics](#)
- [To vary other parameters](#)
- [Best practices for using pseudo-dynamics](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **MD_pseudodyn** as the project name, click the **OK** button.

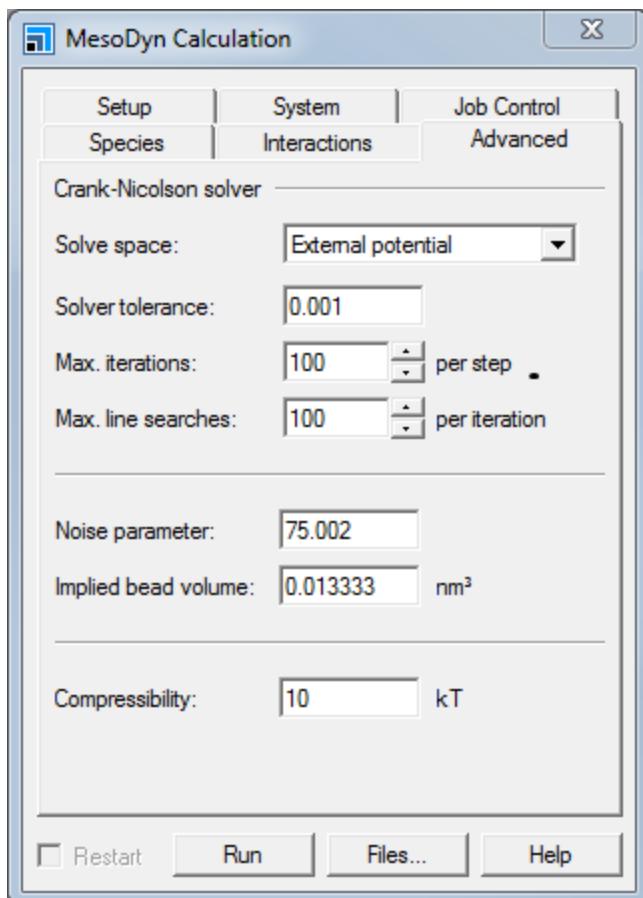
The new project is created with *MD_pseudodyn* listed in the Project Explorer.

2. To set up a MesoDyn calculation with fast pseudo-dynamics

To select the fast pseudo-dynamics option it is necessary to use an external potential for the solve space.

Click the MesoDyn button  on the **Modules** toolbar and select **Calculation** to open the MesoDyn Calculation dialog.

On the **Advanced** tab change the **Solve space** to **External potential**.



MesoDyn Calculation dialog - Advanced tab

You will change several parameters in order to improve numerical stability in the pseudo-dynamics calculation. It is advisable to reduce the time step to about half of its default value, and to double the run length.

On the **Setup** tab change the **Time step** to **25 ns**. Set **Number of steps** to **200**, and click the **Run** button.

Wait for the job to finish. Typically a calculation of this type takes about 75% as long as a traditional mixed density/potential integration scheme. While this may not seem particularly impressive, a comparison of the evolution of the system shows that the pseudo-dynamic run has progressed much further.

For comparison, run the system again, with the traditional potential and density field solver option. Double the time step and halve the number of steps, returning them to their default values.

On the **Setup** tab change the **Time step** to **50 ns**, and the **Number of steps** to **100**.

Return the Solve space to its original value.

On the **Advanced tab** and change the **Solve space** to **Mixed - density & potential**. Click the **Run** button, do not use the *Restart* option.

When the job has completed, compare the two sets of results. Visual inspection reveals little - both structures show broadly similar structures. However, comparison of the order parameter graphs shows that the pseudo-dynamics has moved the simulation considerably further than the standard solver option.

3. To vary other parameters

If numerical instabilities occur, try adjusting the following parameters.

Compressibility - The compressibility, which more accurately would be described as the incompressibility of the fluid, may be altered to improve numerical stability. Use lower values for compressibility when using pseudo-dynamics. The *Compressibility* parameter is found on the *Advanced* tab.

Solver tolerance - It may be necessary to use a value for solver tolerance that is lower than the specified default value. In general, a value leading to 5-20 iterations per time step should be used. The *Solver tolerance* parameter is found on the *Advanced* tab.

Max. iterations - Increasing the maximum number of iterations may improve numerical stability but should be used as a last resort. The *Max. iterations* parameter is found on the *Advanced* tab.

Noise parameter - A lower value implies more noise. Increasing the noise, and thus decreasing the value, may allow the system to escape from numerical traps. The *Noise* parameter is found on the *Advanced* tab.

4. Best practices for using pseudo-dynamics.

It is best to use the pseudo-dynamics in the equilibration stages of a simulation. This rapid algorithm allows a speedy approach to an equilibrium morphology. When the free energy and order parameter begin to asymptotically approach their equilibrium values, it is advisable to restart the job with the full potential and density field solver space.

This is the end of the tutorial.

References

Maurits, N. *Mathematical modeling of complex systems*, Ph.D. thesis, Rijksuniversiteit Groningen: Groningen (September 1998).

Chapter 16: Morphology tutorials

The following tutorials illustrate how to use Morphology's capabilities.

- [Morphology prediction for Pigment Red](#)
- [Calculating morphology using Crystal Graph](#)

Morphology prediction for Pigment Red

Purpose: Illustrates how to predict crystal morphology from the atomic structure of a crystal using Morphology

Modules: Materials Visualizer, Morphology, Forcite, COMPASS

Time:  

Prerequisites: Using the Crystal Builder Visualizer Tutorial

Background

Morphology allows you to predict crystal morphology from the atomic structure of a crystal. The bulk shape of crystals is critically important to many industrial processes. There are numerous examples of processes in the chemical and pharmaceutical industries where crystal shape is an important factor, including:

- Dissolution rate of chemicals and biological availability of drugs
- Handling, packaging, and storage of crystalline products
- Slurry handling, caking, and filtration during processing
- Milling, grinding, fragmentation, and dusting
- Density and texture optimization
- Wax and scale formation in petrochemicals

The relationship between the crystal morphology and the internal arrangement of atoms in the crystal is therefore of great interest to chemists, chemical engineers, and process engineers. Rationalization of this relationship allows the prediction of crystal shape, the development of tailor-made additives, and the control of solvent and impurity effects. Morphology's application areas include pharmaceuticals, agrochemicals, food sciences, petrochemicals, cements, and commodity and specialty chemicals.

Introduction

This tutorial demonstrates that computational chemistry methods offer a powerful means of deriving the morphology of a molecular crystal. They allow you to examine the molecular landscape of crystal faces using graphic visualization.

Pigment Red (a diphenyl derivative of 1,4-diketopyrrolo(3,4-c)pyrrole, DPP) is a high quality heterocyclic pigment, offering good heat stability, high coloring strength and hiding power, and excellent light and weather fastness. It can be produced as transparent or opaque color by controlling the particle size during manufacture.

To optimize certain physico-chemical properties, such as shade, it can be beneficial to change the morphology of the crystal from a plate-like habit to a more isometric shape.

This tutorial shows you how to determine the crystal morphology for Pigment Red using the Morphology module.

This tutorial covers:

- [Getting started](#)
- [To load and optimize the crystal structure of Pigment Red](#)
- [To set up and run Morphology](#)
- [To analyze the Morphology results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Pigment Red** as the project name, click **OK**.

This creates a new project with *Pigment Red* listed in the Project Explorer.

2. To load and optimize the crystal structure of Pigment Red

Select **File | Import...** from the menu bar to open the Import Document dialog. Navigate to and select **Structures\molecular-crystals\pigments\pigment_red.xsd**, click **Open**.

Now optimize the crystal structure of Pigment Red using Forcite and the COMPASS forcefield, first minimizing only the molecules, then including the cell.

On the **Modules** toolbar, click **Forcite**  and choose **Calculation** from the dropdown list to open the Forcite Calculation dialog. On the **Setup** tab, select **Geometry Optimization** from the **Task** dropdown list and for the **Quality** choose **Medium**.

On the **Energy** tab of the Forcite Calculation dialog, for the **Forcefield** select **COMPASSIII**. Choose **Ewald** for both the **Summation method** values.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click **More...** to open the Forcite Job Control Options dialog. Select the **Live updates** checkboxes for **structure**, **graphs**, and **textual results** and close the dialog.

Click **Run**.

This creates new folder called **pigment_red Forcite GeomOpt** in the Project Explorer. The calculation takes less than a minute to complete. When the calculation finishes, this saves the minimized structure as a **pigment_red.xsd** document in the new folder and displays it in the Materials Visualizer. Now include the cell parameters in a second minimization.

Ensure that the optimized structure is the active document. On the **Setup** tab of the Forcite Calculation dialog, click **More...** to open the Forcite Geometry Optimization dialog. Select the **Optimize cell** checkbox and close the dialog.

Click **Run** and close the dialog.

Compare the cell parameters of the minimized structure with those of the experimental structure to make sure that none of them have changed significantly. This indicates that the forcefield is adequate for the structure.

Note: Before starting a Morphology calculation, select an appropriate energy expression and verify that it describes the crystal geometry as well as the configurations of the molecules forming the crystal. Also, optimize the geometry of the input crystal structure using the same energy expression, including optimization of the cell parameters.

Tip: The COMPASS forcefield is parameterized with non-zero forcefield charges and uses the bond increment approach. Since charge assignments are part of the parameters stored in the forcefield definition, you can accept the default option to use forcefield-assigned charges instead of assigning specific charges manually.

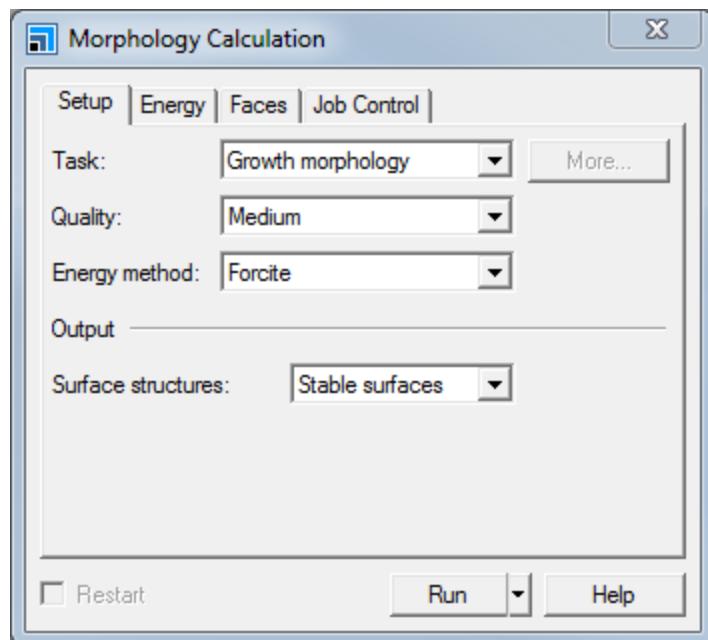
3. To set up and run Morphology

In this section, calculate the crystal morphology of Pigment Red by applying the growth morphology method in Morphology. The growth morphology algorithm assumes that the growth rate of a crystal face is proportional to its attachment energy (the potential energy released on attachment of a growth slice to a growing crystal surface in a vacuum). This method attempts to simulate crystal habits obtained under non-equilibrium growth conditions.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **pigment_red.xsd** in the **pigment_red** **Forcite GeomOpt/pigment_red** **Forcite GeomOpt** folder.

Click **Morphology**  and choose **Calculation** from the dropdown list to open the Morphology Calculation dialog.

On the **Setup** tab, change the **Task** to **Growth morphology**. For the **Quality**, select **Medium** and for the **Energy method** select **Forcite**.



Morphology Calculation dialog, Setup tab

Morphology: Morphology prediction for Pigment Red

The *Quality* option offers a fast, single-click method of choosing all the parameters that control the simulation speed and accuracy. In a real-life situation, use the **Fine** or **Ultra-fine** options. For this tutorial, use the *Quality* level of **Medium** so that the calculation does not take too long.

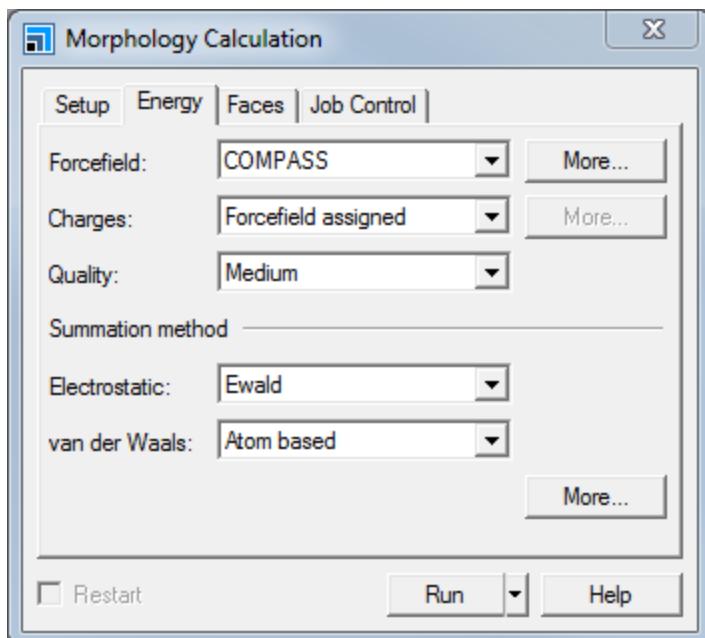
The *Energy method* control allows you to select the source of the energy expression to use for the Morphology calculations. The **Forcite** option uses the Forcite energy server to compute interaction energies according to the options on the *Energy* tab.

On the **Setup** tab, select **Stable surfaces** for **Surface structures**.

This option defines the parameters determining which surfaces to report and whether to produce surface structure documents for the reported surfaces as part of growth morphology and equilibrium morphology calculations. The **Stable surfaces** option reports data only for the most stable surface for each face and generates surface structure documents for the reported surfaces.

On the **Energy** tab, change the **Forcefield** to **COMPASSIII**.

The *Quality* remains **Medium**, as specified on the *Setup* tab earlier.

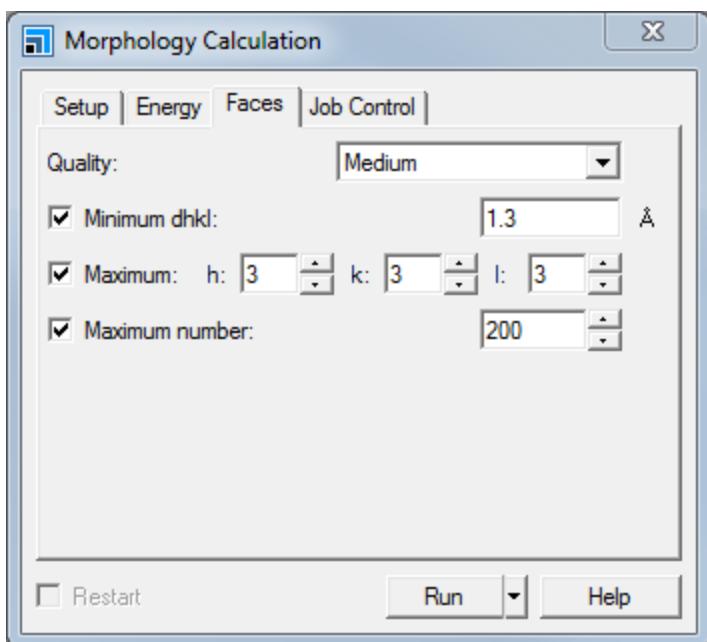


Morphology Calculation dialog, Energy tab

Note: For forcefields that include their own charges, such as COMPASS, cvff, and pcff, the default is to use the **Forcefield assigned** charges. For the other forcefields, such as Dreiding and Universal, the default is **Use current** charges assigned to the input model. In these cases, ensure that you use the same charges for all Morphology runs and that they are the same as those in the input optimized crystal structure.

Note: The *Quality* controls here and on the *Faces* tab propagate from the quality level selected for the overall calculation on the *Setup* tab. As a result, altering these other *Quality* controls results in a **Customized** quality level for the overall calculation.

On the **Faces** tab, make sure that the **Quality** remains **Medium**.



Morphology Calculation dialog, Faces tab

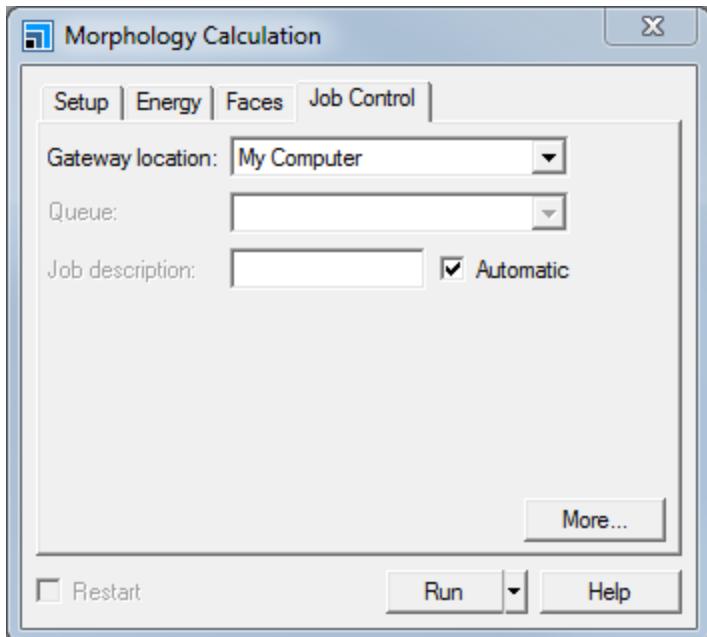
Note: Typically, increasing the *Quality* for a calculation increases the computation time. It is usually sufficient to use a [Coarse](#) or [Medium](#) to ensure that the calculation includes all of the growth faces that build the crystal habit.

The *Quality* controls the extent of the list of growth faces produced by a Morphology calculation. Three variables control the face list generation:

- *Minimum dhkl* - the minimum interplanar spacing for faces appearing on the face list.
- *Maximum h, k, l* - the absolute values of the Miller indices of faces appearing on the face list must be less than or equal to these specified values.
- *Maximum number* - the maximum number of faces to appear on the face list. Face list generation ceases when this number of faces are added to the face list, even if faces that satisfy the other criteria remain.

Note: According to the Donnay-Harker rules, only higher orders of some Miller indices may appear on the morphology surface. In such cases, if the original Miller index satisfies the *Maximum h, k, l* criteria, this adds the relevant higher order Miller index to the list, even if the higher order index violates these criteria.

On the **Job Control** tab, select **My Computer** as the **Gateway location**.



Morphology Calculation dialog, Job Control tab

Click **Run** on the Morphology Calculation dialog and close the dialog and the **pigment_red.xsd** 3D Viewer.

The Job Explorer informs you about the progress of the calculation. After some time, this displays a text document, **Status .txt**, updated regularly as the job progresses. **Status .txt** informs you about:

- The task being performed, for example a growth morphology calculation.
- The total number of growth faces and the number of processed faces.
- Properties for a list of the most recent processed growth faces, including Miller indices, multiplicity, D_{hkl} , attachment energy, and center-to-plane distance.

When the calculation starts, it creates a new folder called **pigment_red Mph Growth** in the Project Explorer. The job saves its parameters automatically, in a file called **pigment_red - Calculation**. The job also creates a second text file in the new folder, **pigment_red .txt**, but this does not open in the Materials Visualizer. Initially, **pigment_red .txt** contains all of the calculation parameters, with updates for any non-fatal errors that occur during the calculation.

Wait until the job finishes before proceeding.

4. To analyze the Morphology results

In this section, analyze the output from the Morphology run.

When the calculation is finished, this displays two documents automatically:

- Morphology report file, **pigment_red .txt**, containing the values of all the input parameters for the calculation.
- A short summary of the calculation results.

Note: It is important to review this file for warnings about unstable surfaces. If the calculation finds unstable surfaces, it continues with the next face. In most cases, unstable surfaces are a result of the crystal structure not being optimized using the current energy parameters. To prevent this, optimize the geometry of the crystal structure as part of the structure preparation step, using the same energy parameters as those used for the Morphology calculation.

Usually the report does not contain any warning messages.

Close **pigment_red.txt**.

The main outputs of a Morphology calculation are:

- A 3D Atomistic document (called the crystal habit document), **pigment_red.xsd**, containing the unit cell of the input crystal structure overlaid with a projection of the calculated crystal habit.
- A study table document, **pigment_red.std**, providing a detailed list of properties for each growth face.

Then the calculation finishes, this automatically displays the **pigment_red.xsd** crystal habit document in the Materials Visualizer, and adds **pigment_red.std** to the Project Explorer.

Examine the crystal habit document first.

Close **Status.txt** and make **pigment_red.xsd** the active document. Examine the habit document using the tools on the **3D Viewer** toolbar.

You can control the relative scaling of the habit data with respect to the atomistic data, since these two groups of data have different coordinate systems.

Right-click in **pigment_red.xsd** and choose **Display Style** from the shortcut menu to open the Display Style dialog.

On the **Habit** tab, change the **Habit size** to **0.500**, then press **TAB** Repeat this for a **Habit size** of **1.000**. Alternatively, use the spin controls to change the relative scaling of the two objects.

The larger the *Habit size*, the larger the size of the calculated crystal habit relative to the input crystal structure.

Move the **Transparency** slider from left to right before changing it back to the default midpoint position.

The transparency of the habit facets changes from completely opaque (solid) when the slider bar is in its leftmost position to fully transparent (invisible) when in its rightmost position.

Clear the selection of the **Show facets** checkbox and then select it again.

This option allows you to switch on and off display of the facets of the crystal habit. Selecting one or more facets and then clearing the *Show facets* checkbox enables you to switch off the display of particular facets.

To make the crystal habit easier to see, you can switch off the display of the crystal structure.

On the **Lattice** tab, change the **Style** to **None** in the **Display style** section. Close the Display Style dialog.

The crystal habit representation contains two important types of objects - growth faces and habit facets:

Morphology: Morphology prediction for Pigment Red

- Growth faces - represent all slow growing crystal faces included in the Morphology calculation. They are placed at distances from the growth origin equivalent to the calculated center-to-plane distances. Growth faces representation uses arrows normal to the respective planes, with their bases on the planes, not visible by default.
- Habit facets - form the external shape of the crystal. The habit is built from growth faces that enclose the smallest volume around the growth origin. Each habit facet is associated with a growth face. However, the reverse is not necessarily true. Habit facets representation uses solid planes, visible by default.

Right-click in **pigment_red.xsd** and choose **Label** from the shortcut menu to open the Label dialog.

Select **Habit Facet** from the **Object type** dropdown list and choose **FacetMillerIndex** from the **Properties** list. Click **Apply** and close the dialog.

This labels the habit facets with their Miller indices.

Open the **Morphology Calculation** dialog. On the **Setup** tab, change the **Task to Report habit properties**. Click **Run** and close the dialog.

This creates a grid document, **pigment_red.xgd**, summarizing important habit properties in tabular form, in the **Pigment_red Mph Growth** folder. The grid document contains three tabs:

- *Summary* - contains important habit properties, including the point group, aspect ratio (the ratio between the longest and the shortest diameter), surface area, volume, number of symmetrically unique facets, and the total number of facets of the habit.
- *Facets* - lists all the symmetrically unique facets of the habit and reports:
 - the Miller indices representing one of the symmetry-related facets
 - the symmetry multiplicity of the facet
 - the center-to-plane distance
 - the area and percentage area of a single facet
 - the total area and total percentage area of all symmetry-related facets.
- *Angles* - lists the interplanar angles between facets.

Tip: You can export the grid document as a **.CSV** file, compatible spreadsheet applications such as Microsoft Excel.

Review the calculated crystal morphology of Pigment Red, the slowest growing **(0 0 1)** face accounts for more than 70% of the crystal surface. The aspect ratio suggests a plate-like morphology. Inhibition of the growth of the fast growing **(0 1 0)** and **(1 -1 0)** faces might lead to a more isometric crystal morphology.

Close **pigment_red.xgd**, click **Yes** when prompted to save the file.

Make **pigment_red.xsd** the active document. Select the **(0 1 0)** face of the habit. Open the **Display Style** dialog.

On the **Habit** tab, click the **Facet color** control to display the color chooser and select a color. Click once in **pigment_red.xsd** to clear the selection of everything.

Repeat the same procedure for the **(1 -1 0)** face of the habit.

Note: Coloring growth faces does not respect symmetry, so you can color symmetry-related faces individually.

Hold down **SHIFT** and click the **(0 1 0)** face and then the **(1 -1 0)** face of the habit.

This colors the **(0 1 0)** and **(1 -1 0)** faces, indicating that they are selected.

On the **Habit** tab of the Display Style dialog, select the **Show growth faces** checkbox.

This adds representations of the **(0 1 0)** and **(1 -1 0)** growth faces as arrows normal to the growth planes, with their bases on the planes.

Define the **Arrow size** in the **Display style** section as **0.35** and close the dialog.

The **Size** controls the relative size of the arrows representing the growth faces and has a default value of **0.10**.

Note: The *Show facets*, *Show growth faces*, and *Size* controls all respect the symmetry of the system. So, if one facet or growth face has its visibility altered by these controls, this affects all the symmetrically equivalent facets or growth faces in the same way.

Click in the background to clear the selection of all the faces, then select one of the growth face arrows. Hold down the **SHIFT** and **ALT** keys and right-click. Drag the mouse from right to left, then upward to change the center-to-plane distance (growth rate).

As you move the object, this automatically updates the habit. If you move a habit facet and increase the center-to-plane distance to a point where it stops being part of the habit, the facet object disappears. Similarly, reducing the center-to-plane distance (growth rate) of a growth face, such that it becomes part of the habit, automatically creates a habit facet and associates it with the growth face.

Continue to manipulate the center-to-plane distances for the **(0 1 0)** and **(1 -1 0)** faces until you obtain a more isometric morphology. Now find the new center-to-plane distances for the growth faces in the modified crystal habit.

Open the **Morphology Calculation** dialog. On the **Setup** tab, for the **Task** select **Report habit properties**. Click the **Run** and close the dialog.

This creates a new grid file, **pigment_red (2).xgd**, in the **pigment_red Mph Growth** folder.

Close **pigment_red.xsd** and click **No** when prompted to save the file.

In the Project Explorer, double-click **pigment_red.xgd** in the **pigment_red Mph Growth** folder. Select **Window | Tile Vertically** from the menu bar so that you can see both of the grid documents.

On the **Facets** tabs, compare the **Distance** for **(0 1 0)** and **(1 -1 0)** in **pigment_red.xgd** and **pigment_red (2).xgd**.

Repeat the same procedure for other growth faces of interest. After examining the crystal habit document, analyze the surface properties for each growth plane in the study table document.

Select **File | Save Project** from the menu bar and then **Window | Close All**. In the Project Explorer, double-click **pigment_red.std** in the **pigment_red Mph Growth** folder.

Morphology: Morphology prediction for Pigment Red

The study table provides a detailed tabular view of properties for each growth face, as calculated during the Morphology run, including:

- Miller indices
- multiplicity
- interplanar spacing
- surface area
- atomistic surface structures
- attachment energy (*Eatt*) and its non-bond components
- center-to-plane distance
- total facet area
- percentage total facet area.

In addition to making simple changes to the crystal habit document to study the dependence of the morphology on growth rate interactively, you can achieve the same effect by manually editing the center-to-plane distances in the study table.

Click column header **F** to select the column. Hold down **SHIFT**, and select columns **G**, **H**, and **I**. Right-click the header of one of the selected columns in **pigment_red.std** and choose **Hide** from the shortcut menu.

You can now see the Miller indices, atomistic surface structures, and the center-to-plane distances for each growth face in one view.

Double-click the **Distance** corresponding to the (0 1 0) face and change it to **10**, then press **TAB**. Repeat the same procedure for the (1 -1 0) face.

Click column header **A** to select the column. Hold down **CTRL** and click the header of column **J**.

Open the **Morphology Calculation** dialog, change the **Task** to **Generate habit**. Click **Run** and close the dialog.

This gives a more isometric crystal habit.

Tip: The study table infrastructure provides extensive functionality that enables you to sort, filter, process, and plot data, and to calculate additional properties.

Make the new **pigment_red.xsd** the active document and select **File | Save As...** from the menu bar to open the Save As dialog. Enter **pigment_red_isometric** and click **Save**.

Select **Window | Close All** from the menu bar. Click **No to All** when prompted to save the changes.

This embeds the atomistic surface models in the study table, you can also view them independently. Examine the (0 1 0) surface.

In the Project Explorer, double-click **pigment_red.std** to open the study table. Double-click **Surface (0 1 0)** in column **E** to display a Study Table Detail View of the (0 1 0) surface.

You can now examine the surface in detail. At this stage, it would be useful to increase the thickness of the surface model.

Select **Build | Surfaces | Recleave Surface** from the menu bar to display the Recleave Surface dialog. On the **Surface Box** tab, increase the **Thickness** to **3.0** in the **Fractional** column. Close the dialog.

This re-cleaves the surface.

Note: The recleave functionality cleaves the new surface from the crystal structure document **pigment_red.xsd** situated in the results folder of the Morphology calculation. If you turned off [lattice visibility](#) in the crystal habit document to better investigate the habit, turn it on again.

Otherwise, all the objects in the surface structure are invisible. You can make the lattice visible again by changing the **Style** back to **Default** on the *Lattice* tab of the Display Style dialog.

Copy the entire document by clicking **Copy** . In the Project Explorer, right-click the project **Pigment Red** and choose **New | 3D Atomistic Document** from the shortcut menu. Paste the structure into the empty document using **Paste** . In the Project Explorer, right-click **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Change the name of the document to **pigment_red_010.xsd**.

Close **pigment_red Detail View: E2 (Surface (0 1 0))**.

This displays a dialog asking if you want to commit the edits made to the study table.

Click **No** when prompted to save the changes.

Repeat the same procedure for **pigment_red.std**, then select **File | Save Project** from the menu bar.

Note: If you modify any surface and commit the change to the study table, the changes are permanent.

An additive can interact with the fast growing (0 1 0) faces, acting as a growth inhibitor for these faces. Slowing down the growth rate of the (0 1 0) faces could result in the Pigment Red crystals developing a more isometric morphology. You need the attachment energy of the growth face for comparison to such a calculation.

Open **pigment_red.std** and find the value of **Eatt(Total)** in column **F** for the (0 1 0) face.

You can study interactions between the Pigment Red (0 1 0) surface and the inhibitor through dynamics simulation. This is described in the [Modeling inhibitor adsorption onto a Pigment Red crystal face](#) Adsorption Locator tutorial.

This is the end of the tutorial.

Calculating morphology using Crystal Graph

Purpose: Illustrates how to use crystal graph to identify interactions between molecular fragments in a crystal.

Modules: Materials Visualizer, Morphology, COMPASS

Time:  

Prerequisites: [Morphology prediction for Pigment Red](#)

Introduction

Pigment Red (a diphenyl derivative of 1,4-diketopyrrolo(3,4-c)pyrrole, DPP) is a high-quality heterocyclic pigment, offering good heat stability, high coloring strength and hiding power, and excellent light and weather fastness. It is produced as either transparent or opaque color by controlling the particle size during manufacture.

Instead of performing an energy calculation as part of the Morphology calculation, you can use the Crystal Graph functionality to identify interactions between molecular fragments in a crystal. You can then calculate the bond energies for all these interactions and use them as input for growth morphology or equilibrium morphology calculations to determine the crystal's habit.

The Hartman-Perdok theory ([Hartman-Perdok, 1955](#); [Bennema, 1996](#); [Grimbergen et al., 1998](#)) starts from the concept that crystals are stable because molecular fragments can form strong attractive intermolecular interactions. A crystal graph describes interactions between molecular fragments in a crystal structure. This enables you to explore the effect of intermolecular interaction strength on crystal morphology.

This tutorial covers:

- [Getting started](#)
- [To set up and run Crystal Graph](#)
- [To analyze the Crystal Graph results](#)
- [To calculate morphology using the Crystal Graph outputs](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Pigment Red CG** as the project name, click **OK**.

This creates a new project with *Pigment Red CG* listed in the Project Explorer. Now, import the input file to study.

In the Project Explorer, right-click the project root and select **Import...** to open the Import Document dialog. Navigate to the location where you saved the **Pigment Red** project in [Morphology prediction for Pigment Red](#). Open **Pigment Red Files\Documents\pigment_red** **Forcite GeomOpt\pigment_red** **Forcite GeomOpt\pigment_red Mph Growth\pigment_red.xsd** and click **OK**.

Right-click **pigment_red.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Enter **pigment_red_input** as the name and press **ENTER**.

Save the project.

Select **File | Save Project** from the menu bar.

2. To set up and run Crystal Graph

Click **Morphology**  on the toolbar and choose **Crystal Graph** from the dropdown list to open the Crystal Graph Calculation dialog.

On the **Setup** tab, for the **Forcefield** select **COMPASSIII**, for **Charges** select **Forcefield assigned**, and for the **Quality** select **Medium**.

Note: It is important that you use the same energy settings for the Crystal Graph calculation as you used to optimize the crystal structure. So, the energy settings (forcefield and preparation options) are linked to the corresponding settings on the Morphology Calculation dialog. The *Quality* setting is not linked, because Crystal Graph does not need a cutoff when it does its energy calculation, so the energy *Quality* setting is not relevant. The Crystal Graph *Quality* relates solely to Crystal Graph calculation parameters, such as Maximum unit cell separation.

Make sure the **Assign molecules automatically** checkbox is selected.

Enabling this option automatically assigns all the atoms in the crystal structure to molecules.

Tip: Alternatively, to define molecules manually, use the tools on the **Molecules** tab of the Crystal Graph Calculation dialog to group manually selected atoms in the crystal structure into molecules.

Note: When you choose to automatically assign molecules, all the atoms in a covalently bonded fragment comprise a molecule. This assigns individual atoms in, for example, an ionic structure as separate molecules. These are the only two possibilities recognized.

When you are manually assigning molecules, the only recognizable selection is either an entire covalently bonded fragment or individual atoms that do not have any covalent bonds to other atoms, for example elemental metals. You cannot create a molecule from part of a molecular fragment or from multiple atoms or fragments that are held together by non-covalent bonding, such as ionic or hydrogen bonding.

Select the **Maximum unit cell separation** option.

This option specifies the maximum molecular center-to-center distances along each lattice vector for molecular interactions in multiples of the unit cell dimensions. Crystal Graph calculation do not consider interactions that extend over distances greater than the specified values.

Morphology: Calculating morphology using Crystal Graph

Alternatively, you can select the *Maximum molecular separation* option to specify the maximum distance allowable between the nearest two atoms in the interacting molecules. In this tutorial, use the default spatial range of *Maximum unit cell separation*.

On the **Setup** tab, make sure the **Apply initial energy filter** checkbox is selected.

The energy filter applies an energy cutoff to exclude the weakest interactions. The default value of **0.596 kcal mol⁻¹** represents the thermal energy at room temperature, that is, interactions with energies weaker than this value are not stable at room temperature.

Click **Create** and close the dialog.

Wait until the calculation finishes before proceeding.

3. To analyze the Crystal Graph results

In this section, analyze the outputs from the Crystal Graph run.

Once the calculation finishes, this displays a crystal graph in the **pigment_red_input.xsd** document, overlaid on the unit cell view. You can control the rendering and coloring of the molecular interactions in a crystal graph.

Make **pigment_red_input.xsd** the active document and select **File | Save As...** from the menu bar to open the Save As dialog. Enter **pigment_red(CG)** as the **File name** and click **Save**.

Right-click in the **pigment_red(CG).xsd** 3D Viewer and choose **Display Style** from the shortcut menu to open the Display Style dialog. On the **Molecule Interaction** tab, change the **Display style** setting from **Dashed line** to **Line**.

This renders all the molecular interactions as solid lines, rather than the default display style of dashed lines. You can control the relative line width of the interactions.

Change the **Line width** to **1.00**.

You can color the interactions according to their bond energies.

In the **Coloring** section, select the **Color by energy** option.

In the current selection, blue indicates the strongest interactions and red indicates the weakest. The colors smoothly graduate between these two extremes for interactions with intermediate bond energies.

Note: The interaction coloring does not update dynamically following re-evaluation of the energies. For the interaction coloring to reflect current property values correctly, recolor the molecule interactions whenever you make any changes to their bond energies.

In **pigment_red(CG).xsd**, select one of the interactions colored in blue. Right-click in the 3D Viewer and choose **Label** from the shortcut menu to display the Label dialog.

For the **Object type**, choose **Energy**. Select **PotentialEnergy** from the **Properties** list and click **Apply**.

Repeat the same procedure for one of the interactions colored in red.

This labels the two interactions with their potential energy.

Next, review the molecular fragments in the crystal.

Click once in **pigment_red(CG.xsd)** to cancel all selections. On the Label dialog, click **Remove All** and **close** the dialog.

Select the **Molecule** tab on the Display Style dialog, change the **Display style** from **None** to **Polyhedron**, and then **Ellipsoid**.

When you select the *Polyhedron* display style, this renders all the molecules as polyhedra. The locations of the atoms in each molecule determine the vertices of the polyhedra. When you select the *Ellipsoid* display style, this renders the molecules as ellipsoids covering the approximate extent of the atoms contained in each molecule.

Click the **Color** control to display the color chooser and select a color.

This colors all the molecule objects with the chosen color. To make the crystal graph easier to see, you can switch off the display of the molecules.

On the **Molecule** tab of the Display Style dialog, change the **Display style** back to **None** and **close** the dialog.

It is common for a Crystal Graph calculation to produce a large number of interactions. You can filter the interactions according to energy to hide the less significant interactions and focus only on those that appear to have the greatest influence on the crystal morphology.

Open the **Crystal Graph Calculation** dialog. On the **Analysis** tab, move the **Weakest** slider in the **Energy filter** section from its rightmost position one notch to the left. You can also enter a specific value in the text box.

This defines the weakest energy as about $-3.9 \text{ kcal mol}^{-1}$ and selects all the interactions with energies that fall outside the defined range.

Click **Apply** on the Crystal Graph Calculation dialog.

This deletes all the selected interactions with energies that fall outside the defined range.

Select **Edit | Undo Apply Crystal Graph Criteria** from the menu bar.

This restores the crystal graph to its original state with the weakest energy filter specified at about $-0.9 \text{ kcal mol}^{-1}$.

On the **Analysis** tab of the Crystal Graph Calculation dialog, move the **Weakest** slider in the **Energy filter** section from its rightmost position one notch to the left.

When you apply graph augmentation, this restores all the interactions that fail the energy filter, but that are different from every other interaction sharing the same molecule by more than 45° . This selects and clears the selection of a specific group of interactions in **pigment_red(CG.xsd)** according to the energy filter, as well as the crystal graph augmentation.

Morphology: Calculating morphology using Crystal Graph

Note: When you apply augmentation, Crystal Graph tries to restore interactions that fall outside the defined energy filter range. It starts with the strongest rejected interaction and continues with the second strongest, until it cannot add any more interactions that conform to the specified angle constraint.

The crystal graph augmentation method is intended to ensure that sufficient interactions exist to define a suitable habit when used in an appropriate Morphology calculation.

With the **Perform graph augmentation by directional criterion** checkbox selected, click **Apply**.

This deletes fewer interactions from the crystal graph comparison with the same operation without graph augmentation applied.

Select **Edit | Undo Apply Crystal Graph Criteria** from the menu bar.

Click **Export crystal graph as grid document** on the Crystal Graph Calculation dialog and **close** the dialog.

This creates a grid document in the Project Explorer, `pigment_red_CG.xgd`, listing all the interactions in the crystal graph, along with their lengths and bond energies.

Note: This permanently removes filtered or deleted interactions from a crystal graph, so they are not listed in the grid document.

The grid document contains the following columns:

- *Molecule1, Molecule2* - list the atomic compositions of the molecules, along with the symmetry transformations that uniquely identify each individual molecule.
- *Unit Cell of Molecule2* - reports the coordinates, in unit cell lengths, of the unit cell containing Molecule2 in relation to that containing Molecule1, taken as located at the origin.
- *Multiplicity* - reports the symmetry multiplicity.
- *Center-Center Length* - reports the length, in Å, of the interaction, that is the distance between the centers of the two molecules.
- *Energy* - reports the bond energy, in kcal mol⁻¹, of the interaction.

Note: Crystal Graph considers molecular interactions that span unit cells to operate bidirectionally and reports them as such. In the case of two isolated molecules in different unit cells, this reports both the interaction Molecule1…Molecule2 and its inverse, Molecule2…Molecule1, even though their lengths and bond energies are identical. This ensures that all interactions 'entering' a unit cell have a matching interaction 'leaving' the unit cell, as in the visual representation of the crystal graph.

Note: A crystal graph is associated with the crystal structure from which it was derived. Modifying the atomic arrangement of the crystal structure, by moving or deleting atoms, invalidates the crystal graph.

Tip: You can export this grid document as a `.CSV` file compatible with spreadsheet applications such as Microsoft Excel.

4. To calculate morphology using the Crystal Graph outputs

In this section, calculate the growth morphology of Pigment Red by using the orientation and bond energies of the interactions reported in the crystal graph as input.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **pigment_red(CG).xsd**.

Open the **Morphology Calculation** dialog. On the **Setup** tab, make sure that the **Task** is **Growth morphology** and the **Quality** is **Medium**. Change the **Energy method** to **Crystal Graph**.

When you select **Crystal Graph** as the *Energy method*, this automatically disables the *Energy* tab of the Morphology Calculation dialog. Morphology calculates the attachment energies using the bond energies of the interactions reported in the active crystal graph document. Since this requires fewer energy calculations, the calculation time is shorter.

On the **Faces** tab, for the **Quality** select **Medium**. Click **Run** and **close** the dialog.

Close **pigment_red(CG).xsd**.

Once the calculation starts, a new folder called **pigment_red(CG) Mph Growth** is created in the Project Explorer. Wait until the job finishes before proceeding.

Examine the results of the calculation, starting from the text output file **pigment_red(CG).txt**. Usually, there are no warning messages in this report file.

Scroll through **pigment_red(CG).txt**. Verify that this reports no errors or warnings, then close the text document.

Make **pigment_red(CG) Mph Growth\pigment_red(CG).xsd** the active document and examine the habit document using the tools on the **3D Viewer** toolbar.

Next, explore the effect of the intermolecular interaction strength on the crystal morphology.

Open **pigment_red(CG).xsd** and select one of the interactions highlighted in red.

Select **View | Explorers | Properties Explorer** from the menu bar. Choose **Energy** from the **Filter** dropdown list. Double-click **PotentialEnergy** to display the **Edit PotentialEnergy** dialog. Enter **-10** and click **OK**. Click in the 3D Viewer to clear selection of the molecular interaction.

The potential energy for this interaction is now **-10 kcal mol⁻¹**. This automatically applies the same potential energy value to all its symmetry images.

Open the **Morphology Calculation** dialog. Click **Run** and close the dialog.

Close the **pigment_red(CG).xsd** document and click **No** when prompted to save the changes.

When the calculation is complete, examine the crystal habit document. Increasing the bond strength for these weak interactions improves the stability of the growth planes constructed from them. Stable growth planes are more likely to have smaller center-to-plane distances, leading to a more isometric morphology, in agreement with the Hartman-Perdok theory.

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Select **File | Save Project** from the menu bar and close all of the open documents, apart from **pigment_red(CG Mph Growth)\pigment_red(CG.xsd)**.

Next, import the crystal morphology obtained using the Forceite energy method in [Morphology prediction for Pigment Red](#) and compare it with the morphology obtained using the Crystal Graph method.

In the Project Explorer, right-click the project root and select **Import...** to open the Import Document dialog. Navigate to the location where you saved the **Pigment Red** project in [Morphology prediction for Pigment Red](#). Open **Pigment Red Files\Documents\pigment_red Forceite GeomOpt\pigment_red Forceite GeomOpt\pigment_red Mph Growth\pigment_red.xsd** and click **OK**. Import the **pigment_red.xgd** grid document from the same location.

Right-click **pigment_red.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Enter **pigment_red_forcite** as the name and press **ENTER**. Repeat this to rename **pigment_red.xgd** as **pigment_red_forcite.xgd**.

Hide the facets, lattice, and molecules from both predicted morphologies to leave only the crystal shape, to ease comparison.

With the focus on **pigment_red(CG Mph Growth)\pigment_red(CG.xsd)**, right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog.

On the **Lattice** tab, change the **Style** from **Default** to **None** in the **Display style** section.

On the **Habit** tab, clear the **Show facets** checkbox. Choose green as the **Edge color**. Repeat these steps for **pigment_red_forcite.xsd** but choose red as the **Edge color**.

You can overlay the two documents by inserting them into a 3D Atomistic Collection document.

In the Project Explorer, right-click the project root **Pigment Red CG** and select **New | 3D Atomistic Collection Document** from the shortcut menu.

In the Project Explorer, right-click **3D Atomistic Collection.xod** and select **Rename** from the shortcut menu. Change the name of the new collection document to **morphology_overlay.xod**.

A collection document allows you to display multiple structures in the same 3D space, while keeping them isolated in all other respects. For example, there are no physical interactions between systems in a collection document.

In the Project Explorer, hold down **CTRL** and select **pigment_red(CG Mph Growth)\pigment_red(CG.xsd)** and **pigment_red_forcite.xsd**. Right-click one of the selected files and choose **Insert Into** from the shortcut menu. Click **3D Viewer Reset View** .

This overlays the two habits in the collection document. If there is a size discrepancy between the habits, you can change this using the Display Style dialog.

Open the **Display Style** dialog and select the **Habit** tab. Right-click in **morphology_overlay.xod** and select **Physical Systems** from the shortcut menu.

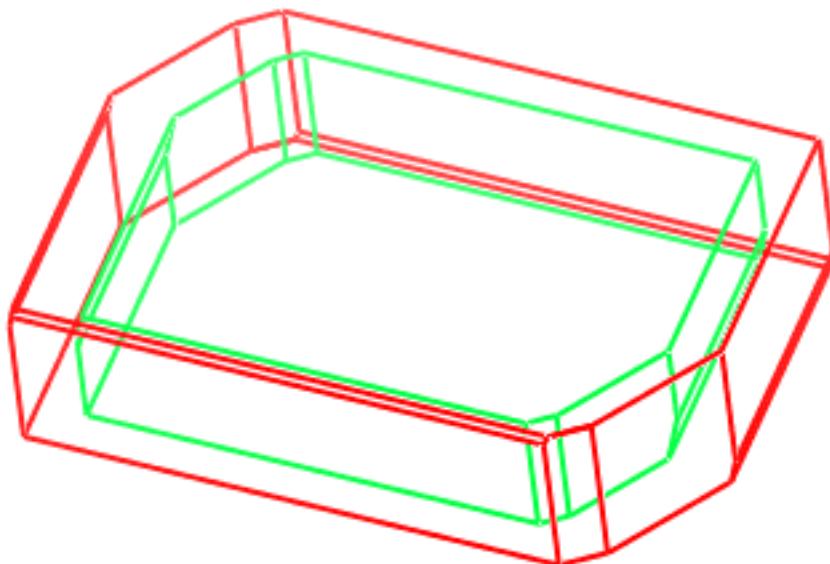
This opens the Physical Systems dialog that enables you to select and work with multiple systems in a collection document.

On the Physical Systems dialog, select **pigment_red_forcite** followed by **pigment_red(CG)**.

The *Habit size* value on the *Habit* tab of the Display Style dialog changes if you have different values for the two structures. Specify the *Habit size* parameter as the same value for both structures.

Select **pigment_red_forcite** on the Physical Systems dialog. On the **Habit** tab of the Display Style dialog, specify the **Habit size** as **0.6**. Repeat this process for **pigment_red(CG)** and **close** the Physical Systems dialog.

The two crystal morphologies are now displayed in the same 3D space, colored in red and green. They are in excellent agreement with each other, as shown below.



Overlay of the morphology of Pigment Red obtained using the Forcite energy method (red) and the Crystal Graph energy method (green)

You can examine the finer details of the two crystal morphologies.

Close **morphology_overlay.xod** and click **Yes** when prompted to save the file as part of the project.

In the Project Explorer, double-click **pigment_red(CG) Mph Growth\pigment_red(CG.xsd**.

Open the **Morphology Calculation** dialog and, on the **Setup** tab, for the **Task** select **Report habit properties**. Click **Run** and **close** the dialog.

This creates a new grid file, **pigment_red(CG).xgd** in the **pigment_red(CG) Mph Growth** folder. Compare this with the habit properties from the Forcite morphology calculation in the **pigment_red_forcite.xgd** document that you imported.

Morphology: Calculating morphology using Crystal Graph

Close **pigment_red(CG).xsd** and click **Yes** when prompted to save the file as part of the project.

In the Project Explorer, double-click **pigment_red_forcite.xgd** to make it the active document.

Select **Window | Tile Horizontally** from the menu bar.

There are six habit facets in the crystal morphology calculated by the Crystal Graph energy method and also identified by the Forcite energy method. However, two minor facets produced by Forcite, (0 1 -1) and (1 1 -1), (each less than 1% of the total surface area), are not present in the crystal morphology obtained using the Crystal Graph energy method.

The observation is not unexpected. The Crystal Graph energy method only considers bond energies for the interactions between molecular fragments in a crystal structure. As a result, the energy evaluation is less accurate than a full energy evaluation using the Forcite energy method. In addition, you can use the Ewald summation with the Forcite energy method. This is extremely important if individual molecules have a net charge, such as in ionic systems, or for a morphology consisting of planes having a dipole moment. In cases without Ewald summations, the calculation does not converge properly because the interaction radius often contains a non-zero net charge. This leads to arbitrary energy oscillations as a function of interaction radius. For non-ionic systems, decide whether the increased accuracy obtained by using Ewald summations justifies the greater computation time.

In the example presented here, the two energy methods provide results that are in excellent agreement.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Hartman, P.; Perdok, W. *Acta Crystallogr.*, **8**, 521 (1955).

Bennema, P. *J. Cryst. Growth*, **166**, 17 (1996).

Grimbergen, R. F. P.; Bennema, P.; Meekes H. *Acta Crystallogr., Sect. A*, **54** 491 (1998).

Chapter 17: ONETEP tutorials

The following tutorial illustrates how to utilize ONETEP's capabilities.

LiF density of states (DOS) with ONETEP and CASTEP

Purpose: Introduces how to use the ONETEP module in Materials Studio, paying special attention to comparison with CASTEP results.

Modules: Materials Visualizer, ONETEP, and CASTEP

Time: 

Prerequisites: None

Background

Lithium fluoride is a white, inorganic, crystalline, ionic, solid salt under standard conditions. It transmits ultraviolet radiation more efficiently than any other known substance. Uses include specialized UV optics and as a material used to record gamma and neutron exposure in thermoluminescent dosimeters.

Lithium fluoride also has a very high electrical resistance resulting from its wide band gap. Griceite is the name for the very rare mineralogical form of LiF.

Lithium fluoride (highly enriched in the common isotope lithium-7) forms the basic constituent of the preferred fluoride salt mixture used in liquid-fluoride nuclear reactors. Typically a mixture of lithium fluoride with beryllium fluoride forms a base solvent, into which fluorides of uranium and thorium are introduced. Lithium fluoride is exceptionally chemically stable; LiF/BeF₂ mixtures have low melting points and the best neutronic properties of fluoride salt combinations appropriate for reactor use.

In this tutorial, you use ONETEP and CASTEP to study the electronic structure of lithium fluoride and to obtain the corresponding density of states (DOS) charts. The ONETEP calculation also illustrates how to generate DOS charts for selected atoms, which can be very helpful for large systems.

This tutorial covers:

- [Getting started](#)
- [To prepare the structure](#)
- [To run the ONETEP calculation](#)
- [To run the CASTEP calculation](#)
- [To compare the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Note: The calculations in this tutorial are demanding in terms of CPU time and could require an hour or more computation time depending on your hardware. Error messages in ONETEP or CASTEP output files containing "Out of RAM" or similar statements indicate that the memory on the server is not sufficient. You can also find the output files from both the ONETEP and CASTEP calculations described in this tutorial in the Examples/Projects/ONETEP/LiF_Files/Documents directory of your Materials Studio installation.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **LiF_DOS** as the project name, click the **OK** button.

The new project is created with *LiF_DOS* listed in the Project Explorer.

2. To prepare the structure

The first thing that you need to do is to prepare the structure of the lithium fluoride crystal.

From the menu bar, select **File | New...** to open the New Document dialog. Select **3D Atomistic** from the options and click **OK**.

From the menu bar, select **Build | Crystals | Build Crystal...** to open the Build Crystal dialog. On the **Space Group** tab, enter **FM-3M** for **Enter group**. On the **Lattice Parameters** tab, enter **4.03** as the **a** length in Å. Click **Build**.

A new window with the crystal lattice opens. Now, you need to add the Li and F atoms.

From the menu bar, select **Build | Add Atoms** to open the Add Atoms dialog. Select **Li** as **Element** and click **Add**.

Enter for **F** as the **Element** and specify **a** as **0.5**. Click **Add** and close the dialog.

The unit cell that you have created only contains 8 atoms. For this tutorial, you want to perform a calculation on a larger system, so you need to build a $2 \times 2 \times 2$ supercell.

From the menu bar, select **Build | Symmetry | Supercell** to open the Supercell dialog. Enter **2** for the values of **A**, **B**, and **C**. Click **Create Supercell** and close the dialog.

Right-click in the 3D Viewer and select **Display Style** to open the Display Style dialog. On the **Lattice** tab, ensure that the **Style** uses **Default**. On the **Atom** tab, select **Ball and stick** and close the dialog.

Rename the document **LiF.xsd**.

The final LiF structure containing 64 atoms in the unit cell is depicted in Figure 1 (the **Default** display style adds periodic images for some atoms, so the image in Figure 1 shows 125 atoms).

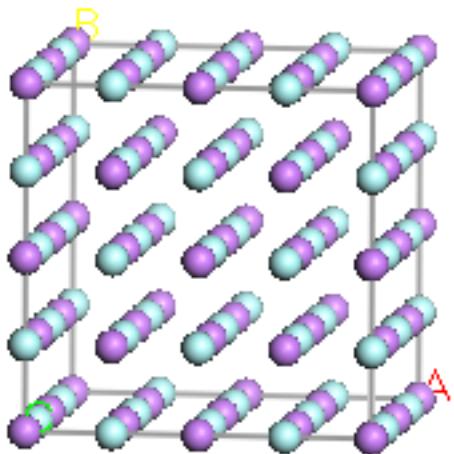


Figure 1. LiF structure

Next, prepare the sets required for identifying which part of the DOS belongs to each type of ion.

Press **ALT** and double-click one of the F atoms.

From the menu bar, select **Edit | Edit Sets** to open the Edit Sets dialog, and click **New....** Type **L DOS_1** and press **ENTER**.

Repeat this to create a second set, **L DOS_2**, which contains the Li ions.

3. To run the ONETEP calculation

The next step is to setup the ONETEP calculation.

With **LiF.xsd** as the active document, click **ONETEP**  on the **Modules** toolbar and select **Calculation** to open the ONETEP Calculation dialog.

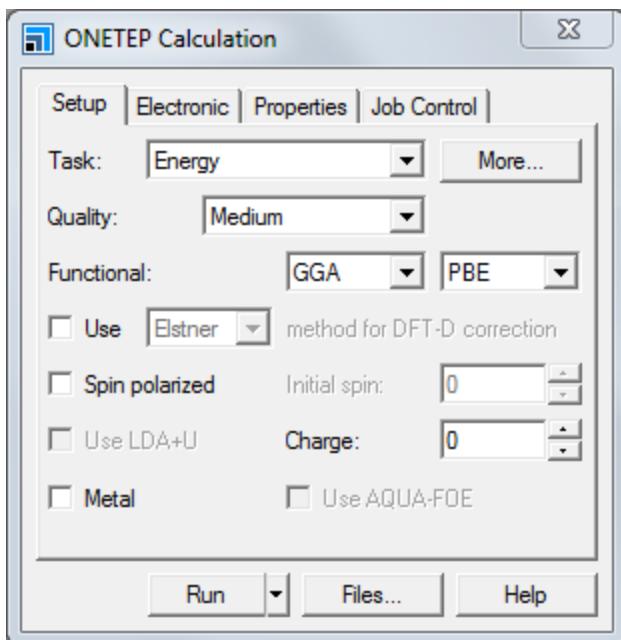


Figure 2. ONETEP Calculation dialog, Setup tab.

On the **Setup** tab, select **Energy** as the **Task** and **Medium** for the **Quality**. Choose **GGA-PBE** as the **Functional**.

On the **Properties** tab, select **Density of states projections** and, in the related options, select **Local density of states**.

To obtain results in a reasonable amount of time, change the Li and F radii. Do not make this type of change for production calculations.

On the **Electronic** tab, click **More...** to open the ONETEP Electronic Options dialog. Choose the **Basis Set** tab, change the Li and F radius values to **3.3 Å** and close the dialog.

To complete the ONETEP calculation in a reasonable amount of time, you need to run the calculation in parallel.

On the ONETEP Calculation dialog, select the **Job Control** tab. Enter the number of cores on which you want to run the calculation in the **Run in parallel on** textbox.

Now you are ready to run the calculation.

Click **Run** and close the dialog.

Tip: While the job is running, you can proceed to [step 4](#).

Depending on your hardware, this calculation may take around 30 minutes to complete. The results of the calculation save in the **LiF_ONETEP_Energy** folder. The **LiF.onetep** file is the output of the calculation and includes the SCF progress, the final converged energy, the population analysis results, and a summary of orbitals and occupancies.

To visualize the DOS or the orbitals, you need to use the ONETEP Analysis dialog. You can find the output of this calculation in the Examples/Projects/ONETEP/LiF Files/Documents directory in the LiF ONETEP Energy folder.

When the calculation has completed, open the final **LiF.xsd** document. Click **ONETEP**  on the **Modules** toolbar and select **Analysis** to open the ONETEP Analysis dialog.

Select **Density of states** from the list and click **View**.

A new window with a chart of the DOS displays.

The final DOS graph is depicted in Figure 3 below.

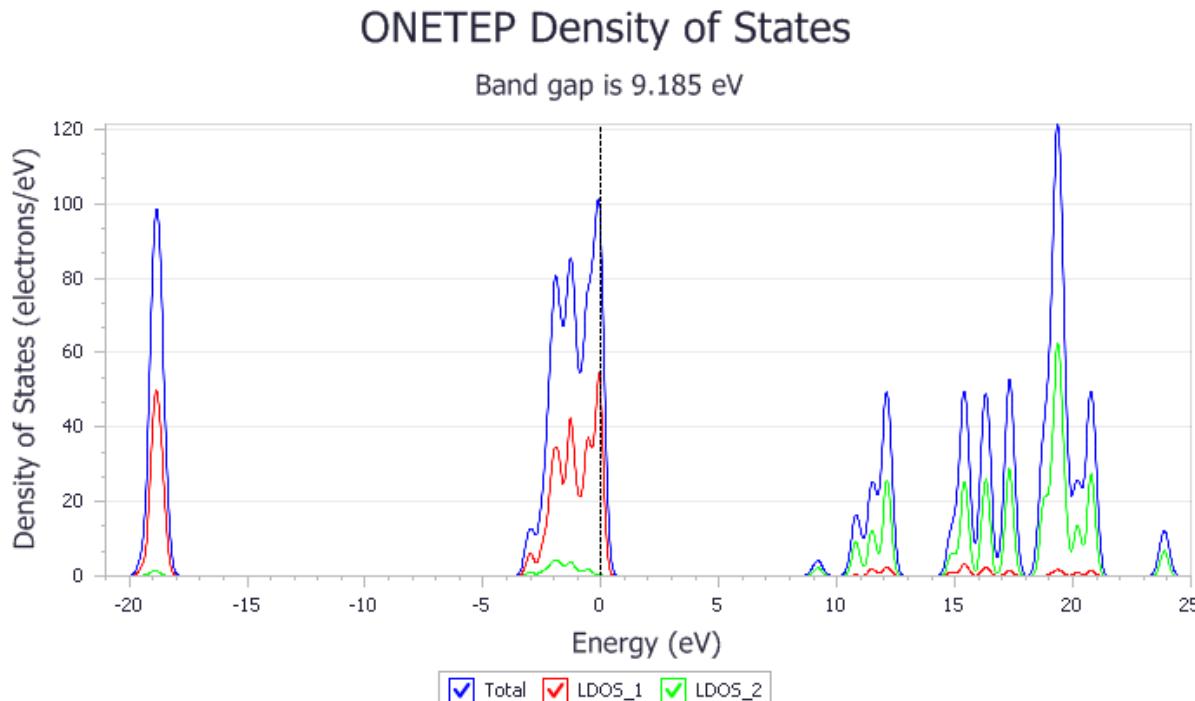


Figure 3. ONETEP DOS for a LiF crystal containing 64 atoms.

The blue line shows the total density of states, the red line the local density of states of the F ions, and the green line the local DOS of the Li ions. This shows that the valence band primarily involves F, while the conduction band is almost exclusively Li.

Tip: If you select specific sets, the DOS projections only display for those sets of atoms. The *Edit Sets* dialog helps you to select the correct sets.

You can proceed in a similar way to display other properties (orbitals, potentials, etc), if requested during the energy calculation. You can also repeat this calculation with a substitution defect and additional sets to explore the location of defect states.

4. To run the CASTEP calculation

Now, proceed to setup the CASTEP calculation. To obtain similar results with both modules, run a CASTEP calculation with a single k-point (Gamma point) and the same norm conserving pseudopotentials.

With the original **LiF.xsd** document as the active document, click **CASTEP**  on the **Modules** toolbar and select **Calculation** to open the CASTEP Calculation dialog.

On the **Setup** tab, select **Energy** as the **Task** and **GGA-PBE** as the **Functional**. Clear selection of **Metal** as the compound is definitely dielectric.

On the **Electronic** tab, select **Gamma** as the **k-point set** and set the **Pseudopotentials to Norm conserving**.

Click **More...** to open the CASTEP Electronic Options dialog. Choose the **Potentials** tab and select **Reciprocal space for Representation**. Close the dialog.

To be able to get information about the conduction band, you need to define the number of empty bands used in the DOS CASTEP calculation. An energy range of 25 eV is enough to get the first conduction band for LiF.

On the **Properties** tab of the CASTEP Calculation dialog, select **Density of states**, and change the **Energy range** to **25 eV**. Select **Gamma** from the **k-point set** list. Clear selection of **Population analysis**.

Before running the calculation, you need to define the number of processors where you want to run the calculation.

On the **Job Control** tab, enter the number of cores on which you want to run the calculation in the **Run in parallel on** textbox.

Now you are ready to run the calculation.

Click **Run**.

Click **No** on the warning dialog so that the calculation proceeds using P1 symmetry.

Close the CASTEP Calculation dialog.

The results of the calculation save in the **LiF CASTEP Energy** folder. Depending on your hardware, this calculation may take around 2 minutes to complete. You can find the output of this calculation in the **Examples/Projects/ONETEP/LiF Files/Documents** directory in the **LiF CASTEP Energy** folder. To visualize the DOS, you need to use the CASTEP Analysis dialog.

When the calculation is complete, open the **LiF CASTEP Energy/LiF.xsd** document, select **Modules | CASTEP | Analysis** from the menu bar to open the CASTEP Analysis dialog.

Select **Density of states** from the list and click **View**.

A new chart of the DOS displays.

The final CASTEP DOS graph is depicted in Figure 4 below.

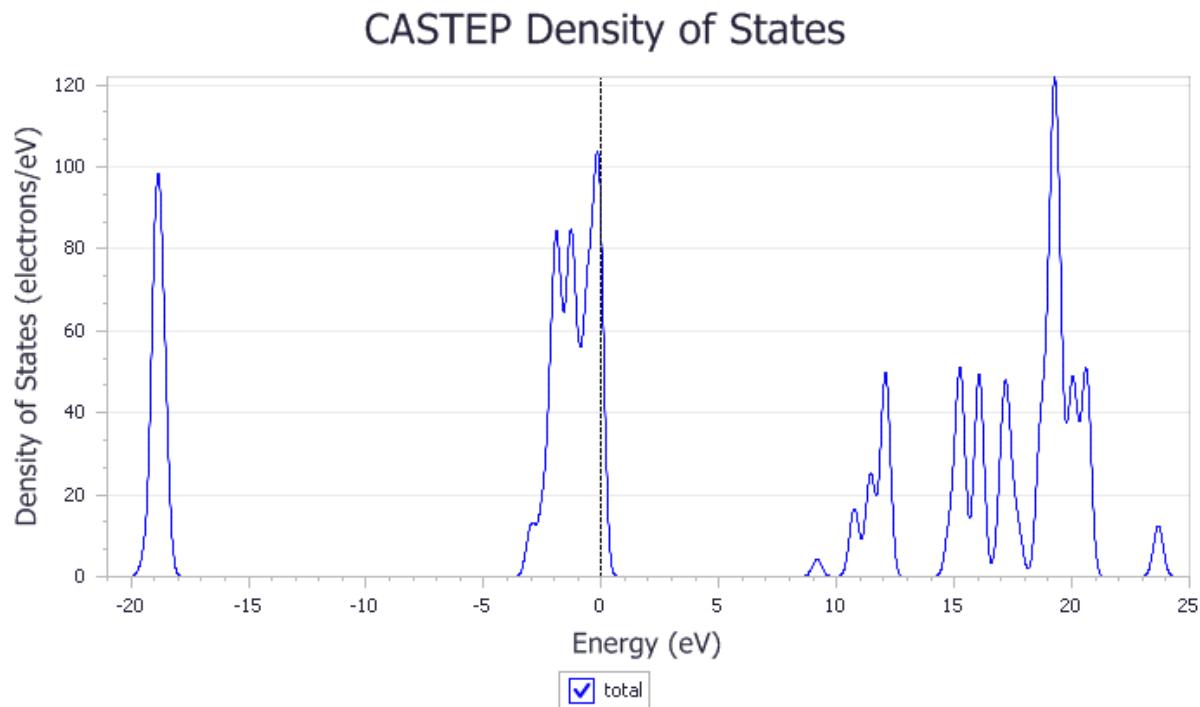
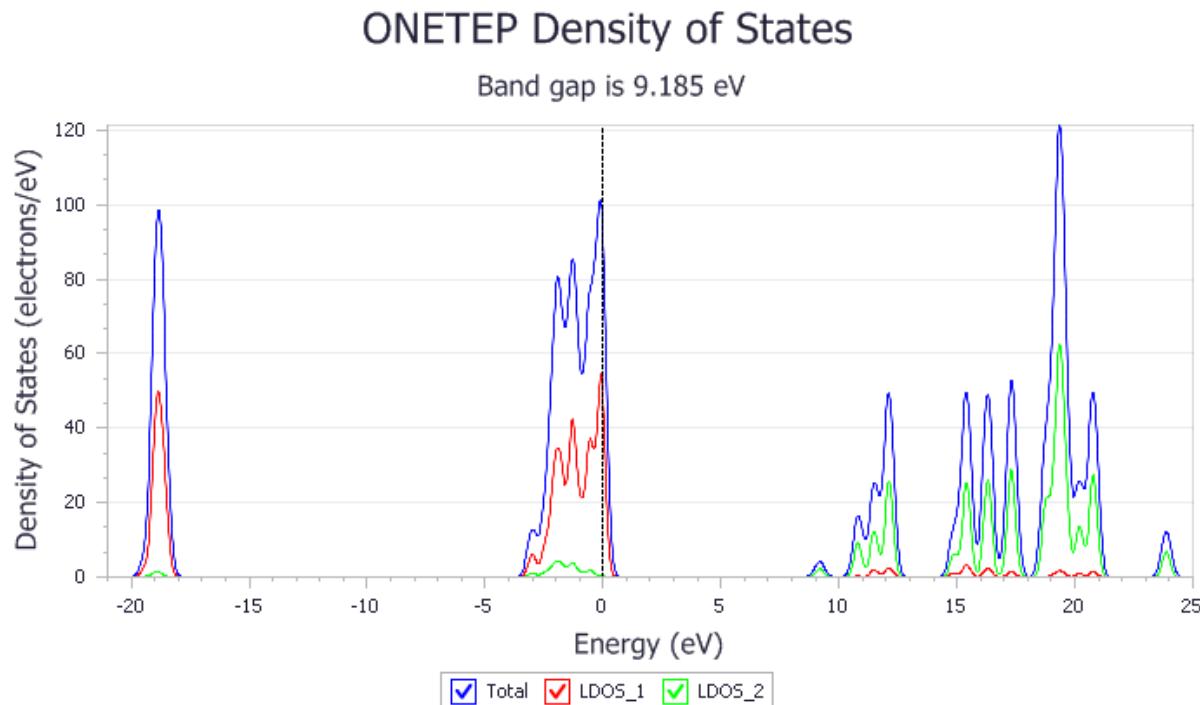
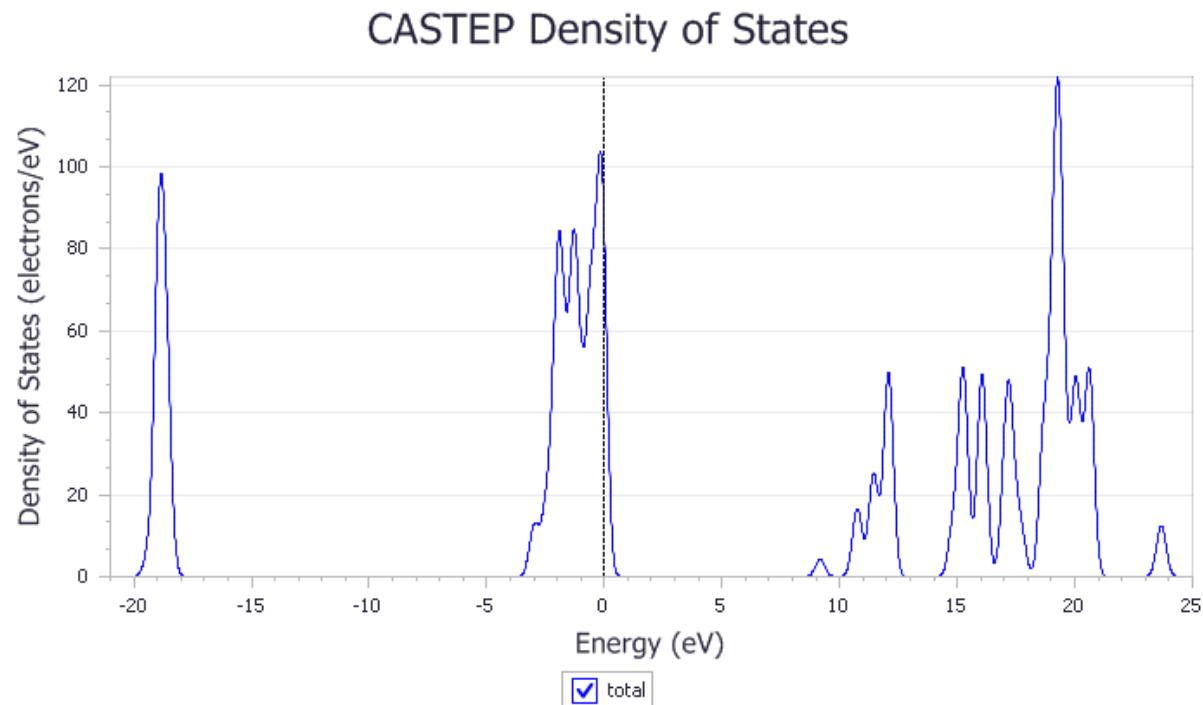


Figure 4. CASTEP DOS for a LiF crystal containing 64 atoms.

5. To compare the results

If you check the final energies obtained with ONETEP and CASTEP, you can see that those are of the same order of magnitude: 790.8 Ha with ONETEP (around -21519 eV) and -21522 eV with CASTEP. The DOS results are also very similar.





This is the end of the tutorial.

Chapter 18: Polymorph tutorials

The following tutorials illustrate how to utilize Polymorph's capabilities.

- [Predicting the Crystal Structure of 3-oxabicyclo\(3.2.0\)hepta-1,4-diene](#)
- [Predicting a polymorphic form of a potential anti-cancer drug - conformational analysis](#)
- [Predicting a polymorphic form of a potential anti-cancer drug](#)
- [Using Materials Studio to edit a forcefield](#)

Predicting the crystal structure of 3-oxabicyclo(3.2.0)hepta-1,4-diene

Purpose: Illustrates how to predict possible crystal packing arrangements based on molecular structure using Polymorph.

Modules: Materials Visualizer, DMol³, Polymorph, Reflex

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Pharmaceuticals, agrochemicals, pigments, dyes, specialty chemicals, and explosives are all, at some stage during the manufacturing process, organic crystalline materials. Polymorphism affects these products during downstream development and formulation because the crystal form determines many of the properties of the material, including:

- Shelf life
- Vapor pressure
- Solubility
- Bioavailability
- Morphology
- Density
- Shock sensitivity

It is vital that researchers involved in crystalline product formulation select the polymorph with the correct properties and can anticipate problems such as competing crystallization of undesirable polymorphs. To do this, you need to establish the most likely polymorphic forms. Knowledge of polymorphic forms is also important for patenting and registration purposes.

It is often impossible or impractical to use single crystal X-ray diffraction, the standard experimental procedure for elucidating the structure of a molecular crystal. Thus, computational techniques that predict crystal structures without experimental data are of great value.

Polymorph uses forcefield technology to propose stable packing arrangements. This method keeps the molecular geometry fixed during the Monte Carlo simulation and only allows full optimization during the energy minimization stage. Therefore, when dealing with flexible molecules, you must perform parallel calculations for each stable molecular conformation of the compound under investigation.

Introduction

You can determine possible crystal structures of 3-oxabicyclo(3.2.0)hepta-1,4-diene (OHD) using Polymorph. The molecule was used in a blind test organized by the Cambridge Crystallographic Data Centre (CCDC) to assess the performance of the available methods for crystal structure prediction [1](#).

The success rate of crystal structure prediction depends critically on the accuracy of the forcefield employed. In this tutorial, you use the COMPASS III forcefield, which proved to be suitable for crystal structure prediction when used with atomic charges calculated by high-level ab initio calculations.

This tutorial covers:

- [Getting started](#)
- [To build and optimize the molecule with DMol³ and calculating ESP-fitted charges](#)
- [To configure and run Polymorph](#)
- [To analyze the results using a study table](#)
- [To compare the results with a known OHD crystal structure](#)
- [To identify the best match with an experimental powder pattern](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

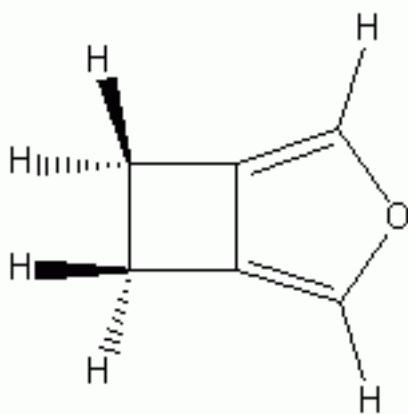
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **OHD** as the project name, click **OK**.

The new project is created with *OHD* listed in the Project Explorer.

2. To build and optimize the molecule with DMol³ and calculating ESP-fitted charges

In the Project Explorer, right-click **OHD** and select **New | 3D Atomistic Document**. Change the name of the new structure document to **OHD-mol**. Use the Sketch tools to sketch an OHD molecule (shown below) and then clean the structure by clicking **Clean** .



Molecular structure of OHD

Now, optimize the molecule with DMol³ and calculate the ESP-fitted charges.

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On the **Modules** toolbar, click the **DMol3** arrow  and select **Calculation** to open the DMol3 Calculation dialog.

On the **Setup** tab, select **Geometry Optimization** as the **Task**. Select **GGA** and **PBE** as the **Functional**. Leave the **Quality** as **Medium**.

On the **Electronic** tab, for the **Basis** set select **DNP**.

On the **Properties** tab, select **Electrostatics** and **Population analysis**. For **Electrostatics**, select **Electrostatic potential**. For **Population analysis**, select **ESP charges**.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click **Run** and close the dialog.

A new folder, called **OHD-mol DMol3 GeomOpt**, displays in the Project Explorer and presents the progress of the job in the form of chart and text documents. The calculation can take some time, depending on the speed of the processor in your computer. Wait until the job finishes before proceeding.

Next, analyze the DMol³ results and extract information on the ESP-fitted charges.

In the Project Explorer, double-click **OHD-mol.outmol** in the **OHD-mol DMol3 GeomOpt** folder. Press **CTRL + F** and search for **ESP-fitted charges**.

You reach a part of the document that looks like this:

ESP-fitted charges :				
n	Elem	chg	vdw(in)	vdw(ex)
1	O	-0.121	1.72	3.22
2	C	-0.188	2.00	3.50
3	C	0.058	2.00	3.50
4	C	0.058	2.00	3.50
5	C	-0.188	2.00	3.50
6	C	-0.220	2.00	3.50
7	C	-0.220	2.00	3.50
8	H	0.184	1.30	2.80
9	H	0.184	1.30	2.80
10	H	0.113	1.30	2.80
11	H	0.113	1.30	2.80
12	H	0.113	1.30	2.80
13	H	0.113	1.30	2.80

Note: The actual ESP charge values might be slightly different if the initial drawn structure and optimization level differ.

The file lists the ESP-fitted charges for each atom, as calculated by DMol³. Now, assign all these charges to the fully optimized structure of OHD.

In the Project Explorer, double-click **OHD-mol.xsd** in the **OHD-mol DMol3 GeomOpt** folder. From the menu bar, select **Modules | DMol3 | Analysis** to open the DMol3 Analysis dialog. Select **Population analysis** and change the **charges to structure** to **ESP**. Click **Assign** and close the dialog.

The ESP-fitted charges generated by DMol³ do not sum to exactly zero because of truncation errors. So, before proceeding, modify the charges slightly so that they do add up to zero.

From the menu bar, select **Modify | Charges** to open the Charges dialog. On the **Edit** tab, select **Set total charge to** and specify a value of **0.0**. Click **Assign** and close the dialog.

Now display the charges on each atom.

Right-click in the **OHD-mol.xsd** 3D Viewer and select **Label** to open the Label dialog. From the **Properties** list, select **Charge**, and click **Apply**.

When you have examined the charges, click **Remove All** to remove the charges from the display, and close the dialog.

3. To configure and run Polymorph

In this section, use Polymorph to predict various possible crystal packing arrangements for OHD. OHD is a rigid molecule, so you do not need to analyze its conformation.

According to the Cambridge Structural Database (CSD), the 17 most frequent space groups cover about 90% of all organic and organometallic crystal structures. Without prior knowledge of the crystal symmetry (for example, from an indexable powder pattern), you must run the calculations for at least five of the most common space groups.

From the menu bar, select **File | Save Project**, and the close all the open documents, apart from **OHD-mol DMol3 GeomOpt\OHD-mol.xsd**.

Click the **Polymorph** arrow  on the **Modules** toolbar and select **Calculation** to open the Polymorph Calculation dialog. On the **Setup** tab, click **Assign automatically**. Select **Fine** as the **Quality**.

In this tutorial, you run a Polymorph prediction sequence. You could do this by running each step in the sequence separately or all of them in a single consecutive calculation. The Polymorph prediction sequence consists of four steps: packing (Monte Carlo simulation), preclustering, optimization, and clustering. The entire sequence can take hours or even days, during which time Polymorph:

- Runs a Monte Carlo simulation to generate thousands of potential crystal structures for OHD in the selected space groups
- Runs a preclustering analysis to group the crystals into clusters of similar structures
- Minimizes each cluster to get a group of optimized structures
- Runs a second clustering analysis to check whether any of the optimized structures converge to the same energy minima

The preclustering step sorts the crystal structures generated by Monte Carlo simulations into groups of similar structures. The geometric tolerances defined on the control panel determine the similarity. The preclustering step reduces the total number of structures before the next stage of the calculation: optimization. Since optimization is the most computationally expensive step, preclustering can help accelerate the calculation significantly. However, there is a risk of losing possible solutions at the preclustering stage. The number of structures retained depends on the tolerances and the maximum number of clusters you define. Since the crystal structures generated by the Monte Carlo simulation are not optimized before the preclustering, the measure of similarity is not very precise. By default, the preclustering step is not included, to prevent discarding structures.

In this tutorial, include this step to accelerate the calculation.

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On the **Setup** tab of the Polymorph Calculation dialog, for the **Task** select **Prediction**. Click **More...** to open the Polymorph Prediction dialog.

Select both **Clustering** options and click **More...** for **Packing** to open the Polymorph Packing dialog.

The *Quality* remains **Fine**, as specified on the *Setup* tab of the Polymorph Calculation dialog.

Seven parameters control the Monte Carlo temperature cycles including:

- *Cooling Factor* (on the *Space Groups* tab, as indicated below)
- *Heating factor*
- *Maximum number of steps*
- the number of *Steps to accept before cooling*
- *Minimum move factor*
- *Maximum temperature*
- *Minimum temperature*

By changing the *Quality* from **Coarse** to **Ultra-fine**, you increase both the probability of generating all relevant crystal packing arrangements and the total amount of CPU time required.

Polymorph optimizes each specified parameter. So, select a set of parameters rather than try to define individual parameters manually. In a real-life situation, use the **Medium**, **Fine**, or **Ultra-fine** search levels. In this tutorial, leave the search level as **Fine**.

Make sure you can see the **Setup** tab of the Polymorph Calculation dialog. On the Polymorph Packing dialog, change the **Quality** to **Coarse**, then to **Medium**, and then back to **Fine**.

As you change the *Quality* for the packing task, the overall quality on the *Setup* tab of the Polymorph Calculation dialog changes automatically from **Fine** to **Customized**, and finally returns to **Fine**.

Close the Polymorph Packing dialog.

If you want, you can observe the effect on the global *Quality* parameter of modifying other settings by repeating the same procedure for the Polymorph Clustering and Polymorph Geometry Optimization dialogs.

The clustering procedure depends on several parameters. Again, it is advisable to select one of four predefined parameter sets, rather than to choose individual parameters manually (except, in certain cases, for the maximum number of clusters).

On the Polymorph Prediction dialog, click **More...** for **Clustering** to open the Polymorph Clustering dialog.

In the **Cluster generation** section, change the **Maximum clusters** to **2000**. Close the Polymorph Clustering dialog.

Increasing the quality reduces the likelihood of clustering different structures together and consequently increases the number of clusters produced.

In a real-life calculation, define the search level as **Fine** or **Ultra-fine**, so that you do not lose the correct crystal structure during the clustering process. The geometry optimization procedure also depends on several parameters. Select one of the four predefined parameter sets, rather than choosing individual parameters manually. You can also choose the maximum number of iterations, whether to apply

external pressure, or whether to optimize the atomic coordinates only or to include the cell parameters as well. For real-life calculations, use the *Optimize cell* option.

In this tutorial, use the default settings.

Tip: By default, Polymorph optimizes the geometry of each unique structure with respect to all degrees of freedom. However, you can apply rigid body constraints for fixed relative distances between a group of atoms. Rigid body constraints can prevent the geometry optimizer from exploring unrealistic regions of configuration space. Defining rigid bodies tends to reduce the number of degrees of freedom required to describe the configuration of a system, so calculations run faster. To use rigid body optimization, select *Keep motion groups rigid* on the Polymorph Geometry Optimization dialog.

Note: Different polymorphic crystal structures usually differ by only a fraction of a kcal/mol in energy. Therefore, optimize all degrees of freedom of the crystal, including the cell parameters. Ensure that all atoms can move. You must use exactly the same energy expression for all geometry optimization runs that you want to compare.

Close the Polymorph Prediction dialog.

Next, choose the COMPASS III forcefield and use the ESP charges obtained with DMol³ earlier.

On the **Energy** tab of the Polymorph Calculation dialog, select **COMPASS III** as the **Forcefield** and select **Use current** from the **Charges** list.

Polymorph can search all space groups. However, by default, it searches only the five most common space groups. The crystal structure of OHD is in space group PBCA. So, to accelerate the tutorial, search in only the two orthorhombic space groups, P212121 and PBCA. Typically, you include all the other common space groups in the search.

You can specify a cooling factor independently for each space group. In this tutorial, use the default value of **0.001** for both space groups.

On the **Space Groups** tab of the Polymorph Calculation dialog, select space groups **P212121** and **PBCA** and clear selection of all the others.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Clear selection of **Automatic** and enter **OHD-Fine** as the **Job description**. Click **Run** and close the Polymorph Calculation dialog.

The Job Explorer informs you about the progress of the calculation. After some time, two new windows appear: a text document, **Status.txt**, and a chart document. These documents update regularly as the job progresses.

The text document displays information about:

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1. The task performed, for example *Polymer Packing* or *Polymer Geometry Optimization* (you do not see *Polymer Clustering* as the calculation finishes quite rapidly).
2. The space group for the search. The search follows the order listed on the *Space Groups* tab.
 - For Polymer packing: space group, current step number, current crystal structure acceptance, temperature, total energy for the current crystal structure (including the contributions of the H-bond, van der Waals, and electrostatics energies), and the density of the current crystal structure.
 - For Polymer geometry optimization: space group, total number of frames, current frame number, optimization convergence, total energy for the current crystal structure, total non-bond energy (including a breakdown of the H-bond, van der Waals, and electrostatics contributions), and total bonded energy (including a breakdown of the bond, angle, torsion, inversion, and cross-terms contributions).

The chart document varies depending on the current step of the prediction sequence and the space group. Polymer packing creates a chart document called OHD-Fine [space group name] Ener-Dens.xcd, which shows the density and energy information for each potential crystal structure found so far. The Polymer geometry optimization generates a chart document called OHD-Fine [space group name] Energy.xcd, which shows the energy for each optimized crystal structure.

Once the calculation starts, a new folder called OHD-Fine PMP Predict displays in the Project Explorer. The parameter settings for this job automatically save in a file called OHD-Fine - Calculation.

In the new folder, the job creates four subfolders as it progresses:

1. **Input** - contains the input molecular structure required for restart if the job stops for any reason.
2. **Packing** - includes four types of files for each space group:
 - a trajectory file containing all the potential crystal structures generated by the Monte Carlo simulation
 - a chart document showing the acceptance ratio and temperature profile for the Monte Carlo simulation
 - a second chart document showing the density and energy for each potential crystal structure
 - a text file showing the acceptance, temperature, energy, and density for all the structures generated
3. **GeomOpt** - includes a trajectory file for each space group, containing the lowest energy structure for each cluster, and a chart document showing the energy for each optimized crystal structure.
4. **Pre-clustering** - includes a trajectory file for each space group that groups together similar crystal structures generated by the Monte Carlo process. Each cluster is represented by the structure that has the lowest lattice energy.

The whole process generates hundreds of crystal structures. Many of these are very similar and minimize to the same crystal structure. It is useful to group together similar crystal structures and to represent each cluster by the structure with the lowest lattice energy. These final results of the Polymer Prediction sequence, save in the top level of the OHD-Fine PMP Predict folder. The job creates a trajectory file containing all non-redundant energy minima for each space group.

Note: The search in Polymorph relies on a Monte Carlo simulation, which is a stochastic method. Therefore a single calculation does not always guarantee identification of all low energy crystal structures in a given space group. To assess the completeness of the Polymorph search, run the Polymorph prediction more than once with the same settings. If separate runs with identical settings produce the same low energy crystal structures, then you can consider the search complete. If you obtain different results, repeat the search until it finds no new crystal structures.

Now, start a second Polymorph job using the same settings.

From the menu bar, select **File | Save Project**, and close all the open documents, apart from **OHD-mol.xsd** in the **OHD-mol DMol3 GeomOpt** folder.

Open the **Polymorph Calculation** dialog. On the **Job Control** tab, select **My Computer** as the **Gateway location**, and enter **OHD-Fine 2** as the **Job description**. Click **Run** and close the dialog.

Wait until the job finishes before proceeding.

4. To analyze the results using a study table

In this section, you analyze the output from the Polymorph run.

From the menu bar, select **File | Save Project**, and then **Window | Close All**.

Click the **Polymorph** arrow  and select **Analysis** to open the Insert Polymorph Results File dialog.

Navigate to the **OHD-Fine PMP Predict** directory, hold down **CTRL**, and select **OHD-Fine PBCA.xtd** and **OHD-Fine P212121.xtd**. Click **Open**.

Repeat the same procedure to navigate to the **OHD-Fine 2 PMP Predict** directory and insert the trajectories **OHD-Fine 2 PBCA.xtd** and **OHD-Fine 2 P212121.xtd** into the study table.

All the frames in the four trajectory files display in the study table. The study table provides you with detailed information about each potential polymorph, including:

- *crystal Structures* (column A)
- *Frame number* (column B, the lower the frame number the lower the total energy for the structure)
- *Space group* (column C)
- *Cell Volume* (column D)
- *Density* (column E)
- *Total energy* (column F)
- the contribution of *van der Waals* (column G)
- *Electrostatic* (column H) energy to the non-bond energy
- the cell parameters (columns I-N)

The name of each structure has the format: *[job name] [space group name] - [frame number]*. By default, the sorting of the structures in each space group uses their total energy values. The lowest energy frames display at the top of the table. To locate the global minimum structure, you can sort the study table across different space groups and/or obtained by different calculation runs.

Polymorph: Predicting the crystal structure of 3-oxabicyclo(3.2.0)hepta-1,4-diene

From the menu bar, select **Tools | Sort Rows...** to open the Sort Rows dialog. Select **F : Total energy** from the **Sort by column** list, select **Ascending**, and click **OK**.

The study table now ranks all the structures by their total energy, with the lowest energy structures at the top of the table. In this tutorial, the lowest energy structure is either OHD–Fine PBCA – 1 (the structure in frame 1 of the trajectory for space group PBCA) or OHD–Fine 2 PBCA – 1, with essentially the same total energy value. Since you performed two separate runs using the same settings here, any given low energy structure might be found more than once. Therefore, you need to perform a clustering analysis to remove the duplicates.

Select all the cells by clicking in the top left heading cell in the study table.

Click **Models**  on the **QSAR Models** toolbar. Click the **Category** heading to sort by category and locate the **Crystallization** category. Select the **Polymorph clustering** row. Click **Run** and close the dialog.

Note: You can only perform Polymorph clustering for 3D crystal structures that either have the same asymmetric unit formula or at least contain the same cluster groups (same forcefield type, or element types, or names). However, all the crystals do not necessarily have the same space group symmetry. If the study table contains structure documents that do not conform to these restrictions, Polymorph enters #N/A in the results column.

The outputs produced by the Polymorph clustering model include:

- **cluster number**
- **Rank in cluster** - Similarity ranking with respect to the reference structure in that particular cluster
- **Similarity to cluster reference** - Crystal similarity measure with respect to the reference structure in that particular cluster

The clustering classified OHD–Fine PBCA – 1 and OHD–Fine 2 PBCA – 1 in the same cluster – Cluster 1, with the crystal similarity measure value of 0. In other words, your initial calculations found the same lowest energy structure twice. Remove the duplicate crystal structures in any given cluster, and create a subset of the unique structures.

Open the **Sort Rows** dialog.

Select **P : Rank in cluster (Polymorph Clustering)** from the **Sort by column** list, and then select **Ascending**.

Select **O : Cluster number (Polymorph Clustering)** from the **Then by column** list, and then select **Ascending**.

Click **OK**.

In the study table, click row 1. Hold down **SHIFT**, and click the last row that has a value of 1 in column **P : Rank in cluster (Polymorph Clustering)**. From the menu bar, select **Tools | Filter**.

The lowest energy representative of each cluster filters into a new sheet - Sheet 2. This sheet already sorts the structures according to their total energy values. You can examine the energy profiles for all the structures.

Note: Since the filtered structures can come from either Polymorph execution, the term OHD–Fine PBCA – 1 refers to the lowest energy structure regardless of its original trajectory.

In the study table, ensure that **Sheet 2** is active and select column **F (Total energy)** by clicking the column heading. Click **Quick Plot**  on the **Study Table Viewer** toolbar.

The lattice energies of all the crystal structures display in a chart document. The most likely candidate for the experimentally observed crystal structure is the frame with the lowest lattice energy in the trajectory files.

Close the chart document and click **No** when prompted to save the document.

To find the most likely stable polymorphs, you can also sort the study table using different criteria; for example, density, van der Waals energy, etc.

Note: Structures with low lattice energies generally have relatively high densities. Examine the density profile to investigate.

Ensure that the study table document is active and open the **Sort Rows** dialog. Change the **Sort by column** to **E : Density**, select **Descending**. Click **OK**.

Now, the study table sorts all the structures by density. The structure OHD–Fine PBCA – 1 has a high density value and, consequently, appears near the top of the table.

In the study table, select column **E (Density)** by clicking the column heading. Click **Quick Plot**  on the **Study Table Viewer** toolbar.

After you have finished examining the density chart, sort the table by total energy once more. You can also generate a density-energy plot.

Close the chart document and click **No** when prompted to save the document.

Open the **Sort Rows** dialog. Change the **Sort by column** back to **F : Total energy**, select **Ascending**, and click **OK**.

In the study table, click the heading of column **E** and then, holding down **SHIFT**, click the heading of column **F**. Click **Quick Plot** .

By default, the plot uses the leftmost of the two selected columns for the x-axis and the other column for the y-axis.

The density-energy plot also shows that the lowest energy structures normally have higher densities.

Close the chart document and click **No** when prompted to save it.

Note: To distinguish different crystal structures, it is usually sufficient to compare their total energies and densities.

Now create a subset of the five lowest energy structures and examine them in greater details.

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In the study table, select **Sheet 2**. Click row **1**, hold down **SHIFT**, then click row **5** to select the top five structures. From the menu bar, select **Tools | Filter**.

A new sheet contains the five selected structures. Examine each of the structures carefully. Start with the lowest energy structure, OHD-Fine PBCA - 1.

In column **A**, right-click the first structure, **OHD-Fine PBCA - 1**, and choose **Extract To Collection**.

A new 3D Atomistic Collection Document opens, containing the crystal structure of OHD-Fine PBCA - 1.

Click **3D Viewer Rotation Mode**  and rotate the structure.

To make the crystal structure clearer, you can switch off the display of the motion groups.

Hold down **ALT** and double-click a motion group.

You have selected all the motion groups. Next, hide them.

From the menu bar, select **View | Visibility | Hide**. Press **CTRL + D** to clear selection of the motion groups.

Examine the crystal structure.

Note: The name of the file has an asterisk appended. This indicates a modification to the structure so that it differs from that saved in the trajectory file.

In the Project Explorer, right-click **Extracted From Polymer Analysis.xod** and select **Rename**, change the name of the document to **overlay.xod**.

You use this collection document later to compare this structure with an experimental structure.

From the menu bar, select **File | Save Project**, and close all the open documents, apart from **Polymer Analysis.std**.

5. To compare the results with a known OHD crystal structure

Frequently, Polymorph is used to find the crystal structure of a compound for which experiments have already determined the crystal structures of other polymorphic forms. In such cases, you can assess the reliability of the Polymorph prediction procedure by verifying that the generated crystal structures with lowest lattice energies include the experimentally observed crystal structures. You can use the same clustering similarity measure to determine the agreement between the experimental structure and the calculated structures.

In this tutorial, compare the calculated crystal structures with one of the known crystal structures of OHD.

Load the experimental crystal structure for comparison.

In the Project Explorer, select the project **OHD**. Click **Import**  to open the Import Document dialog. Navigate to **Examples\Polymorph\Structures** and import the file **ohd_pm1.xsd**.

Make **Polymorph Analysis.std** the active document, on the **Sheet 2** tab select all the cells by clicking in the top left heading cell in the study table.

Click **Models** .

This opens the Models dialog, which allows you to choose a list of properties to calculate. The study table automatically includes the results. Use the *Crystal Similarity Measure* model to compare the experimentally determined crystal structure with all the structures calculated by Polymorph.

Click the **Category** heading to sort by category and locate the **Crystallization** category. Select the **Crystal similarity** row and click **Edit Model** .

This opens the Model Editor - Crystal Similarity Measure dialog.

On the **Inputs** tab, click in the **Value** cell for **Reference crystal** and select **ohd-pm1.xsd** from the list.

On the **Outputs** tab, select **Calculate** for **Crystal similarity** and click **Save**. Close the Model Editor - Crystal Similarity Measure dialog.

Click **Run** on the Models dialog, and close the dialog.

The study table now has a new column called *Crystal Similarity Measure*.

Ensure that **Polymorph Analysis.std** is the active document.

From the menu bar, select **Tools | Sort Rows...** to open the Sort Rows dialog. Change the **Sort by column** to **R : Crystal Similarity Measure**, select **Ascending**. Click **OK**.

Now, the study table sorts all the structures by their similarity to the experimental structure. The similarity measure is based on interatomic distances. Sometimes the structure with the lowest similarity measure does not necessarily correspond best to the experimentally observed polymorph. In the present case, the first 30 structures in the list include OHD-Fine_PBCA - 1.

The choice of unit cell does not necessarily match for the experimental crystal structure and the predicted crystal structures. So, to compare the crystal structures visually, overlay the experimental crystal structure with the predicted structures, looking at the molecular arrangement, rather than the size and shape of the unit cell.

Tip: Calculating hydrogen bonding patterns can help identify similar structures. However, in the present case, there is no hydrogen bonding in the structure.

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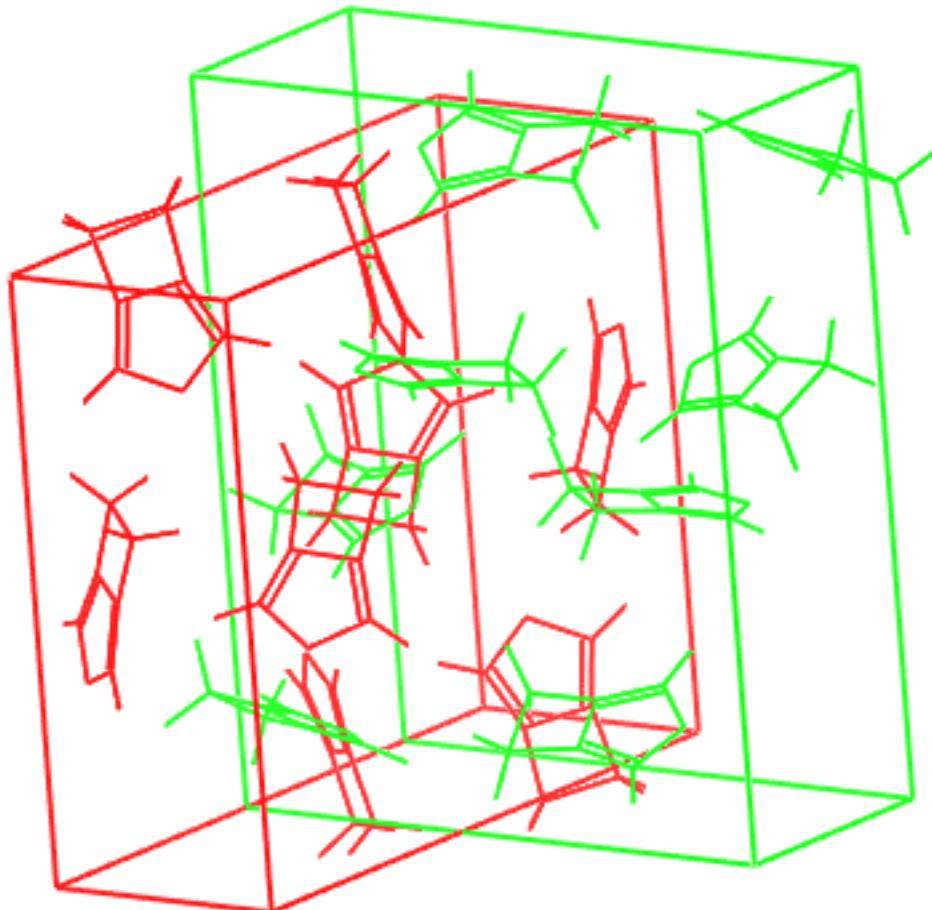
Minimize the study table by clicking the  icon. In the Project Explorer, double-click **overlay.xod** to open the predicted structure in a 3D Viewer.

Right-click in **overlay.xod** and select **Display Style** to open the Display Style dialog. On the **Atom** tab, select **Custom** in the **Coloring** section. Click the color control to display the color chooser and select **green**. On the **Lattice** tab, specify the **Color** as green as well.

Make **ohd-pm1.xsd** the active document. Click **Copy**  to copy the entire unit cell. Click in **overlay.xod** and select **Edit | Paste** from the menu bar to paste the experimental unit cell into the collection document. Change the **Atom** and **Lattice** colors to **red** using the Display Style dialog.

Expand the **overlay.xod** window by clicking the  icon. Click once in the 3D Viewer to clear the entire selection.

The experimental crystal structure and the lowest energy frame from the Polymorph run now display in the same 3D space, colored red and green, respectively.



Overlay of the experimental structure of OHD (red) and the lowest energy frame (green) from the Polymorph run

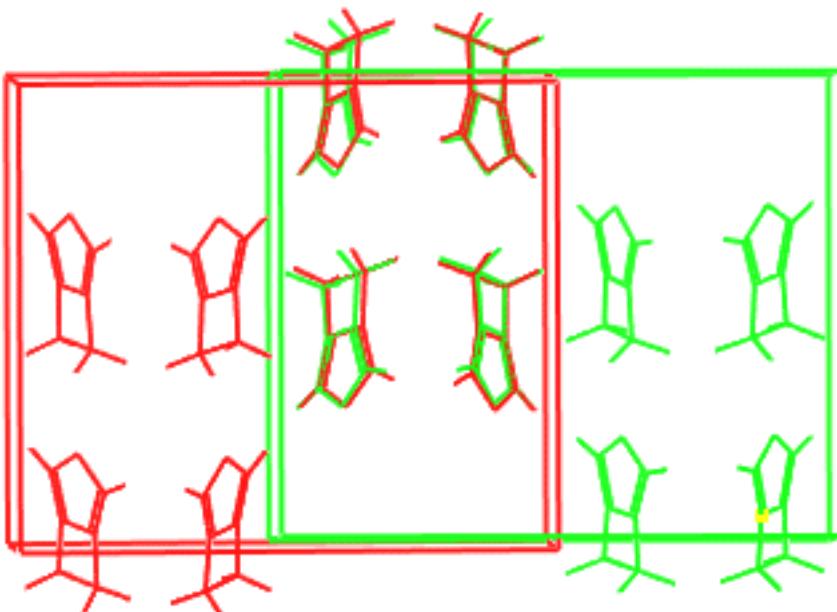
Double-click the green unit cell in **overlay.xod** to select the lowest energy frame.

To translate this unit cell independently, hold down the **SHIFT** and **ALT** keys and the right mouse button while dragging the mouse.

To rotate this unit cell independently, hold down **SHIFT** and the right mouse button while dragging the mouse.

Tip: If you have a three-button mouse or a mouse with a wheel, you can translate a selection by pressing the center mouse button or wheel and *SHIFT* while dragging the mouse.

Position the green (calculated) unit cell so as to maximize the overlap with the red (experimental) unit cell. Matching up the unit cells as closely as possible produces a view like that shown below.



Experimental structure of OHD (red) and the lowest energy frame (green) from the Polymorph run aligned for maximum overlap

You can see that the packing arrangements for the two overlaid structures are essentially the same, although the unit cell choice is different. Repeat these steps to compare other frames with the experimental structure.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

6. To identify the best match with an experimental powder pattern

You can use Polymorph for structure determination in cases where an experimental powder diffraction pattern is available but is of insufficient quality for structure determination. By comparing the experimental pattern to simulated diffraction patterns for all the crystal structures found by Polymorph, you can identify the correct crystal structure.

You can use the Powder Comparison model for this task.

Unit cell parameters calculated with Polymorph typically differ by a few percent from experimental lattice parameters, resulting in a mismatch of calculated and experimental diffraction peaks. To improve the overlap between the peak positions, broaden the experimental peak profile by convolution with a

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Gaussian function. Make sure that you use the same Gaussian function for the calculation of the simulated powder patterns. In addition, always subtract the background from the experimental powder pattern.

In the Project Explorer, select the project **OHD** and click **Import**  to open the Import Document dialog. Choose **Chart Files** from the file types list for the **File name**. Navigate to the **Examples\Reflex\Experimental Data** folder and select the file **ohd.xcd**. Click **Open**.

Click the **Reflex** arrow  on the **Modules** toolbar and select **Pattern Processing** to open the Reflex Pattern Processing dialog.

On the **Pattern Preparation** tab, in the **Background** section, increase the **Number of iterations** to **300**. Click **Calculate** and then **Subtract**.

A new chart document, **ohd (Background Removed).xcd**, displays the powder pattern without the background. You can now smooth the powder diffraction pattern. The best choice of Gaussian width for smoothing depends on the noise level and the peak width. You must find this empirically.

Select the **Pattern Processing** tab on the Reflex Pattern Processing dialog. In the **Smoothing** section, define the **Gaussian width** as **1.0**. Click **Smooth** and close the dialog.

A new chart document, **ohd (Background Removed) (Smoothed).xcd**, opens, containing the smoothed powder diffraction pattern.

Make **Polymorph Analysis.std** the active document and choose **Sheet 1**. Select all the cells by clicking in the top left heading cell in the study table.

Click **Models**  to open the Models dialog. Locate **Crystallization** in the **Category** column. Click the row for **Figure of merit** and click **Edit Model** .

On the **Inputs** tab of the Model Editor - Powder Comparison dialog, click the **Value for Experimental data** and select **ohd (Background Removed) (Smoothed).xcd** from the list. For the **Profile FWHM W**, specify **1**.

On the **Outputs** tab, select **Calculate** for **R_p**, **R_w**, and **CMACS**, and then click **Save**. Close the Model Editor - Powder Comparison dialog.

Click **Run** and close the Models dialog.

The study table has three new columns: *R_w (Powder Comparison)*, *R_p (Powder Comparison)*, and *CMACS (Powder Comparison)*. These different measures describe the level of agreement between the powder patterns. Low numbers indicate good agreements.

Ensure that the **Polymorph Analysis.std** study table is the active document.

From the menu bar, select **Tools | Sort Rows...** to open the Sort Rows dialog. Change the **Sort by column** to **S : Rp (Powder Comparison)**, select **Ascending**, and click **OK**.

Repeat the same procedure to sort the table by column **T**.

In both cases, the structure in frame 1 of the trajectory for space group PBCA appears near the top of each table. This indicates good correspondence with the experimental powder diffraction pattern. The same structure also has the lowest lattice energy, confirming that the structure in frame 1 of the trajectory for space group PBCA matches the experimental crystal structure.

From the menu bar, select **File | Save Project**, followed by **Window | Close All**.

This is the end of the tutorial.

References

Lommerse, J. P. M.; Motherwell, W. D. S.; Ammon, H. L.; Dunitz, J. D.; Gavezzotti, A.; Hofmann, D. W. M.; Leusen, F. J. J.; Mooij, W. T. M.; Price, S. L.; Schweizer, B.; Schmidt, M. U.; van Eijck, B. P.; Verwer, P.; Williams, D. E. "A test of crystal structure prediction of small organic molecules", *Acta Crystallogr., Sect. B*, **56**, 697-714 (2000).

Predicting a polymorphic form of a potential anti-cancer drug - conformational analysis

Purpose: Illustrates how to set up a molecular structure for a subsequent Polymorph calculation.

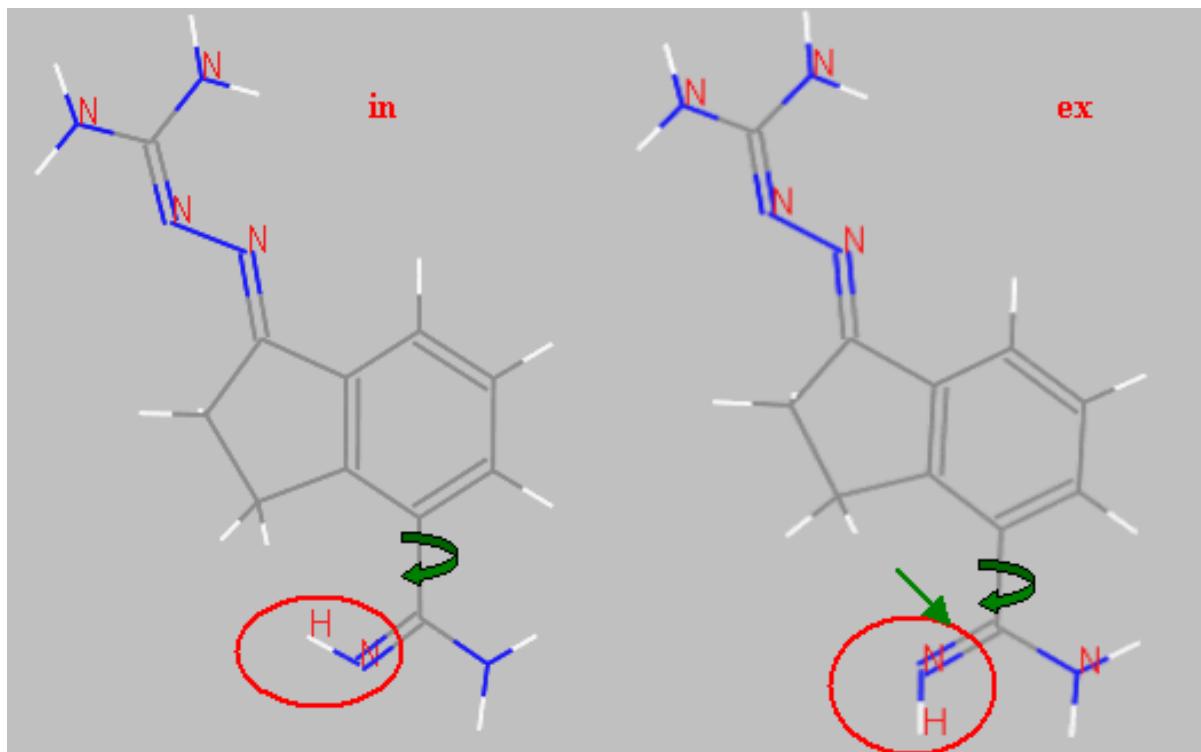
Modules: Materials Visualizer, Conformers, DMol³

Time:

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

Polymorph uses forcefield technology to propose stable packing arrangements. This method keeps the molecular geometry fixed during the Monte Carlo simulation, allowing full optimization only during the energy minimization stage. Therefore, when dealing with flexible molecules, parallel calculations must be performed for each stable molecular conformation of the compound under investigation.



The two conformers of the hydrogen atom in the terminal imino group

The ESP charges are calculated from the full electrostatic potential of the molecule. See Fitting atomic point charges to the electrostatic potential (ESP) for more details. Partial atomic charges, such as ESP charges, depend on the conformation of the molecule under consideration. Therefore they need to be recalculated for each conformer.

This tutorial shows how to perform a conformational analysis of 4-Amidino-indanone guanyl-hydrazone (AIGH) using Conformers, and how to calculate ESP-fitted charges using DMol³. AIGH was recently

suggested by scientists of Novartis as a new selective inhibitor of S-adenosyl-methionine decarboxylase, which is an anti-cancer drug (Stanek et al., [1993](#)). This example is a typical case for polymorphism of pharmaceutical compounds. Two anhydrous polymorphs are known to exist, but only one crystal structure has been determined experimentally, as suitable single crystals of the other polymorph could not be grown. Karfunkel (Karfunkel et al., [1996](#)) describes how his group used Polymorph to determine the unknown polymorphic form on the basis of ab initio packing calculations.

Introduction

The molecular conformation of AIGH differs in the rotation of the terminal amino and imino groups around the C-C bond connecting them to the ring fragment. Also, the hydrogen for the imino group can adopt one of two orientations: "in", where the hydrogen is pointing toward the ring; or "ex", where the hydrogen is pointing away from the ring.

The Conformers module is designed specifically to enable the searching of conformational space of a molecule. You can search by random, boltzmann jump, or systematic search methods. In this tutorial, you will perform two systematic searches of the C-C bond.

This tutorial covers:

- [Getting started](#)
- [To prepare the AIGH molecule](#)
- [To generate the conformers](#)
- [To calculate ESP-fitted charges using DMol³](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

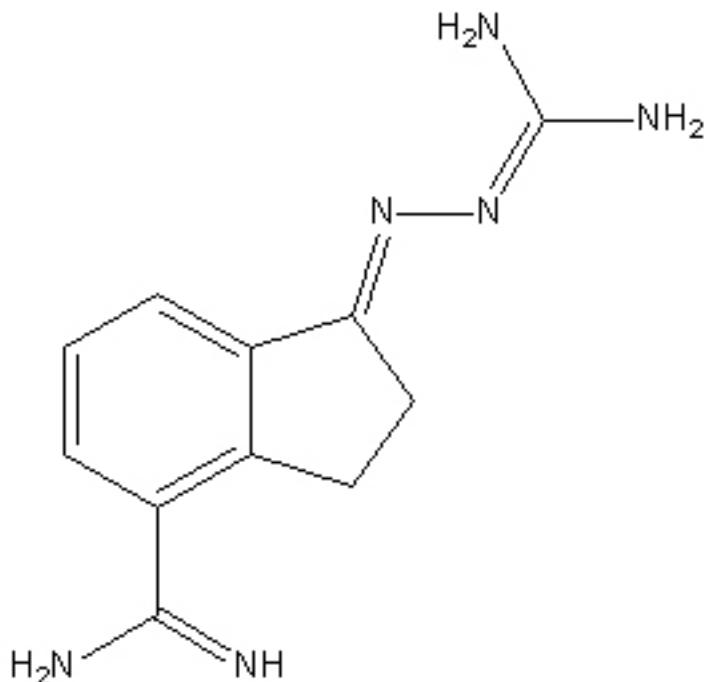
Open the **New Project** dialog and enter **AIGH_conf** as the project name, click the **OK** button.

The new project is created with *AIGH_conf* listed in the Project Explorer. Now you will import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Polymorph\Structures** folder and double-click on **AIGH-mol.xsd**.

2. To prepare the AIGH molecule

You will create two copies of the input molecule, one with the C=N torsion angle in the "in" position and the other with the torsion angle in the "ex" position.



The molecular structure of AIGH

There are many different ways to make a copy of the document in Materials Studio. In this example, you will add the C-C torsion angle, save the document, modify the "in/ex" torsion angle, and save it as a different name.

Click on the **Measure/Change** arrow on the **Sketch** toolbar, and select **Torsion** from the dropdown list. Click on the C-C single bond, identified by the curly arrow in the [sketch](#) of the *in* conformer.

You can now rename the structure as **AIGH-mol_in.xsd**.

In the **Project Explorer**, right-click on **AIGH-mol.xsd** and select **Rename** from the shortcut menu, enter **AIGH-mol_in.xsd** and press **ENTER**. Choose **File | Save Project** from the menu bar.

Modify the structure to change the imino group to the [ex position](#).

Click on the **C=N double bond** to add another torsion, identified by the straight arrow in the [sketch](#) of the *ex* conformer. Click the **3D Viewer Selection Mode** button and left click the torsion that you just created. Select **View | Explorers | Properties Explorer** from the menu bar.

The value in the *Filter* dropdown list should be **Torsion**. If it is **Bond**, the bond, and not the torsion, is selected. Click on the torsion in the structure.

In the **Properties Explorer**, double-click on **Angle**, and enter a value of **180**.

The torsion angle is now 180° . You should save the structure as the *ex* version and remove the $\text{C}=\text{N}$ torsion angle.

Select **File | Save As...** from the menu bar. Enter the filename **AIGH-mol_ex.xsd**. With the torsion still selected, press **DELETE**. Select **File | Save Project** from the menu bar.

You have created both the *in* and *ex* conformers, which will be used as the input files for the conformational search.

3. To generate the conformers

In this section, you will use the Conformers module to perform a conformational analysis independently for the *in* and *ex* structures.

Note: This section will only deal with the parts of Conformers that are applicable to this tutorial. For a more detailed introduction, please complete the dedicated Conformers tutorial.

In addition to the difference in the hydrogen orientation for the imino group, an examination of the molecular structure suggests the molecular conformation differs in a rotation of the terminal amino and imino groups around the C-C bond connecting them to the ring structure. To find the most stable conformers, you can set up a systematic search for the torsion angle.

Change the focus back to **AIGH-mol_in.xsd**. On the **Modules** toolbar, click the **Conformers** button  and choose **Calculation** from the dropdown list.

This opens the Conformers Calculation dialog. The first step is to setup the torsion angle that you want to rotate.

Click the **Torsions...** button.

This opens the Conformers Torsions dialog. Any torsion monitors that are defined on the molecule are displayed. If you have no torsions, you can use the Find functionality to search for rotatable torsions. However, you should already have the C-C torsion defined so you just need to set the # Steps. In this example, you want to minimize the structure every 1 degree whilst keeping the torsion that you are changing fixed.

Change the # Steps to **360**. Check the **Restrained** checkbox and close the dialog.

On the Conformers Calculation dialog, the Estimated conformers should be 360.

You are going to optimize the conformers as they are generated. The default optimization values are set to coarse but this can lead to some conformers not optimizing and giving odd torsion-energy plots. For this system, you should set the optimization convergence criteria to ultra-fine.

On the **Search** tab of the Conformers Calculation dialog, check the **Optimize geometry** checkbox and click the **More...** button to open the Conformers Geometry Optimization dialog. In the **Convergence tolerance** section, change the **Quality** to **Ultra-fine**. Close the dialog.

You now have to set the forcefield preferences.

On the **Energy** tab of the Conformers Calculation dialog, change the **Forcefield** to **pcff**.

Click the **More...** button for the **Summation method** to open the Conformers Non-Bond Options dialog. Change the **Truncation** to **None** and close the dialog.

The non-bond options treat the Van der Waals and Coulomb interactions. By nature, these are long range interactions and are computationally expensive so a truncation method is generally used as their

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effects decrease with distance. For this case, you are treating the non-bond interactions with no-cutoff so they are calculated for all the atoms to give you very accurate non-bond energies.

You are now ready to run the calculation. This may take a few minutes to calculate.

Click the **Run** button and close the Conformers Calculation dialog.

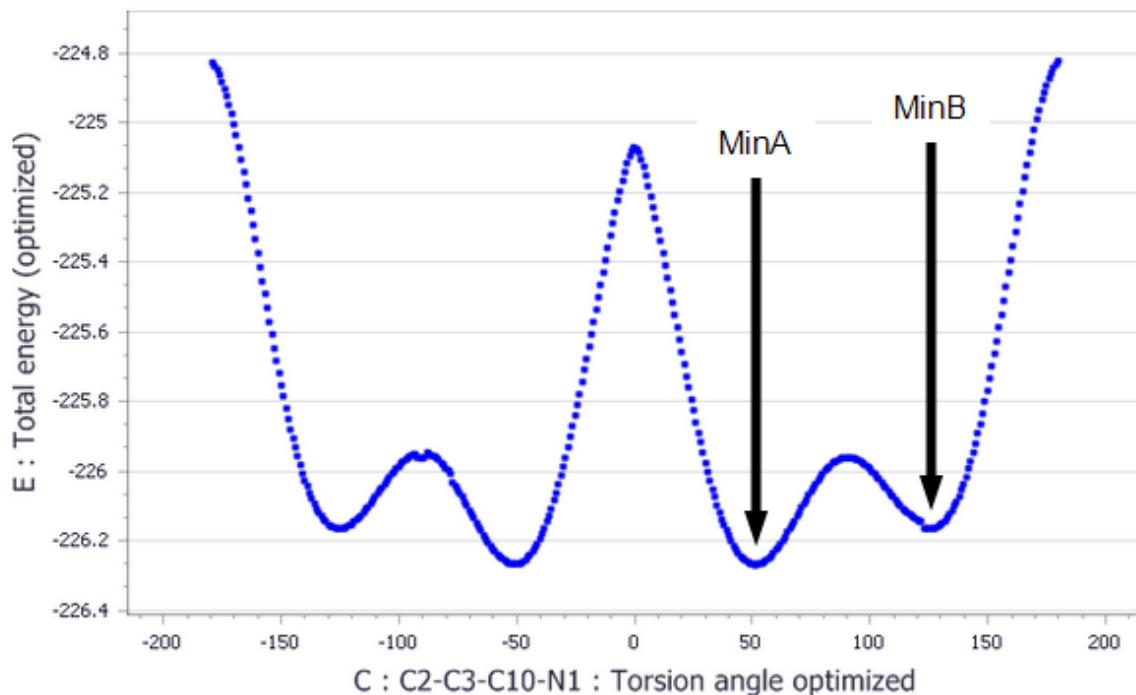
A new folder, called **AIGH-mol_in** **Conformers Calculation** is created. When the calculation completes, this will contain several documents but the one of interest is the study table as this holds the structures and energies.

When the calculation completes, select **File | Save Project** followed by **Window | Close All** from the menu bar. Re-open **AIGH-mol_in.std**.

The study table contains the structure, the optimized structures, the torsion angle that was varied, the energy of the unoptimized structure and the energy of the optimized structure. You will focus on the optimized energy and structure.

Select columns **C** and **E** and click the **Quick Plot** button .

The following chart is generated:



Energy profile for the *in* conformer

From the energy profile you can see that there are four energy minima for this system. The energy profile is almost symmetrical, so the conformers at +50° and -50° will give the same results from the polymorph search. You need to find the conformers at MinA and MinB on the chart.

Finding the lowest energy conformer can be achieved by sorting the study table by energy.

Select column **E** in the study table and click the **Sort Ascending** button.

Polymorph: Predicting a polymorphic form of a potential anti-cancer drug - conformational analysis

You will see that the two lowest energy structures are at +50 ° and -50 ° and the energy difference between them is minimal. The lowest energy conformer is AIGH-mol_in-182 optimized. This is the conformer at Min A on the chart. To find the lowest energy conformer at Min B, you should select the points on the chart, and then examine the study table.

Change focus back to **AIGH-mol_in Scatter Plot.xcd**. Draw a rectangle around the points at the bottom of the energy well in Min B.

Using the selection tools to select the points on the chart means that they will also be selected in the study table. As the rows in the study table are sorted by their energy, you just have to locate the row nearest to the top that is highlighted and this will be the minimum energy structure in the energy well.

In the Project Explorer, double-click on **AIGH-mol_in.std**. Scroll up and down the study table to find the selected row that is closest to the top of the table.

This should be AIGH-mol_in-257 optimized. You can now create two new xsd documents to hold this. You can use copy and paste to do this or you can use the collection document.

Select column **B** and click the **Sort Ascending** button. Scroll down and **select** the cell in column **B** containing **AIGH-mol_in-257 optimized**. Scroll up and hold down **CTRL** and select **AIGH-mol_in-182 optimized**. With your mouse over the selected cell, **right-click** and select **Extract To Collection** from the shortcut menu.

A new collection document is displayed with the two molecules overlaid. You can now extract these into .xsd documents.

Right-click in **Extracted from AIGH-mol_in.xod** and select **Extract to Atomistic Documents** from the shortcut menu.

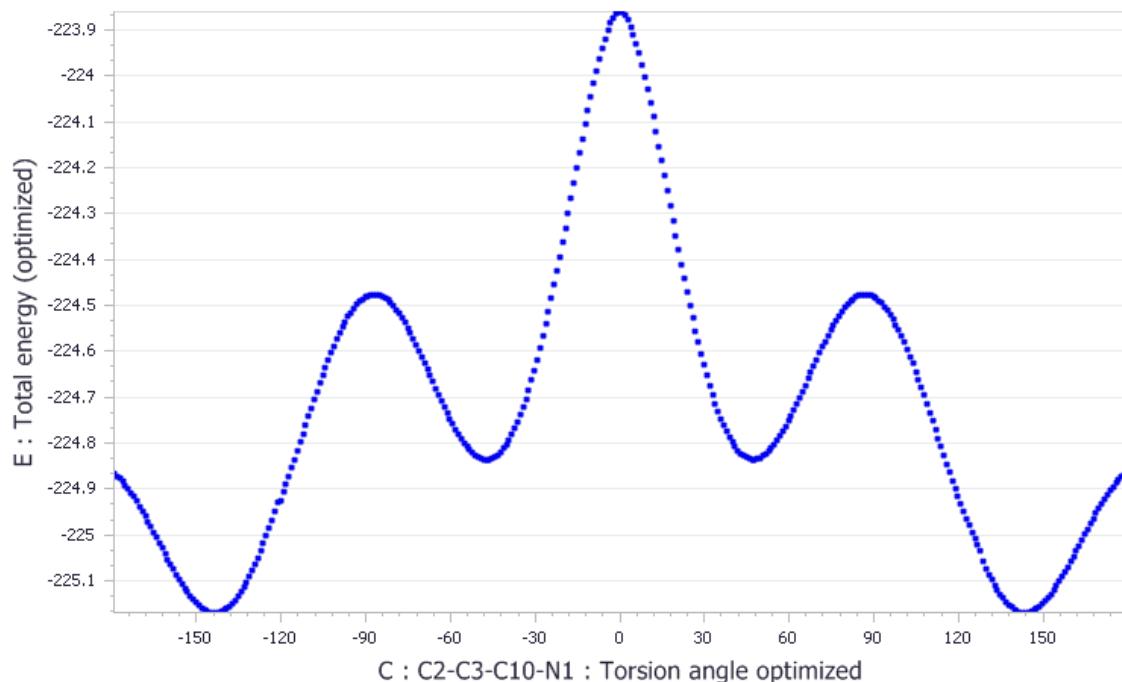
In the Project explorer, two new atomistic documents are created. You can now rename these to reflect their place in the energy profile.

Rename **AIGH-mol_in-257 optimized.xsd** to **AIGH-mol_in_MinB.xsd**. Rename **AIGH-mol_in-182 optimized.xsd** to **AIGH-mol_in_MinA.xsd**.

You will use these documents in the next section. However, you should repeat the above Conformers calculation for **AIGH-mol_ex.xsd**.

Change the focus to **AIGH-mol_ex.xsd**. Repeat the steps from the start of [section 3](#) again on this document.

You should find that you will have to reset the torsion angle for the new document but the energy setup will remain the same. Again, you can extract the frames for the two minima for further calculation. The energy profile should look similar to the one below.



Energy profile for the ex conformer

4. To calculate ESP-fitted charges using DMol³

Now you will calculate the ESP-fitted charges with DMol³. To maintain the conformation from the Conformer calculations, only a single point energy calculation will be carried out here.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**. Re-open **AIGH-mol_in_MinA.xsd**.

On the Modules toolbar, click on the **DMol3**  button and choose **Calculation** from the dropdown list. On the **Setup** tab, change the **Task to Energy**. Set the **Quality to Fine**. Select **GGA** and **PBE** from the **Functional** dropdown list.

On the **Properties** tab, check **Population analysis** and then, with this option highlighted, also check **ESP charges**. Click the **Run** button.

A new folder, called **AIGH_in_MinA DMol3 Energy**, is created in the Project Explorer. The progress of the job during the computation is presented in the form of chart and text documents. The calculation may take some time, depending on the speed of the processor in your computer. You should wait until the job finishes before proceeding.

Tip: To speed up the calculation, you can set the *Quality* to **Medium**. However, you must ensure that you choose the **DNP** basis set on the *Electronic* tab. The charges obtained from these two sets of settings are comparable.

Next you should analyze the DMol³ results and extract information on the ESP-fitted charges.

In the **Project Explorer**, double-click on **AIGH-mol_in_MinA DMol3 Energy\AIGH-mol_in_MinA.xsd**.

Click the **DMol3**  button and choose **Analysis** to open the DMol3 Analysis dialog. Select **Population analysis** from the **DMol3 Analysis** dialog. Choose **ESP** and click the **Assign ESP charges to structure** button. Close the dialog.

The ESP fitted charges are assigned to the molecule.

Right-click on the **AIGH-mol_in_MinA.xsd** document and choose **Label** from the shortcut menu. On the **Label** dialog, select **Charge** from the **Properties** and click the **Apply** button.

Once you finish examining the charges, click the **Remove All** button on the **Label** dialog to remove the charges from the display. Close the dialog.

You have now generated your first conformer ready for the polymorph calculation run.

Repeat [section 4](#) to calculate the ESP-fitted charges for the other three conformer molecules you have generated.

Tip: You should only have to re-open the DMol3 Calculation dialog and click the **Run** button as the settings will be the same.

You can now use these four conformers of AIGH as inputs to Polymorph simulations.

This is the end of the tutorial.

References

Stanek, J., Caravatti, G., Frei, J., Furet, P., Mett, H., Schneider, P., Regenass, U., *J. Med. Chem.*, **36**, 2168 (1993).

Karfunkel, H.R., Wu, Z.J., Burkhard, A., Rihs, G., Sinnreich, D., Bürger, H.M., Stanek, J., *Acta Cryst.*, **B52**, 555 (1996).

Predicting a polymorphic form of a potential anti-cancer drug

Purpose: Illustrates how to predict possible crystal packing arrangements based on molecular structures using Polymorph.

Modules: Materials Visualizer, Polymorph

Time:   

Prerequisites: [Predicting a polymorphic form of a potential anti-cancer drug - Conformational analysis](#)

Introduction

This tutorial shows how to perform a polymorph search on 4-amidinoindanone guanylhydrazone (AIGH). Four possible conformations for the AIGH molecule were obtained in the [Predicting a polymorphic form of a potential anti-cancer drug - Conformational analysis](#) tutorial. In case you have not completed this tutorial, the necessary results files are provided as part of the Polymorph installation for you to import.

You will use Polymorph to predict various crystal packing arrangements for all four conformers independently. Only one of the four conformations will lead to successful prediction of the polymorphs of AIGH.

This tutorial covers:

- [Getting started](#)
- [To set up and run Polymorph](#)
- [To analyze the results using a study table](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **AIGH** as the project name, click the **OK** button.

The new project is created with **AIGH** listed in the Project Explorer. In this tutorial, you will use Polymorph to predict crystal packing arrangements for one of the low energy conformers obtained from the previous tutorial.

Click the **Import** button  to open the Import Document dialog. Navigate to the project folder in which you saved the four results of the previous tutorial. Select the file **AIGH-mol_in_MinA.xsd** and click the **Open** button. Rename the file **aigh_in_minA.xsd**.

Alternatively, navigate to **Examples/Polymorph/Results** and select the file **aigh_in_129.xsd**. Click the **Open** button, then rename the file **aigh_in_minA.xsd**.

2. To set up and run Polymorph

According to the Cambridge Structural Database (CSD), about 90% of all organic and organometallic crystal structures are covered by the 17 most frequent space groups. Without prior knowledge of the crystal symmetry (for example from an indexable powder pattern), you will have to run the calculations in a minimum of the 5 most common space groups, or better still, in the 17 most common ones.

Make **aigh_in_minA.xsd** the active document. Click the **Polymorph** button  on the toolbar and choose **Calculation** from the dropdown list to open the Polymorph Calculation dialog. On the **Setup** tab, if the motion group is not defined click the **Assign automatically** button. Change the **Quality** to **Fine**.

In this tutorial, you will run a Polymorph prediction sequence. You could do this by running each step in the sequence separately or all of them in a single consecutive calculation. The Polymorph prediction sequence consists of four steps, namely: packing (Monte Carlo simulation), pre-clustering, optimization, and clustering. The entire sequence can take hours or even days, during which time:

- A fast and reliable Monte Carlo simulated annealing process searches the lattice energy hypersurface for probable crystal packing alternatives for the AIGH molecule, typically generating thousands of possible structures.
- Optionally, these potential structures are clustered into unique groups based on packing similarity.
- The geometry of each unique structure is optimized with respect to all degrees of freedom.
- The optimized structures are clustered again to remove duplicates. The final structures are ranked according to lattice energy.

On the **Setup** tab of the Polymorph Calculation dialog, set the **Task to Prediction**. Click the **More...** button to open the Polymorph Prediction dialog.

Check both the **Clustering** checkboxes and close the dialog.

Next, you will choose the Dreiding forcefield and use the ESP charges obtained with DMol³ earlier.

On the **Energy** tab of the Polymorph Calculation dialog, select **COMPASS III** as the **Forcefield** and set the **Charges to Use current**.

Polymorph can search all space groups. However, by default, it searches only the five most common space groups (these are the ones in the list). To speed up this demonstration of the technique, you are setting the Polymorph Predictor to search just one space group, P-1. In a real case, you would have to include all other common space groups.

On the **Space Groups** tab of the Polymorph Calculation dialog, check the **Use** checkbox for the space group **P-1** and uncheck all the others.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Uncheck the **Automatic** checkbox and enter **aigh_in_minA** as the **Job description**. Click the **Run** button and close the dialog.

The Polymorph Prediction calculation is now running and you will get regular updates about the progress of the job. You should wait until the job finishes before proceeding.

3. To analyze the results using a study table

In this section, you will analyze the output from the Polymorph run.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Click the **Polymorph** button  and choose **Analysis** to open the Insert Polymorph Results File dialog. Navigate to the **aigh_in_minA PMP Predict** directory and select **aigh_in_minA P-1.xtd**. Click the **Open** button.

All of the frames in the trajectory file are now displayed in a study table named **Polymorph Analysis.std**. The study table provides you with detailed information about each potential polymorph, including crystal *Structures* (column A), *Frame number* (column B, the lower the frame number the lower the total energy for the structure), *Space group* (column C), *Cell Volume* (column D), *Density* (column E) and *Total energy* (column F), the contribution of *van der Waals* (column G), *Electrostatic* (column H), and *H-bond energy* (column I) to the non-bond energy, and the cell parameters (columns J-O).

The name of each structure has the format: **[job name] [space group name] - [frame number]**. By default, the structures are already sorted, within each space group, according to their total energy values. The lowest energy frames are at the top of the table.

To find the most likely stable polymorphs, you can now sort the study table using different criteria, for example total energy, density, and so on.

Select **Tools | Sort Rows...** from the menu bar to open the Sort Rows dialog. Change the **Sort by column** setting to **F : Total energy**, select **Ascending**, and click the **OK** button.

All the structures are now ranked by their total energy, with the lowest energy structures at the top of the table. In this tutorial, **aigh_in_minA P-1 - 1** (which is the structure in frame 1 of the trajectory for space group P-1), is the lowest energy structure. You can also examine the energy profiles for the other structures.

You could also sort the table by density (column E). You should generate a density energy plot.

In the study table, click on the heading of column **E** and then hold down **SHIFT** and click on the heading of column **F**. Click the **Quick Plot** button .

The density-energy plot also shows that the lowest energy structures normally have higher densities.

You can now examine each possible polymorph. Start with the lowest energy structure, that in frame 1 of the trajectory.

Make **Polymorph Analysis.std** the active document. In column **A**, right-click on the first structure, **aigh_in_minA P-1 - 1**, and choose **View** from the shortcut menu.

The crystal structure of **aigh_in_minA P-1 - 1** is displayed.

Copy the entire document by pressing the **Copy** button  on the toolbar.

In the Project Explorer, right-click on the project **AIGH** and choose **New | 3D Atomistic Document**.

Paste the structure into the empty document using the **Paste** tool . In the Project Explorer, right-click on **3D Atomistic.xsd** and select **Rename** to change the name of the document to **aigh_in_minA_frame1.xsd**.

Right-click anywhere in the **aigh_in_minA_frame1.xsd** 3D Viewer and choose **Display Style** from the shortcut menu to open the Display Style dialog. On **Lattice** tab, select **Default** from the **Style** dropdown list. Set the **Max** value for **A** to **2**. Close the dialog.

To make the crystal structure clearer, you can switch off the display of the motion groups.

Hold down **ALT** and double-click on a motion group.

All the motion groups should now be selected.

To switch off the display of the motion groups, select **Visibility | Hide** from the **View** menu. Press **CTRL + D** to deselect the motion groups.

Now you will examine the hydrogen bonding patterns in the structure.

Click the **Calculate Hydrogen Bonds** arrow  and select **Monitor Hydrogen Bonding** from the dropdown list.

The hydrogen bonds are drawn as pale blue dotted lines. You can also check for close contacts in the packing arrangement.

Select **Build | Close Contacts** from the menu bar to open the Close Contact Calculation dialog. Click the **Calculate** button and close the dialog.

The close contacts are drawn as purple dotted lines in the crystal structure. There are no undesirable close contacts in this structure. All the hydrogen bonds are classified as close contacts, but are not undesirable.

To remove the display of the close contacts, hold down **ALT** and double-click on one of the purple dotted lines to select all the close contacts. Right-click on the structure and select **Delete** from the shortcut menu.

Open the **Display Style** dialog. On the **Lattice** tab, set the **Max** value for **A** to **1**.

Select all the hydrogen bonds, select **Visibility | Hide** from the **View** menu. Press **CTRL + D** to deselect hydrogen bonds.

This is the predicted structure with the lowest calculated lattice energy (for 0 K) in space group P-1.

In the Polymorph Predictor sequence, you were only considering one low energy conformation of AIGH. To get reliable results, you have to compare the results of the other conformations.

Polymorph: Predicting a polymorphic form of a potential anti-cancer drug

You also need to take into account the fact that the calculations were performed in a single space group. Without prior knowledge of the crystal symmetry (for example, from an indexable powder pattern), you should run the calculations in a minimum of the 5 most common space groups, or better still, in the 17 most common ones.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Chapter 19: QMERA tutorials

The following tutorials illustrate how to utilize QMERA's capabilities.

- [QM/MM calculation of the SW1 defect formation energy for a carbon nanotube](#)
- [QM/MM geometry optimization of a Ru\(H\)₂\(diphosphine\)\(diamine\) complex](#)

QM/MM calculation of the SW1 defect formation energy for a carbon nanotube

Purpose: Introduces how to use the QMERA module in Materials Studio. Special attention is paid to preparing the system and which type of embedding scheme to use.

Modules: Materials Visualizer, QMERA

Time: 

Prerequisites: None

Background

The Stone-Wales (SW) defect is a common defect on carbon nanotubes that is thought to have important implications for their mechanical properties (see [Andzelm et al., 2006](#)). The 90° rotation of two carbon atoms around the midpoint of the C-C bond transforms four hexagons into two pentagons and two heptagons. This substructure is known as Stone-Wales defect. In this tutorial you will calculate the formation energy of a nonchiral SW defect (SW1).

This tutorial covers:

- [Getting started](#)
- [QM region definition](#)
- [QMERA calculation](#)
- [Analysis of results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the [Creating a project](#) tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Stone-Wales** as the project name, click the **OK** button.

The new project is created with *Stone-Wales* listed in the Project Explorer.

2. Structure preparation

The first thing you need to do is prepare the structure of the single-walled nanotube (SWNT).

Select **Build | Build Nanostructure | Single-Wall Nanotube** from the menu bar. Change the **N** and **M** indices to **8** and **0** respectively.

This corresponds to a nanotube of 6.26 Å diameter.

Uncheck the **Periodic nanotube** box and change the number of **Repeat units** to **7**, this gives a nanotube length of 29.82 Å. Select **Both ends** from the **Hydrogen termination** dropdown list. Click the **Build** button and **close** the dialog.

Now you have to create the defect in the middle of the nanotube.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Click the **Stick** radio button and close the dialog.

Press the **LEFT** arrow key twice to rotate the nanotube so that you can see its full length horizontally.

The **Z** axis should be pointing to the left and the **Y** axis should be pointing up, on the axis orientation display, see [Figure 1](#).

Select two carbon atoms which are near the center of the nanotube wall and which are connected by a horizontal bond and then select the remainder of benzene rings at each end of the bond.

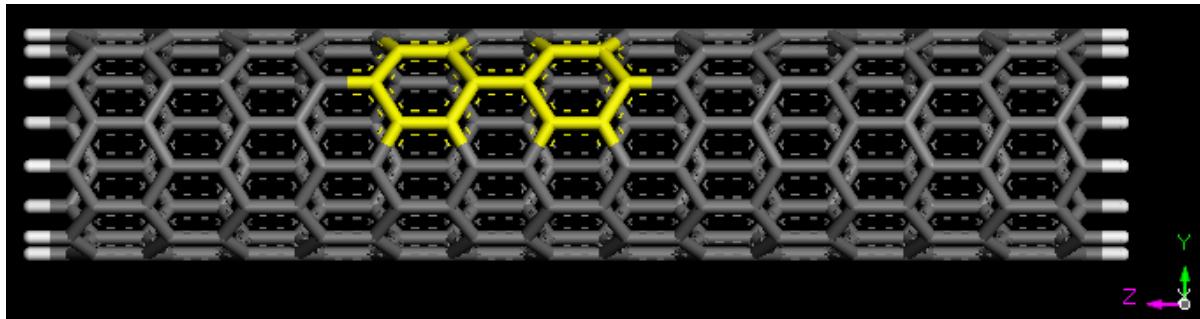


Figure 1. SWNT with two central carbon atoms and their pendant benzene rings selected.

Click on the arrow for the **3D Viewer Recenter** from the toolbar and select **View Onto** from the dropdown list. Click anywhere in the 3D Viewer to deselect everything and **reselect** the central two carbon atoms.

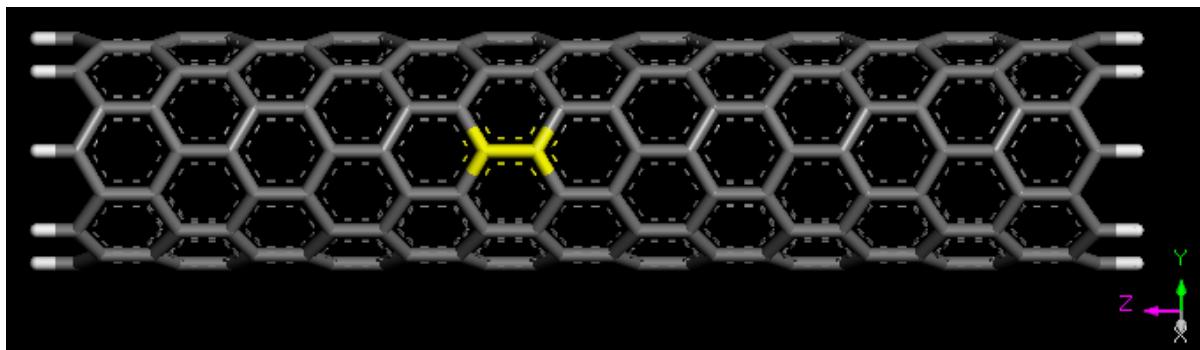


Figure 2. SWNT viewed from above, with two central carbon atoms selected.

Select the **Movement tools** from the toolbar, change the **Angle** to **90.0** and click the **Move Around Z** button. Close the dialog.

This creates the defect by rotating the two carbon atoms 90° around the screen Z axis.

To view the appropriate connectivity select **Build | Bonds** from the menu bar to open the **Bond Calculation** dialog. Uncheck **Calculate bond type**, set the **Convert representation to** option to **Resonant**. Click the **Calculate** button and close the dialog.

Rename the **SWNT .xsd** document to **SW1.xsd**.

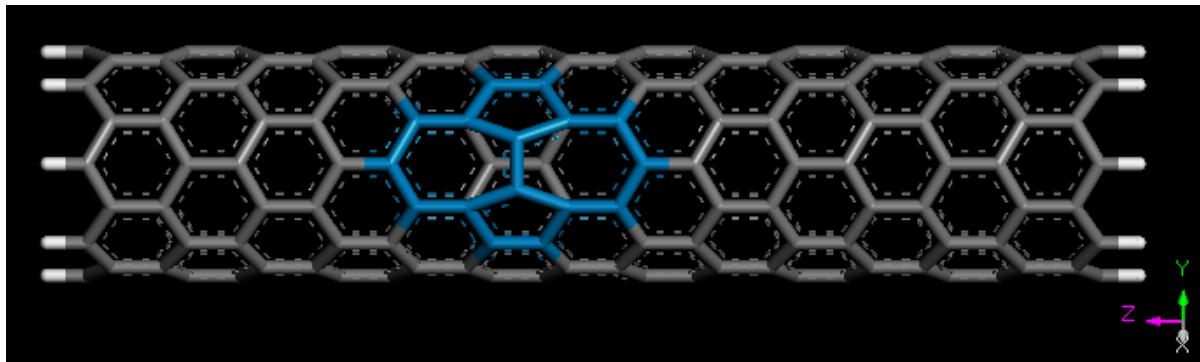


Figure 3. SW1 defect (highlighted here in blue) on an SWNT.

Tip: The input files can also be found in the *Examples* folder in the following location **Examples/Projects/QMERA/Stone-Wales Files/Documents**. The **SW1.xsd** file contains the defect structure and **SWNT.xsd** contains the defect-free nanotube.

3. QM region definition

The next step is to define the QM region that you want to use in the simulation. It is necessary to include full rings in the calculation to avoid possible clashes between hydrogen link atoms, and to leave enough space between the defect and the boundary QM-MM atoms. In this case you will include the defect plus a crown of full rings around it in the QM region (see Figure 4).

With the two carbon atoms central to the defect still selected, choose **Edit | Atom Selection** from the menu bar to open the Atom Selection dialog. Select **Connected** from the **Select by Property** dropdown list and choose the **Add to the existing selection** radio button. Click the **Select** button four times and **close** the dialog. Hold down **SHIFT** and select the **four** carbons needed to complete the crown of six-membered rings.

Select  | **Calculation** from the modules toolbar to open the QMERA Calculation dialog. Click the **Add** button to add the selected atoms to the **QuantumAtoms** set.

Click anywhere in the 3D Viewer, the atoms in the set will be highlighted in purple.

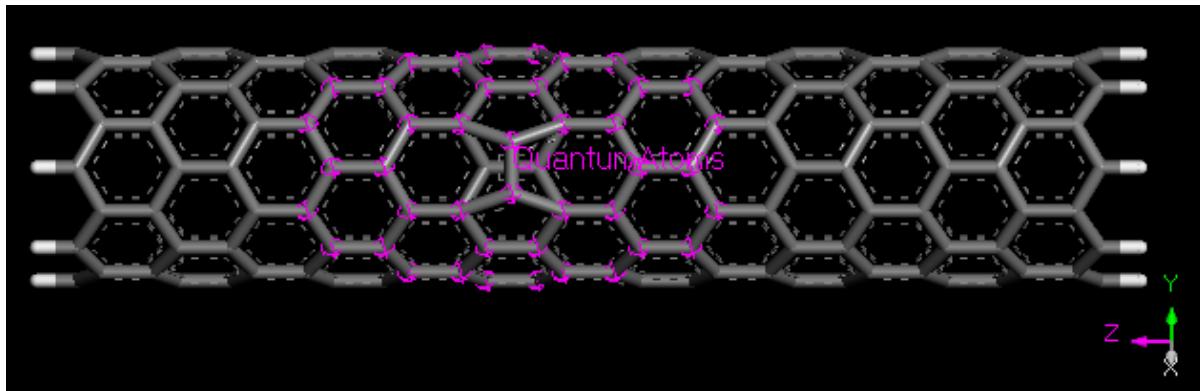


Figure 4. SW1 defect with the QuantumAtoms set defined.

If you want to visualize the hydrogen link atoms to be sure that there are no problems related to their position, you can use the **View** button on the QMERA Calculation dialog.

On the **Setup** tab of the **QMERA Calculation dialog** click the **View** button. A new window will open, double-click on the **LinkAtoms** label. Check that the position of the hydrogen link atoms makes sense and **close** the window. Click the **No** button on the dialog asking whether to save the document.

4. QMERA calculation

You are now ready to run the QMERA calculation. In this case the polarization effects are negligible and the charges of all atoms will be left as zero, which is compatible with the Dreiding forcefield. It is also sufficient to choose a mechanical embedding approach for the QM/MM calculation.

Note: By assigning charges to all atoms (for example using a charge equilibration method or using the charges from a forcefield) for this kind of embedding, the QM/MM electrostatic interaction is accounted for by the classical Coulomb interaction between all atoms. So the MM region charges do not enter the QM calculation. When non-zero charges are used, the net charges of the QM and MM regions must be integer values.

There are two different models available for mechanical embedding: QM-Pot and additive. You will use the QM-Pot model which uses a subtractive expression to calculate the total energy. Forcefield parameters are therefore required for all atoms of the system.

On the **Setup** tab of the **QMERA Calculation dialog** select **Geometry Optimization** as the **Task** and ensure that the **Quality** of the calculation is set to **Medium**.

In order to complete the tutorial more quickly, you could use the **Coarse** quality setting.

Click the **More...** button associated with the task, to open the **QMERA Geometry Optimization** dialog. Select **HDLC** as the **Method** and **close** the dialog.

The HDLC minimizer combines the use of highly decoupled delocalized internal coordinates with the linear scaling BFGS update of the Hessian (L-BFGS) method. This usually achieves faster convergence than normal BFGS or conjugate gradient methods for covalent systems of this size.

Click the **More...** button for the **QM server** to open the **QMERA DMol3 Parameters** dialog. Select **GGA** and **PBE** for the functional and **close** the dialog.

Click the **More...** button for the **MM server** to open the **QMERA GULP Parameters** dialog. Ensure that **Dreiding** is selected as the **Forcefield** and **Use current** is selected for **Charges**, **close** the dialog.

Select the **Options** tab of the **QMERA Calculation dialog**, ensure that **Mechanical** is selected as the **Embedding scheme** and **Model** is set to **QM-Pot**. Click the **Run** button.

GGA functionals provide a good description of the electronic subsystem and the PBE exchange-correlation functional has previously been identified as efficient for QM/MM calculations on nanotubes, see [Andzelm et al., 2006](#) for similar calculations.

Depending on your hardware, this calculation may take several hours to complete. If you wish to examine and analyze the results directly the output files are provided in the **Examples/Projects/QMERA/Stone-Wales Files/Documents/** directory in the **SW1 QMERA GeomOpt** and **SWNT QMERA GeomOpt** folders.

5. Analysis of results

The results of the calculation will be returned in a new folder called **SW1 QMERA GeomOpt**.

Open the **SW1.xsd** file in the **SW1 QMERA GeomOpt** folder to see the optimized geometry.

The final energy for this structure can be found in the **SW1.csout** file, the **QM/MM Energy** heading reports the corresponding energy in a.u., which is Hartree in this case.

Double-click on **SW1.csout** to open the energy file, press **CTRL + F** and enter **Energy (subtractive)** into the Find dialog.

The end of the file is displayed. Scroll up a little and examine the **QM/MM Energy**.

To examine the relationship between the energy and the structure you can compare the energy chart with the trajectory. You will need to analyze the results to obtain the trajectory and chart documents, even if you already have some charts with intermediate updates.

Select **Modules | QMERA | Analysis** from the menu bar to open the QMERA Analysis dialog. Select **Energy evolution** and click the **View** button. **Close** the dialog.

The energy evolution either creates or opens two chart documents, called **SW1 Energies.xcd** and **SW1 Convergence.xcd**.

Make **SW1.xtd** the active document and, on the animation toolbar, click on the **Play**  button.

As the animation proceeds the seven-membered rings widen.

Stop the animation and open **SW1 Energies.xcd**.

Click on a point on the graph near the beginning of the optimization.

The 3D Viewer displays the structure at the corresponding step in the calculation. In this way you can examine the structure at specific energies during the calculation.

To obtain the formation energy for the SW1 defect you need to perform a QMERA calculation with the same settings for the defect free nanotube. To do this you should use a QM region of four fused C₆ rings and a surrounding crown. The resultant QM region will be similar to the one shown in Figure 4, except that the central C-C bond of the QM region in Figure 4 will be horizontal rather than vertical. The output files for this calculation are provided in the Examples/Projects/QMERA/Stone-Wales Files/Documents/SWNT_QMERA_GeomOpt/ folder.

Once you have both calculations you can calculate the formation energy of the SW1 defect as the difference in *QM/MM Energy*, converting from atomic units to eV according to:

1 a.u. (Hartree) = 27.2113845 eV.

You should obtain a value of around 2.1 eV.

This is the end of this tutorial.

Reference

Andzelm, J., Govind, N., Maiti, A., *Chem. Phys. Lett.*, **2006**, (421), 58-62.

QM/MM geometry optimization of a Ru(H)₂(diphosphine)(diamine) complex

Purpose: Introduces how to use the QMERA module in Materials Studio with special attention paid to which type of embedding scheme to use.

Modules: Materials Visualizer, QMERA

Time:

Prerequisites: None

Background

The preparation of enantiomerically pure alcohols is of high importance in drug design. A breakthrough in this field was the discovery, by Noyori and co-workers, of highly efficient ruthenium catalysts for the enantioselective hydrogenation of ketones (*R. Noyori, Angew. Chem., Int. Ed.*, 2002, **41**, 2008). Among the best catalysts for carbonyl hydrogenation are octahedral complexes where Ru(II) is coordinated by a chiral diphosphine and a chiral diamine.

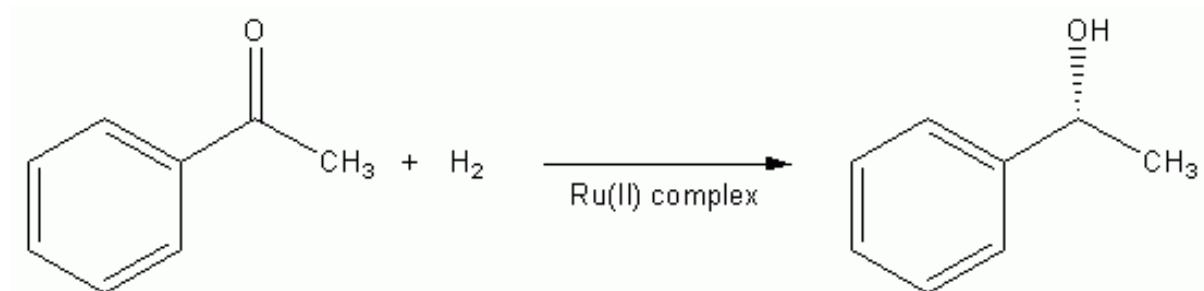


Figure 1. Conversion of a ketone to a chiral secondary alcohol.

In this tutorial you will use the QMERA module in Materials Studio to optimize the structure of a Ru(H)₂(diphosphine)(diamine) complex. You will use DMol³ to describe the QM region and the Dreiding forcefield to describe the MM region.

This tutorial covers:

- [Getting started](#)
- [Structure and QM/MM setup](#)
- [QMERA calculation](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Ru_complex** as the project name, click the **OK** button.

The new project is created with *Ru_complex* listed in the Project Explorer.

2. Structure and QM/MM setup

The structure you will use is shown below:

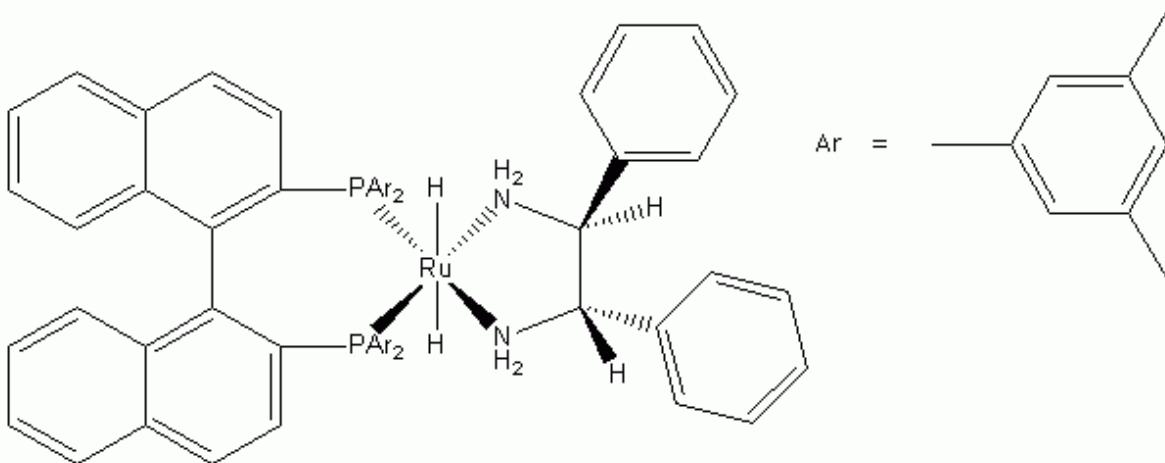


Figure 2. Ru(II) complex used as an asymmetric hydrogenation catalyst for ketones.

Select **File | Import...** from the menu bar and browse to **Examples\Projects\QMERA\Ru_complex Files\Documents\Ru_start.xsd**. Click the **Open** button.

Once you have the structure of the complex you can prepare the QMERA calculation. For this system you will include the polarization of the QM region due to the MM region. To this end, you will include the MM point charges in the SCF part of the QM calculation. This type of approach is called electrostatic embedding and it does not require forcefield parameters for the QM region, for either atom types or charges, because an additive expression is used to calculate the total energy of the system.

You need to define the QM region first. The atoms to include in the QM region are shown in Figure 3. The QM region includes the Ru center, the two hydrides (H), the two P atoms and the H₂NCH₂NH₂ diamine backbone.

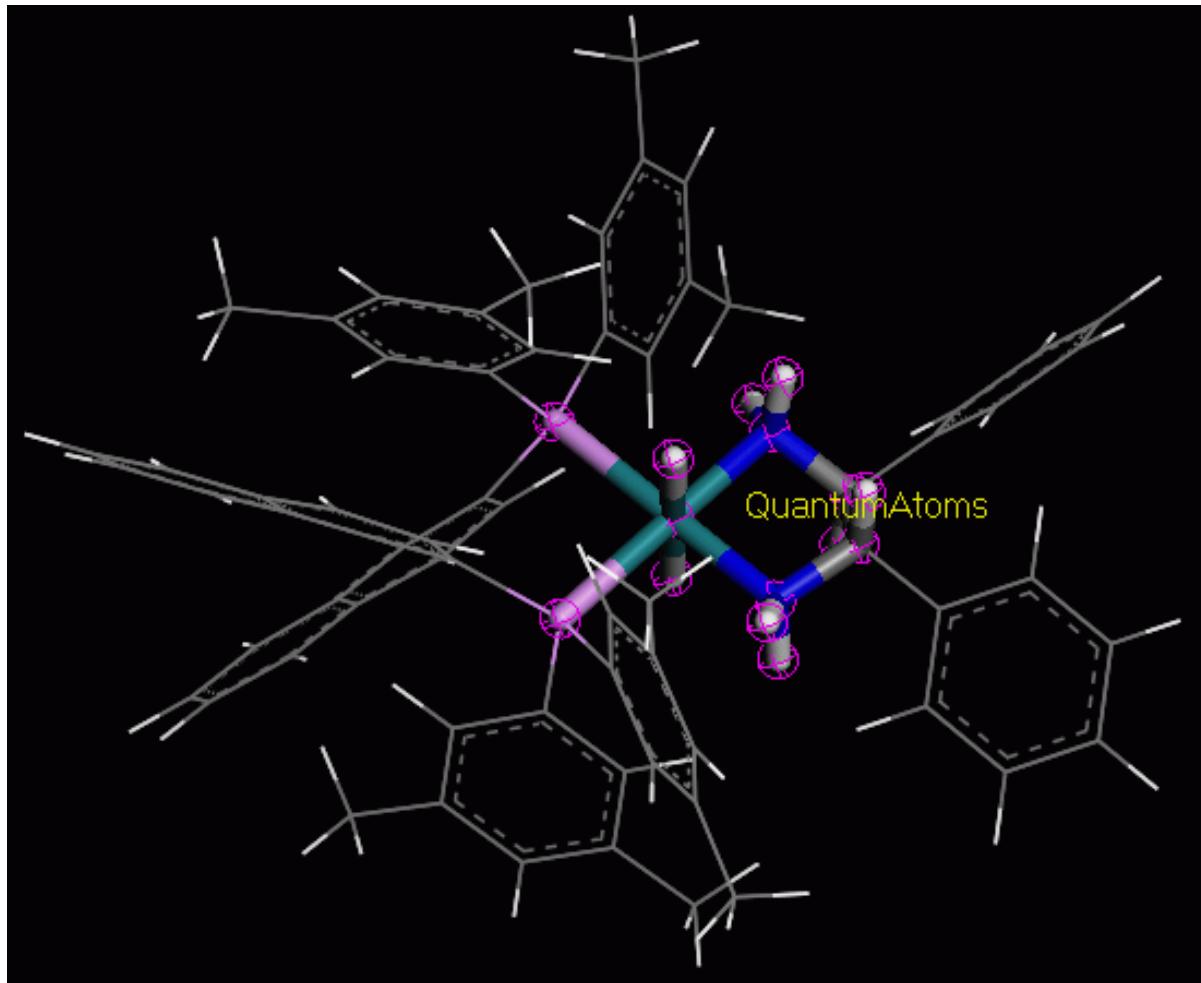


Figure 3. Ru(II) complex with the QM region indicated using stick representation.

Use the selection tool to select the QM region indicated above. Select the **QMERA** module from the Modules toolbar and choose **Calculation** to open the QMERA Calculation dialog. Click the **Add** button to add the selected atoms to the **QuantumAtoms** set.

Click anywhere in the 3D Viewer, the atoms in the set will be highlighted in purple.

If you want to visualize the hydrogen link atoms to be sure that there are no problems related to their position, you can use the **View** button in the QMERA Calculation dialog.

On the **Setup** tab of the QMERA Calculation dialog click the **View** button. A new window will open with the *LinkAtoms* selected. Check that the position of the hydrogen link atoms makes sense and **close** the window. Click the **No** button on the dialog which asks if you want to save this document.

You need to setup and modify the ligand charges. In electronic embedding methods, the basic requirement for the choice of charges is that net charge of the MM atoms must be integer. In this case this is achieved by using the QEq method to calculate separately the charges of each ligand bound to the QM region, under the constraint that the net charge must be zero.

Select **Modify | Charges** from the menu bar to open the Charges dialog. On the **Calculate** tab choose **QE_Q** as the **Method**. Select one of the MM ligand residues (for example a phenyl ring) and click the **Calculate** button. The ligand charges have been determined now. Repeat this procedure for all the other MM ligands.

Close the Charges dialog.

Note that the atoms in the QM region do not need to have charges assigned.

The prepared structure can also be imported from **Examples\Projects\QMERA\Ru_complex Files\Documents\Ru_complex.xsd**.

You can now run the QMERA calculation.

3. QMERA calculation

On the **Setup** tab of the QMERA Calculation dialog, select **Geometry Optimization** as the **Task** and **Medium** for the **Quality** of the calculation. Click the **More...** button for the **Task** to open the QMERA Geometry Optimization dialog.

Select **HDLC** as the **Method** and **close** the dialog.

Click the **More...** button for the **QM server** to open QMERA DMol3 Parameters dialog. Select **GGA** and **PBE** for the **Functional** and **close** the dialog.

This Ru(II) complex has a zero net QM charge, the two hydride ligands act as electron donors (2×-1) to compensate for the metal's $2+$ charge and no other QM atoms contribute charges (all other ligands coordinate the Ru center through dative bonding). So the DMol³ charge can remain at a value of zero for this system.

For the **MM server** click the **More...** button to open the QMERA GULP Parameters dialog. Select **Dreiding** as the **Forcefield** and **Use current** for the **Charges**, close the dialog.

On the QMERA Calculation dialog, click on the **Options** tab and select **Electronic** as the **Embedding** scheme and **Disperse boundary charge** as the **Model**. Click the **Run** button.

Depending on your hardware, this calculation may take several hours to complete. If you wish to examine and analyze the results directly the output files are provided in the **Examples\Projects\QMERA\Ru_complex Files\Documents** directory in the **Ru_complex** QMERA GeomOpt folder.

After performing the calculation for the Ru(II) complex you can proceed to include the substrate (ketone) in the calculation. The ketone will belong to the QM region and as a consequence you do not need charges or atom types for that structure. You can draw the ketone in the same document as the Ru(II) complex and add it to the QM region using the **Add** button on the QMERA Calculation dialog.

The prepared structure for the complex and substrate can be found at **Examples\Projects\QMERA\Ru_complex Files\Documents\Ru_complex+ketone_2.xsd**. If you wish to examine and analyze the results of the QM/MM calculation on the ketone system directly, the output files from the QMERA run can be found in the **Examples\Projects\QMERA\Ru_complex Files\Documents\Ru_complex+ketone_2** QMERA GeomOpt folder.

This is the end of this tutorial.

Chapter 20: Reflex tutorials

The following tutorials illustrate how to utilize Reflex's capabilities.

- [Working with powder diffraction patterns](#)
- [Indexing powder patterns](#)
- [Indexing of 4-nitrophenylhexylurethane using X-Cell](#)
- [Indexing a flat unit cell with X-Cell](#)
- [Rietveld refinement of inorganics](#)
- [Rietveld refinement with energetic considerations](#)
- [Determining the degree of crystallinity of lactose monohydrate samples](#)

Working with powder diffraction patterns

Purpose: Introduces the Reflex tools for calculating and comparing theoretical and experimental powder diffraction patterns.

Modules: Materials Visualizer, Reflex

Time: 

Prerequisites: Project management Visualizer Tutorial

Background

Simulation and analysis of X-ray, electron, and neutron diffraction patterns in Materials Studio is handled by the Powder Diffraction tool in the Reflex module. Reflex supports real-time simulation during structure manipulation, allowing you to monitor the effects of structural changes on diffraction patterns. It can also be used to compare simulated and experimental data.

Introduction

This tutorial covers:

- [Getting started](#)
- [The Powder Diffraction tool](#)
- [To use different types of radiation](#)
- [To compare two similar structures](#)
- [To manipulate the graph](#)
- [To compare experimental data with simulated data](#)
- [To export study table data files](#)
- [To monitor changes in diffraction patterns](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Indigo** as the project name, click the **OK** button.

The new project is created with *Indigo* listed in the Project Explorer. Now you will import the input file you will be studying.

Crystal structures can be imported into Materials Studio in various file formats such as **.cif** and **.PDB** files. Two structure files have been provided containing different polymorphs of the dye indigo. This is the main constituent in the color of blue jeans.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Structures** folder and double-click on **indigo_a.xsd**.

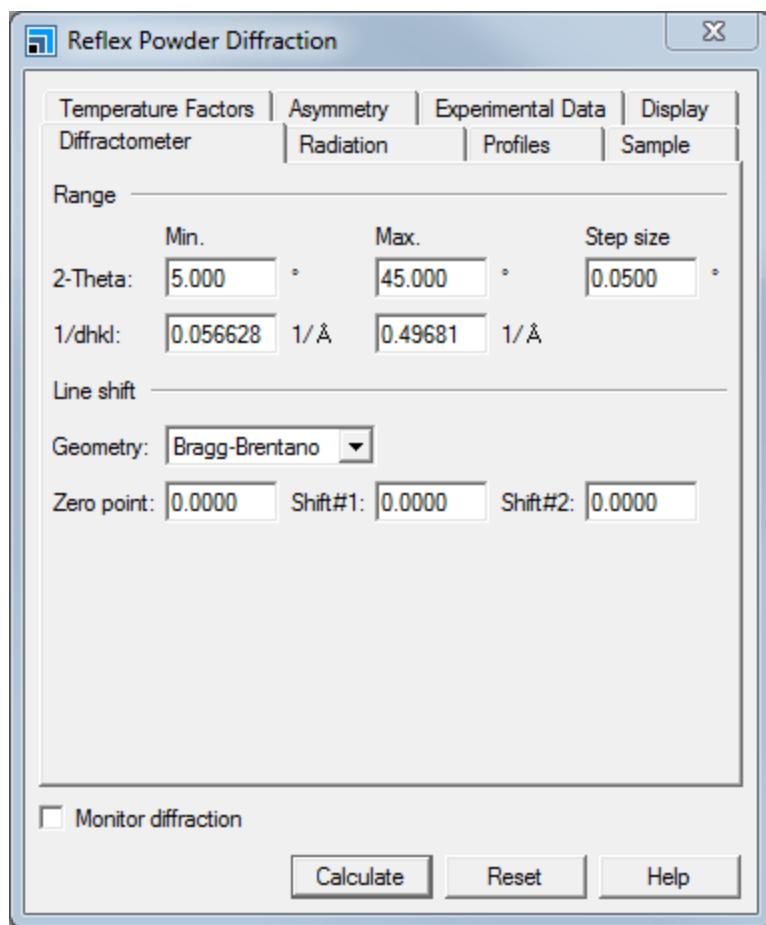
A unit cell containing six molecules is displayed in the 3D Viewer.

2. The Powder Diffraction tool

The Powder Diffraction tool is part of the Reflex module.

Click the **Reflex**  arrow on the **Modules** toolbar and select **Powder Diffraction**.

This opens the Reflex Powder Diffraction dialog.



Reflex Powder Diffraction dialog

The Reflex Powder Diffraction dialog consists of eight tabs containing all the settings you might need for the simulation and analysis of diffraction patterns.

The first step is to calculate a diffraction pattern.

Click the **Calculate** button on the Reflex Powder Diffraction dialog.

This creates a new chart document entitled **indigo_a.xcd**. This chart plots 2-theta values on the x-axis versus intensity values on the y-axis. Diffraction peaks are indicated by green markers.

3. To use different types of radiation

Different types of radiation can be used to generate powder diffraction patterns. You will now calculate powder patterns for the three different types of radiation available. The relevant parameters are on the *Radiation* tab.

On the **Reflex Powder Diffraction** dialog, select the **Radiation** tab.

This tab is split into four sections, relating to the three different types of radiation and monochromator options for X-ray diffraction. The default radiation type is X-ray and you used this to calculate your first pattern. In the X-ray radiation options section, you can choose which type of anode you would like to use as the source and if a polarization correction should be included. As you have already generated an X-ray powder diffraction pattern, you will now generate a neutron diffraction pattern.

Select **Neutron** radiation from the **Type** dropdown list.

The **Calculate** button is not active because the structure document is not in focus. To perform another calculation, you must make the 3D Atomistic document containing the indigo structure active.

Click on the 3D Viewer to make it active or double-click on **indigo_a.xsd** in the **Project Explorer**.

Now generate the powder pattern.

Click the **Calculate** button.

The chart document is updated with the diffraction pattern based on the new radiation source. You can repeat this for electron radiation.

Select **Electron** radiation from the **Type** dropdown list.

Remember to make the 3D Viewer active.

Make **indigo_a.xsd** the active document and click the **Calculate** button.

The chart document is updated again with the diffraction pattern for the new radiation source. Before continuing, return the radiation source to X-ray.

Set the radiation **Type** to **X-ray**.

4. To compare two similar structures

A second polymorph of indigo exists and its diffraction pattern can be compared with that for indigo_a.

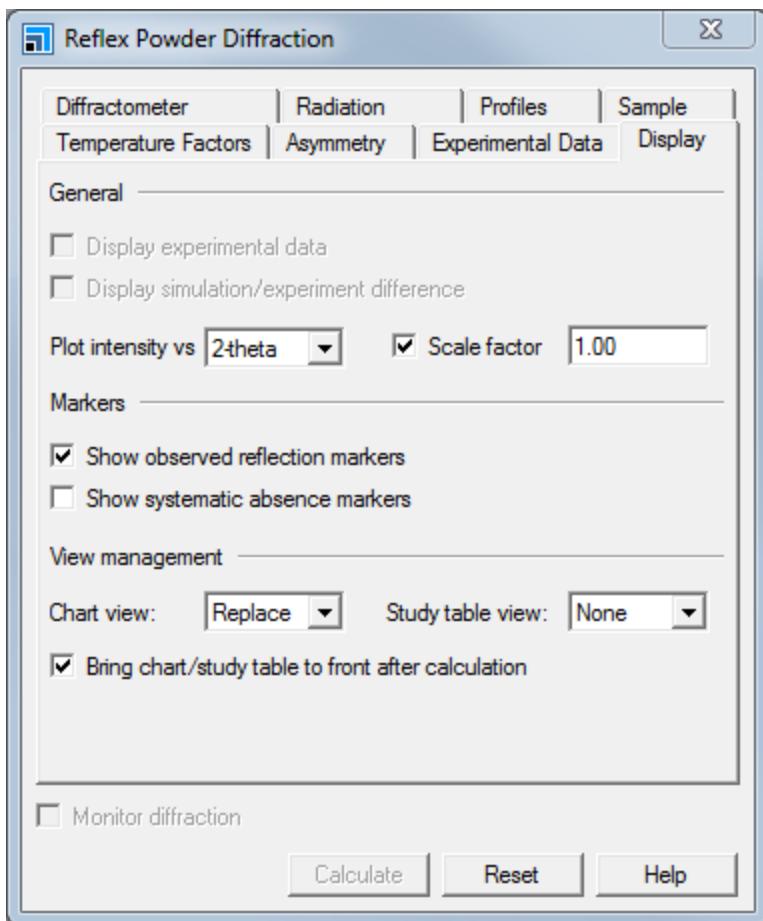
Import the crystal structure **Examples\Reflex\Structures\indigo_b.xsd**.

There are now two 3D Atomistic documents and one chart document open. You should load both sets of diffraction data into one chart document, so that you can compare them.

Make **indigo_a.xsd** the active document. Click the **Calculate** button on the Reflex Powder Diffraction dialog.

If you calculate the diffraction pattern for indigo_b now, the new graph will replace that of indigo_a, so you should first change the graph display options.

Select the **Display** tab on the Reflex Powder Diffraction dialog.



Reflex Powder Diffraction dialog, Display tab

The top section of the *Display* tab deals with the generation of graphs from experimental data. The second section controls the appearance of markers on the graph. The final section, entitled *View management*, allows you to specify the chart and study table options. The *Study table* view option allows you to output information directly to a spreadsheet style study table, as well as a graph.

The default Chart view option is *Replace* but you should change this so that the chart plots are added together.

Select **Add** from the **Chart view** dropdown list.

Now you can calculate the diffraction pattern for polymorph *indigo_b*.

Make **indigo_b.xsd** the active document and click the **Calculate** button.

A second line is added to the Chart Document. A legend is displayed at the bottom of the Chart Document indicating that the *indigo_a* data is plotted in blue and the *indigo_b* data is plotted in green.

5. To manipulate the graph

You can manipulate your view of the chart using the zoom and translate tools.

Select the **Zoom** tool  on the **Chart Viewer** toolbar. Left-click and hold in the **Chart Viewer** and move the mouse to the left and right and up and down.

Moving the mouse to the left and right compresses and expands the chart document horizontally.

Moving the mouse up and down the screen expands and compresses the chart vertically.

Select the **Translation** tool . Click in the **Chart Viewer** and move the mouse around.

The *Translation* tool acts in the same way for the Chart Viewer as it does in the 3D Viewer. You can also translate using the scroll bars.

Click on the scroll bar on the bottom of the **Chart Viewer**. Scroll across the x-axis of the document.

You can reset the view of the chart by using either the **Reset View** button or pressing HOME on your keyboard, this applies to both Chart and 3D Viewers.

Click on the **Reset View** button  on the **Chart Viewer** toolbar.

Note: If you are using a mouse with a wheel, you can use the wheel to mimic the zoom function by simply moving the wheel up and down. You can also translate by holding down the wheel and moving your mouse around the screen.

If you wish to hide a data set from the chart you can do this by unchecking the corresponding checkbox in the legend.

In the chart legend uncheck the **Observed Reflections** checkbox.

The green observed peaks are removed from the chart. Now remove the current graph from the project.

Select **indigo_b.xcd** in the **Project Explorer** and click the **Delete** button . When a dialog opens asking if you are sure, click the **Yes** button.

Having removed the chart document, you should now save the project.

Select **File | Save Project** from the menu bar.

Finally, you should change the *Chart view* option back to *Replace*.

On the **Display** tab of the Reflex Powder Diffraction dialog, select **Replace** from the **Chart view** dropdown list.

6. To compare experimental data with simulated data

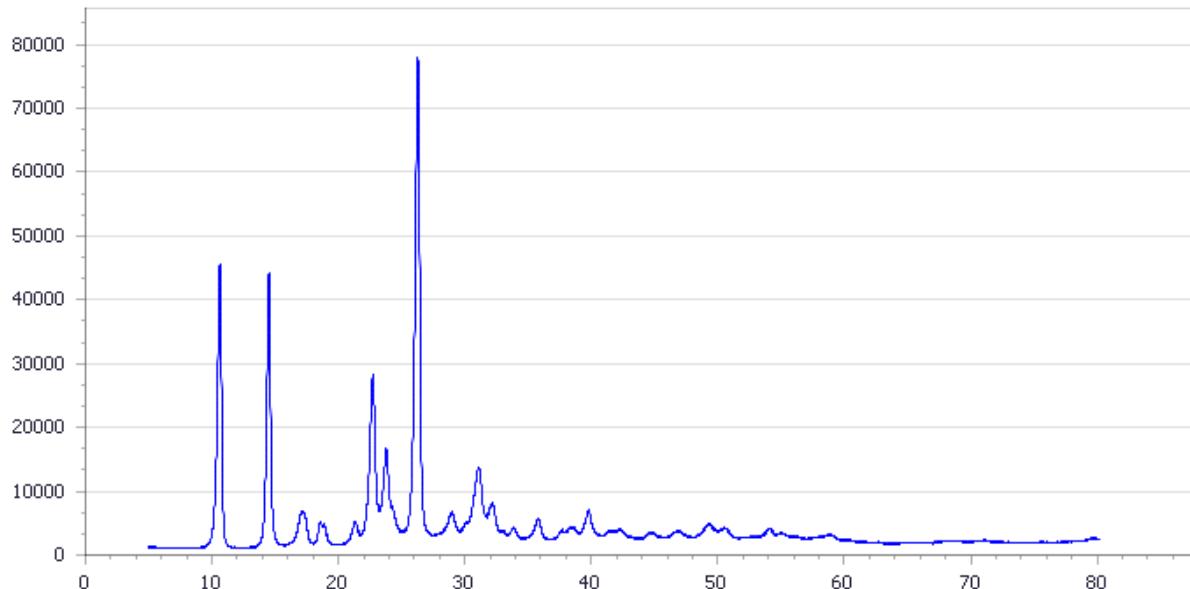
An important feature of the Powder Diffraction tool is the ability to compare simulated diffraction patterns with those obtained experimentally. Materials Studio accepts many different experimental data formats but in this tutorial you will import data in the .3cam file format developed at Cambridge University.

Now import the experimental data, which was obtained using X-ray radiation.

Click on the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and open **indigo_1.3cam**.

The diffraction pattern is opened in a new Chart Viewer.

Reflex: Working with powder diffraction patterns



Select the **Experimental Data** tab, to display information about the experimental data file that you have imported.

On the Reflex Powder Diffraction dialog, select the **Experimental Data** tab and choose **indigo_1.xcd**. Click the **View** button.

The data consists of a filename, pattern, start and end values and step size. Now tell the program that you want to display the experimental data in your next chart.

On the **Display** tab check the **Display experimental data** checkbox.

The *Display simulation/experiment difference plot* option is now active.

Check the **Display simulation/experiment difference** checkbox.

X-ray radiation was used to obtain the experimental results, so you must make sure that the simulated data are also based on X-rays.

On the **Radiation** tab, ensure that the radiation **Type** is set to **X-ray**.

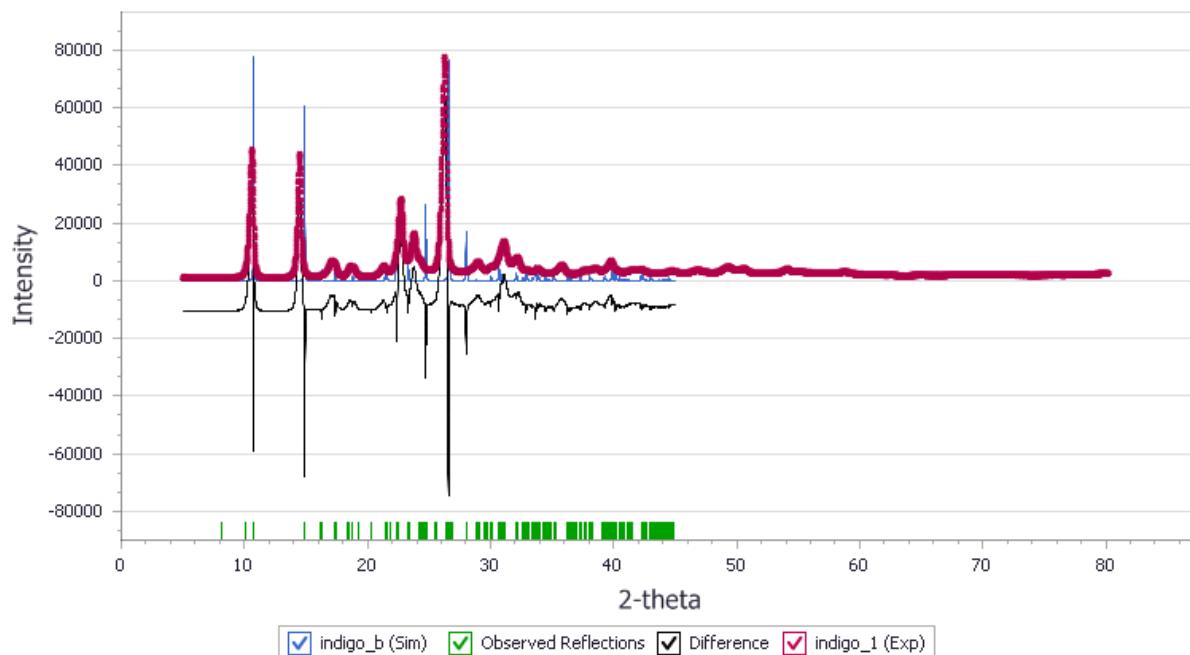
Before you display the plot, you must select the structure you would like to run the calculation on. This is done by making the required structure the active document.

Double-click on **indigo_b** in the **Project Explorer**.

Now generate the diffraction pattern for the **indigo_b** structure and compare it with the experimental data.

Click the **Calculate** button.

The generated plot should look similar to this.



The chart shows the experimental data in red, the simulated data in blue, and the difference between the two in black. Green observed check marks are also displayed.

You can see that the experimental data and the simulated data do not fit well. There are peaks in the experimental data that do not exist in the simulated data and vice versa. For example, there are simulated peaks at 2-theta values of approximately 25 and 28 that do not appear in the experimental pattern.

You will also notice that the experimental information range ends at 80.170, whereas the simulated data ends at 45. You can specify the range of the simulated data on the *Diffractometer* tab.

On the **Diffractometer** tab change the **2-Theta Max** value from 45 to **80.00**.

Now repeat the calculation with the wider 2-theta range.

Double-click on **indigo_b** in the **Project Explorer** and click the **Calculate** button on the Reflex Powder Diffraction dialog.

The chart is updated with the full range of the 2-theta values displayed.

Next compare the experimental data with the simulated pattern of the **indigo_a** polymorph.

Double-click on **indigo_a** in the **Project Explorer** and click the **Calculate** button on the Reflex Powder Diffraction dialog.

The new simulated diffraction pattern is in good agreement with the experimental data. There are no peaks that do not match up and the difference plot is much improved. This indicates that this is the polymorph identified experimentally.

You can improve the quality of the match by changing the sample crystallite size or the experimental resolution. Try reducing the crystallite size first and then the experimental resolution. The crystallite size can be specified using the *L** parameters.

On the **Sample** tab in the **Crystallite size** section, check the **Use in broadening calculation** checkbox. Change the values of L_a , L_b and L_c from **500** to **300**.

The crystallite size is the average size of the crystals in the powder. Generally, powders consist of different sizes of crystallites and these affect the broadness of the peaks in the experimental results. To improve the fit between the experimental results and the simulated results, you can change the simulated crystallite size.

Make **indigo_a** the active document and click the **Calculate** button.

Now change the experimental resolution on the *Profiles* tab.

On the **Profiles** tab change the **W** parameter to **0.24**.

Make **indigo_a** the active document and click the **Calculate** button.

The width of the simulated data peaks increases and the peaks above a 2-theta value of 35 match much better with the experimental data.

7. To export study table data files

It is also possible to export the diffraction data in study table form, that is as a spreadsheet. This is useful if you need the precise values of the peak intensities. The data can also be copied and pasted into most spreadsheet packages.

Select **File | Save Project** from the menu bar.

On the **Display** tab of the Reflex Powder Diffraction dialog, in the **View management** section, change the **Study table view** from **None** to **Replace**.

When you generate a powder diffraction pattern, you will also generate the spreadsheet style study table information to go with it.

Make **indigo_a** the active document and click the **Calculate** button.

The Chart Document is updated and a new Study table Document is displayed with several columns containing information about the calculations.

Note: The study table contains only the simulated data. It does not include the experimental data.

You can either leave this information in the Study Table (.std) file or you can copy and paste it into a spreadsheet package.

Before you continue, remove the Chart Document.

Select **indigo_a.xcd** in the **Project Explorer** and click the **Delete** button . When a dialog opens asking if you are sure, click the **Yes** button.

8. To monitor changes in diffraction patterns

The Monitor diffraction tool in Materials Studio allows you to make changes to a structure and watch the effects of those changes in real-time. These changes can include stretching or compressing bonds or changing the orientation of the molecules within the cell. In this section, you will monitor the changes in the diffraction pattern as you rotate the molecule in the cell and then as you stretch a bond in the indigo_a structure.

The first step is to close the other documents in the Visualizer.

Close the **indigo_b** 3D Viewer.

This does not remove the structure from the project but only from the Visualizer. Now set the Powder Diffraction options to monitor the diffraction.

Select the **Display** tab on the Reflex Powder Diffraction dialog and change the **Study table view** option to **None**. Ensure that **indigo_a.xsd** is the active document and check the **Monitor diffraction** checkbox.

The text at the bottom of the Powder Diffraction dialog changes to read Monitor diffraction: **indigo_a**. The chart document is displayed as normal. At this point, it is best to close the Powder Diffraction dialog as you are going to need room for visualization.

Close the **Reflex Powder Diffraction** dialog.

You can also move and resize the Chart and 3D Viewers so that you have a good view of both of these. Now select a fragment from the **indigo_a** structure to rotate.

Select any atom in one of the fragments, right-click and choose **Select Fragment** from the shortcut menu.

One of the structures in the cell is selected. Since the molecules in the cell are all related by symmetry, when you rotate one structure, you will automatically rotate the rest.

Hold down **SHIFT** and the right mouse button. Move the mouse.

As you rotate the fragment, the chart data changes because the relative positions of the groups have changed. You can also change the diffraction pattern by changing the bond lengths. Try stretching and moving one of the carbonyl oxygen atoms.

Click on one of the red oxygen atoms. Hold down **SHIFT + ALT**, right-click and drag the mouse.

Tip: If you have a three button mouse or a mouse with a wheel, you can translate the fragment by holding down **SHIFT** and the middle mouse button or wheel.

The oxygen is dragged as you move the mouse and the position and length of the bond changes. This has an immediate and observable effect on the diffraction pattern.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Indexing powder patterns

Purpose: Introduces the Powder Indexing tool and chart document manipulation enabling you to index powder patterns and determine cell parameters from experimental data.

Modules: Materials Visualizer, Reflex

Time: 

Prerequisites: [Working with powder diffraction patterns](#)

Background

Certain compounds are difficult to crystallize. Often it is impossible to grow single crystals of such compounds of sufficient quality for X-ray analysis and subsequent structure solution. Instead, the crystallization experiments result in the formation of a crystalline powder. Such polycrystalline materials can be analyzed using powder diffractometry. A powder diffraction pattern is a 2D representation of the 3D crystal structure. The peak positions are related to the unit cell parameters, while the intensities of the peaks carry information about the space group and the arrangement of atoms in the unit cell.

Using modern software tools, crystal structures can now be solved routinely from powder diffraction data. In general, the determination of unit cell parameters from peak positions, a process known as indexing, is the first step toward determining the crystal structure.

Introduction

This tutorial shows how the Powder Indexing tool can be used to index powder diffraction patterns within Materials Studio. You will learn how to create peak lists for analysis and how to set up an indexing calculation.

Two powder patterns will be indexed, belonging to an organic and an inorganic compound. You will use different methods to establish a list of diffraction peaks.

This tutorial covers:

Getting started

Indexing the powder pattern of an organic compound

- To import the powder data
- To create a peak list
- To use the Marker tool on the Chart Viewer toolbar
- To recalculate the peak list
- To index the powder pattern

Indexing the powder pattern of an inorganic compound

- To import the data
- To remove the background noise
- To use a Study Table document to add markers
- To index the powder pattern
- To compare the indexing result to a crystal structure

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Getting started

Begin by creating a new project.

Open the **New Project** dialog and enter **Indexing** as the project name, click the **OK** button.

The new project is created with *Indexing* listed in the Project Explorer.

Indexing the powder pattern of an organic compound

1. To import the powder data

First create a folder for the powder pattern of cholamide dihydrate.

Right-click on the **Indexing** project root  in the Project Explorer and select **New | Folder**. Rename the folder **dihydrate**.

Next import the chart document containing the powder diffraction pattern into the dihydrate folder.

Click the **Import** button  to open the Import Document dialog. Select **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder. Locate and load the **dihydrate.xcd** file.

The powder pattern of cholamide dihydrate opens in a new Chart Viewer.

2. To create a peak list

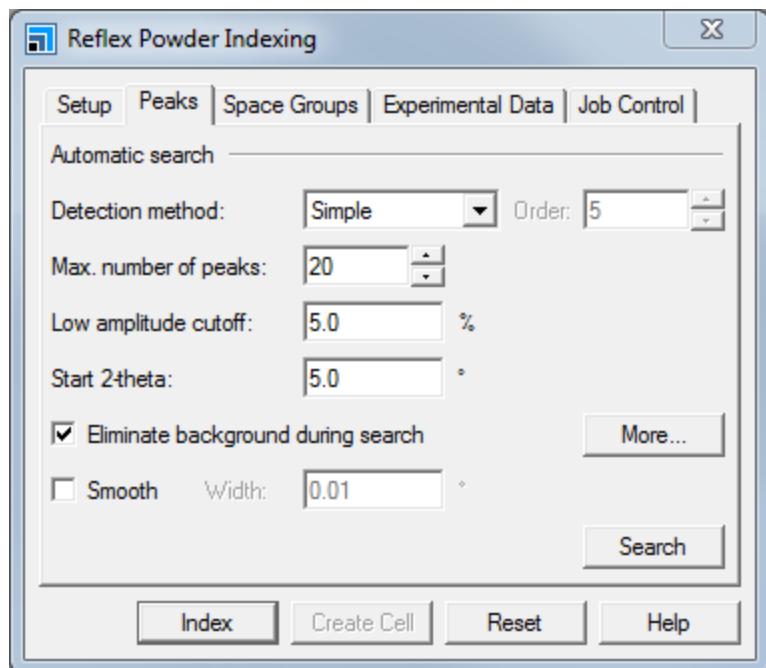
Next identify the peaks that will be used to index the pattern. This is done initially using the automatic peak search functionality.

Click the **Reflex** arrow  on the **Modules** toolbar and select **Powder Indexing** from the dropdown list.

This opens the Reflex Powder Indexing dialog.

Select the **Peaks** tab.

Reflex: Indexing powder patterns



Reflex Powder Indexing dialog, Peaks tab

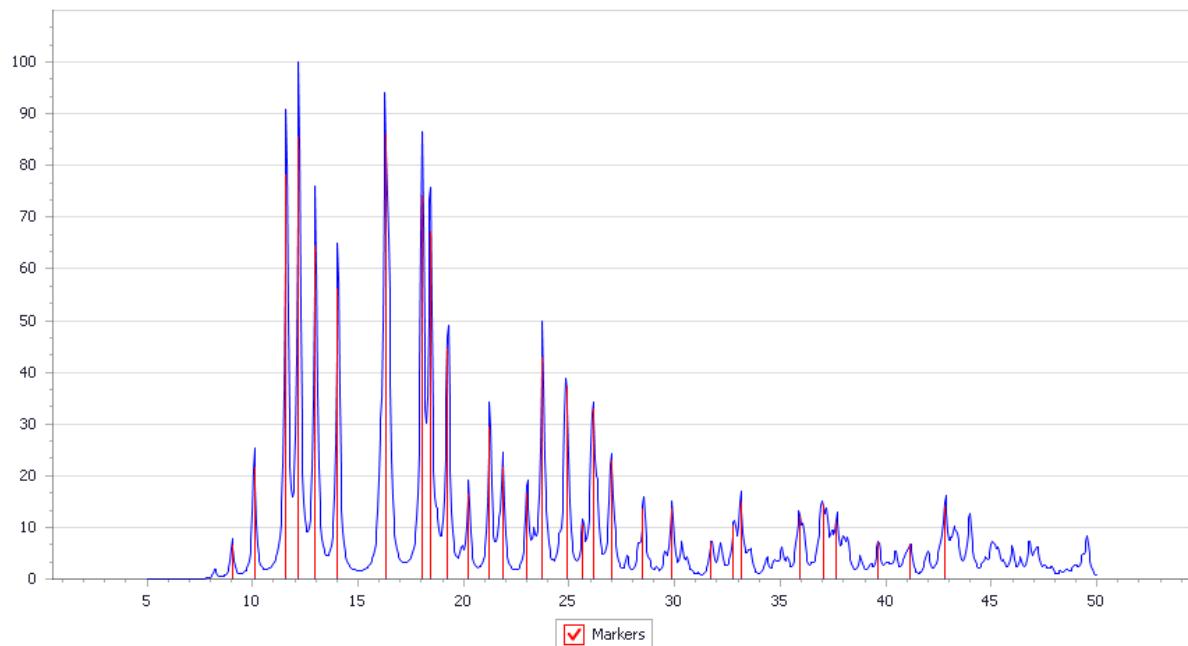
You can change the maximum number of peaks you wish the search algorithm to detect. The appropriate value for this parameter will vary between powder patterns, in this example you should use a value of 30.

Increase the **Max. number of peaks** to **30** and select **Savitzky-Golay** from the **Detection method** dropdown list.

The Low amplitude cutoff is the percentage of the maximum peak height below which peaks will not be selected. This value depends on the intensity distribution of the background noise. For this example, there is no need to edit this, or any of the other parameters on the *Peaks* tab.

Click the **Search** button and close the Reflex Powder Indexing dialog.

Markers identifying the peaks that have been located are displayed in light blue in the Chart Viewer.



The chart document with peak markers.

If the automatic peak search gives unsatisfactory results, you can remove markers easily. If, for example, there are one or two markers identifying very small peaks, these can be removed individually.

Alternatively, if many very small peaks are marked, the peak search can be rerun with a different Low amplitude cutoff.

3. To use the Marker tool on the Chart Viewer toolbar

New markers can be added using the Marker tool on the Chart Viewer toolbar.

Click the **Marker** button  on the **Chart Viewer** toolbar. Left click to place the marker.

You can force the marker to jump to the nearest data point by holding down **CTRL** while placing the marker.

Left-click on a data point for another marker, then hold down **CTRL** and drag the marker.

You can move an existing marker by left-clicking and dragging. Hold down **CTRL** while you drag to jump to the nearest data point. If you subsequently decide the original position was correct, you can press **ESC** to cancel the operation.

Left-click on one of the markers, keep the mouse button held down and move the cursor. Press **ESC**.

The X and Y coordinates of the marker can be examined and edited in the Properties Explorer.

Select **View | Explorers | Properties Explorer** from the menu bar to display the Properties Explorer.

Choose the **Selection** tool  and click on a marker in the Chart Viewer to select it. In the Properties Explorer, set the **Filter** to **Chart Markers**.

The Properties Explorer lists the attributes of the marker, including *IsUsed*, *X*, and *Y*.

Reflex: Indexing powder patterns

Click on the **Value** for **Y** in the Properties Explorer to make the value editable. If the marker is not the same height as the peak it is marking change the value of **Y** and press **Enter**.

Tip: Alternatively you can view the X and Y coordinates of markers and other points using the crosshair. To show the crosshair, right-click on the chart and choose **Show Crosshair** from the context menu. The coordinates of data points and markers that are close to the mouse pointer are displayed in a tooltip.

You can delete one or more markers by selecting them and pressing **DELETE**.

Hold down **SHIFT** and left-click on several markers. Move the cursor away from the selected markers and press **DELETE**.

The selected markers are identified a blue circle with yellow fill at their tip. Pressing **DELETE** removes all of the currently selected markers. You can select all of the markers in a chart, and all the points, using **CTRL + A**.

Press **CTRL + A**, then press **DELETE**.

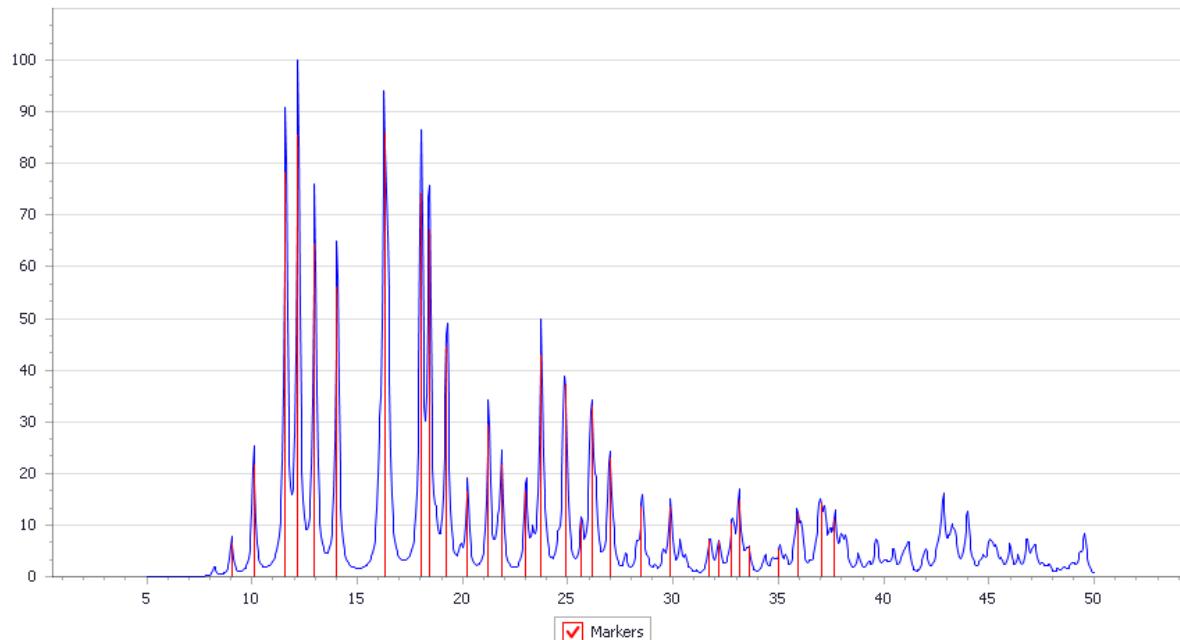
Only the markers are deleted, because points cannot be deleted.

4. To recalculate the peak list

Since you have added and removed peaks, you should perform the peak search again. This time you will change the *Low amplitude cutoff* to 3%.

Open the **Reflex Powder Indexing** dialog. On the **Peaks** tab, change the **Low amplitude cutoff** to 3 %. Click the **Search** button.

The new search results are displayed.



This time, the smaller peaks have not been marked as they are less than 3% of the height of the highest peak. This has improved the peak search but, before you index the pattern, there are still some peaks

that need to be added and removed. You can remove the peaks by selecting them and pressing **DELETE**. You can add peaks using the *Marker* tool.

You are now ready to index the powder pattern.

5. To index the powder pattern

The selected peaks will be used to index your powder pattern. Four methods for indexing powder patterns are available with Materials Studio. TREOR90 ([Werner et al., 1985](#)) is a non-exhaustive trial-and-error method. DICVOL91 ([Boultif and Louër, 1991](#)) is a quasi-exhaustive algorithm that gives the user additional control over the peak position error, cell parameter limits and density constraints. ITO ([Visser, 1969](#)) searches for unit cells by first identifying groups of diffraction peaks that belong to the same plane of the reciprocal lattice. These planes are then combined to find the reciprocal lattice. X-Cell ([Neumann, 2003](#)) is a novel indexing algorithm, developed at BIOVIA, that makes use of systematic absences to facilitate the search for possible indexing solutions.

You will use the TREOR90 indexing program in this example. Before performing the indexing calculation you should specify which crystal systems you want to examine.

On the **Setup** tab of the Reflex Powder Indexing dialog, check all of the **Crystal systems to test** checkboxes. Click the **Index** button.

When the job is finished a dialog reports the status as completed.

Click the **OK** button on the Job Completed dialog.

A study table document containing the results of the calculation is displayed, as shown below.

dihydrate Reflex TREOR\dihydrate.std												
	A	B	C	D	E	F	G	H	I	J	K	L
#	F O M	Peaks Found	System	a	b	c	alpha	beta	gamma	Volume	Program	
1	1 11.00000000	30 of 30	Monoclinic	11.36406100	10.80309500	10.33639300	90.00000000	108.74907000	90.00000000	1.201630e+003	TREOR90	

Study table document showing results of indexing calculation.

TREOR90 only reports one solution. By contrast, the other indexing methods frequently find more than one possible unit cell and the various solutions are listed in separate lines of the study table document. These are rated according to their Figure of Merit (FOM). Each line contains information about the crystal system, the cell lengths, a , b , c , the cell angles, α , β , γ , and the cell volume.

Compare your results with the following: $a = 11.3620(7)$ Å, $b = 10.8162(7)$ Å, $c = 10.3344(7)$ Å, $\beta = 108.730(6)^\circ$, $V = 1202.8(3)$ Å³, P21, monoclinic - see Wahle et al. ([1997](#)).

The final step in the indexing procedure is to create an empty unit cell using the new lattice parameters.

Click on the first row marker, **1**, in the study table document and click the **Create Cell** button on the Reflex Powder Indexing dialog, close the dialog.

A new 3D Atomistic document containing the empty unit cell is displayed in the Visualizer, called **dihydrate1.xsd**.

You might like to repeat the indexing procedure with different parameter settings. For example, try changing the Low amplitude cutoff to 1.0 or alter the number of peaks included in the analysis to more than 30.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

Indexing the powder pattern of an inorganic compound

1. To import the data

First create a new folder to work in.

Right-click on the **Indexing** project and select **New | Folder** from the shortcut menu. Rename the folder **fin31**.

Now import the files containing the powder diffraction data into the fin31 folder.

Select the **fin31** folder. Click the **Import** button  to open the Import Document dialog. Ensure that **Chart Files** is selected from the **Files of type** dropdown list. Open **fin31.3cam**.

2. To remove the background noise

You can use the Pattern Processing tool to remove background noise from an experimental powder pattern.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. Select the **Pattern Preparation** tab and click the **Calculate** button.

The background noise is highlighted in red on the chart document.

Click the **Subtract** button on the **Pattern Preparation** tab.

A new chart document entitled **fin31 (Background Removed).xcd** is added to the project and the background noise is removed from the powder pattern.

3. To use a Study Table document to add markers

In the first example you added markers directly to the chart document. However, you can instead type peak positions into a single column in a study table document, then copy and paste them into the chart document.

Click on the options arrow associated with the **New** button  on the toolbar and select **Study Table Document** from the dropdown list.

An empty study table document opens in the Visualizer. Now type in the positions of the peaks.

Type the following values in column A: **16.82, 21.84, 22.89, 25.81, 28.08, 29.04, 31.86, 32.20, 33.04, 34.08, 35.58, 39.26, 39.98, 42.16, 43.84, 46.82, 48.22, 49.52**.

These are the values of 2-theta where the peak markers will be placed. Now copy and paste column A into the chart document.

Click and hold on cell **A1**, and move the cursor down to **A18**. All the cells in column A are selected. Select **Edit | Copy** from the menu bar.

Make **fin31 (Background removed).xcd** the active document, right-click and select **Paste Markers** from the shortcut menu.

Markers are added to the chart document. The height of the markers defaults to 50% of the height of the highest peak

4. To index the powder pattern

Before running the indexing calculation, you should make sure that the correct experimental data are selected, as two data sets are available.

Select the **Experimental Data** tab on the Reflex Powder Indexing dialog and double-click on **fin31 (Background removed).xcd**.

Double-clicking ensures that the correct data set is used for indexing and makes the chart document active. Alternatively, you can simply single-click to select the powder pattern. You can now run the Indexing calculation.

On the **Setup** tab check all of the **Crystal systems to test** check boxes. Click the **Index** button.

After a few seconds, the study table document containing a solution is displayed. You can compare this result with the actual crystal structure.

When the job is finished a dialog reports the status as completed.

Click the **OK** button on the Job Completed dialog.

5. To compare the indexing result with the crystal structure

The crystal structure of fin31 is available in Materials Studio XSD format.

Use the Import Document dialog to import **Examples\Reflex\Structures\fin31.xsd**.

A 3D Viewer containing the crystal structure of fin31 is displayed in the Visualizer. You can use the Properties Explorer to compare the values of the cell parameters you calculated earlier with those of the known crystal structure. To access the unit cell parameters from the 3D Atomistic document, change the **Filter** to **Lattice 3D**.

Select **Lattice 3D** from the **Filter** dropdown list. Scroll down the Properties Explorer to view the cell parameters LengthA, LengthB, and so on.

The unit cell parameters LengthA, LengthB, LengthC, AngleAlpha, AngleBeta and AngleGamma relate to the parameters a , b , c , α , β , and γ in the study table document. The values should be similar.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank Dr. S. Byrn of Purdue University for supplying some of the material for this tutorial.

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Indexing of 4-nitrophenylhexylurethane using X-Cell

Purpose: Illustrates how to use X-Cell to index challenging powder patterns.

Modules: Materials Visualizer, Reflex

Time: 

Prerequisites: [Indexing powder patterns](#)

Background

X-Cell ([Neumann, 2003](#)) is a novel indexing algorithm that has been developed at BIOVIA. It uses an extinction-specific dichotomy procedure to perform an exhaustive search of parameter space, to establish a complete list of all possible indexing solutions. Unlike DICVOL91 ([Boultif and Louër, 1991](#)), X-Cell allows for a certain number of impurity peaks among the experimentally observed reflections. The zero point shift of the diffraction pattern is determined as part of the search procedure. Systematic absences are explicitly taken into account and parameter space is searched in such a way that the number of observed diffraction peaks in the angular range being considered is gradually increased. This approach guarantees that the correct solution is found quickly if a high quality powder diffraction pattern is available. Regardless of whether or not a promising unit cell has already been found, the algorithm continues to search larger and larger portions of parameter space until the search is complete or until it is interrupted by the user. Demanding problems can be solved by running the algorithm for an extended period of time on a fast server. X-Cell has a significantly higher success rate than DICVOL91 ([Boultif and Louër, 1991](#)), TREOR90 ([Werner et al., 1985](#)) and ITO15 ([Visser, 1969](#)) combined.

Introduction

This tutorial shows you how to setup and run an X-Cell job using Materials Studio. It also describes how to analyze the results of the X-Cell run. You will index the powder diffraction pattern of 4-nitrophenylhexylurethane (NPHU). This powder pattern is strongly affected by preferred orientation and attempts to index it with ITO15 ([Visser, 1969](#)), TREOR90 ([Werner et al., 1985](#)) or DICVOL91 ([Boultif and Louër, 1991](#)) have, so far, failed.

This tutorial covers:

- [Getting started](#)
- [To pick diffraction peaks](#)
- [To set up the X-Cell job](#)
- [To run an X-Cell job](#)
- [To analyze the results](#)
- [Pawley refinement](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by creating a new project.

Open the **New Project** dialog and enter **NPHU** as the project name, click the **OK** button.

The new project is created with *NPHU* listed in the Project Explorer. Now import the experimental data you will be studying.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder, choose **Chart Files** from the **Files of type** dropdown list and double-click on **NPHU.xcd**.

2. To pick diffraction peaks

Next use the Reflex module in Materials Studio to pick the diffraction peaks for indexing automatically. The selection of diffraction peaks is a crucial part of the indexing procedure.

At low 2-theta values, peak intensities are high and peak overlap is small. Therefore, the probability of detecting peaks is fairly high and allowed reflections are likely to be selected for indexing. However, at high 2-theta values, peak intensities are low and peak overlap is strong so the detection probability is lower.

The performance of X-Cell depends strongly on the detection ratio - the number of reflections selected for indexing divided by the number of allowed reflections, within a given angular range - with the best performance being obtained if the detection ratio is high.

To obtain a high detection ratio, you should choose a maximum 2-theta value and try to assign peak markers to all of the features below this value that can be identified as diffraction peaks. Although the peak list should be as complete as possible, you should also try to avoid selecting spurious features. In principle, X-Cell can treat a certain number of reflections that do not correspond to the main crystalline phase as impurity peaks. In practice, however, the efficiency of X-Cell strongly decreases with the number of impurity peaks that are considered. Therefore, you should be careful not to select low intensity peaks that may be statistical noise. Furthermore, you may decide not to select weak peaks in the shoulder of stronger peaks as their position is frequently not very well defined. You should never select a couple of seemingly well defined peaks at high angle in addition to the low angle peaks as this will reduce the detection ratio significantly.

As a rule of thumb, you should always try to select at least 20 - 25 reflections. However, if the diffraction peaks are poorly resolved, you can attempt to run X-Cell with fewer peaks. In this tutorial, you will select only 15. If the unit cell to be determined is fairly flat or if the impurity content of the sample is high, it may be necessary to select significantly more than 25 reflections.

To facilitate the automatic peak picking, you should first subtract the background from the powder pattern.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. On the **Pattern Preparation** tab, in the **Background** section, increase the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document, **NPHU (Background Removed) . xcd**, is created, in which the background has been subtracted from the powder pattern. Now smooth the powder pattern. The best choice of the Gaussian width for smoothing depends on the noise level and the peak width and has to be found by trial and error. Begin by estimating the average peak width (Full Width Half Maximum).

Zoom in on the peak at **8.2 °** and determine the peak width.

An order of magnitude estimate will suffice. The peak width should be about **0.2 °**.

Reflex: Indexing of 4-nitrophenylhexylurethane using X-Cell

Select the **Pattern Processing** tab. In the **Smoothing** section, set the **Gaussian width** to **0.1** and click the **Smooth** button. Close the Reflex Pattern Processing dialog.

A new chart document, NPHU (Background Removed) (Smoothed). xcd, is created, containing the smoothed powder diffraction pattern. Now select diffraction peaks using the automatic peak picking tool. Because you have already removed the background and smoothed the data you can turn off the automatic background elimination.

Click on the **Reflex** arrow  on the **Modules** toolbar and choose **Powder Indexing** from the dropdown list to open the Reflex Powder Indexing dialog.

On the **Peaks** tab set the **Max. number of peaks** to **15**, the **Low amplitude cutoff** to **2.5** and the **Start 2-Theta** to **5**. Uncheck the **Eliminate background during search** checkbox and click the **Search** button.

Use the **Zoom**  and **Translate**  tools to examine the powder diffraction pattern closely.

You should always examine the results of the automatic peak picking carefully. In this particular case, all of the peak markers are well positioned and no manual changes are required. The two intense peaks at about 38.5 and 44.5 ° can be attributed to scattering from the aluminum sample holder.

3. To set up the X-Cell job

Now you must specify the settings for the X-Cell search.

Begin by selecting the X-Cell algorithm.

On the **Setup** tab of the Reflex Powder Indexing dialog, choose **X-Cell** from the **Program** dropdown list.

Now specify the dimensionality of the X-Cell search. X-Cell can search for 1D (rows), 2D (zones) and 3D unit cells. In this case, you should use a 3D search.

Click the **More...** button on the **Setup** tab to open the X-Cell Options dialog. Ensure that **3D** is selected from the **Dimensionality of search** dropdown list on the **General** tab.

X-Cell is able to handle a certain number of impurity peaks among the experimentally observed peaks, through an impurity level setting.

In this case, you should use an impurity level of 1.

Set the **Impurity level** to **1** on the **General** tab of the X-Cell Options dialog.

If an impurity level greater than 0 is chosen, you can select an impurity mode which controls how the search will proceed.

Include lower levels has significant advantages and is selected by default. It ensures that solutions with a high number of calculated peaks and a low number of impurity peaks can be found, even if a high impurity level is specified.

Select **Include lower levels** from the **Impurity mode** dropdown list.

The number of calculated peaks considered is gradually increased until a maximum value is reached. This maximum value is defined by specifying the detection level.

The detection level can have any value between 0.0 and 1.0. Values are expressed as a percentage.

The default value for the detection level is 25%, which means that the number of calculated peaks can be four times higher than the number of observed peaks. In some cases, it may be necessary to set the detection level to lower values. However, in this case a detection level of 33% is more appropriate.

Change the **Detection level** to **33%**.

X-Cell also allows you to specify the expected zero point correction and the zero point search range.

Change the **Zero point search range** from 0.01 to **0.1 °**. Leave the **Zero point correction** at the default value of **0.0 °**.

Finally, you should specify the peak width you determined in the previous section.

Change the **Average peak width** from 0.15 to **0.2**. Click the **OK** button to close the X-Cell Options dialog.

If a 3D search is performed, you can specify which crystal systems should be searched. By default, the search is carried out in only the Cubic, Hexagonal and Tetragonal crystal systems. You should expand the search to include all crystal systems apart from Triclinic.

Ensure that all of the boxes apart from **Triclinic** are checked, in the **Crystal systems to test** section on the **Setup** tab of the Reflex Powder Indexing dialog.

4. To run an X-Cell job

X-Cell in Powder Indexing uses the client-server architecture implemented in Materials Studio. So, if your PC is connected to other computers on a network, it is possible to set up gateways to these computers and run the calculation remotely, thus avoiding using the resources of your own PC. However, your own PC is probably set up as a server and the gateway "My Computer" will be used by default.

Select the **Job Control** tab on the Reflex Powder Indexing dialog. Choose a suitable server from the **Gateway location** dropdown list. Click the **More...** button to open the Job Control Options dialog. Ensure that **Update study table** and **Update textual results** are checked and close the dialog.

Click the **Index** button on the Reflex Powder Indexing dialog to launch the X-Cell job on the selected gateway.

The Job Explorer appears, which informs you about the progress of the calculation. After some time, two new windows appear; a text document, **Status .txt**, and a study table document, **NPHU (Background Removed) (Smoothed) .std**. These documents are updated regularly, as the job progresses.

The study table document consists of two sheets. The first sheet, labeled **Best**, contains all the solutions obtained by indexing which meet the selection criteria. A complete list of solutions is presented in the second sheet, labeled **All**.

The text document informs you about:

- The impurity level at which the search is currently being performed and the range of calculated peaks that is currently being considered.
- The crystal system in which the search is currently being performed. For a given impurity level and peak number range, the crystal systems are searched in the following order: hexagonal/trigonal, cubic, tetragonal, orthorhombic, monoclinic, triclinic.
- The number of possible indexing solutions found so far above (best) and below (total) a certain threshold. Solutions above the threshold are likely candidates for the correct unit cell.
- For each impurity level, you are informed about the maximum number of calculated peaks considered so far, the value of two additional control parameters called status and factor and the number of search steps.

You should wait until the X-Cell job finishes before proceeding. This may take some time, depending on the specification of the server machine on which you run the job.

5. To analyze the results

All of the solutions found by X-Cell are listed in the study table document, **NPHU (Background Removed) (Smoothed).std**. They are sorted by Relative Figure of Merit (Rel. FOM). The best solutions appear at the top of this list.

Make **NPHU (Background Removed) (Smoothed).std** the active document and select the **All** tab. Inspect the top ranked solutions.

The top ranked solution is in extinction class P21 and has a cell volume of about 692 Å³, the next unique solution is a C2 cell, with a volume of around 1382 Å³.

In order to identify which is the correct unit cell it is necessary to carry out Pawley refinement for the two best solutions. To do this, you must first create 3D Atomistic documents containing the different unit cells.

Select the row in the study table document, **NPHU (Background Removed) (Smoothed).std**, that contains the top ranked, P21 cell. Click the **Create Cell** button on the Reflex Powder Indexing dialog.

A new 3D Atomistic document, **NPHU (Background Removed) (Smoothed)1.xsd**, is created which contains the empty P21 unit cell.

Right-click on **NPHU (Background Removed) (Smoothed)1.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Rename the document **P21 Cell**. The .xsd extension is added automatically.

Now repeat the same procedure for the highest ranked C2 solution with the cell volume of approximately 1382 Å³.

Select the row in the study table document, **NPHU (Background Removed) (Smoothed).std**, that contains the highest ranked solution with C2 extinction class. Click the **Create Cell** button and close the Reflex Powder Indexing dialog.

Right-click on the new file, **NPHU (Background Removed) (Smoothed)5.xsd**, in the Project Explorer and select **Rename** from the shortcut menu. Rename the document **C2 Cell**. The .xsd extension is added automatically.

6. Pawley refinement

Note: By default, Pawley refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run synchronously** from the **Job Control** tab.

Pawley refinement of the trial unit cells against the experimental data will indicate which is the correct cell. This is performed using the Powder Refinement tool in Reflex.

Open the **Reflex Powder Refinement** dialog.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

Changing the *Number of cycles* automatically changes the *Convergence quality* setting from *Medium* to *Customized*.

On the **Setup** tab, set the **2-Theta** range **Min** to **5 °** and **Max** to **30 °**.

On the **Exp. Data** tab, select **pattern 1** of the document **NPHU.xcd**.

On the **Pattern** tab, check the checkboxes for the refinement of **U**, **V**, **W** and **NA**. For the **Zero point**, enter the value from the X-Cell study table document, but do not refine this parameter. In the **Asymmetry** section choose **Finger-Cox-Jephcoat** from the **Correction** dropdown list. Change the **2-Theta limit** to **20**, and check the checkboxes for the refinement of the parameters **H/L** and **S/L**.

On the **Display** tab, check the **Display simulation/experiment difference** plot checkbox.

Ensure that **P21 Cell.xsd** is the active document and click the **Refine** button.

Note: If you run this refinement job on a remote computer the refined unit cell will be in the **P21 Cell Reflex Pawley\P21 Cell.xsd** file.

Now add the cell parameters and the zero point shift to the refinement.

On the **Setup** tab, click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **10** and click the **OK** button.

On the **Pattern** tab, check the checkbox for the refinement of **Zero point** shift.

Ensure that **P21 Cell.xsd** is the active document. On the **Lattice** tab, check the checkboxes for the refinement of all cell parameters. Click the **Refine** button.

After 10 cycles of refinement, the R_{wp} value should be about 15%.

Now repeat the Pawley refinement for the next best unique solution.

Reflex: Indexing of 4-nitrophenylhexylurethane using X-Cell

Click the **Reset** button on the Reflex Powder Refinement dialog.

Choose the **Setup** tab and click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to 5 and click the **OK** button.

On the **Setup** tab, set the **2-Theta** range **Min** to 5 ° and **Max** to 30 °.

On the **Exp. Data** tab, select **pattern 1** of the document **NPHU.xcd**.

On the **Pattern** tab, check the checkboxes for the refinement of **U**, **V**, **W** and **NA**. For the **Zero point**, enter the value from the X-Cell study table document, but do not refine this parameter. In the **Asymmetry** section choose **Finger-Cox-Jephcoat** from the **Correction** dropdown list. Change the **2-Theta limit** to 20, and check the checkboxes for the refinement of the parameters **H/L** and **S/L**. Check the **Background coefficients** checkbox.

On the **Display** tab, check the checkbox for the **Display simulation/experiment difference** plot and choose **New** from the **Chart view** dropdown list.

Ensure that **C2 Cell.xsd** is the active document and click the **Refine** button.

Note: If you run this refinement job on a remote computer the refined unit cell will be in the **C2 Cell Reflex Pawley\c2_Cell.xsd** file.

Once again, perform 10 additional cycles of refinement, including the cell parameters and the zero point shift.

On the **Setup** tab, click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to 10 and click the **OK** button.

On the **Pattern** tab, check the checkbox for the refinement of **Zero point** shift.

Ensure that **C2 Cell.xsd** is the active document. On the **Lattice** tab, check the checkboxes for the refinement of all cell parameters. Click the **Refine** button and close the dialog.

After 10 cycles, the R_{wp} for the C2 cell should be around 18%.

The lower residual factor obtained for the P21 cell suggests that it is correct. A single crystal diffraction study of NPHU ([Yakimanski et al., 1997](#)) confirms this. The P21 cell obtained by X-Cell is indeed the correct solution to the indexing problem.

As an exercise, you may like to try to index this diffraction pattern using ITO, TREOR or DICVOL.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank Dr. Ute Kolb for providing the experimental powder diffraction pattern of NPHU.

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Indexing a flat unit cell with X-Cell

Purpose: Illustrates how to use X-Cell to index challenging powder patterns for flat unit cells.

Modules: Materials Visualizer, Reflex, X-Cell

Time:  

Prerequisites: [Indexing of 4-nitrophenylhexylurethane using X-Cell](#)

Background

Flat unit cells in real space have two short axes and one long axis in reciprocal space. Therefore, the first few diffraction peaks at low 2-theta values belong to a single zone in reciprocal space and define only the two short reciprocal axes and the angle between them. Flat unit cells are difficult to index for two main reasons:

- The number of low angle reflections belonging to a single zone may be quite high. As a result, it is possible that all of the reflections selected for indexing may belong to the same zone. This means that unit cell is not uniquely determined.
- Even if you are aware that a large number of low angle peaks belong to the same zone, it may be difficult to select enough peaks that define the remaining unit cell parameters because of peak overlap and the decrease in the scattering intensity at higher 2-theta values.

To facilitate the indexing of flat unit cells, X-Cell makes it possible to divide the task into two steps. Using only a small number of reflections at low 2-theta values, you first search for zones. If a zone is found that fits the experimental data, accurate 2D cell parameters and the zero point shift of the diffraction pattern can be determined by Pawley refinement. Comparing the reflections belonging to the zone with the experimental powder diffraction pattern, it is possible to identify the reflections that characterize the remaining cell parameters. In the second step, the peak positions, the lattice constants of the zone and the zero-point shift are used as the input to the 3D unit cell determination.

A similar approach can be used to index long unit cells.

Introduction

This tutorial will show you how to index the powder diffraction pattern of form II of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide (DFIYA). The powder diffraction pattern of DFIYA is particularly difficult to index, as it is strongly affected by preferred orientation. The intensities of the reflections belonging to the dominant zone are enhanced, while the intensities of reflections that define the remaining parameters are reduced.

This tutorial covers:

- [Getting started](#)
- [To pick diffraction peaks for a zone search](#)
- [To set up the X-Cell job for a zone search](#)
- [To run X-Cell for a zone search and analyze the results](#)
- [Pawley refinement of the dominant zone](#)
- [To pick diffraction peaks for a unit cell search](#)
- [To set up the X-Cell job for a unit cell search](#)
- [To run X-Cell and analyze the results of a unit cell search](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **DFIYA** as the project name, click the **OK** button.

The new project is created with *DFIYA* listed in the Project Explorer. Now import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click on **DFIYA_II.xcd**.

2. To pick diffraction peaks for a zone search

Next pick the diffraction peaks to be used for the determination of the dominant zone. If the scattering at low 2-theta values is dominated by a single zone, about 10 reflections should be sufficient to find it.

To facilitate automatic peak picking, you should first subtract the background from the powder diffraction data.

Select **Modules | Reflex | Pattern Processing** from the menu bar to open the Reflex Pattern Processing dialog. On the **Pattern Preparation** tab, in the **Background** section, increase the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document, *DFIYA_II (Background Removed)*.**xcd**, is created, in which the background has been subtracted from the powder pattern. Now smooth the powder pattern.

Begin by estimating the average peak width.

Use the **Zoom** tool  to zoom in on the peak at **6.2 °** and determine the width of the peak at half of its maximum height (FWHM).

The peak width should be about **0.15 °**.

Select the **Pattern Processing** tab. In the **Smoothing** section, set the **Gaussian width** to **0.05** and click the **Smooth** button. Close the Reflex Pattern Processing dialog.

Reflex: Indexing a flat unit cell with X-Cell

A new chart document, DFIYA_II (Background Removed) (Smoothed).xd, is created, containing the smoothed powder diffraction pattern. Now select diffraction peaks using the automatic peak picking tool.

Click the **Reflex** button  on the **Modules** toolbar and choose **Powder Indexing** from the dropdown list to open the Reflex Powder Indexing dialog.

Select the **Peaks** tab. Set the **Max. number of peaks** to **10**, the **Low amplitude cutoff** to **3.0** and the **Start 2-theta** to **5**. Click the **Search** button.

Use the **Zoom**  and **Translate**  tools on the **Chart Viewer** toolbar to examine the powder diffraction pattern closely.

You should always examine the results of the automatic peak picking carefully. In this particular case, all of the peak markers are well positioned and no manual changes are required.

3. To set up the X-Cell job for a zone search

Now specify the settings for the X-Cell search.

Select the **Setup** tab on the Reflex Powder Indexing dialog. Uncheck the λ_2 checkbox to ignore the contribution of the second wavelength. Choose **X-Cell** from the **Program** dropdown list.

Next specify the dimensionality of the X-Cell search.

Click the **More...** button on the **Setup** tab to open the X-Cell Options dialog. Select **2D** from the **Dimensionality of search** dropdown list on the **General** tab.

In case one of the selected reflections is an impurity peak (for example one belonging to another zone), you should set the impurity tolerance level to 1, and choose to search the impurity levels 0 and 1 in parallel. An *Impurity level* of **1** including lower levels is sufficient for this tutorial.

At low 2-theta values, the probability of observing symmetry allowed reflections is fairly high. You can therefore set the detection level to 50%. This means that X-Cell will consider all zones for which the number of calculated peaks in the selected 2-theta range is less than twice the number of experimental peaks.

Change the **Detection level** to **50%**.

X-Cell also allows you to specify the expected zero point correction and the zero point search range.

Change the **Zero point search range** from **0.01** to **0.1 °**. Leave the **Zero point correction** at the default value of **0.0 °**.

Finally, specify the peak width you determined in the previous section.

Ensure that the **Average peak width** is set to **0.15**. Click the **OK** button.

4. To run X-Cell for a zone search and analyze the results

Select the **Job Control** tab on the Reflex Powder Indexing dialog. Choose a suitable server from the **Gateway location** dropdown list.

Click the **Index** button on the Reflex Powder Indexing dialog, to launch the X-Cell job on the selected gateway.

You should wait until the X-Cell job finishes before proceeding. All of the solutions found by X-Cell are listed in the study table document, **DFIYA_II (Background Removed) (Smoothed).std**.

For rows and zones, a relative figure of merit cannot be calculated. So, in all output files, the solutions are ranked according to the figure of merit, and only the solution with the best figure of merit is given if the same zone is found in more than one 2D space group. The cell parameters a , b and γ specify the 2D unit cell in real space that is equivalent to the dominant zone in reciprocal space.

One of the two solutions in the study table document has a significantly higher figure of merit. In the next section you will verify that this solution corresponds to the dominant zone, using Pawley refinement. For both the solutions, the study table document indicates that there is one impurity peak. This may not mean that there really is a low angle peak that cannot be attributed to the dominant zone. In fact, the impurity peak may correspond to one of the calculated peaks, but if the deviation between the calculated and the observed peak position is fairly large, treating the observed peak as an impurity peak may significantly increase the figure of merit.

5. Pawley refinement of the dominant zone

The refinement carried out in this section is a multi-stage process. First, you limit the refinement to the angular range covered by the peaks used for indexing, to obtain an appropriate first guess of all parameters involved.

Then, you repeat the refinement for the full angular range, adjusting only the background parameters and the peak intensities. By visual comparison of the calculated and the experimental patterns, you can then determine the 2-theta value up to which all of the diffraction peaks belong to the dominant zone.

Next, you carry out another Pawley refinement of all parameters over the angular range identified in the previous step. The zero point shift and the 2D cell parameters obtained at this stage will be used as input parameters for 3D indexing in a later section.

Finally, you carry out a second Pawley refinement over the full angular range, with all parameters held fixed except for the background parameters and the peak intensities. The difference plot of the calculated and the experimental patterns obtained in this step is used for peak picking in the next section.

First you must build a model of the 2D unit cell, on which to perform the Pawley refinement.

Select the row in the study table document, **DFIYA_II (Background Removed) (Smoothed).std**, which contains the top ranked **p1** unit cell. Click the **Create Cell** button and close the Reflex Powder Indexing dialog.

A new 3D Atomistic document, **DFIYA_II (Background Removed) (Smoothed)1.xsd**, is created which contains the empty P1 unit cell.

Right-click on **DFIYA_II (Background Removed) (Smoothed)1.xsd** in the Project Explorer and select **Rename** from the shortcut menu. Rename the document **cell_2D**. The **.xsd** extension is added automatically.

Now carry out the first Pawley refinement.

On the **Modules** toolbar, click the **Reflex** button  and select **Powder Refinement** to open the Reflex Powder Refinement dialog.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to 5 and click the **OK** button.

The *Convergence quality* on the *Setup* tab will change to **Customized**.

On the **Setup** tab, set the **2-Theta** range to **5-18 °**.

On the **Exp. Data** tab, select the original experimental pattern, **DFIYA_II.xcd pattern 1**, which has not had the background subtracted or been smoothed.

On the **Pattern** tab, check the checkboxes for the refinement of **U**, **V**, **W** and **NA**. For the **Zero point**, enter the value given in the **Zero** column of the study table document, **DFIYA_II (Background Removed) (Smoothed).std** for the top ranked 2D cell and check the checkbox for its refinement.

On the **Display** tab, check the checkbox for **Display simulation/experiment difference** in the **General** section.

Make **cell_2D.xsd** the active document. On the **Lattice** tab, check the checkboxes for the refinement of the cell parameters **a**, **b** and **gamma**.

Click the **Refine** button.

Examine the comparison of the calculated and the experimental powder diffraction patterns. All peaks within the chosen range can be attributed to the dominant zone. Now you will find out where the reflections that do not belong to the dominant zone begin to appear.

Ensure that **cell_2D.xsd** is still active. On the **Setup** tab, change the **2-Theta range** to **5-50°**.

On the **Pattern** tab, uncheck the checkboxes for the refinement of **U**, **V**, **W**, **NA**, and the **Zero point**.

On the **Lattice** tab, uncheck the checkboxes for the refinement of the cell parameters **a**, **b**, and **gamma**.

Click the **Refine** button.

Examine the comparison of the calculated and the experimental powder diffraction patterns. All peaks up to 19.5 ° belong to the dominant zone. The first feature that cannot be attributed to the dominant zone can be found at about 19.75 °.

Next repeat the Pawley refinement of all parameters over a slightly wider angular range.

Make **cell_2D.xsd** the active document. On the **Setup** tab, change the **2-Theta range** to **5-19.5 °**.

On the **Pattern** tab, check the checkboxes for the refinement of **U**, **V**, **W**, **NA** and the **Zero point**.

On the **Lattice** tab, check the checkboxes for the refinement of the cell parameters **a**, **b** and **gamma**.

Click the **Refine** button.

Finally, note down the zero point shift and the cell parameters generated by the latest Pawley refinement, for later use and generate a comparison of the calculated and the experimental patterns over the full angular range.

Make **cell_2D.xsd** the active document. On the **Setup** tab, change the **2-Theta range** to **5-50 °**.

On the **Pattern** tab, uncheck the checkboxes for the refinement of **U**, **V**, **W**, **NA** and the **Zero point**. Note down the value of **Zero point** for later use.

On the **Lattice** tab, uncheck the refinement of the cell parameters **a**, **b** and **gamma**. Note down the values of these parameters for later use.

Click the **Refine** button and close the dialog.

Examine the comparison of the calculated and the experimental powder diffraction patterns.

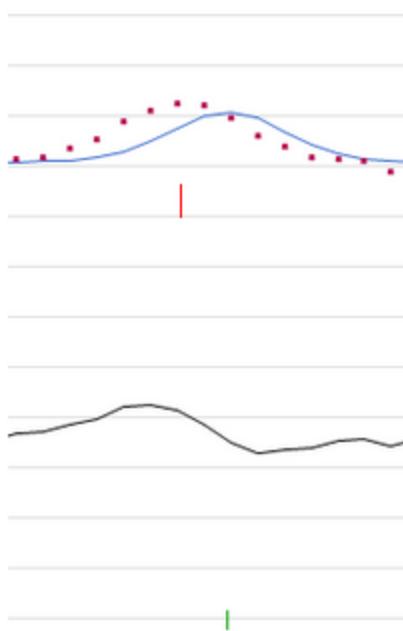
6. To pick diffraction peaks for a unit cell search

In this section, you pick the diffraction peaks used for indexing. The peak list has to contain reflections belonging to the dominant zone and reflections that define the remaining cell parameters. Within the angular range chosen for peak picking, you should try to identify as many reflections as possible.

The reflections defining the remaining cell parameters are all fairly weak and you should not rely on the automatic peak picking tool to find these. Instead, you should pick the peaks manually.

Since the dominant zone has already been refined, you can use the tick marks from the refinement to accurately position the peak markers for reflections that belong to it.

The reflections that define the remaining cell parameters should be picked very carefully. Many of these reflections are in the vicinity of reflections from the dominant zone (see below). In the Pawley refinement carried out in the last section, the intensity of reflections belonging to the dominant zone is overestimated in such cases. For peak positioning, you should use the experimental data rather than the difference plot.



Ensure that **cell_2D.xcd** is the active document. Use the **Zoom** tool to zoom in on the patterns for peak selection.

Use the **Chart Viewer Marker** to select all the diffraction peaks in the range from **5 °** to **29.5 °**. Use the tick marks from the previous refinements to help guide you to accurately position the peak markers for reflections that belong to the dominant zone. In this range, you should also be able to identify **10 reflections** that do not belong to the dominant zone.

These reflections can be found at the following 2-theta positions: 19.767112, 20.196377, 23.219712, 24.253705, 25.311651, 27.011796, 27.442203, 28.040301, 28.607701, and 29.264913.

If you are uncertain about your selection, you should inspect the sample file, **DFIYA_II_3D_peak_selection.xcd**, which is provided for comparison.

Now transfer the peak list from **cell_2D.xcd** to the original experimental pattern, before setting up the X-Cell unit cell search.

Make **cell_2D.xcd** your active document. Press **CTRL + A** to select all the peaks. Right-click on the chart and choose **Copy Markers** from the shortcut menu to copy them to the clipboard.

In Project Explorer, double-click on **DFIYA_II.xcd** to open it. Right-click on the document, and choose **Paste Markers** from the shortcut menu.

7. To set up the X-Cell job for a unit cell search

Now you must specify the settings for the 3D X-Cell search, in the same way as you did for the 2D search.

Select **File | Save Project** from the menu bar and close all of the windows except **DFIYA_II.xcd**.

Open the **Reflex Powder Indexing** dialog. On the **Setup** tab choose **X-Cell** from the **Program** dropdown list.

Now specify the dimensionality of the X-Cell search. This time you should use a 3D search.

Click the **More...** button to open the X-Cell Options dialog. Select **3D** from the **Dimensionality of search** dropdown list on the **General** tab.

In case one of the selected reflections is an impurity peak, you should set the impurity tolerance level to 1, and choose to search the impurity levels 0 and 1 in parallel.

This time, you should use a detection level of 33%.

Change the **Detection level** to **33%**.

The zero point shift is known from the 2D Pawley refinement.

Change the **Zero point correction** to the value obtained from the Pawley refinement of the 2D zone.

Change the **Zero point search range** to **0.0 °**.

You should also keep the cell parameters of the dominant zone constant.

Select the **Cell Parameters** tab of the X-Cell Options dialog. Choose **a, b, gamma** from the **Known parameters** dropdown list.

Enter the cell parameters obtained from the previous Pawley refinement. Leave the **Error** at the default value of **0.0**. Click the **OK** button.

Ensure that all of the boxes are checked in the **Crystal systems to test** section of the **Setup** tab.

8. To run X-Cell and analyze the results of a unit cell search

Select the **Job Control** tab on the Reflex Powder Indexing dialog. Choose a suitable server from the **Gateway location** dropdown list.

Click the **Index** button to launch the X-Cell job on the selected gateway.

The indexing calculation is now running. Constant updates about the progress of the calculation are provided. You should wait until the X-Cell job finishes before proceeding.

In the Project Explorer, double-click on the study table document **DFIYA_II.std** in the folder of **DFIYA_II Reflex X-Cell**.

This study table document should contain several possible indexing solutions. As an exercise, you can try to identify the correct unit cell by Pawley refinement. The crystal structure of DFIYA_II has been determined by single crystal X-ray diffraction and the correct unit cell has a cell volume of about 963 \AA^3 with $a \sim 15.1 \text{ \AA}$, $b \sim 13.9 \text{ \AA}$, $c \sim 5.0 \text{ \AA}$, $\alpha \sim 86.9^\circ$, $\beta \sim 97.7^\circ$ and $\gamma \sim 111.0^\circ$.

The list of solutions will depend on which peaks were selected. If you chose the peak list provided in the file **DFIYA_II_3D_peak_selection.xcd** the top solution will be the correct one. If you used a different input you should be able to identify the correct unit cell by Pawley refinement.

Reflex: Indexing a flat unit cell with X-Cell

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank P.G. Varlashkin, M. Sacchetti, and J. Zhu from GlaxoSmithKline for supplying the experimental data.

Rietveld refinement of inorganics

Purpose: Introduces the Powder Refinement tool and applies it to refine a trial structure against its powder diffraction pattern.

Modules: Materials Visualizer, Reflex

Time: 

Prerequisites: [Working with powder diffraction patterns](#)

Introduction

This tutorial shows how the Powder Refinement tool can be used to refine a trial crystal structure. There are two different types of refinement implemented in Materials Studio. You will use Rietveld refinement, which iteratively improves an approximate (trial) structure to maximize the agreement between simulated and experimental diffraction patterns.

In this tutorial, you will use the experimental X-ray diffraction data provided to refine a suggested trial structure for the mineral akermanite.

This tutorial covers:

- [Getting started](#)
- [To calculate the powder diffraction pattern for akermanite](#)
- [To set the Rietveld refinement](#)
- [To refine the structure](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **akermanite** as the project name, click the **OK** button.

The new project is created with *akermanite* listed in the Project Explorer. Now you will import the input file you will be studying.

Now import the akermanite structure.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Structures** folder and double-click on **ak100.xsd**.

Before you calculate the diffraction pattern, you should also load the experimental powder pattern.

Open the **Import Document** dialog and choose **Chart Files** from the **Files of type**. Navigate to the **Examples\Reflex\Experimental Data** folder, locate and load the file **ak100.3cam**.

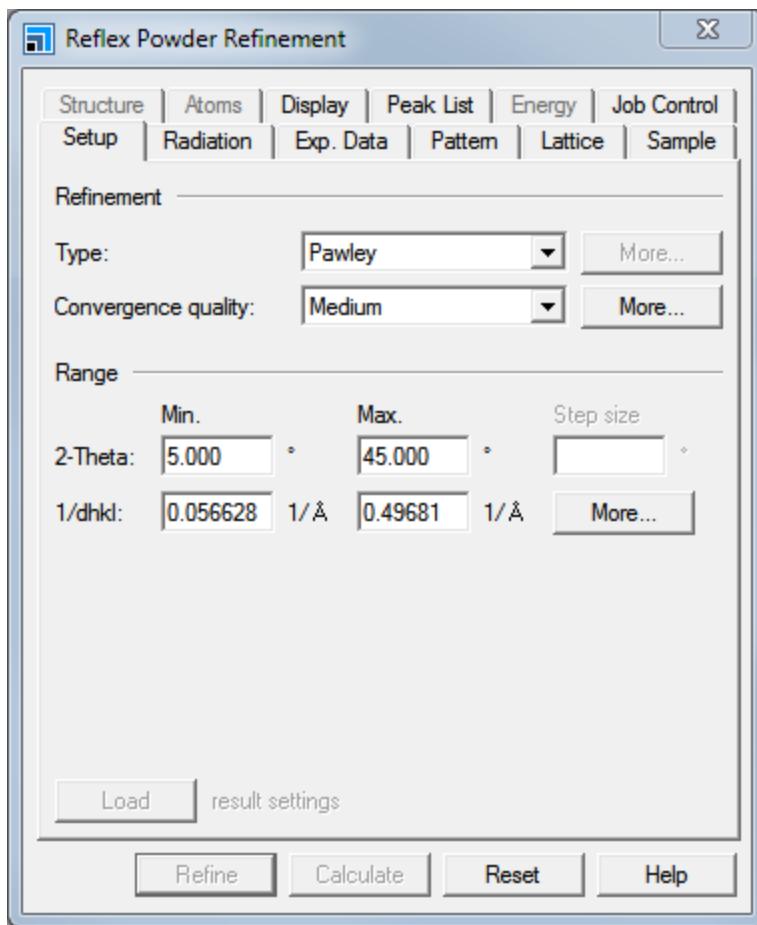
2. To calculate the powder diffraction pattern for akermanite

The next step is to calculate the powder diffraction pattern and display it on the same graph as the experimental data.

Note: It is also possible to begin refinement at this stage, but for the purposes of the tutorial, you will make a comparison between the simulated and experimental data, to determine the starting value of R_{wp} .

Click the **Reflex** arrow  on the **Modules** toolbar and select **Powder Refinement**.

This opens the Reflex Powder Refinement dialog displayed.



Reflex Powder Refinement dialog, Setup tab

Now change some of the default variables.

Change the **Min. 2-Theta** value from 5.00 to **10.00** and the **Max. 2-Theta** value from 45.00 to **90.00**.

Change the refinement **Type** from Pawley to **Rietveld**.

Next you are going to change the graphical display settings.

Select the **Display** tab.

As the chart will already contain a lot of information, you should remove the observed markers that normally appear with the calculated pattern.

Uncheck the **Show observed reflection markers** checkbox.

Now calculate the powder pattern.

Select the **Exp. Data** tab and choose **ak100.xcd** to indicate that this data should be used for the calculation.

Make sure that **ak100.xsd** is the active document and click the **Calculate** button.

A chart document is created displaying the simulated and experimental powder patterns for akermanite. You should see that the *Structure* and *Atoms* tabs become active. This is because, unlike the Pawley method, the Rietveld method allows you to refine the structure and atom parameters.

Note: The step you have just performed is not a refinement calculation but merely the first step in the procedure. It is comparable to performing a single point energy calculation, as opposed to an energy minimization.

You can compare the patterns in more detail by zooming in using the selection rectangle and translating the pattern.

Hold down the **R** key and left-click on the chart. Drag the mouse to draw a bounding box around the area you wish to magnify. Release the mouse button.

Examine the fit in detail. Although the calculated pattern clearly matches the experimental one, there is an offset between the two. The Rietveld R_{wp} - and R-factors are displayed at the top of the chart.

An R-factor can be considered to be a figure of merit for the quality of the structure.

$$R = 100 \cdot \frac{\sum_{i=1}^n |I_{obs}^i - I_{calc}^i|}{\sum_{i=1}^n |I_{obs}^i|}$$

Where:

I_{obs}^i is the observed (experimental) intensity

I_{calc}^i is the calculated intensity with all the refined parameters

n is the number of data points in the range

The R_{wp} -factor is much the same except that a weighting, w_i , is applied to give more importance to the fit at higher angles.

$$R_{wp} = 100 \cdot \frac{\sum_{i=1}^n w_i (I_{obs}^i - I_{calc}^i)^2}{\sum_{i=1}^n w_i (I_{obs}^i)^2}$$

3. To set up the Rietveld refinement

Now you are going to set up the Rietveld calculation ready for refinement. The first step is to change the 2-theta range to 10 - 50.

Note: Certain parts of the Reflex module are linked, so for example, if you change the 2-theta range in the Powder Diffraction dialog, it changes in the Powder Refinement dialog. The radiation type used is also set globally.

On the **Reflex Powder Refinement** dialog select the **Setup** tab, change the **Max. 2-Theta** from 90 to **50**.

Now check that the radiation type is set correctly.

Select the **Radiation** tab.

Confirm that the default values of λ_1 and λ_2 for a copper source, of 1.540562 and 1.54439 respectively, are being used.

4. To refine the structure

Next you must set up the Rietveld refinement by fitting a background function and modifying the unit cell dimensions. The scale factor is adjusted automatically by Reflex.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **2** and click the **OK** button.

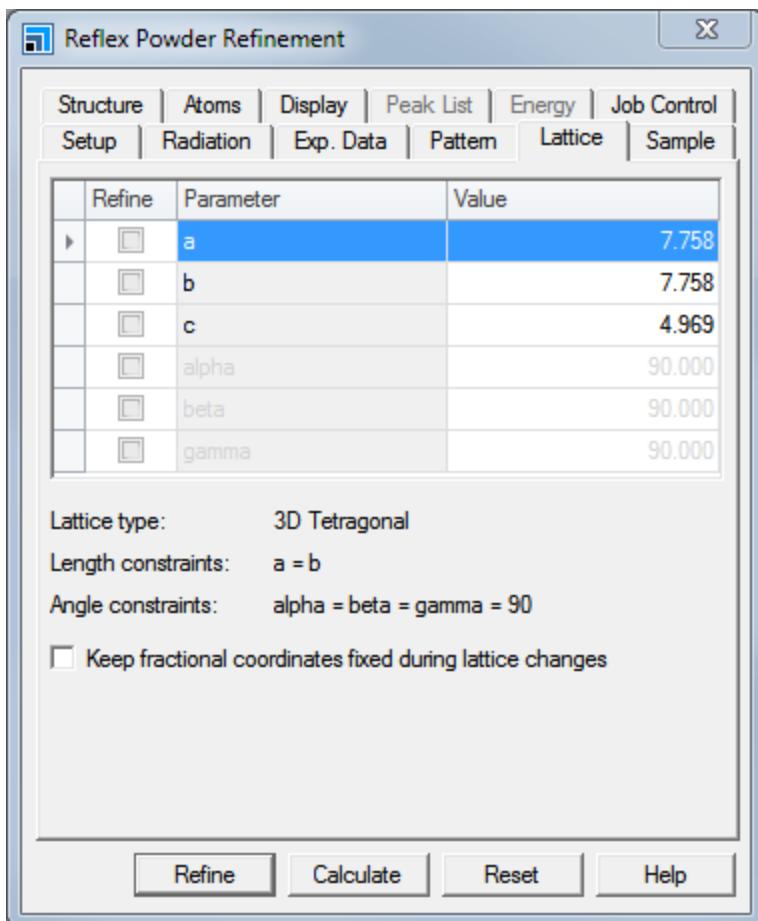
Now set the background settings.

In Rietveld refinement, the X-ray or Neutron background is refined as a polynomial of whatever order you choose. The default is a polynomial with 20 coefficients and that is sufficient for most calculations. Scroll down the grid on the *Pattern* tab and you will see that the refine checkbox is automatically checked on for the background coefficients.

Note: In this case, you are not going to refine the zero point. Although an error in zero point does lead to a systematic peak shift, such as you see in this example, the peak shift may also be due to inaccurate cell dimensions. If you ever do choose to refine the zero point, then the refinement should always be carried out after cell dimension refinement.

You will however refine the lattice parameters.

Choose the **Lattice** tab and make **ak100.xsd** the active document.



Reflex Powder Refinement dialog, Lattice tab

Note: If no information is displayed in this tab, you should ensure that the structure you are refining is active.

Now choose which cell parameters you wish to refine.

Check the **a** and **c** checkboxes in the **Refine** column.

Note: When you select the *a* parameter, the *b* parameter is automatically selected and you cannot select the α , β , and γ angles. This is because of the tetragonal symmetry of the structure.

Before you continue, you should ensure that the fractional coordinates are kept fixed during the calculation.

Check the **Keep fractional coordinates fixed during lattice changes** checkbox.

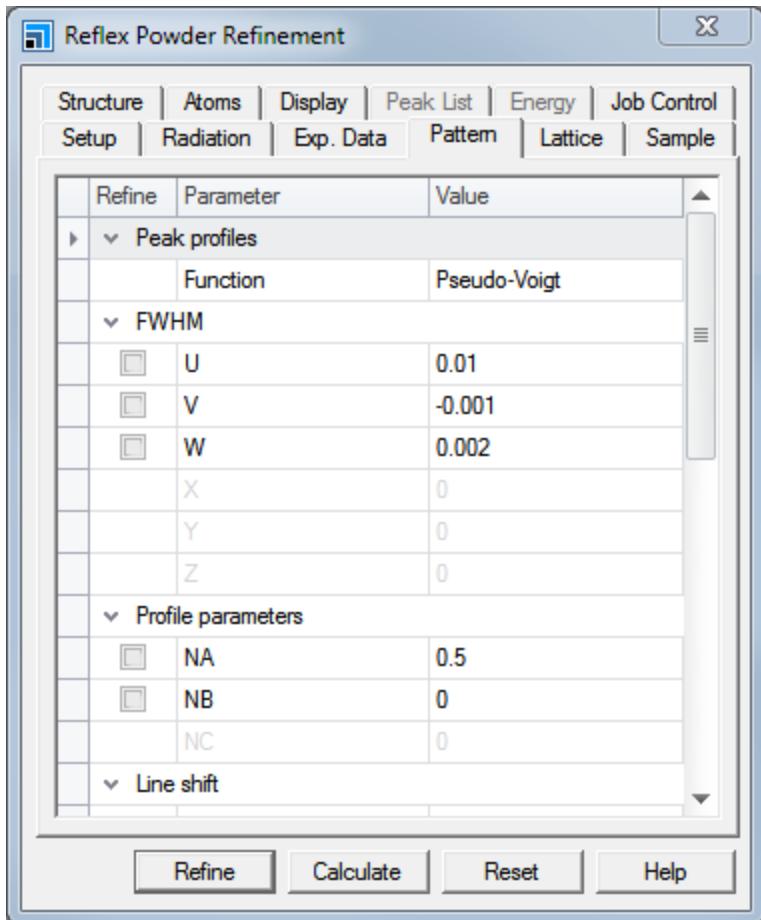
Now you can set up the refinement of the peak profiles. Rietveld refinement offers a choice of nine profile types. The default is Pseudo-Voigt. A Pseudo-Voigt (*pV*) peak is a mixture of the Gaussian (*G*) and Lorentzian (*L*) peak forms:

$$pV = \eta L + (1 - \eta)G$$

$$\eta = A + B(2\theta)$$

Where *A* and *B* are refinable "mixing" parameters.

Select the **Pattern** tab.



Reflex Powder Refinement dialog, Pattern tab

Check the **U**, **V**, and **W** options in the **FWHM** section. Change the value of **W** to **0.2** and the values of both **U** and **V** to **0.00**. In the **Profile parameters** section check the **NA** and **NB** mixing parameters.

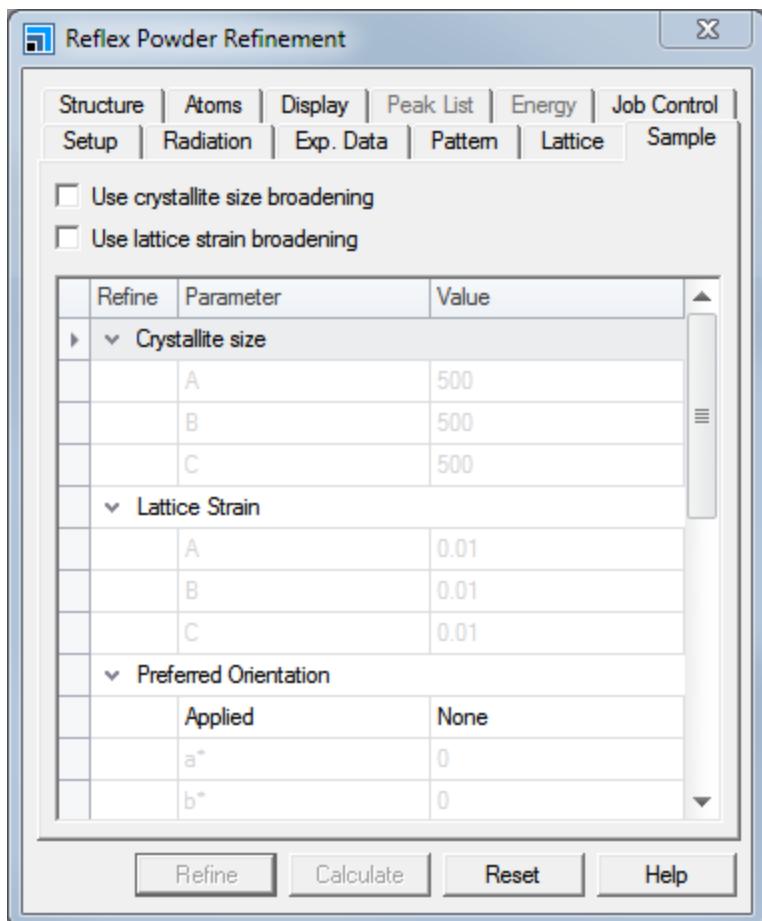
The *FWHM* parameters define how the profiles vary with diffraction angle, and the mixing parameters define the relative Lorentzian/Gaussian character of the profiles. If the initial lattice parameters are a long way from the true values, you get no overlap between the experimental and the observed values. This means that the refinement is likely to fail. Changing the values of *U* and *V* to 0.00, you increase the width of the peaks being refined and so you have a better chance of performing the refinement correctly.

Now you are ready to perform the refinement.

Click the **Refine** button on the Reflex Powder Refinement dialog.

The R_{wp} value should refine to around 10% and R_p should refine to around 7%. These are very low and indicate that the structure is almost certainly the correct one.

The final step is to refine the preferred orientation parameter. This is located on the *Sample* tab.



Reflex Powder Refinement dialog, Sample tab

In the **Preferred orientation** section choose **March-Dollase** from the **Applied** dropdown list. Check the **R0** checkbox.

Refining the orientation parameter will account for some of the texture in the sample, which, when present, can grossly alter the relative intensities of peaks. The direction of the texture may be chosen using the *Direction* boxes but the default of (0 0 1) is fine in this case.

Ensure that **ak100.xsd** is the active document. Click the **Refine** button.

This time there is a slight improvement in the fit quality. The R_{wp} value should decrease to around 8%.

Note: By default, Rietveld refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run synchronously** on the **Job Control** tab.

The low R-factor indicates that this is probably the correct crystal structure of akermanite. You can examine the chart document to see how well the simulated pattern fits to the experimental one.

Use the **Zoom** and **Translation** tools to inspect the chart.

Now that you have performed a refinement of the structure, try some different refinement strategies.

Reflex: Rietveld refinement of inorganics

You should repeat the calculation but try refining after each change you make. Why does this give a higher R-factor than the one observed if you refine all in one go?

This is because if you refine one variable at a time, you can get trapped in a local minimum. When performing these calculations, you should generally refine all the variables in one go. If this does not converge as you thought it would, you can repeat the steps individually but generally this will not give you a better result.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Rietveld refinement with energetic considerations

Purpose: Illustrates how the incorporation of energy information into an all-atom Rietveld refinement process allows for structure solutions being both chemically viable and in close agreement with the experimental diffraction pattern.

Modules: Materials Visualizer, Reflex, COMPASS

Time:  

Prerequisites: [Rietveld refinement of inorganics](#)

Background

Occasionally, the available powder diffraction data do not contain enough information for a successful Rietveld refinement. For example, in systems with a large number of degrees of freedom such as all-atom refinements or refinements using low-quality powder data. In these instances, Rietveld refinements typically lead to chemically unviable structures because the information content of the powder pattern is too low to accurately determine all the degrees of freedom.

To overcome this problem, Reflex allows you to incorporate an accurate description of potential energy in conjunction with the R_{wp} in the Rietveld refinement process, optimizing a combined figure of merit. The aim is to find solutions that optimally meet two different and possibly conflicting objectives:

- The simulated pattern has to match the experimental diffraction data.
- The potential energy of the structure has to be close to the minimum.

A priori elucidation of the energy weight factor determining the relative importance of the energy contribution might not be intuitive. In such cases, you can use a Pareto optimization (*a posteriori* preference calculation) to obtain an appropriate value.

Introduction

In this tutorial, you refine the crystal structure of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide using Rietveld refinement and Rietveld refinement with energies. You include March-Dollase preferred orientation correction in the structure refinement. The correction factors were determined by crystal structure solution based on powder diffraction data, as described in the Reflex Plus tutorial [Structure solution in the presence of preferred orientation](#).

This tutorial covers:

- [Getting started](#)
- [Refinement with Pawley fitting](#)
- [Rietveld refinement](#)
- [Rietveld refinement with energies and Pareto optimization](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Start Materials Studio and create a new project called **Rietveld with energies**.

Now load the powder diffraction pattern of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide.

Click **Import**  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list and navigate to the **Examples\Reflex\Experimental Data** folder, double-click **(E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.xcd**. In the Project Explorer, right-click the imported document and select **Rename** from the shortcut menu. Change the filename to **data**, this automatically appends the **.xcd** file extension.

Next load the crystal structure of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide.

Open the **Import Document** dialog, select **3D Atomistic Files** from the **Files of type** dropdown list. Navigate to the **Reflex** folder, which is one level up from the **Experimental Data** directory. Double-click the **Structures** folder and select the file **(E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.xsd**. Click **Open**.

In the Project Explorer, right-click the imported document and select **Rename** from the shortcut menu. Change the filename to **structure**, this automatically appends the **.xsd** file extension.

2. Refinement with Pawley fitting

The purpose of Pawley refinement is to provide cell parameters, background parameters, profile parameters, and the zero-point shift of the diffraction pattern for the structure solution step. The peak intensities are not related to the unit cell contents at this stage.

In Reflex, the fitting algorithm is stable enough to refine all parameters simultaneously.

Click **Reflex**  on the **Modules** toolbar and select **Powder Refinement** from the dropdown list to display the Reflex Powder Refinement dialog.

On the **Pattern** tab enable refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and of the **Zero point Line shift** using the checkboxes. The refinement of **20** background coefficients is enabled by default.

Make sure that the 3D Atomistic document **structure.xsd** is active and select the appropriate checkboxes to enable refinement of all cell parameters on the **Lattice** tab.

On the **Display** tab, select the **Display simulation/experiment difference** checkbox.

Since the CPU time required for structure solution is approximately proportional to the number of diffraction peaks, limit the 2θ range used for structure solution and Pawley refinement to a subsection of the complete powder diffraction pattern.

On the **Setup** tab, select **Pawley** as the refinement **Type**. Click **More...** for **Convergence quality** to open the Refinement Convergence Options dialog. Specify the **Number of cycles** as **5** and click **OK**.

Changing the *Number of cycles* automatically changes the *Convergence quality* setting from *Medium* to *Customized*.

On the **Setup** tab, change the **Max. 2-Theta** value from 45 to **40 °**.

On the **Exp. Data** tab, select the **data.xcd** data set.

The powder pattern was recorded using a copper anode and a graphite (0 0 2) monochromator. The (0 0 2) reflection of graphite corresponds to a d-spacing of 3.4 Å.

On the **Radiation** tab, all the default settings are appropriate except for the monochromator settings. In the **X-ray** section, select a **Single** monochromator and for **d_{hkl}** specify **3.4 Å**.

Click **Refine** on the Reflex Powder Refinement dialog.

During the Pawley refinement, the bottom of the Materials Visualizer window displays the cycle number and the current R_{wp} value. After five cycles, the R_{wp} value is about 6.7%. Repeat the Pawley refinement until you obtain no further improvement in the R_{wp} value.

Ensure that **structure.xsd** is active and click **Refine** and close the Reflex Powder Refinement dialog.

You obtain a minimum value for R_{wp} of about 6.3%.

Note: By default, Pawley or Rietveld refinement jobs run synchronously on the Materials Studio client. However, the client-server architecture in Materials Studio allows you to run all refinement jobs on a remote server. To do this, clear selection of the *Run synchronously* checkbox on the *Job Control* tab of the Reflex Powder Refinement dialog.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

3. Rietveld refinement

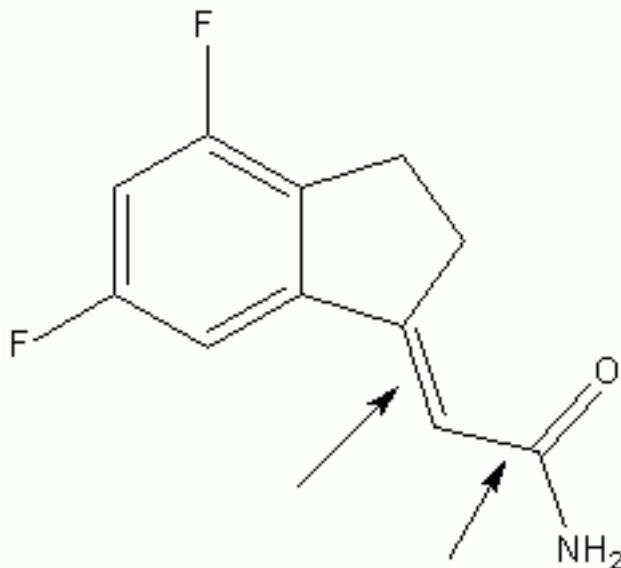
Next perform Rietveld refinement of some parameters. Start by making a copy of the structure solution.

In the Project Explorer, double-click **structure.xsd** and select **Edit | Copy** from the menu bar.

Right-click the project name and choose **New | Folder** from the shortcut menu. Change the name of the new folder to **refinement**.

Right-click **refinement** in the Project Explorer and select **New | 3D Atomistic Document** from the shortcut menu. Change the filename of the new document to **refined structure.xsd**. Select **Edit | Paste** from the menu bar. Click anywhere in the 3D Viewer for **refined structure.xsd** to clear selection of everything.

For the Rietveld refinement, add two flexible torsions (as shown below) to the parameters refined so far.



Molecular structure of (E)-2-(4,6-difluoroindan-1-ylidene)acetamide

Click the **Measure/Change** arrow on the **Sketch** toolbar and select **Torsion** from the dropdown list.

Choose one molecule in **refined structure.xsd** and click the double bond that links the acetamide fragment to the carbon ring system. This creates a new torsion monitor. Repeat the same procedure for the other torsion.

Choose the **Selection** tool .

Now define the whole molecule as a motion group. This allows description of the position and orientation of all atoms in the molecule by a single set of translational and rotational parameters, in addition to the torsional degree of freedom you defined.

In the 3D Viewer for **refined structure.xsd**, click one of the atoms to select it. Right-click the structure and choose **Select Fragment** from the shortcut menu to select the entire molecule.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Setup** tab, change the **Type** from Pawley to **Rietveld**.

On the **Structure** tab, click **Create motion group(s) from selection as Single group** and select all of the structural parameters checkboxes for refinement. Click anywhere in **refined structure.xsd** to clear selection of everything.

For Rietveld refinement, this adds the global isotropic temperature factor to the refinable parameter list.

On the **Sample** tab, in the **Temperature factors** section for the **Applied** temperature factor choose **Global Isotropic**. Select the checkbox to refine the **Global isotropic** temperature factor.

Next enter the preferred orientation correction factors. For Rietveld refinement, you need a good estimate of the preferred orientation vector. You can use Powder Solve to determine the crystal structure and the preferred orientation parameters simultaneously as described in the Reflex Plus tutorial [Structure solution in the presence of preferred orientation and energetic considerations in structure refinement](#).

Alternatively, you can make a reasonable estimate for the correction factors based on the length of the lattice vectors. In this tutorial, a good starting point seems to be $a^* = 1.0$, $b^* = 3.0$, $c^* = 1.0$, with the default value $R0 = 1.0$.

On the **Sample** tab of the Reflex Powder Refinement dialog, in the **Preferred orientation** section for the **Applied Preferred orientation** method choose **March-Dollase**.

Specify **a^*** , **b^*** , **c^*** , and **$R0$** as **1.0**, **3.0**, **1.0**, and **1.0**, respectively. Select the checkboxes to refine all preferred orientation parameters.

For Rietveld refinement, use the full range of the powder diffraction pattern. In addition, you want the comparison between the calculated and the experimental patterns to be displayed in a new chart document.

On the **Setup** tab, click **More...** for **Convergence quality** to open the Refinement Convergence Options dialog. For the **Number of cycles** specify **5** and click **OK**.

On the **Setup** tab, change the **Max. 2-Theta** value to **50 °**.

On the **Display** tab, in the **General** section, select the **Display simulation/experiment difference** checkbox. In the **View management** section, change **Chart view** from Replace to **New**.

Click **Refine**.

The R_{wp} value for the Rietveld refinement is about 12.4%. Next, examine the crystal structure.

In the Project Explorer, double-click **refinement\refined structure.xsd**.

Right-click in the 3D Viewer and choose **Display Style** from the shortcut menu to open the Display Style dialog. Select the **Lattice** tab and for the **Max** values for **A**, **B**, and **C** specify **2.00**. Close the dialog.

Click **Calculate Hydrogen Bonds**  on the **Atoms and Bonds** toolbar, then click **Calculate Close Contacts** .

To make the crystal structure clearer, you can switch off the display of motion groups.

Reflex: Rietveld refinement with energetic considerations

Press **ALT** and double-click a motion group to select all motion groups. To switch off the display of the motion groups, select **Visibility / Hide** from the **View** menu. Click anywhere in **refinement\refined structure.xsd** to clear selection of everything.

Examine the crystal structure - there are some minor close contacts. Next, examine the comparison of the simulated and the experimental powder diffraction patterns.

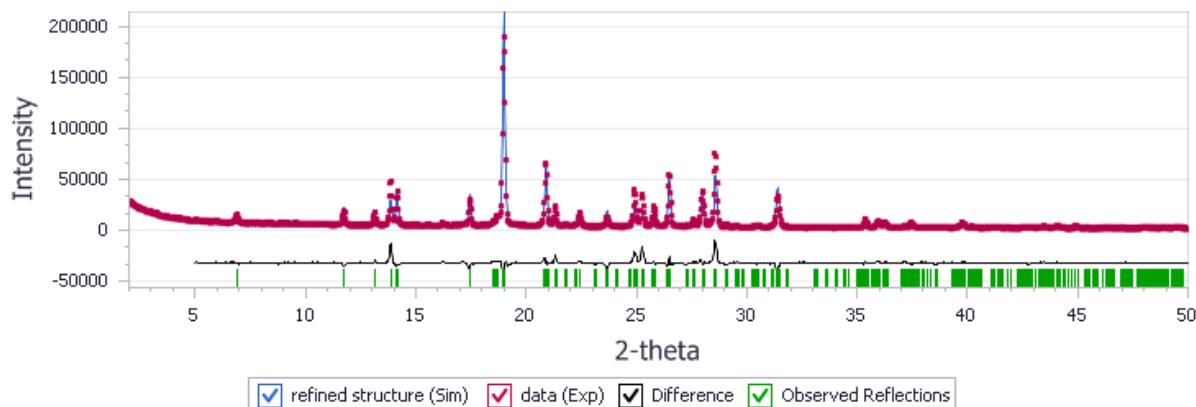
Click the **Hydrogen Bonds** arrow  and select **Delete Hydrogen Bonds** from the dropdown list.

Click the **Close Contacts** arrow  and select **Delete Close Contacts**.

In the Project Explorer, double-click the chart document **refined structure.xcd** and examine it.

This reproduces well overall intensity distribution of the experimental powder diffraction pattern, although some regions show intensity differences as indicated in the difference plot in the chart document below.

Powder Refinement: $R_{wp} = 14.65\%$ $R_{wp(w/o bck)} = 25.65\%$
 $R_p = 10.62\%$



Comparison between the simulated powder pattern obtained by Rietveld refinement and the experimental powder pattern

Optionally, you can generate an HTML document that summarizes the results of the Rietveld refinement.

Ensure that **refined structure.xsd** is the active document. Select the **Display** tab of the Reflex Powder Refinement dialog. In the **View management** section, select the **Generate HTML report** checkbox. Click **Calculate**, close the Reflex Powder Refinement dialog, and examine the HTML report.

The HTML document contains all the refined parameters.

Select **File | Save Project** from the menu bar. Close all of the open documents, apart from **refined structure.xsd**.

4. Rietveld refinement with energies and Pareto optimization

Now improve the structure solution by including energy information in the Rietveld refinement by optimizing a combined figure of merit.

First you must select the energy weight factor determining the relative importance of the energy contribution. The optimum value of this parameter depends not only on the quality of the experimental data and the accuracy of the forcefield energy expression, but also on your chosen objective: is it more important that the solution matches the experimental pattern or that the lattice energy is close to its minimum? In this case, you can use Pareto optimization to calculate automatically a set of possible optimum refinement solutions using a sequence of Rietveld refinement with energies calculations with differing energy weights.

Select **File | Save As...** from the menu bar to open the Save As dialog. Enter the filename **pareto** and click **OK**.

Next you define each atom as an individual motion group for an all-atom Pareto optimization calculation. This means three translational parameters describe each atom. Start by deleting the motion groups and torsions defined previously.

Open the **Display Style** dialog and select the **Lattice** tab. Choose **In-Cell** from the **Style** dropdown list and close the dialog.

Select **Edit | Select All** from the menu bar and then **View | Visibility | Unhide** to display all the motion groups. Select all the motion groups and press **DELETE**.

Select all the torsions and press **DELETE**.

Select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu to select one complete molecule.

Open the Reflex Powder Refinement dialog. On the **Structure** tab, choose **Individual groups** for the motion group selection and click **Create**. Ensure selection of the refinement checkboxes and the **Use hydrogens** checkbox.

Click anywhere in the 3D Viewer to cancel selection of everything.

Now use Pareto optimization to calculate a set of possible optimum refinement solutions automatically.

On the **Setup** tab, for the **Refinement Type** choose **Pareto optimization**. Click **More...** to open the Pareto Optimization Options dialog.

The number of points specify the total number of points to calculate on a Pareto curve. The energy window describes the tolerance window above the global minimum within which you can expect realistic structure solutions. In this tutorial, use the default settings.

Close the Pareto Optimization Options dialog.

On the **Energy** tab, of the Reflex Powder Refinement dialog, change the **Forcefield** to **COMPASSIII** and ensure selection of **Forcefield assigned** from the **Charges** dropdown list.

On the **Job Control** tab, select an appropriate **Gateway location**. Click **Refine** and **close** the Reflex Powder Refinement dialog.

Close the **pareto.xsd** 3D Viewer and click **Yes** when asked if you want to save the changes.

Notes:

- Before you start a Pareto optimization, it is important that you choose an appropriate energy expression/forcefield and verify that it calculates the geometry and potential energy surface of the molecular fragments with sufficient accuracy.
- Pareto calculations run as remote jobs.

Once the calculation starts, this creates a new folder called **pareto Reflex Pareto** in the Project Explorer and automatically saves the parameter settings for this job in the **pareto - Powder Diffraction** file.

The Job Explorer informs you about the progress of the calculation. After some time, two new windows appear, a text document, **Status.txt**, and a chart document **pareto E vs Rwp.xcd**. As the job progresses it regularly updates these documents.

The text document informs you about:

- The number of optimization cycles performed so far.
- The energy weight factor (mixing factor).
- R_{comb} (combined figure of merit), R_{wp} , and R_{e} (energetic figure of merit).
- The total potential energy for the current structure and the energy difference between that and the global minimum.

The chart document contains the set of optimum solutions found so far and the corresponding energetic and R_{wp} values. Wait until the job finishes before proceeding.

Note: The first step of a Pareto optimization is a minimization of the potential energy of the crystal with fixed lattice parameters. This energy minimum provides the reference for the energy contribution to the combined figure of merit.

Next analyze the Pareto optimization results.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

In the **Project Explorer**, double-click **pareto.txt** in the **pareto Reflex Pareto** folder.

The text file contains the values of all the settings used as input for the calculation and a short summary of the calculation results.

Close **pareto.txt**.

In the **Project Explorer**, double-click **pareto.xtd** followed by **pareto E vs Rwp.xcd** in the **pareto Reflex Pareto** folder.

Select **Window | Tile Vertically** from the menu bar.

In the energy versus R_{wp} chart, the optimum solutions form a curve called the Pareto front. The continuum of all potential solutions exists only in the region above the Pareto front, whereas no solutions are possible below. In nearly all cases, the absolute optimum solution having minimum energy and minimum R_{wp} is part of an inaccessible region. **pareto . xtd**, which contains all the optimum solutions links dynamically with the chart file.

Choose the **Selection** tool  and click any point in **pareto E vs Rwp.xcd**.

You can see how the points on the chart relate to the trajectory frames. Alternatively, you can use the animation controls to select a trajectory frame and relate it to the corresponding point on the graph.

If the **Animation** toolbar is not visible, select **View | Toolbars | Animation** from the menu bar.

Make **pareto.xtd** the active document. Click the **Animation Mode** arrow  and choose **Options** from the dropdown list to open the Animation Options dialog. Enter **1** in the **Current frame** textbox and press **TAB**. Alternatively, use the spin controls to specify the frame number.

Next examine the optimized parameters for frame 1 and the weight of the energy contribution to the R_{comb} .

Open the **Reflex Powder Refinement** dialog.

On the **Setup** tab, click **Load result setting**. Click **More...** for **Refinement Type** in the **Refinement** section to open the Rietveld with Energies Options dialog. Examine the **Weight** and click **OK**.

Repeat the same procedure for other frames in **pareto.xtd**, reloading the results settings each time.

The **Weight** reported on the *Rietveld with Energies Options* dialog is different for each frame.

Close the **Animation Options** and **Reflex Powder Refinement** dialogs.

Select **Window | Close All** from the menu bar. Click **No to All** when asked if you want to save the changes.

The Pareto optimization suggests the best solution that is closest to the absolute optimum (minimum R_{wp} , minimum E). In the energy versus R_{wp} chart **pareto E vs Rwp . xcd**, this solution has the shortest distance from the origin. On completion of the Pareto optimization, this is saved automatically in the project. Examine the crystal structure.

Reflex: Rietveld refinement with energetic considerations

In the **Project Explorer**, double-click **pareto.xsd** in the **pareto Reflex Pareto** folder.

Click **Calculate Hydrogen Bonds**  then **Calculate Close Contacts** .

To make the crystal structure clearer, you can switch off the display of motion groups. Press **ALT** and double-click a motion group. To switch off the display of the motion groups, select **Visibility | Hide** from the **View** menu. Press **CTRL + D** to clear selection of the motion groups.

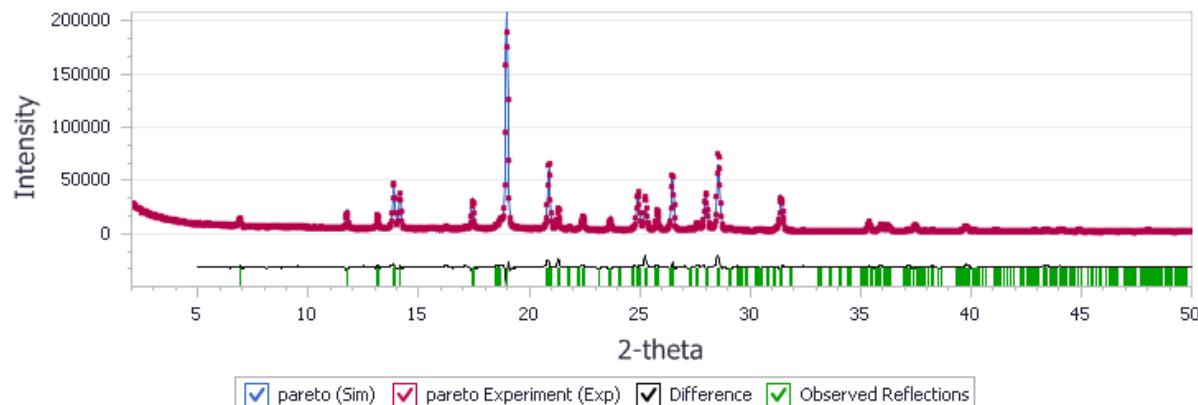
Close **pareto.xsd** and click **No** when asked if you want to save the changes.

Next examine the comparison of the simulated and the experimental powder diffraction pattern.

In the **Project Explorer**, double-click the Chart Document **pareto Reflex Pareto\pareto.xcd** and examine it.

The R_{wp} reduces to 11.2% compared to 12.40% obtained from regular Rietveld refinement. This reproduces well the overall intensity distribution of the experimental powder diffraction pattern. The inclusion of energy information into the Rietveld refinement process optimizing a R_{comb} allows for an improved structure solution.

Powder Refinement: $R_{wp} = 11.07\%$ $R_{wp}(w/o bck) = 19.31\%$
 $R_p = 8.34\%$



Comparison between the simulated powder pattern obtained by Rietveld refinement and experimental powder pattern

Note: Pareto optimization only provides the set of optimum solutions. Although it suggests a 'best solution', it by no means indicates the solution that is actually the best solution. The decision on which of the optimum solutions to select cannot be automated and has to be taken by the user according to specific criteria: is it more important in this particular case to have a good fit with the experimental pattern or is it critical that the energy is close to its minimum?

Compare the crystal structure obtained from Rietveld refinement with energies with that obtained from Rietveld refinement by overlaying the two structures.

Close **pareto.xcd**. Right-click the project root and select **New | Folder** from the shortcut menu. Rename the new folder **preferred_orientation**.

In the **Project Explorer**, double-click **pareto.xsd** in the **refinement\pareto** Reflex Pareto folder. Press **ALT** and double-click a motion group, then press **DELETE**.

Copy the contents of the document by clicking **Copy** . In the **Project Explorer**, right-click the folder **preferred_orientation** and choose **New | 3D Atomistic Collection Document** from the shortcut menu. Click **Paste** .

In the **Project Explorer**, right-click **3D Atomistic Collection.xod** and select **Rename** from the shortcut menu. Change the name of the document to **overlay.xod**.

Right-click the **overlay.xod** structure and select **Display Style** from the shortcut menu to open the Display Style dialog. On the **Atom** tab, for **Coloring** choose **Custom**, click the color chooser and select **red**.

On the **Lattice** tab, for the **Color** choose red.

Close **pareto.xsd** and click **No** when asked if you want to save the changes.

In the **Project Explorer**, double-click **refined structure.xsd** in the **refinement** folder. Press **ALT** and double-click a torsion, press **DELETE**.

Copy the contents of the document by selecting **Edit | Copy** from the menu bar. In the Project Explorer, double-click **overlay.xod** and select **Edit | Paste** from the menu bar.

On the **Atom** tab of the Display Style dialog, for **Coloring** choose **Custom**, click the color chooser and select **white**. Close the Display Style dialog.

Close **refined structure.xsd** and click **No** when asked if you want to save the changes.

Expand the **overlay.xod** window by clicking **Maximize** . Click once in the window to cancel selection of everything.

The two structures (**pareto.xsd** in red and **refined structure.xsd** in white) are quite similar, with the differences mainly in the hydrogen positions. Examine the hydrogen bonding scheme and close contacts.

Reflex: Rietveld refinement with energetic considerations

Double-click one of the atoms in red to select all of the **pareto.xsd** molecular fragment. Click **Calculate**

Hydrogen Bonds



Click anywhere in the 3D Viewer to clear selection of everything. Repeat the same procedure for **refined structure.xsd**.

The two structures have very similar hydrogen bonding schemes. Next, examine the close contacts.

Press **ALT** and double-click a hydrogen bond, then press **DELETE**.

Double-click one of the atoms in red to select all of the **pareto.xsd** molecular fragment. Click **Calculate**

Close Contacts



Click anywhere in the 3D Viewer to clear selection of everything. Repeat the same procedure for **refined structure.xsd**.

There are fewer close contacts for the structure solution obtained by Rietveld with energies. The inclusion of energy contribution in this case provides more accurate atomic positions, for example the hydrogen atoms.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank P. G. Varlashkin, M. Sacchetti, and J. Zhu from GlaxoSmithKline for supplying the experimental data.

Determining the degree of crystallinity of lactose monohydrate samples

Purpose: Illustrates how to estimate the degree of crystallinity from powder X-Ray data

Modules: Materials Visualizer, Reflex Powder Crystallinity

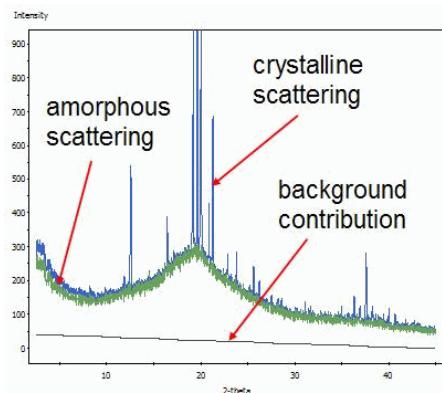
Time:  

Prerequisites: [Indexing powder patterns](#), Using scripting to calculate the interaction energy between two layers

Background

In many cases crystallization does not result in a 100% pure single crystalline phase. Instead it can yield a mixture of crystalline phases, a mixture of a single crystalline phase and an amorphous phase, or mixtures of different crystalline and amorphous phases. Powder X-ray diffraction data can be used to probe for these conditions, for example identifying and quantifying different crystalline phases from powder diffraction data, as described in the tutorial [Quantitative phase analysis of organic mixture samples](#).

In order to determine the degree of crystallinity based on X-ray data, the pattern needs to be deconvoluted into three scattering contributions: crystalline, amorphous, and background. The area difference between the crystalline and amorphous contributions determines the degree of crystallinity whereas the background contribution represents the background noise caused by, for example, the scattering from the sample holder.



Scattering contributions relevant for estimating the amorphous content

This tutorial discusses two methods for estimating the degree of crystallinity: background subtraction and phase analysis. Background subtraction can estimate the amorphous content from only the X-ray pattern. By contrast, the more accurate phase analysis method requires a diffraction pattern of the purely crystalline and amorphous phases as input.

Introduction

Lactose is an excipient used in pharmaceutical formulations as a binder and filler. In this tutorial you will analyze a series of X-ray powder diffraction patterns where lactose monohydrate, a common crystalline form of lactose, has been mixed with amorphous lactose at controlled weight ratios.

This tutorial covers:

- [Getting started](#)
- [To estimate the degree of crystallinity using the background subtraction method](#)
- [To estimate the degree of crystallinity using the phase analysis method](#)
- [To compare both methods using the scripting API](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **lactose** as the project name, click the **OK** button.

The new project is created with *lactose* listed in the Project Explorer. Now import the input files you will be studying.

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder and find all relevant files by typing **lactose*** into the **File name** textbox, press **ENTER**.

Several files are displayed. You should see eleven files of the type **lactose_XX%.xrdml** where "XX" indicates the degree of crystallinity, ranging from 10% to 100% ([Moizan et al., 2004](#)). You should also see **lactose_amorphous.xrdml** and **lactose_empty.xrdml**.

On the **Import Document** dialog, hold **SHIFT** and click on the first file then the last file in the list to select all files. Click the **Open** button.

All files are imported into Materials Studio. Now save the project and close all open windows.

Choose **File | Save Project** from the menu bar followed by **Window | Close All**.

2. Estimating the degree of crystallinity using the background subtraction method

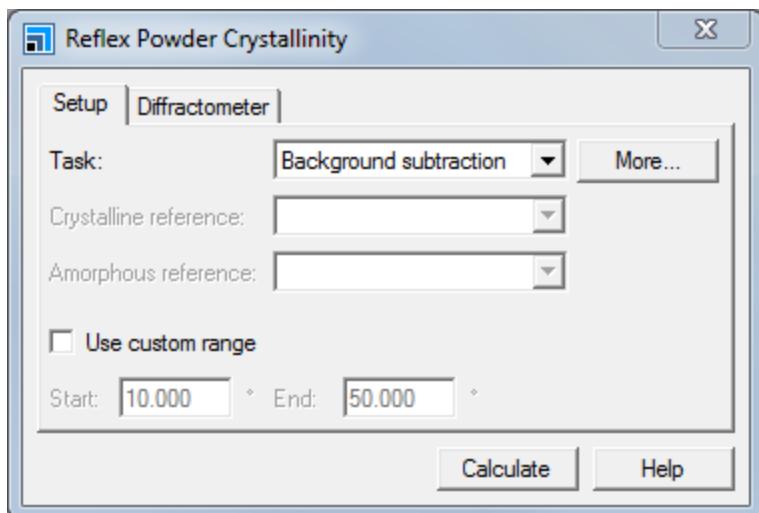
In this section you will use the background subtraction method to estimate the degree of crystallinity of some of the files you have just imported. Initially, you will use the Powder Crystallinity tool without providing any supplementary information.

Open the diffraction pattern for the sample with a degree of crystallinity of 20%.

In the Project Explorer double-click on **lactose_20%.xcd**.

Open the Reflex Powder Crystallinity tools.

Select **Modules | Reflex | Powder Crystallinity** from the menu bar.



Reflex Powder Crystallinity dialog

The **Task** dropdown list lets you choose between the background subtraction and phase analysis methods. The *Crystalline reference* and *Amorphous reference* options allow you to select the respective reference patterns. These are enabled only if the *Task* is set to *Phase analysis*. *Use custom range* allows you to restrict the range over which the analysis is performed.

On the Reflex Powder Crystallinity dialog set the **Task** to **Background subtraction** and click the **Calculate** button.

A new document entitled **lactose_20% Decomposition.xcd** is generated. The degree of crystallinity is estimated at 52.4%. *Coverage* indicates the fraction of intensity that was fitted. In this case all of the intensity was accounted for by the algorithm, so the coverage is 100%.

The degree of crystallinity has been significantly overestimated. To improve this result, you will now load a background reference pattern.

In the Project Explorer double-click on **lactose_20%.xcd** to make it the active document. On the Reflex Powder Crystallinity dialog, click the **More...** button for **Task** to open the Background Subtraction Options dialog. Click the **Use background reference** radio button and select **lactose_empty.xcd** from the dropdown list and close the dialog. On the Reflex Powder Crystallinity dialog click the **Calculate** button.

A new document named **lactose_20% Decomposition (2).xcd** is generated. The degree of crystallinity is estimated to 32.8%, in better agreement with the experimental value of 20%.

Now inspect both decompositions using the zoom and translate tools.

Select the **Zoom** tool on the **Chart Viewer** toolbar. Click in the **Chart Document** and move the mouse to the left and right and up and down while holding down the left mouse button. Select the **Translation** tool and move the mouse around the **Chart Document**.

Notice that there is a clear difference in the decomposition for high 2-Theta values. In **lactose_20% Decomposition (2).xcd** the background has lower intensities. The remaining intensity primarily affects the amorphous scattering intensity which explains the lower degree of crystallinity. For **lactose_20% Decomposition.xcd**, where no experimental background was provided, the

Reflex: Determining the degree of crystallinity of lactose monohydrate samples

background intensity was estimated to be significantly higher, leading to a significantly lower estimate of the amorphous scattering and higher estimate of the degree of crystallinity.

If you want try using the *Use custom range* feature on the *Setup* tab to verify that changing the low 2-Theta values has little effect on the estimates of the degree of crystallinity.

Select **Window | Close All** from the menu bar and click the **No to All** button when asked whether you want to save any documents as a part of this project. Choose **File | Save Project** from the menu bar.

3. Estimating the degree of crystallinity using the phase analysis method

In this section you will use crystalline and amorphous reference patterns to obtain a high quality prediction of the degree of crystallinity.

Double-click on **lactose_80%.xcd** in the Project Explorer. On the **Reflex Powder Crystallinity** dialog change the **Task to Phase analysis**. Select **lactose_100%.xcd** from the **Crystalline reference** dropdown list. Select **lactose_amorphous.xcd** from the **Amorphous reference** dropdown list. Click the **Calculate** button.

The degree of crystallinity is reported to be 80.9%, which is in excellent agreement with experiment. *Coverage* is reported at 93.0% which means that 7.0% of the scattering intensity could not be fitted. Again, inspect the pattern by using the *Zoom* and *Translate* tools.

Select **Window | Close All** from the menu bar, click the **No to All** button when asked whether you want to save any documents as a part of this project. Choose **File | Save Project** from the menu bar.

4. To compare both methods using the scripting API

To compare the performance of both methods you could run calculations for each of the ten data files by hand. However, a much faster and more convenient way is to use the scripting capabilities of this module. For a general introduction on how to use the Materials Studio scripting API please see the tutorial *Using scripting to calculate the interaction energy between two layers*.

First open a new Perl document.

Select **File | New** from the menu bar to open the New Document dialog, double-click on **Perl Script**.

A new Script Viewer opens. Next, create a Perl script by copying the script below into the empty Perl document.

Copy and paste the following Perl script into the new Script document.

```
# "@docs" is the list of diffraction files to analyze
my @docs = ("lactose_95%.xcd", "lactose_90%.xcd", "lactose_
80%.xcd",
            "lactose_70%.xcd", "lactose_60%.xcd", "lactose_50%.xcd",
            "lactose_40%.xcd", "lactose_30%.xcd", "lactose_20%.xcd",
            "lactose_10%.xcd");

# Alias some shortcuts for the modules
my $reflex = Modules->Reflex;
my $crystallinity = $reflex->PowderCrystallinity;

# assign the amorphous, crystalline, and background reference
```

```
$crystallinity -> SetAmorphousReference( $Documents{"lactose_amorphous.xcd"} );
$crystallinity -> SetCrystallineReference( $Documents{"lactose_100%.xcd"} );
$crystallinity -> SetBackgroundReference( $Documents{"lactose_empty.xcd"} );

# These are the settings for the phase analysis
my @SettingsPA = (
    CrystallinityMethod => "Phase analysis",
    WriteLevel      => "Silent"
);

# These are the settings for the phase background subtraction
my @SettingsBG_empty = (
    CrystallinityMethod => "Background subtraction",
    WriteLevel      => "Silent",
    UseAutoBackground  => "No"
);

# These are the settings for the phase background subtraction
my @SettingsBG = (
    CrystallinityMethod => "Background subtraction",
    WriteLevel      => "Silent",
    UseAutoBackground  => "Yes"
);

# Create a study table to hold the results
my $StudyTable = Documents->New("Crystallinity Report.std");

#Setup some Header information in the StudyTable
$StudyTable->ColumnHeading(0) = "Diffraction file";
$StudyTable->ColumnHeading(1) = "Crystallinity (Background Subtraction)";
$StudyTable->ColumnHeading(2) = "Crystallinity (Background Subtraction, empty sample holder)";
$StudyTable->ColumnHeading(3) = "Crystallinity (Phase Analysis)";

# "index" is the row index in the results study table
my $index = 0;

# This executes the Powder Crystallinity calculation for all files
foreach my $file (@docs) {

    # Load in the chart document
```

```
my $chartDoc = $Documents{$file};

# Run the Background subtraction method
$reflex->ChangeSettings(\@SettingsBG);
my $resultsBG = $crystallinity->Run($chartDoc);

# Run the Background subtraction method
$reflex->ChangeSettings(\@SettingsBG_empty);
my $resultsBG_empty = $crystallinity->Run($chartDoc);

# Run the Phase analysis method
$reflex->ChangeSettings(\@SettingsPA);
my $resultsPA = $crystallinity->Run($chartDoc);

# Store the results into the study table
$StudyTable->Cell($index, 0) = $file;
$StudyTable->Cell($index, 1) = $resultsBG->Crystallinity;
$StudyTable->Cell($index, 2) = $resultsBG_empty->Crystallinity;
$StudyTable->Cell($index, 3) = $resultsPA->Crystallinity;

# Close the chart document
$chartDoc->Close;

# increment "index" to store the next row of results
++$index;

}
```

Now run the script.

Make sure **Perl Script.pl** is in focus by double-clicking on it in the Project Explorer. Change the name of the Perl script to **Crystallinity Report.pl**.

Click on the **Run on Server** tool  on the **Scripting** toolbar.

Once the calculation finishes the results are collected in a folder called *Crystallinity Report Script*. The important information is collected in a study table called *Crystallinity Report.std*.

In the **Project** explorer double-click on **Crystallinity Report.std**, which should contain the following data:

Diffraction file	Crystallinity (Background Subtraction)	Crystallinity (Background Subtraction, empty sample holder)	Crystallinity (Phase Analysis)
lactose_95%.xcd	74.2	83.3	95.6
lactose_90%.xcd	80.9	79.3	85.0

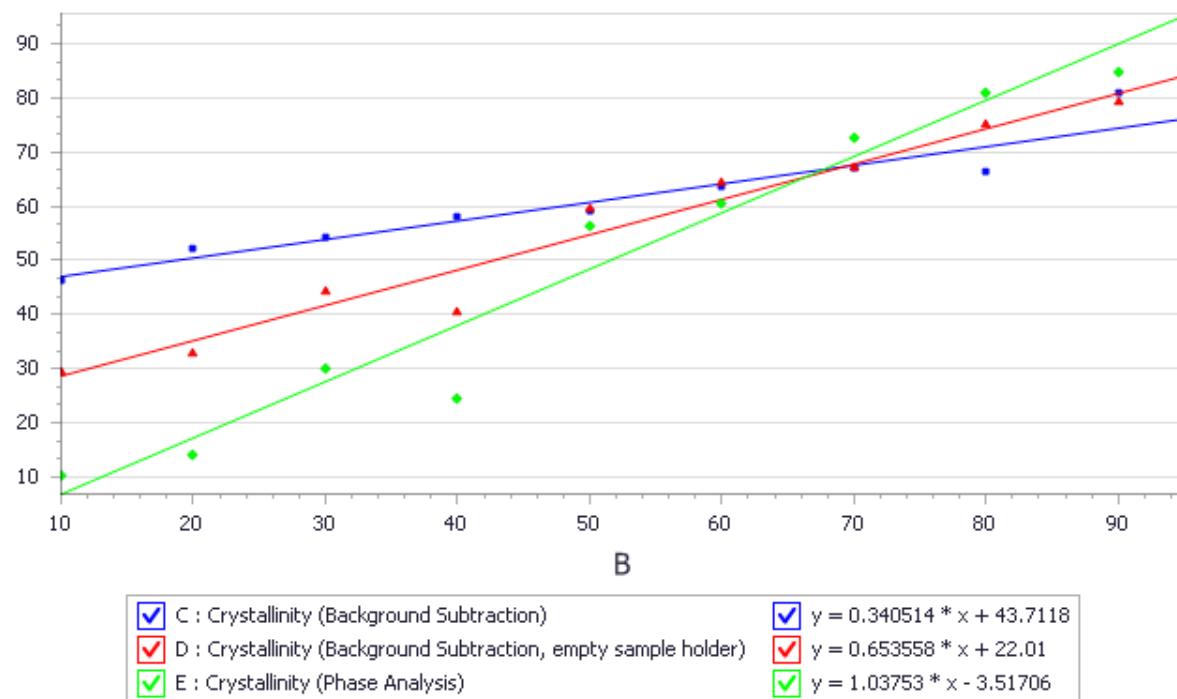
Diffraction file	Crystallinity (Background Subtraction)	Crystallinity (Background Subtraction, empty sample holder)	Crystallinity (Phase Analysis)
lactose_80%.xcd	66.5	75.0	80.9
lactose_70%.xcd	67.2	67.3	72.8
lactose_60%.xcd	63.8	64.4	60.6
lactose_50%.xcd	59.1	59.7	56.3
lactose_40%.xcd	58.0	40.6	24.4
lactose_30%.xcd	54.3	44.4	30.2
lactose_20%.xcd	52.4	32.8	14.3
lactose_10%.xcd	46.3	29.4	10.2

Next you will analyze this data using the plotting capabilities of Materials Studio.

Select column **B**, right-click and select **Insert | Left** from the shortcut menu. Type in the experimental values for the degrees of crystallinity (**95** next to **lactose_95%.xcd**).

Hold **SHIFT** and click **B** then **E** to select the columns to plot. Select **Tools | Plot Graph** from the menu bar to open the Plot Graph dialog. Set **Graph type** to **Scatter (2-D)** and **X-axis** to **B**. Check **Show best fit line** checkbox and click the **Plot** button.

The scatter plot should look like this:



Scatter plot for the various predictions of the degree of crystallinity

Note that all methods correctly reproduce the trend in the change of the degree of crystallinity. Furthermore, overall the phase analysis method is in excellent agreement with experiment.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank V. Moizan, T. Larsson, L. Briggner, and J. Giovannini from Astra Zeneca for supplying the experimental data.

References

Virginie Moizan^{1,2}, Tomas Larsson¹, Lars-Erik Briggner¹, Julien Giovannini¹, 2004, "in silico procedures for phase identification and quantitative phase analysis using state-of-the-art in X-Ray Powder Diffraction", MSc Thesis report, ¹AstraZeneca, ²Rennes University.

Chapter 21: Reflex QPA tutorials

The following tutorial illustrates how to utilize the capabilities of Powder Quantitative Phase Analysis.

Quantitative phase analysis of organic mixture samples

Purpose: Illustrates how to determine the relative amounts of different phases in a mixture from a powder diffraction pattern of the mixture.

Modules: Materials Visualizer, Reflex, Reflex QPA

Time:  

Prerequisites: [Rietveld refinement with energetic considerations](#)

Background

Quantitative phase analysis (QPA) refers to the determination of the relative amounts of different phases in multi-phase samples. It is widely used to analyze the phase composition of a material in a rapid and simple manner. Its applications include forensic analysis, mineral assays, fiber analysis, characterization of pharmaceuticals, corrosion products, intermetallics, and contaminants.

Introduction

In Reflex QPA, the pure component phases that comprise a mixture may be represented by:

- crystal structures (Rietveld method) - pattern, sample, lattice, and structural parameters can be refined for each phase.
- experimental powder diffraction patterns (standardless method or internal standard method) - parameters associated with line shift corrections can be refined for each phase.
- a mixture of crystal structures and experimental powder diffraction patterns.

This tutorial aims to explain the different steps involved in the analysis of an acetohexamide mixture. Acetohexamide is used to treat type II (non insulin-dependent) diabetes, particularly in people whose diabetes cannot be controlled by diet alone.

This tutorial covers:

- [Getting started](#)
- [To prepare the pure phase crystal structures](#)
- [To set up, run, and analyze the results of QPA with the Rietveld method](#)
- [To prepare the powder diffraction patterns with an internal standard](#)
- [To set up, run, and analyze the results for internal standard QPA](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **QPA** as the project name, click the **OK** button.

The new project is created with *QPA* listed in the Project Explorer. Now you will import the input file you will be studying.

You will load the powder diffraction pattern of a three-component-phase mixture, comprising 40% of the stable polymorphic form of acetohexamide (Form A), 40% of the metastable polymorphic form of acetohexamide (Form B), and 20% corundum (internal standard).

Click the **Import** button  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder, change the **Files of type** to **Chart Files**, and double-click on **Acetohexamide_Mixture.xcd**.

Close **Acetohexamide_Mixture.xcd** and click the **Yes** button when asked if you want to save the document as part of the project.

Tip: After loading the experimental powder diffraction pattern, you may wish to process it further using the Pattern Processing tool. You could, for example, remove $K\alpha_2$ peaks due to the secondary emission lines of the X-ray anode, or smooth the pattern and remove any noise. These $K\alpha_2$ stripping and smoothing steps are optional and are not prerequisites for a successful Powder QPA calculation.

You will now import the crystal structures of Form A, Form B, and corundum.

Open the **Import Document** dialog. Select **3D Atomistic Files** from the **Files of type** dropdown list. Navigate to the folder **Examples\Reflex\Structures**. Hold down **CTRL** and select the files **Acetohexamide_FormA.xsd** and **Acetohexamide_FormB.xsd**. Click the **Open** button.

Open the **Import Document** dialog. Navigate to and select the file **Structures\metal-oxides\Al2O3.xsd**, then click the **Open** button.

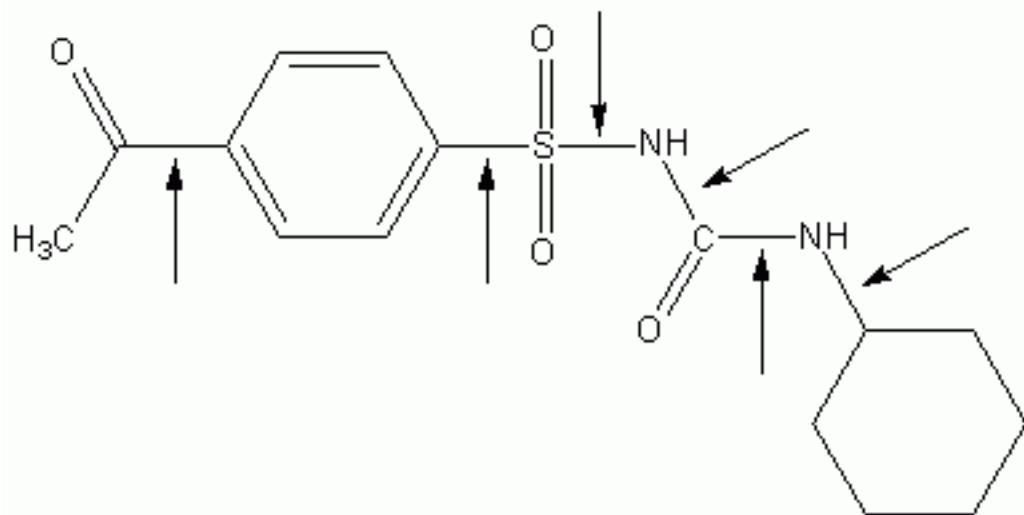
2. To prepare the pure phase crystal structures

This section shows you how to prepare the input files for a Powder QPA calculation using the Rietveld method, where the pure component phases are represented by their crystal structures. The diffraction pattern of the mixture is decomposed into a superposition of powder diffraction patterns simulated from these structures.

You will define the structural degrees of freedom for each of the crystal structures starting by specifying the intramolecular torsions of the molecular fragment in the unit cell.

Make **Acetohexamide_FormA.xsd** the active document. Click the **Measure/Change** arrow  on the **Sketch** toolbar and select **Torsion** from the dropdown list.

Choose one molecule in **Acetohexamide_FormA.xsd**. Six flexible single bonds are identified in the figure below. Click on them in turn, starting from one end of the chain and working your way through the others.



Molecular structure of acetohexamide

Note: You can define the measurements on any symmetry image of a molecular fragment in the periodic structure. You do not need to define all measurement degrees of freedom on the same molecular fragment. However, you need to ensure that you do not define the same measurement twice on two different symmetry images since in such a case you artificially increase the number of degrees of freedom and it will take a longer time to locate the optimal structure.

In the next step, you will define the whole molecule as a motion group. This means that the position and orientation of all atoms in the molecule are described by a single set of translational and rotational parameters in addition to the torsional degree of freedom you have just defined.

Choose the **Selection** tool from the **3D Viewer** toolbar.

In the 3D Viewer for **Acetohexamide_FormA.xsd**, click on one of the atoms to select it. Right-click on the structure and choose **Select Fragment** from the shortcut menu to select the entire molecule.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Setup** tab, change the refinement **Type** from Pawley to **Rietveld**.

On the **Structure** tab choose **Single group** for the motion group selection and click the **Create** button.

All the checkboxes for the structural degrees of freedom (torsions and motion groups) are switched on automatically for refinement.

Note: It is recommended that you turn off the refinement of the structural degrees of freedom by default. Once the major phases have been identified from an initial QPA run, the results may be improved by enabling the refinement of the structural degrees of freedom just for the major phases.

On the **Structure** tab, switch off the **Refine** checkboxes for all the structural degrees of freedom.

Close **Acetohexamide_FormA.xsd** and click the **Yes** button when asked if you want to save the document as part of the project.

Repeat the same procedure to define the torsional degrees of freedom and motion groups for **Acetohexamide_FormB.xsd**. Ensure that none of the structural parameters checkboxes are switched on for refinement. Close **Acetohexamide_FormB.xsd** and save the document as part of the project.

Next you will define the structural degrees of freedom for corundum.

Make **Al2O3.xsd** your active document and press **CTRL + A** to select the entire structure.

On the **Structure** tab of the Reflex Powder Refinement dialog, choose **Individual groups** for the motion group selection and click the **Create** button. Ensure that none of the structural parameters checkboxes are checked for refinement.

Close **Al2O3.xsd** and click the **Yes** button when asked if you want to save the changes.

There are a range of non-structural parameters that can be refined for a crystal structure as part of a Powder QPA calculation, including profile, background, and sample parameters. The default settings for all these parameters are imported from the current settings in Reflex and applied to each pure component phase. Therefore, you need to define the general settings for these refinement parameters.

On the **Setup** tab of the Reflex Powder Refinement dialog, change the **Max. 2-Theta** value from 45° to 70.001° .

The data for this tutorial were measured with copper λ_1 radiation only, so you should deselect λ_2 radiation for the refinement.

On the **Radiation** tab, uncheck the λ_2 checkbox in the **X-ray** section.

On the **Pattern** tab, enable refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and of the **Zero point Line shift**. The refinement of 20 **Background coefficients** is enabled by default.

In the Project Explorer, double-click on **Acetohexamide_Mixture.xcd** to make it your active document.

On the **Exp. Data** tab, select the chart document **Acetohexamide_Mixture.xcd** as the experimental powder diffraction data. Close the Reflex Powder Refinement dialog.

3. To set up and run a Powder QPA with the Rietveld method

In this section, you will perform a Powder QPA calculation using the Rietveld method. Two separate Powder QPA tasks are available in Materials Studio, full refinement and refine weights. In this tutorial, you will run a full refinement calculation.

Click the **Reflex** arrow  on the **Modules** toolbar and select **Powder QPA** from the dropdown list to open the Reflex Powder QPA dialog.

On the **Setup** tab, set the **Type** to **Full refinement**.

Note: The calculation of weight fraction is only available for X-ray diffraction data. If you use electron or neutron diffraction sources, you will be able to calculate the scattering intensity fraction of each phase in the mixture but not the weight fractions.

On the **Setup** tab the **Convergence quality** should be set to **Medium**. Check the **Create individual chart document for each phase** checkbox.

This option determines whether the chart documents containing the calculated powder diffraction patterns will be inserted into the Powder QPA study table when a calculation is complete.

Tip: Since the chart documents are produced for all the component phases, the size of the study table containing the results of a Powder QPA job can become very large.

Next you will define the potential pure component phases in the mixture.

On the **Phases** tab, click the **Add new phases** button to open the Add QPA Phases dialog. Hold down **CTRL** and select **Acetohexamide_FormA.xsd**, **Acetohexamide_FormB.xsd**, and **Al2O3.xsd**. Click the **Open** button.

A study table called **Powder QPA.std** is automatically created in the Project Explorer. In addition to the structures, the corresponding cell formulas for the pure component phases are extracted and entered into the study table. A phase ID is assigned to each phase with the name being taken from the crystal structure file.

You may wish to examine or edit the refinement parameters settings for individual phases.

Click on the **Al2O3** row in the study table document **Powder QPA.std** to select it. Click the **Edit parameters** button for **Al2O3 parameters** on the Reflex Powder QPA dialog.

This opens the Phase Al2O3 dialog.

When a phase is loaded into the input study table, default settings for the refinement parameters are also imported. In the case of crystal structures, the lattice parameters, structural degrees of freedom, and atomic temperature factors are taken from the **.xsd** document. All the other non-structural refinement parameters, for example pattern parameters and sample parameters, are imported from Reflex.

On the **Pattern** tab of the Phase Al₂O₃ dialog, make sure that the appropriate checkboxes are checked to enable the refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and of the **Zero point Line shift**. The refinement of **20 Background coefficients** should also be enabled.

On the **Lattice** tab, check on the refinement of the cell parameters **a**, **b** and, **c**, and check the **Keep fractional coordinates fixed during lattice changes** checkbox.

On the **Structure** tab, make sure that the checkboxes for all the structural degrees of freedom are switched off. Click the **OK** button.

Click anywhere in the study table document to deselect the **Al₂O₃** row.

For molecular crystals, it is advisable to keep the Cartesian coordinates fixed in order to avoid distortion of bond angles and distances in the asymmetric unit as a result of lattice parameter refinement. However, this is not possible for Al₂O₃ because the Al and O atoms are sitting in special positions, and therefore you need to preserve their fractional coordinates. This is very common for many inorganics. If you wish, you can continue to review the refinement settings for component phases Acetohexamide_FormA and Acetohexamide_FormB.

In the study table document **Powder QPA.std**, click the **Acetohexamide_FormA** row to select it. Click the **Edit** button for **Acetohexamide_FormA parameters** to open the Phase Acetohexamide_FormA dialog.

On the **Pattern** tab, check on refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and of the **Zero point Line shift**.

On the **Lattice** tab, check on the refinement of the cell parameters **a**, **b**, and **c**, and ensure that the checkbox of **Keep fractional coordinates fixed during lattice changes** is unchecked.

On the **Structure** tab, make sure that the checkboxes for all the structural degrees of freedom are switched off. Click the **OK** button.

Repeat the same procedure for Acetohexamide_FormB. Click anywhere in the study table document **Powder QPA.std** to deselect everything.

Tip: You can propagate the refinement settings from one structure document to any or all of the others in the input study table using the Export parameters to Powder Refinement and Import parameters from Powder Refinement functionalities on the *Phases* tab of the Reflex Powder QPA dialog. These tools allow Powder Refinement to be used as an intelligent clipboard - refinement settings for one structure can be sent to the Powder Refinement dialog, modified if required, and then imported into any or all of the other structures in the study table. Refinement parameters can be exported to or imported from Powder Refinement for crystal structures in the study table.

You should now check that the correct experimental powder pattern for the mixture is selected for the calculation.

Select the **Experimental Data** tab on the Reflex Powder QPA dialog. Make sure that **Acetohexamide_Mixture.xcd** is selected.

The background contribution of the mixture diffraction pattern can be fitted as part of the Powder QPA run. In this tutorial you will use the default setting of a *Polynomial order* equal to **20** to refine the background.

On the **Job Control** tab on the Reflex Powder QPA dialog, select **My Computer** as the **Gateway location**. Uncheck the **Automatic** checkbox and enter **no struct DOF** as the **Job description**.

Ensure that **Powder QPA.std** is the active document. Click the **Refine** button and close the Reflex Powder QPA dialog.

Close **Powder QPA.std** and click the **Yes** button when asked if you want to save the document as part of the project.

The Job Explorer informs you about the progress of the calculation. Once the calculation starts, a new folder called **no_struct DOF Reflex QPA Job** is created in the Project Explorer. The parameter settings for this job are automatically saved in a file called **no_struct DOF - Powder Diffraction**. The input experimental powder diffraction document and study table document are also listed in the folder.

After some time, a new text document, **Status.txt** appears, which gives a summary of the calculation as it currently stands. In addition, a chart document **no_struct DOF.xcd** is created in the **no_struct DOF Reflex QPA Job** folder to show the contribution of the individual pure phases to the input mixture powder pattern. These documents are updated regularly as the job progresses.

Wait until the job finishes before proceeding.

Once the calculation is finished, the main output is inserted into the input study table document and displayed as the active document. The calculated dataset includes the weight fraction of each potential component phase in the experimental mixture and chart documents showing the contribution of each potential phase to the experimental mixture pattern. The weight fractions for FormA, FormB, and corundum are approximately 44%, 36%, and 20%, respectively.

Now examine the text output file.

In the Project Explorer, double-click on the text document **no_struct DOF Reflex QPA Job\no_struct DOF.txt**.

The document contains all the calculation settings and a summary of the main results of the Powder QPA calculation. The R_{wp} value is quite large at about 36.3%. The integrated residual intensity is approximately 13.2%, which indicates that a significant amount of the intensity in the mixture powder diffraction pattern is not accounted for. Next, you should look at the chart file.

In the Project Explorer, double-click on the chart document **no_struct DOF Reflex QPA Job\no_struct DOF.xcd**.

The intensity distributions of the simulated and experimental powder patterns are significantly different, confirming that the refinement has not been completed successfully. One reason for this is that the refinement has not been performed including the structural degrees of freedom parameter. Since there

Reflex QPA: Quantitative phase analysis of organic mixture samples

is no prior knowledge of the potential phases, the Powder QPA job results indicate that the three input component phases are the major phases.

Next you will perform a second Powder QPA job, this time including the structural degrees of freedom parameter.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Open the **Reflex Powder QPA** dialog and select the **Phases** tab. In the Project Explorer, double-click on **no struct DOF Reflex QPA Job\no struct DOF.std** to make it your active document.

Select the **Al2O3** row in the **no struct DOF.std** Study Table Viewer. On the Reflex Powder QPA dialog click the **Edit** button for **Al2O3 parameters** to open the Phase Al2O3 dialog.

On the **Structure** tab, check the checkboxes for motion groups and all the torsions. Click the **OK** button.

Repeat the same procedure for **Acetohexamide_FormA** and **Acetohexamide_FormB**.

The structural degrees of freedom for Al2O3, Acetohexamide_FormA, and Acetohexamide_FormB are [2](#), [12](#), and [12](#), respectively. All of the other settings, from the previous run, should remain unchanged. You are now ready to start the job.

Click anywhere in the study table document **no struct DOF.std** to deselect everything.

Select the **Job Control** tab from the Reflex Powder QPA dialog and enter **struct DOF** as the **Job description**.

Click the **Refine** button and close the dialog. Close **no struct DOF.std** and click the **No** button when asked if you want to save the changes to the document.

The Job Explorer informs you about the progress of the calculation.

When the calculation is complete, examine the results, starting with the study table document. The calculated weight fractions for Acetohexamide_FormA, Acetohexamide_FormB, and corundum are approximately [43.0%](#), [38.7%](#), and [18.3%](#), respectively.

Next you will examine the text output.

In the Project Explorer, double-click on the text document **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF.txt**.

The R_{wp} value is about [21.5%](#), this is a significant improvement on the R_{wp} value of [36.3%](#) which was obtained above without employing the structural degrees of freedom parameter in the refinement.

The integrated residual intensity has reduced to [4.5%](#), which indicates that a majority of the intensity in the mixture has been attributed to the three component phases.

In the Project Explorer, double-click on the chart document, **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF.xcd**.

There is still a discrepancy between the intensity of the simulated and experimental powder diffraction patterns. There are several reasons which can account for this, one of them being preferred orientation.

The lattice parameters of corundum are $a = b = 4.76 \text{ \AA}$, $c = 12.99 \text{ \AA}$. As the c -axis is about three times longer than the other two axes, the c^* -axis of the reciprocal unit cell is about three times shorter than the a^* -axis and the b^* -axis. Preferred orientation might be playing a role here. It is therefore appropriate to try a QPA calculation again, this time including a preferred orientation correction.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Open the **Reflex Powder QPA** dialog and select the **Phases** tab.

In the Project Explorer, double-click on **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF.std** to make it your active document. Select the **Al2O3** row of **struct DOF.std** and, on the Reflex Powder QPA dialog, click the **Edit** button for **Al2O3 parameters** to open the Phase Al2O3 dialog.

On the **Sample** tab, scroll down to **Preferred orientation**. Change the **Applied** correction from **None** to **March-Dollase** and check the checkboxes for **a^* , b^* , c^*** and **R0**. Click the **OK** button.

Repeat the same procedure for **Acetohexamide_FormA** and **Acetohexamide_FormB**.

Tip: The Powder QPA results can vary slightly depending on the starting values of the preferred orientation a^* , b^* , and c^* . Experimental microscope data on crystal morphology can help provide some educated guesses on the potential preferred orientation. Alternatively, you can calculate the crystal morphology for a crystal structure using the Morphology module in Materials Studio.

In this tutorial, you will use the default values for the preferred orientation and coefficients. All of the other settings, from the previous run, should remain unchanged. You are now ready to start the calculation.

Click anywhere in the study table document **struct DOF.std** to deselect everything.

Select the **Job Control** tab from the Reflex Powder QPA dialog. Enter **struct DOF PO** as the **Job description**. Click the **Refine** button and close the dialog.

Close **struct DOF.std** and click the **No** button when asked if you want to save the changes to the document.

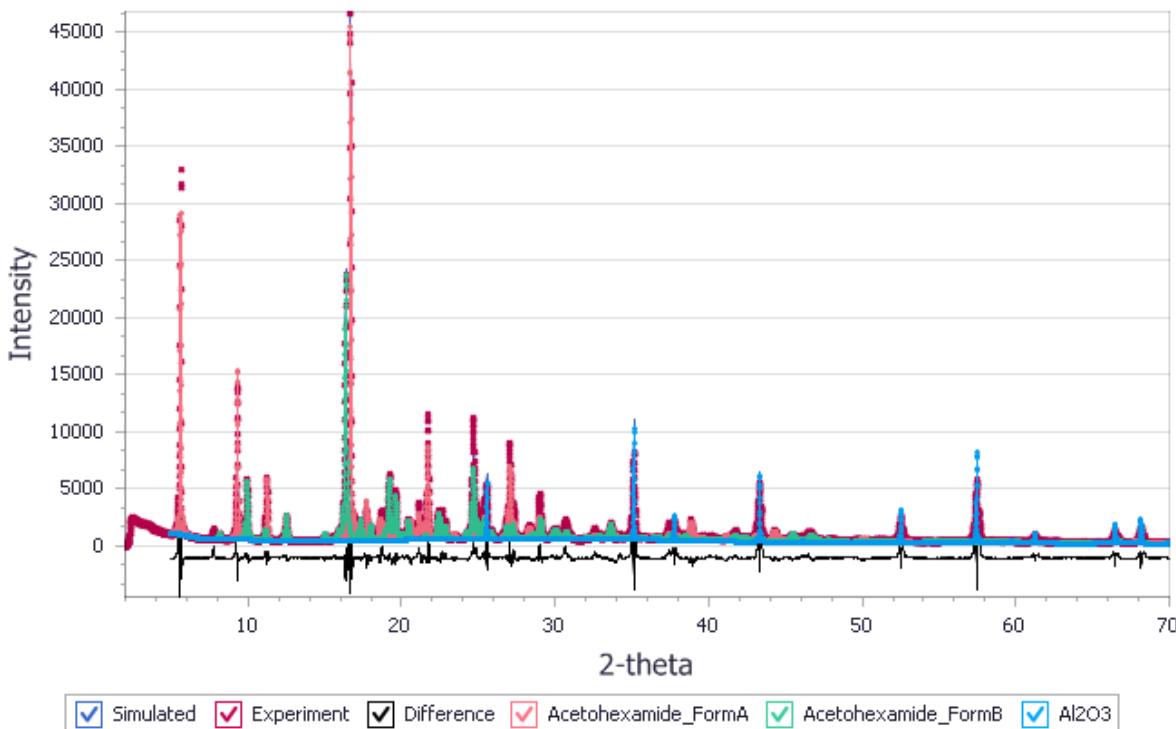
When the calculation is complete, examine the results, starting with the study table document. The results show that the weight fractions for Acetohexamide_FormA, Acetohexamide_FormB, and corundum are approximately **37.3%**, **39.5%**, and **23.2%**, respectively. These values are in good agreement with the actual composition of 40%, 40%, and 20% for the respective phases.

Now examine the text output.

In the Project Explorer, double-click on the text document **no struct DOF Reflex QPA Job\struct DOF Reflex QPA Job\struct DOF PO Reflex QPA Job\struct DOF PO.txt**.

The R_{wp} value is about **11.8%**, and the integrated residual intensity is about **1.4%**. The overall intensity distribution of the experimental powder diffraction pattern is well reproduced, although some regions show intensity differences as indicated in the difference plot in the chart document below.

$R_{wp}=11.86\%$ $R_{wp(w/o\ bck)}=24.56\%$ $R_p=8.98\%$



Comparison between the simulated powder pattern obtained by QPA and the experimental powder pattern of the mixture phase

You may wish to explore the effects of other refinement parameters, for example temperature factors, crystallite size broadening, or lattice strain broadening among others, on the final results of the weight fractions.

Note: The number of degrees of freedom can become quite large so that the information contained in the experimental powder diffraction pattern of the phase mixture may not be sufficient to uniquely determine all the refinable parameters. As a result, parameter or structure values may become unphysical, leading to incorrect results. To avoid this, it is recommended that you refine only those parameters that strongly affect the simulated diffraction pattern and include only those phases that make large contributions to the intensity of the powder diffraction pattern of the phase mixture.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To prepare the powder diffraction patterns with an internal standard

This section describes how to prepare the input files for an internal standard QPA calculation.

The internal standard method uses the experimental powder diffraction patterns of the potential pure component phases as input. A fixed weight fraction of a standard material (corundum in this tutorial) is added to all pure phases as well as the mixture phase before their powder diffraction patterns are recorded. In order to calculate the component weight fraction, the internal standard method requires that all the powder diffraction patterns are rescaled such that the scattering intensity contribution from the standard is the same for all the patterns. This approach provides a means to correct for varying experimental conditions, sample adsorption, and matrix effects.

Note: The standardless method also uses the experimental powder diffraction patterns of the pure component phases as input. It differs from the internal standard method in that all the powder diffraction patterns must be recorded under identical experimental conditions. No scaling is required for the standardless method.

Start by importing the powder diffraction patterns for Acetohexamide Form A and Form B. Both patterns contain 20% corundum.

In the Project Explorer, click on the **QPA** project.

Open the Import Document dialog and select **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** directory, hold down **CTRL** and select **Acetohexamide_FormA.xcd**, **Acetohexamide_FormB.xcd**, and **corundum.xcd**. Click the **Open** button.

Next determine the scaling factor required for normalizing the powder diffraction patterns with respect to the internal standard. To do so, you will first calculate the integrated scattering intensity of the internal standard in any given powder diffraction pattern. The scale factor is calculated as the ratio of the target value for the diffraction contribution of the standard (an arbitrary but constant value for all the component phases and the mixture phase) and the calculated integrated scattering intensity of the standard.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

In the Project Explorer, double-click on **Acetohexamide_FormA.xcd** to make it the active document.

Open the **Reflex Powder QPA** dialog. On the **Phases** tab, click the **Add new phases** button to open the Add QPA Phases dialog. Select **corundum.xcd** and click the **Open** button.

A study table called **Powder QPA (2).std** is automatically created in the Project Explorer.

In the Project Explorer, right-click on **Powder QPA (2).std** and select **Rename** from the shortcut menu. Change the filename to **corundum_FormA**. The file extension **.std** is automatically appended.

Once you have loaded a pattern, you should prepare it in exactly the same way as you prepared the mixture pattern, so if you stripped out the $K\alpha_2$ peaks or smoothed the experimental mixture pattern, you should carry out the same procedure for the pure phase patterns.

When a powder diffraction pattern is inserted into a study table, you will need to manually enter the cell formula for each phase in the *Cell formula* column. Since you are only concerned about the integrated intensity of the corundum, instead of the weight fraction, at this point, you can proceed without entering the cell formula for corundum.

Note: When a phase is loaded into the input study table, defaults settings for the line shift refinement parameters are imported from the current settings in Reflex and applied to all phases that are added to the study table.

In the study table document, **corundum_FormA.std**, click on the row containing **corundum**.

On the **Phases** tab of the Reflex Powder QPA dialog, click the **Edit** button for **corundum parameters** to open the Phase corundum dialog. Make sure the checkbox for **Zero point** is checked on the Phase corundum dialog and click the **OK** button.

Click anywhere in the study table document **corundum_FormA.std** to deselect everything.

Select the **Experimental Data** tab on the Reflex Powder QPA dialog. Make sure that the chart document **Acetohexamide_FormA.xcd** is selected as the experimental powder diffraction data.

On the **Job Control** tab, enter **formA_scaled** as the **Job description**.

Click the **Refine** button and close the dialog.

Close **corundum_FormA.std** and click the **Yes** button when asked if you want to save the document as part of the project.

Note: Refinement parameters cannot be exported to Powder Refinement for powder patterns in the study table. However, you can import refinement settings from Powder Refinement for the powder patterns.

The calculation takes a few seconds. When it is complete, you should examine the results in the study table document.

The integrated intensity for corundum is **1.038259e+004**. Assuming the target value is 1000, the scale factor for the Acetohexamide_FormA powder diffraction pattern is calculated as below:

$$\text{Scale factor (Acetohexamide_FormA)} = 1000 / 1.038259e+004 = 0.096315081$$

Tip: You can select the most appropriate part of the powder patterns for calculating the diffraction contribution from the standard by specifying the 2θ range and/or using excluded regions. For instance, to obtain intensity ratios for a single isolated peak, specify a simulation range comprising just this single peak.

Note: The individual calculated scale factors will strongly depend on the 2θ range used during the QPA analysis. However, the weight fractions calculated during internal standard QPA depend on the ratio of the scale factors only. It is essential that you normalize all patterns to the same value of the diffraction contribution of the standard and that you use the same 2θ range for quantitative phase analysis with an internal standard.

Repeat the same procedure to calculate the scale factors for **Acetohexamide_FormB.xcd** and **Acetohexamide_Mixture.xcd**, rename the study table documents **corundum_FormB** and **corundum_Mixture**.

$$\text{Scale factor (Acetohexamide_FormB)} = 1000 / 9.811742e+003 = 0.101918701$$

$$\text{Scale factor (Acetohexamide_Mixture)} = 1000 / 1.141771e+004 = 0.087583237$$

You are now ready to normalize the experimental powder diffraction patterns using the obtained scale factors.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

In the Project Explorer, double-click on **Acetohexamide_FormA.xcd** to make it your active document.

Open the **Reflex Pattern Processing** dialog. On the **Pattern Processing** tab, set the **Scaling factor** to **0.096315081** and click the **Scale** button.

A new chart document, **Acetohexamide_FormA (Scaled).xcd**, is created, in which the original powder diffraction pattern has been normalized using the scaling factor for **Acetohexamide_FormA**.

You may calculate the contribution from background scattering and then subtract this background contribution. This is necessary if you wish to exclude the background calculation from the quantitative phase analysis. Since the background of a potential component phase pattern is not fitted in a Powder QPA calculation, you will subtract the background from the powder diffraction patterns for the pure component phases.

On the **Pattern Preparation** tab of the Reflex Pattern Processing dialog, in the **Background** section, increase the **Number of iterations** to **300**. Click the **Calculate** button and then the **Subtract** button.

A new chart document, **Acetohexamide_FormA (Scaled) (Background Removed).xcd**, is created, in which the background has been subtracted from the powder pattern.

In the Project Explorer, right-click on **Acetohexamide_FormA (Scaled) (Background Removed).xcd** and select **Rename** from the shortcut menu. Change the filename to **Acetohexamide_FormA (Prep).xcd**. Repeat the same procedure for **Acetohexamide_FormB.xcd**.

It is not recommended to subtract the background from the experimental mixture phase pattern. Instead, the full pattern should be used for evaluating the R_{wp} figure of merit during the QPA optimization. The background contribution of the mixture diffraction pattern should be fitted as part of a QPA run.

In the Project Explorer, double-click on **Acetohexamide_Mixture.xcd** to make it the active document.

On the **Pattern Processing** tab of the Reflex Pattern Processing dialog, set the **Scaling factor** to **0.087583237** and click the **Scale** button.

Close the Reflex Pattern Processing dialog.

5. To set up, run, and analyze the results for the internal standard QPA

In this section, you will perform a Powder QPA calculation using the internal standard method. First you will prepare an input study table document.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

Open the **Reflex Powder QPA**. On the **Setup** tab, set the **Type** to **Full refinement** and check the **Patterns contain internal standard** checkbox.

On the **Phases** tab, click on the **Add new phases** button to open the Add QPA Phases dialog. Hold down **CTRL**, select **Acetohexamide_FormA (Prep).xcd** and **Acetohexamide_FormB (Prep).xcd**, and click the **Open** button.

A study table called **Powder QPA (2).std** is automatically created in the Project Explorer.

In the Project Explorer, right-click on **Powder QPA (2).std** and select **Rename** from the shortcut menu. Change the filename to **Patterns_internstd.std**.

Note: If you are using powder patterns from samples containing an internal standard, cell formula information is not required to calculate weight fractions.

Note: If you use standardless QPA and the cell formula is not known for any of the potential component phases, it is still possible to run a Powder QPA calculation to obtain the intensity fractions. However, weight fractions will not be calculated for any phases for which the cell formula is not given in the input study table.

Select the **Experimental Data** tab on the Reflex Powder QPA dialog. In the Project Explorer, double-click on **Acetohexamide_Mixture (Scaled).xcd** to make it the active document. Make sure that the chart document **Acetohexamide_Mixture (Scaled).xcd** is selected as the experimental powder diffraction data.

On the **Job Control** tab, enter **internal standard** as the **Job description**.

Make **Patterns_internstd.std** the active document.

Click the **Refine** button and close the dialog.

Close **Patterns_internstd.std** and click the **Yes** button when asked if you want to save the document as part of the project.

When the calculation is complete, examine the results, starting with the study table document. The results show that the weight fractions for Acetohexamide_FormA and Acetohexamide_FormB are approximately **39.5%** and **48.1%**, respectively.

Note: Absolute weight fractions may be obtained using the internal standard method, even in cases where not all the pure phases are known or included in the analysis.

For the internal standard QPA method, the reported weight fractions are not normalized to 100% over all phases for which the cell formula information was provided.

For the standardless QPA method, the reported weight fractions are normalized to 100% over all the phases for which the cell formula information was provided. Since these weight fractions cannot take account of any phases for which the cell formula was not supplied, they would not represent the actual absolute weight fraction in the mixture. However, the ratio of the weight fraction of two component phases will still be the same as would be observed in the whole mixture.

In this tutorial, the sum of the total weight fraction is 87.6%.

The underestimation might be due to:

- missing pure component phases
- errors associated with the scaling factors
- preferred orientation
- treatment of background
- micro absorption effects
- crystallinity of the internal standard

A missing component phase is not likely to be the reason in this case, since the integrated residual intensity is only 0.9% (see below). Phases with a higher linear absorption coefficient may display microabsorption effects, which invariably yield an underestimate of the phase weight.

The individual calculated scale factors will strongly depend on the 2θ range used during the QPA analysis. There is no rule of thumb on how to select the 2θ range. The single peak method is widely used in the industry. However, preferred orientation is the major source of variation for this method. In this tutorial, the full powder diffraction pattern corundum was used for the estimation of the scaling factors. Therefore preferred orientation is somewhat compensated.

Higher order polynomials are usually used to model background. However, the extent of the correction is hard to control. A larger number allows a more accurate background fit. However, if the number chosen is too large, the background function may try to model individual peak shapes, which is undesirable. Furthermore, the correlations between the background polynomial coefficients and other parameters are largely unknown, although the polynomial coefficients have been shown to affect displacement parameters.

Now examine the text output.

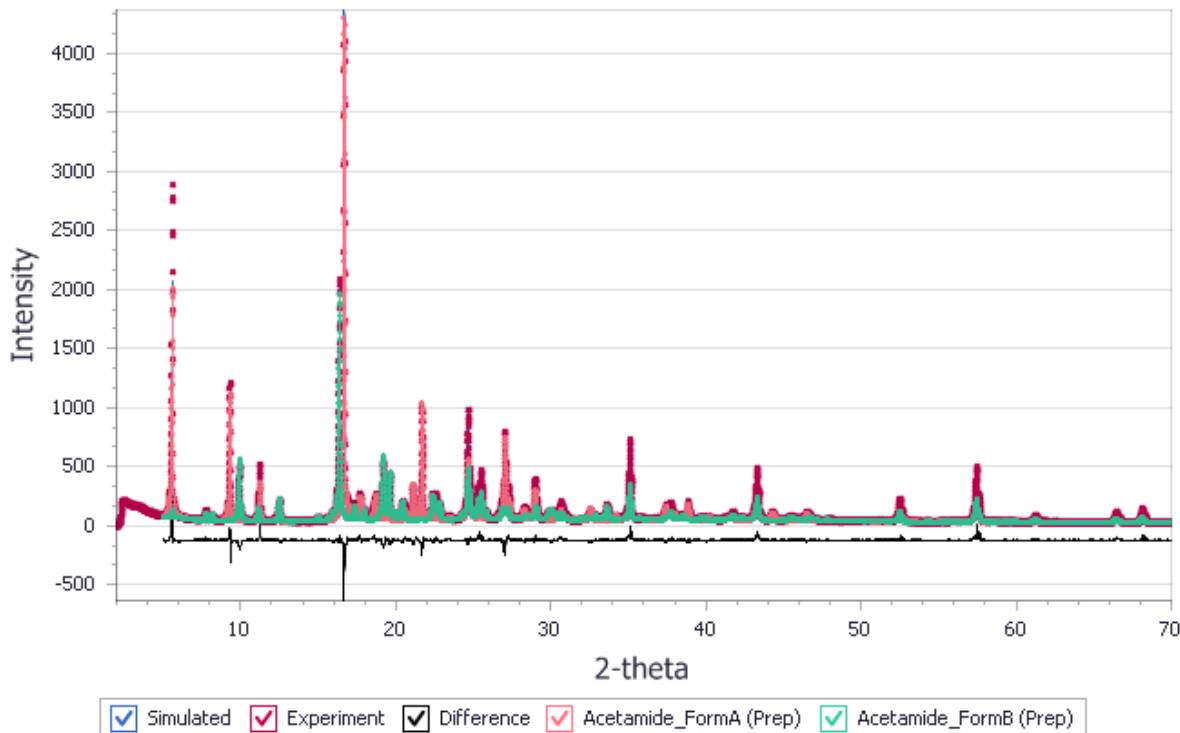
In the Project Explorer, double-click on the text document **internal standard Reflex QPA Job\internal standard.txt**.

The R_{wp} value is about **9.6%**. The integrated residual intensity is **0.9%**, which indicates that a majority of the intensity in the mixture has been accounted for within the two component phases.

In the Project Explorer, double-click on the chart document **internal standard Reflex QPA Job\internal standard.xcd** to examine its content.

The overall intensity distribution of the experimental powder diffraction pattern is well reproduced, although some regions show intensity differences as indicated in the difference plot in the chart document below.

Rwp= 9.62% Rwp(w/o bck)=14.04% Rp=7.12%



Comparison between the simulated powder pattern obtained by QPA and the experimental powder pattern of the mixture phase

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank G. Stephenson, G. Clanton, and B.A. Diseroad from Eli Lilly for supplying the experimental data.

Chapter 22: Reflex Plus tutorials

The following tutorials illustrate how to utilize Powder Solve's capabilities.

- [Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus](#)
- [Structure solution in the presence of preferred orientation and energetic considerations in structure refinement](#)
- [Structure solution of the inorganic compound FIN31](#)
- [Structure solution of 4-nitrophenylhexylurethane using a close-contacts penalty](#)

Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus

Purpose: Introduces the Powder Solve tool and illustrates how to use it to solve crystal structures from experimental powder diffraction data.

Modules: Materials Visualizer, Reflex Plus, Forcite

Time:  

Prerequisites: [Indexing powder patterns](#)

Background

Reflex Plus in Materials Studio is a module for determining a crystal structure from powder diffraction data. Structure determination using Reflex Plus is a four-step process. The steps are indexing, Pawley fitting, structure solution, and Rietveld refinement.

In the first step, you derive the crystal class and approximate lattice parameters from the peak positions in the powder diffraction pattern, using either TREOR90 ([Werner et al., 1985](#)), DICVOL91 ([Boultif and Louér, 1991](#)), ITO15 ([Visser, 1969](#)), or X-Cell ([Neumann, 2003](#)).

Next, you use Pawley fitting to determine accurate lattice constants and various parameters related to the experimental setup and the texture of the sample. The refined parameters include the zero point shift of the diffractogram, background parameters, and profile parameters. At this stage, you treat all peak intensities as independent parameters, not related to the unit cell contents. You can use the peak intensities obtained by the Pawley refinement to automatically determine the most likely space groups in the given crystal system ([Markvardsen et al., 2000](#)).

In the third step, Powder Solve ([Engel et al., 1999](#)) determines the atomic arrangement in the asymmetric unit. You calculate powder diffraction patterns for a large number of trial structures and compare them to the experimental powder pattern. You generate the trial structures using a Monte Carlo with simulated annealing algorithm or a Monte Carlo with parallel tempering algorithm.

Both approaches can locate the global minimum of the weighted R-factor, R_{wp} , which is a measure of the similarity between the experimental powder data and the simulated powder patterns. Lattice symmetry is explicitly taken into account. You gather all the atoms in the asymmetric unit together into motion groups. Each motion group is described by three translational and three rotational degrees of freedom, as well as a certain number of torsional, angular, and distance parameters.

Typically, each molecular fragment in the asymmetric unit corresponds to a motion group. Apart from the specified torsional, angular, and distance degrees of freedom. You must determine the conformation of each motion group before structure solution using potential energy calculations or structural information from related crystal structures. The Monte Carlo search only considers the specified translational, rotational, torsional, angular, and distance degrees of freedom of the motion groups. You attempt the structure solution separately for all relevant space groups.

Finally, you can further improve the result of the structure solution step using a Rietveld refinement.

Introduction

This tutorial shows how to use the Powder Solve tool to solve a crystal structure from powder diffraction data, in Materials Studio. You index a powder pattern, perform a Pawley refinement, select a space group, supply a molecular model, solve the crystal structure, and perform a final Rietveld refinement.

In this tutorial, use the experimental powder diffraction data provided to solve the crystal structure of 3-chloro-trans-cinnamic acid (CTCA). Run the structure solution stage three times allows you to see the effect of using different degrees of freedom.

This tutorial covers:

- [Getting started](#)
- [To index the diffraction pattern](#)
- [To carry out Pawley refinement and select the space group](#)
- [To sketch and optimize the molecule](#)
- [To solve the crystal structure using torsional degrees of freedom](#)
- [To solve the crystal structure using torsional and angular degrees of freedom](#)
- [To solve the crystal structure using torsional, angular, and distance degrees of freedom](#)
- [Rietveld refinement](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **structure_solution** as the project name, click **OK**.

This creates a new project with **structure_solution** listed in the Project Explorer. Now import the input file to study.

Click **Import**  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click **3-Chloro-trans-cinnamic_acid.3cam**.

In the Project Explorer, right-click **3-Chloro-trans-cinnamic_acid.xcd** and select **Rename** from the shortcut menu. Change the filename to **CTCA**, automatically appending the file **.xcd** extension.

2. To index the diffraction pattern

Next, identify the peaks to use to index the pattern. To facilitate the automatic peak search, you must first subtract the background and smooth the powder diffraction pattern. You can do this as part of the peak picking process.

Choose **Modules | Reflex | Powder Indexing** from the menu bar to open the Reflex Powder Indexing dialog. On the **Peaks** tab, change the **Low amplitude cutoff** to **1**. Select the **Eliminate background during search** and **Smooth** checkboxes, and for the **Width** specify **0.05**. Click **Search**.

For indexing, it is very important to select all diffraction peaks in the low angle region of the diffraction pattern and to avoid picking features that do not correspond to diffraction peaks. Therefore, always inspect the results of the automatic peak search, visually.

Use the **Zoom**  and **Translation**  tools to examine the powder diffraction pattern in the range **4°** to **20°**.

Reflex Plus: Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus

See the Chart mouse and keyboard actions topic for more information about how to manipulate charts.

If you need to make changes, you can add and move peaks using the *Chart Viewer Marker Mode*  . However, in this case, no changes are required.

Now you can index the powder diffraction pattern.

Select the **Setup** tab on the Reflex Powder Indexing dialog. From the **Program** dropdown list, select **TREOR90**, and select all the **Crystal systems to test** checkboxes.

The diffraction pattern was measured using copper radiation so you do not have to change the default wavelength in this case.

Click **Index**.

After TREOR90 has finished, a Study Table document opens, containing the results of the indexing procedure. Examine the results. The figure of merit (FOM) measures the quality of the proposed unit cell.

In the case of CTCA, the correct unit cell belongs to the monoclinic crystal system and has a volume of about 856 \AA^3 , with $a \approx 14.0 \text{ \AA}$, $b \approx 5.0 \text{ \AA}$, $c \approx 12.4 \text{ \AA}$, and $\beta \approx 94^\circ$.

Using the result from TREOR90, it is possible to generate a 3D structure for the empty unit cell.

Make the new Study Table the active document. On the **Reflex Powder Indexing** dialog, click **Create Cell**.

This creates a new 3D Atomistic document called **CTCA1.xsd**, containing an empty unit cell matching the solution from the powder indexing run.

In the Project Explorer, rename **CTCA1.xsd** to **CTCA**.

Move the file to the top level of the project by dragging it onto the **structure_solution** item at the top of the project tree.

3. To carry out Pawley refinement and select the space group

Pawley refinement treats all peak intensities as variable parameters and adjusts them together with background parameters, profile parameters, cell parameters, and the zero point shift of the diffraction pattern to obtain the best possible agreement between a simulated and the experimental diffraction pattern.

Pawley refinement can verify the correctness of the unit cell. In general, an incorrect unit cell results in significant differences between the simulated and the experimental powder patterns. The space group associated with the unit cell has no systematic absences at this point and by default, the lattice symmetry of a monoclinic unit cell is P2.

The fitting algorithm is stable enough to refine all parameters simultaneously.

Select the **Space Groups** tab on the **Reflex Powder Indexing** dialog and click **Refine...** to open the Reflex Powder Refinement dialog.

On the **Setup** tab, click **More...** for **Convergence quality** to open the Refinement Convergence Options dialog. Change the **Number of cycles** from 2 to 5 and click **OK**.

Changing the *Number of cycles* automatically changes the *Convergence quality* setting from *Medium* to *Customized*.

The experimental data were measured with copper λ_1 radiation only.

On the **Radiation** tab, clear selection of the λ_2 checkbox.

On the **Pattern** tab, select the **Pseudo-Voigt** function from the **Peak profiles** dropdown list. Switch on the refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB**, and the **Zero point Line shift**.

Change the **Asymmetry Correction** from **None** to **Berar-Baldinozzi** and enable the refinement of the parameters **P1**, **P2**, **P3**, and **P4**. The refinement of 20 background coefficients is switched on by default.

Make sure that the 3D Atomistic document containing the empty unit cell is active and on the **Lattice** tab, switch on the refinement of all the cell parameters.

Select the **Display** tab and select **Display simulation/experiment difference**.

On the **Exp. Data** tab, select **Pattern 1** from the chart document **CTCA.xcd**.

Click **Refine**.

Note: By default, Pawley or Rietveld refinement jobs run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows you to run all refinement jobs on a remote computer server by switching off **Run synchronously** from the **Job Control** tab.

While the Pawley refinement runs, the bottom of the Materials Visualizer window displays the cycle number and the current R_{wp} value. After five cycles, the R_{wp} value is about 7.0%. After the calculation completes, this displays a new chart document.

Compare the simulated and the experimental powder patterns.

A good agreement between the calculated and the experimental powder pattern confirms that the unit cell is correct.

The top of the chart document displays the final R_{wp} value. $R_{wp}(\text{w/o bck})$ is the weighted Rietveld parameter calculated after subtraction of the background.

Now identify the space group to which the crystal structure is likely to belong. Reflex provides functionality to estimate the likelihood of all space groups in a given crystal system, based on the intensities obtained by Pawley refinement.

Ensure that **CTCA.xsd** is the active document and click **Search** on the **Space Groups** tab of the Reflex Powder Indexing dialog.

This generates a study table document, which ranks all monoclinic space groups according to their figure of merit. The space group with the highest figure of merit is P 21/c, the monoclinic space group most frequently observed in nature. Now generate a 3D Atomistic document containing the unit cell with the correct space group settings.

Select the first row of the study table document **CTCA.std**. Click **Create Cell** on the Reflex Powder Indexing dialog.

This creates a new 3D Atomistic document, **CTCA1.xsd**. Using this document, now repeat the Pawley refinement in the chosen space group.

Click **Refine** on the Reflex Powder Refinement dialog.

Once again, the simulated and the experimental powder diffraction pattern show excellent agreement, with a R_{wp} value of about 7%.

Each new Pawley refinement modifies the parameters describing the diffraction profile. Sometimes, it is helpful to save the current group of parameters for later use.

Click the **Reflex** arrow  on the **Modules** toolbar and select **Save Settings...** from the dropdown list to open the **Save Reflex Settings** dialog. Enter **CTCA** and click **OK**.

This creates a settings document called **CTCA - Powder Diffraction** and places it in the current project. By double-clicking this file in the Project Explorer, you can load the corresponding parameters.

Before you go on to the next section of this tutorial, save the results obtained so far.

Close the Reflex Powder Indexing and Reflex Powder Refinement dialogs. Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

4. To sketch and optimize the molecule

You now have to create a structure for the molecule that you want to use in the structure solution step.

In the **Project Explorer**, right-click **structure_solution** and choose **New | 3D Atomistic Document** from the shortcut menu. Change the filename of the new 3D atomistic document to **molecule**, this automatically appends the **.xsd** file extension.

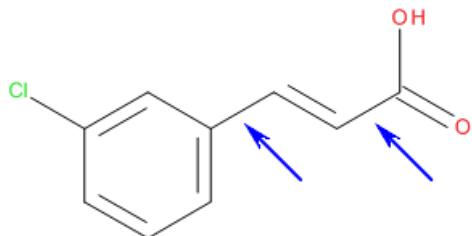
Use the **Sketch** tools to sketch a molecule of CTCA, adjust the hydrogens, and clean the geometry.

See 3D Sketcher for more information about sketching.

To make things easier later on, move the molecule so that its center of geometry automatically falls inside the unit cell placing it in the crystal.

Double-click any atom in the molecule to select all the atoms. Click **Create Centroid** on the **Sketch** toolbar to create a centroid defined by the average position of the atoms. Select **View | Explorers | Properties Explorer** from the menu bar to display the Properties Explorer. Select **Centroid** from the **Filter** dropdown list. Double-click the **CentroidXYZ** property. Enter **1** for each of **X**, **Y**, and **Z** and click **OK**. The molecule moves to be centered on position **1,1,1**.

The figure below shows the molecular structure of CTCA with two specific flexible torsion angles marked.



Molecular structure of CTCA showing flexible torsion angles

Structure solution by Monte Carlo methods or simulated annealing requires that you determine the molecular geometry, apart from the flexible torsion angles, before the structure solution step. Now optimize the molecular geometry using the COMPASS forcefield in Forcite.

Click the **Forcite** arrow on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the Forcite Calculation dialog.

On the **Setup** tab, select **Geometry Optimization** from the **Task** dropdown list and on the **Energy** tab for the **Forcefield** choose **COMPASSIII**.

Click **Run**.

This places the results of the calculation in the new folder, **molecule Forcite GeomOpt**.

Close the Forcite Calculation dialog and the text document **molecule Forcite GeomOpt\molecule.txt**.

molecule Forcite GeomOpt\molecule.xsd is now the active document. This 3D atomistic document contains the optimized molecular geometry. The O-H bond of the hydroxyl group is roughly parallel to the closest C-C bond. Depending on the starting point for the geometry optimization, this may not be the case. The orientation of the hydrogen atom is not important for the structure solution step because X-ray scattering from hydrogen atoms is weak. However, since a non-parallel configuration is rather unlikely, make sure that the O-H bond adopts a parallel conformation.

Click the **Measure/Change** arrow and select **Torsion** from the dropdown list. Click the C-O bond next to the O-H bond to create a torsion monitor.

In the **Properties Explorer**, select **Torsion** from the **Filter** dropdown list. Double-click the value for **Angle** to open the Edit Angle dialog. Enter **180°** or **0°**, depending on which value is appropriate, and click **OK**.

Click **Selection** . Select the **torsion monitor** in the 3D viewer and press **DELETE**.

Close the **Properties Explorer**.

Prepare the molecule by marking the two flexible torsions as shown on the diagram [above](#).

Click the **Measure/Change** arrow . Click each of the two flexible C-C bonds, as indicated in the diagram above to create two new torsion monitors.

Click Selection 

5. To solve the crystal structure using torsional degrees of freedom

You first have to introduce the CTCA molecule into the empty unit cell and select the degrees of freedom to vary during the structure solution search.

Click in the 3D Viewer for **molecule Forcite GeomOpt/molecule.xsd** and press **CTRL + C**.

In the **Project Explorer**, double-click **CTCA1.xsd** to open the 3D Viewer containing the empty unit cell. Press **CTRL + V** to paste the molecule into the unit cell.

Application of the space group symmetry generates four copies of the molecule in the unit cell. The molecule already contains the torsion definitions, but you need to define each molecule as a motion group. A motion group is a group of atoms described by the same translational and rotational degrees of freedom in the structure solution search.

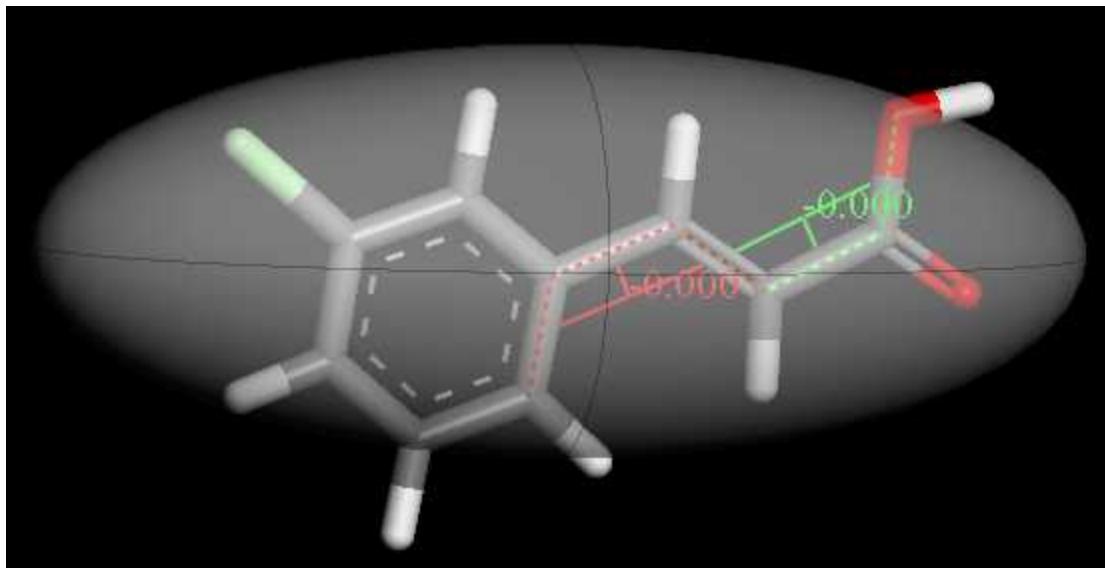
Select **Modules | Reflex | Powder Solve** from the menu bar to open the Reflex Powder Solve dialog.

In the 3D Viewer for **CTCA1.xsd**, select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu, to select one complete molecule.

In the **Reflex Powder Solve** dialog, select the **Structure Params** tab and click **Create motion group(s)**, ensuring that the **selection** type is **Single group**.

Click anywhere in the 3D Viewer to clear selection of everything.

After you have defined the motion groups, the molecule looks like the one shown below, although the torsion angles might be slightly different.



CTCA molecule defined as a motion group with two torsional degrees of freedom.

The **Structure Params** tab summarizes all degrees of freedom.

Ensure selection of all the refinement checkboxes on the **Structure Params** tab.

The amount of CPU time per Monte Carlo step is approximately proportional to the number of atoms, and X-ray scattering from hydrogen atoms is fairly weak compared to other elements. Ignoring scattering from hydrogen atoms increases the speed of the calculation significantly. However, neglecting the weak contribution of scattering from hydrogen atoms to the total scattering intensity introduces a small additional error that can make structure solution more difficult. There is no clear rule whether or not to take into account scattering from hydrogen atoms. In this tutorial, the structure solution step neglects scattering from hydrogen atoms, but does include this in the final refinement step.

Clear selection of the **Use hydrogens** checkbox.

You selected the experimental powder diffraction pattern in the Pawley refinement step. However, sometimes you might want to verify that you are using the right data set.

On the **Experimental Data** tab, make sure that **Pattern 1** of the chart document **CTCA . xcd** is selected as the experimental powder diffraction data.

Several parameters govern the Monte Carlo and simulated annealing procedure in Powder Solve, these include the start temperature, the final temperature, the step width, and the number of Monte Carlo steps. By default, all of these parameters are estimated automatically from the number of degrees of freedom and the roughness of the R_{wp} hypersurface. Because of the stochastic nature of the Monte Carlo and simulated annealing approach, there is no guarantee that the structure solution is found in a single Monte Carlo simulated annealing cycle. Therefore, repeat the Monte Carlo and simulated annealing procedure several times.

On the **Setup** tab, select **Simulated Annealing** from the **Method** dropdown list in the **Solve** section and for the **Number of cycles** specify **10**.

Usually Reflex automatically calculates the number of steps depending on the number of degrees of freedom. In this tutorial, to achieve speedy results, use a fixed number of steps.

Make sure that the 3D Viewer for **CTCA1.xsd** is active. Examine the number of steps proposed by the automatic calculation.

Clear selection of the **Automatic** checkbox and for the **Number of steps** specify **100000**.

Click **More...** for the **Method** on the **Setup** tab to open the Powder Solve Options dialog.

This automatically determines the highest temperature, the lowest temperature, and the step width. The values of these parameters are not yet indicated, since they are calculated at the beginning of the Monte Carlo and simulated annealing run.

Close the **Powder Solve Options** dialog.

Powder Solve makes use of the client-server architecture implemented in Materials Studio. If your PC is connected to other computers on a network, you can configure gateways on other computers and run the calculation remotely. This avoids using the resources of your own PC. Your own PC is probably configured as a server, and the gateway "My Computer" is used by default.

By default, the calculation writes the current structure to a trajectory file each time it obtains a new, best R_{wp} value in the current cycle. At the end of the calculation, you can extract the best solutions found in each cycle from the trajectory file.

You are now ready to start Powder Solve.

Ensure that the 3D Viewer for **CTCA1.xsd** is active. Click **Solve**.

The Job Explorer informs you about the progress of the calculation. After some time, this displays two chart windows. While the calculation is running, you might want to rearrange the open documents and close some of them.

Select **File | Save Project** from the menu bar.

Close all documents, other than those starting with **CTCA1 Reflex PSolve....**

Examine the output in the two chart windows.

After the calculation has finished, the 3D Atomistic document **CTCA1 Reflex PSolve\CTCA1 Solution .xsd** displays the best crystal structure found.

The best crystal structure obtained at the end of several Monte Carlo simulated annealing cycles is not necessarily the right structure solution. The true crystal structure may have been missed because an insufficient number of cycles were performed or because the search did not use the right space group. The structure solution can also fail because the bond lengths and bond angles in the structure were not determined accurately enough before the structure solution step. To decide whether or not the crystal structure has been solved, carefully examine the best proposed crystal structure.

To start, compare the calculated and the experimental powder patterns.

In the **Project Explorer**, double-click the chart document **CTCA1 Reflex PSolve\CTCA1 Solution.xcd**. Compare the calculated and experimental diffraction patterns visually.

The overall intensity distribution of the simulated and the experimental powder patterns look very similar, even though there are significant differences for some of the diffraction peaks. The R_{wp} value falls around 19%, approximately 2.5 times larger than the value obtained by the Pawley refinement. The

exact R_{wp} value of the best crystal structure depends to a certain extent on the molecular conformation used in the forcefield optimization.

Since all peak intensities are independent parameters in the Pawley refinement, the R_{wp} value resulting from it is a lower limit for the R_{wp} value obtained for the structure solution. So, although a difference of 2.5 times between these values after structure solution is quite large, it is not uncommon. Visual inspection of the calculated and the observed diffraction pattern indicates that the crystal structure has been solved.

Another criterion that you can use to assess the success of a structure solution is the number of cycles required to find the best solution. If the calculation obtains the best solution several times and the corresponding R_{wp} value is significantly lower than the best R_{wp} value observed in the other cycles, you can assume that this is the global minimum on the R_{wp} -hypersurface. However, if the best solution has been found only once and several other cycles result in different crystal structures with similar R_{wp} values, it is likely that the R_{wp} -hypersurface has not been sampled correctly. In these circumstances, repeat the calculation with a higher number of Monte Carlo steps per cycle and a higher number of cycles.

In the **Project Explorer**, double-click the text document **CTCA1 Reflex PSolve\CTCA1.txt** and examine its contents.

This finds the solution with the lowest R_{wp} value in several cycles. Differences of about 0.1% are negligible. Therefore you can assume that the global optimum has been found.

Finally, examine the crystal structure that corresponds to the best solution, concentrating on atomic overlap and the hydrogen bonding scheme.

In the **Project Explorer**, double-click the 3D Atomistic document **CTCA1 Reflex PSolve\CTCA1 Solution.xsd**.

Click the **Calculate Hydrogen Bonds** arrow  and select **Hydrogen Bond Options** from the dropdown list to open the Hydrogen Bond Calculation dialog. Select **N, O, S + Halogens + C as Donor** as the H-bonding scheme and click **Calculate**. Close the dialog.

Examine the crystal structure.

To increase the lattice display range for a better appreciation of the hydrogen bonding network, choose **Display Style** from the 3D Viewer shortcut menu to open the Display Style dialog.

Increase the lattice display range in the a, b, and c directions on the **Lattice** tab.

Visual inspection does not reveal any significant atomic overlap. The CTCA molecules pack together forming hydrogen bonded dimers. The crystal structure looks very plausible and it is appropriate to conclude that this is the crystal structure solution.

You can also examine other structures generated during the structure search.

In the **Project Explorer**, double-click the trajectory document **CTCA1 Reflex PSolve\CTCA1.xtd**.

Open the **Reflex Powder Solve** dialog and select the **Analysis** tab. Click **Analyze** and close the dialog.

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This generates a chart showing the R_{wp} values of the crystal structures in the trajectory file. Each new cycle starts with a high R_{wp} value that decreases monotonically throughout the cycle.

Ensure that the chart with the R_{wp} values and the trajectory document **CTCA1 Reflex PSolve\CTCA1.xtd** are both visible in the workspace.

Choose the **Selection**  tool from the Chart Viewer toolbar. Click data points in the chart document to show the corresponding crystal structures in the trajectory document.

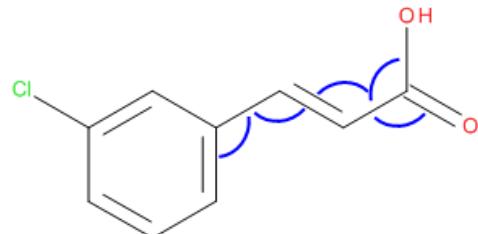
Before finishing this section, save the results obtained so far.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

6. To solve the crystal structure using torsional and angular degrees of freedom

In this section, perform a second Powder Solve calculation, this time allowing flexibility in significant angles in the structure. Powder Solve treats angular and distance degrees of freedom slightly differently from torsional degrees of freedom. Torsional degrees of freedom can vary through the complete 360° range, so the initial value is not important. Angular and distance degrees of freedom can each vary by only a small amount relative to their initial value. So it is important that the initial configuration has these values reasonably optimized. By default, angles can vary by up to 10° from their initial values and distances can vary by up to 10% of their initial values. These defaults are generally satisfactory although you should verify the solution to see if any distances or angles are at the extreme ends of their permitted ranges.

You now have to prepare the molecule with the required angles marked as well as the torsions. These angles are those shown in the figure below.



Molecular structure of CTCA showing angles for variation

Open the document **molecule Forcite GeomOpt\molecule.xsd**.

Click the **Measure/Change** arrow  and select **Angle** from the dropdown list. Create an angle monitor for each of the five angles shown above, in addition to the torsions that are present from the previous stage.

Click **Selection** .

Create a new crystal structure containing the modified molecule as the basis for the new Powder Solve calculation.

In the **Project Explorer**, double-click **CTCA.std** to open the study table showing all the monoclinic space groups.

Select the first row of the study table document. Open the **Reflex Powder Indexing** dialog and click **Create Cell**.

This creates a new 3D Atomistic document called **CTCA1 (2).xsd**. Rename this and then paste in the prepared molecule.

Rename **CTCA1 (2).xsd** to **CTCA2**, this automatically appends the **.xsd** file extension.

Click in the 3D Viewer for **molecule Forcite GeomOpt/molecule.xsd** and press **CTRL + C**.

In the 3D Viewer for **CTCA2.xsd** press **CTRL + V** to paste the molecule into the unit cell.

Repeat the procedures used in [section 5](#) to define the motion groups and to ensure that selection of all the refinement checkboxes on the **Structure Params** tab.

This shows that there are 13 degrees of freedom defined and that all of them can be refined. You are now ready to run Powder Solve again.

Click **Solve**.

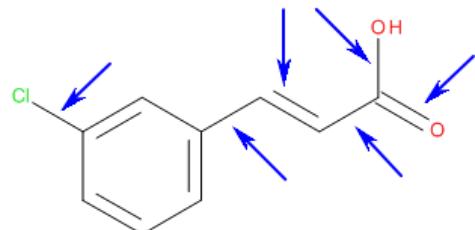
When the job has completed, select **File | Save Project** from the menu bar.

When the job has finished, you can compare the results with those obtained previously where the torsions were the only degrees of freedom within the motion groups. As expected, because there are more degrees of freedom you obtain a better fit to the experimental data. The R_{wp} value obtained from this run is about 16.8%. However, because no account was taken of possible close contacts or energetic considerations, assess for yourself (such as by investigating close contacts or hydrogen bonding patterns) whether the solution presented is viable.

7. To solve the crystal structure using torsional, angular, and distance degrees of freedom

As well as varying angles, you can vary bond distances in a motion group. Although if the original molecular structure is well optimized, you can expect little improvement.

Prepare the molecule with the required distances marked as well as the torsions and angles. The required distances are those shown in the figure below.



Molecular structure of CTCA showing distances for variation

Open the document **molecule** **Forcite GeomOpt\molecule.xsd**.

Click the **Measure/Change** arrow  and select **Distance** from the dropdown list. Create a distance monitor for each of the six distances shown above, in addition to the torsions and angle monitors from the previous stages.

Click **Selection** .

Follow the remainder of the steps in [section 6](#). Rename the new 3D Atomistic document to **CTCA3.xsd**.

You can see that there are now 19 refinable degrees of freedom. This number of degrees of freedom requires more steps in the Powder Solve process, but the current value suffices for this tutorial. However when the job completes you might notice that the best solution has been found in fewer cycles than with only torsion refinement, showing less confidence that the solution found corresponds to the global minimum. In this case, the best solution is about 16.3%, a slight improvement on that with only torsion and angle refinements. As before, assess for yourself whether this solution is viable.

Before finishing this section, close some windows.

Select **File | Save Project** from the menu bar and close all dialogs.

Close all windows apart from **CTCA3 Reflex PSolve\CTCA3 Solution.xsd** and **CTCA.xcd**.

8. Rietveld refinement

Rietveld refinement optimizes various parameters simultaneously to improve the agreement between the calculated and the experimental powder diffraction pattern. Start by refining profile parameters, background parameters, the cell constants, the zero point shift of the diffraction pattern, the position, and orientation of motion groups and torsion angles.

Prepare a new 3D Atomistic document for Rietveld refinement.

In the Project Explorer select **CTCA3 Reflex PSolve\CTCA3 Solution.xsd** and right-click, select **Copy** from the shortcut menu.

In the **Project Explorer**, right-click **structure_solution** and choose **Paste** from the shortcut menu. Rename the new copied document to **CTCA_Rietveld**.

Select **File | Save Project** from menu bar.

Now prepare the Rietveld refinement.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, change the **Type** of refinement from Pawley to Rietveld.

Examine the various tabs on the **Reflex Powder Refinement** dialog. By default, all parameters varied earlier on in the Pawley refinement and the structure solution search remain selected for refinement.

On the **Structure** tab, select the **Use hydrogens** checkbox.

Ensure that the 3D Atomistic document **CTCA_Rietveld.xsd** is active. On the **Lattice** tab, switch on the refinement of all the cell parameters and select the **Keep fractional coordinates fixed during lattice changes** checkbox.

Click **Refine**.

The Rietveld refinement decreases the R_{wp} value by about 2% - 3%. You can improve the R_{wp} value further by increasing the number of refined parameters. However, the crystal structure determination of CTCA is effectively complete.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

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Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

Purpose: Illustrates how the March-Dollase correction implemented in Reflex Plus enables you to solve structures using data with strong preferred orientation. Demonstrates how the incorporation of energy information into an all-atom Rietveld refinement process allows for structure solutions to be both chemically viable and in close agreement with the experimental diffraction pattern.

Modules: Materials Visualizer, Reflex Plus

Time: 

Prerequisites: [Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus](#)

Background

The structure solution process generates huge numbers of trial structures and compares their simulated powder patterns to experimental data. Calculation of a powder diffraction pattern for a trial structure requires the distribution function describing the orientation of crystallites in the powder. In general, a random orientation of the powder particles and an isotropic distribution function are assumed. However, significant deviations from this assumption can occur, especially if the compound under investigation forms plate- or needle-like crystals. Needles and plates tend to align themselves with respect to the sample holder, resulting in a loss of isotropy.

If the orientation of powder particles is not completely random, you need to determine the distribution function and the crystal structure simultaneously. In Rietveld refinement, this approach is quite common and it has been observed that relatively simple preferred orientation corrections frequently describe deviations from isotropy fairly well. The Reflex module implements two of these corrections, March-Dollase ([Dollase, 1986](#)) and Rietveld-Toraya ([Rietveld, 1969](#) and [Toraya and Marumo, 1981](#)). If the preferred orientation is weak, you can solve the crystal structures by assuming an isotropic distribution, and add the preferred orientation correction in a subsequent Rietveld refinement. In the presence of strong preferred orientation, you must determine the preferred orientation correction during the structure solution phase.

The ability to determine the preferred orientation correction during the structure solution phase is a unique feature of Reflex Plus. The preferred orientation corrections add 3 or 4 parameters to the total number of degrees of freedom during the structure solution phase. The use of a preferred orientation correction increases the complexity of the search problem significantly.

Therefore, only apply such a correction if there is a reason to expect preferred orientation, such as microscope images showing plate or needle-like crystals. If possible, it is generally preferable to reduce the effect of preferred orientation experimentally, for example by using a spinning capillary for the experimental measurement.

Both available corrections assume that the correction factor for integrated peak intensities only depends on the angle between the preferred orientation direction and the reciprocal lattice vector corresponding to a given reflection. This assumption is valid for rod or disk shaped crystals that have axial symmetry in combination with cylindrical sample symmetry. While the second condition can always be enforced by spinning the sample, strong deviations of the average particle shape from axial symmetry can occur. This can lead to particle distributions that are not well described by the March-

Reflex Plus: Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

Dollase or the Rietveld-Toraya correction. Despite the Rietveld-Toraya correction offering a higher number of adjustable parameters, the March-Dollase correction is considered more accurate. This is because the functional form of the March-Dollase correction, unlike the functional form of the Rietveld-Toraya correction, is based on physically reasonable assumptions. For structure solution, use the March-Dollase correction.

Occasionally, the available powder diffraction data do not contain enough information for a successful Rietveld refinement. For example, systems with a large number of degrees of freedom as occurring in all-atom refinements and for refinements using low quality powder data. In these instances, Rietveld refinements typically lead to chemically unviable structures because the information content of the powder pattern is too low to accurately determine all degrees of freedom.

To overcome this problem, Reflex allows you to incorporate an accurate description of potential energy with the R_{wp} in the Rietveld refinement process optimizing a combined figure of merit. The aim is to find solutions that optimally meet two different and possibly conflicting objectives:

- The simulated pattern has to match the experimental diffraction data
- The potential energy of the structure has to be close to the minimum

A priori elucidation of the energy weight factor determining the relative importance of the energy contribution might not be intuitive. In such cases, you can use a Pareto optimization (*a posteriori* preference calculation) to obtain an appropriate value.

Introduction

This tutorial solves the crystal structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide using the March-Dollase correction. The preferred orientation present in the sample is rather strong, with certain intensity ratios modified by about a factor of 50.

This tutorial covers:

- [Getting started](#)
- [To build an empty unit cell and specify the space group](#)
- [Pawley fitting](#)
- [To sketch and optimize a molecule](#)
- [To attempt structure solution without preferred orientation correction](#)
- [Structure solution with preferred orientation correction](#)
- [Rietveld refinement](#)
- [Rietveld refinement with energies and Pareto optimization](#)
- [To interpret preferred orientation parameters](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **preferred_orientation** as the project name, click **OK**.

This creates a new project with *preferred_orientation* listed in the Project Explorer. Now import the input file to study.

Reflex Plus: Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

Click **Import**  to open the Import Document dialog. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click **(E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.xcd**.

In the **Project Explorer**, right-click the imported document and select **Rename** from the shortcut menu. Change the filename to **data**, appending the file extension **.xcd** automatically.

2. To build an empty unit cell and specify the space group

The polymorph of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide studied here, crystallizes in space group **P 2₁/c** with **a = 14.26 Å**, **b = 5.11 Å**, **c = 15.06 Å** and **β = 116.9 °**. The diffraction pattern was recorded using a copper anode and the $K_{\alpha 2}$ emission line was not filtered out.

First, you have to create a new 3D Atomistic document.

In the **Project Explorer**, right-click **preferred_orientation** and select **New | 3D Atomistic Document** from the shortcut menu. Rename the new document **cell**.

Now build the unit cell.

Make sure that **cell.xsd** is active and choose **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog.

On the **Space Group** tab, change the space group from **P1** to **P21/c**.

On the **Lattice Parameters** tab, specify:

a as **14.26**

b as **5.11**

c as **15.06**

β as **116.9**

Click **Build**.

3. Pawley fitting

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Pattern** tab, select the checkboxes for the refinement of the profile parameters **U**, **V**, **W**, **NA**, and **NB** and the **Zero point** line shift. The refinement of 20 background coefficients is switched on by default.

Make sure that the 3D Atomistic document **cell.xsd** is active. On the **Lattice** tab, select the checkboxes for the refinement of all cell parameters.

On the **Display** tab, select the **Display simulation/experiment difference** checkbox.

Reflex Plus: Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

The CPU time required for structure solution is approximately proportional to the number of diffraction peaks. Therefore, limit the 2θ range used for structure solution and Pawley refinement to a subsection of the complete powder diffraction pattern.

On the **Setup** tab, select **Pawley** from the refinement **Type** dropdown list. Click **More...** for **Convergence quality** to open the Refinement Convergence Options dialog. For the **Number of cycles** specify **5** and click **OK**.

On the **Setup** tab, change the **Max. 2-Theta** value from **45** to **40 °**.

On the **Exp. Data** tab, select the **data.xcd** data set.

The powder pattern was recorded using a copper anode and a graphite (002) monochromator. The (002) reflection of graphite corresponds to a d-spacing of 3.4 Å.

On the **Radiation** tab, all default settings are appropriate except for the monochromator settings. In the **X-ray** section, select a **Single** monochromator and for **d_{hkl}** specify **3.4 Å**.

Click **Refine**.

After five cycles, the R_{wp} value is about 6.7%. Repeat the Pawley refinement until you obtain no further improvement in the R_{wp} value.

Ensure that **cell.xsd** is active and click **Refine**, close the Reflex Powder Refinement dialog.

You obtain a minimum value for R_{wp} of about 6.3%.

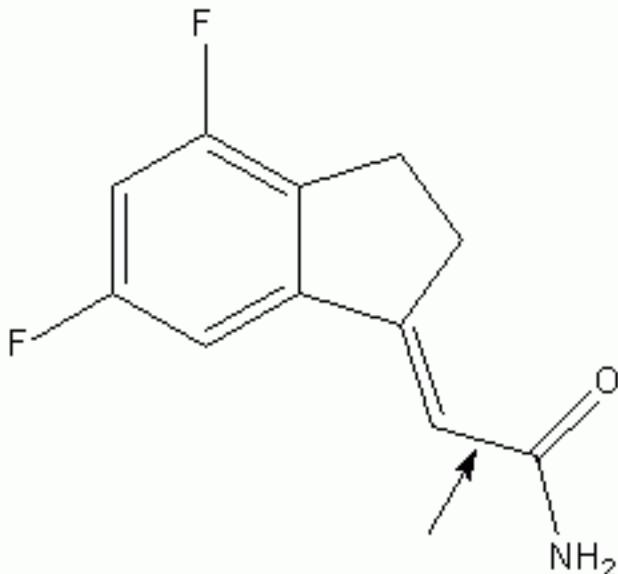
Note: By default, Pawley refinement or Rietveld refinement jobs run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to run on a remote computer server by switching off **Run Synchronously** from the **Job Control** tab.

4. To sketch and optimize a molecule

You now have to create a model of the molecule that you want to use in the structure solution step.

Create a new 3D Atomistic document in the **preferred_orientation** project and rename the file **Molecule**.

Use the tools available on the **Sketch** toolbar to sketch one molecule of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide (shown below). See 3D Sketcher for more information about how to sketch molecules. Remember to adjust the hydrogens and clean the structure.



Molecular structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.

Now optimize the molecular geometry using the COMPASS forcefield in Forcite.

Click the **Forcite** arrow and select **Calculation** from the dropdown list to open the Forcite Calculation dialog.

Change the **Task** from Energy to **Geometry Optimization** and the **Quality** to **Fine**.

On the **Energy** tab, change the **Forcefield** to **COMPASSIII** and ensure that **Forcefield assigned** is selected in the **Charges** dropdown list. Leave all the other settings unchanged.

Click **Run** and close the dialog.

This stores the results of the calculation in the folder, **molecule Forcite GeomOpt**.

Close the text document **Molecule Forcite GeomOpt\Molecule.txt**.

The 3D Atomistic document, **Molecule Forcite GeomOpt\Molecule.xsd**, is now active. This model contains the optimized molecular geometry.

5. To attempt structure solution without preferred orientation correction

In this section, try to solve the crystal structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide without using a preferred orientation correction. To begin with, you have to prepare a starting model for structure solution. Start by defining the torsional degrees of freedom. In this example, there is only one.

Reflex Plus: Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

Ensure that **Molecule Forcite GeomOpt****Molecule.xsd** is the active document.

Click the **Measure/Change** arrow  from the **Sketch** toolbar and select **Torsion** from the dropdown list.

Click the bond indicated by an arrow in the molecular structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide, above. A torsion monitor appears around the bond. Go back to selection mode by clicking **3D Viewer Selection Mode** .

In the next step, you define the whole molecule as a motion group. This means that, in addition to the torsional degree of freedom, a single group of translational and rotational parameters describe the position and orientation of all atoms in the molecule.

Select **Modules | Reflex | Powder Solve** from the menu bar to open the Reflex Powder Solve dialog.

In the 3D Viewer for **Molecule Forcite GeomOpt****Molecule.xsd**, double-click one of the atoms to select the entire molecule.

On the Reflex Powder Solve dialog, select the **Structure Params** tab and click **Create**.

Finally, copy the molecule into the unit cell.

Make sure that **Molecule Forcite GeomOpt****Molecule.xsd** is the active document. Choose **Edit | Copy** from the menu bar.

In the **Project Explorer**, double-click **cell.xsd** to make it the active document. Select **Edit | Paste** from the menu bar.

In this tutorial, you use parallel tempering as the global search algorithm. By default, the approximate number of Monte Carlo steps required for structure solution is estimated from the total number of degrees of freedom. To increase the chances of finding the global minimum, carry out several cycles. If more than one cycle obtains the same best solution, this is a strong indication that this is the global minimum.

On the **Setup** tab in the **Solve** section, select **Parallel Tempering** as the **Method**. Increase the **Number of cycles** from 2 to 5. Examine the proposed **Number of steps**.

Select the **Job Control** tab and examine its contents. Choose the **Gateway location** you want to use.

Switch off the automatic assignment of the **Job description** and enter **no PO correction** as the **Job description**.

All other settings remain correct, since you used them for the Pawley refinement.

Select **File | Save Project** from the menu bar. Close all of the open documents apart from **cell.xsd**.

Click **Solve** on the **Reflex Powder Solve** dialog.

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The Job Explorer informs you about the progress of the calculation. When the calculation is complete, this displays two chart documents. Depending on the specification of your computer, this may take several minutes.

When the calculation is complete, examine the results, starting with the text output.

In the **Project Explorer**, double-click the text document **no PO correction Reflex PSolve\no PO correction.txt** and examine its contents.

The lowest R_{wp} value is about 35.3% and was probably obtained in several cycles, indicating that the global minimum was found for the given choice of variables. Compared to the R_{wp} value of 6.3%, obtained during the Pawley refinement, the R_{wp} value of the best solution is very high and you can conclude that the structure is not yet solved.

Also compare the simulated and the experimental powder diffraction patterns.

In the **Project Explorer**, double-click the chart document **no PO correction Reflex PSolve\no PO correction Solution.xcd** to make it active.

The intensity distributions of the simulated and the experimental powder patterns are somewhat different, confirming that the crystal structure is not solved.

Finally, examine the crystal structure corresponding to the lowest R_{wp} value.

In the **Project Explorer**, double-click the 3D Atomistic document **no PO correction Reflex PSolve\no PO correction Solution.xsd** and examine it.

Right-click the structure and choose **Display Style** from the shortcut menu to open the Display Style dialog. Select the **Lattice** tab and for the **Max** values for **A**, **B**, and **C** specify **2.00**. Close the dialog.

Click **Calculate Close Contacts**  and then **Calculate Hydrogen Bonds**  on the **Atoms and Bonds** toolbar.

To make the crystal structure clearer, switch off the display of motion groups.

Press **ALT** and double-click a motion group. This selects all motion groups.

To switch off the display of the motion groups, select **Visibility | Hide** from the **View** menu. Press **CTRL + D** to clear the selection of the motion groups.

The molecules do not overlap but there are some fairly close contacts and a reasonable hydrogen bonding pattern cannot be found. Once again confirming that the crystal structure is not solved.

6. Structure solution with preferred orientation correction

There are several reasons why a structure solution may fail, such as searching in the wrong space group. If there are no experimental indicators for preferred orientation, trying a different space group would probably be the next step. In this case, however, microscopic examination of the sample revealed needle-like crystals. So it is appropriate to try structure solution in $P\bar{1}/c$ again, this time including a preferred orientation correction.

Reflex Plus: Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

Make sure that **cell.xsd** is the active document. Open the **Reflex Powder Solve** dialog.

On the **Job Control** tab, change the **Job description** to **MD PO correction**.

On the **Sample Params** tab, scroll down to **Preferred Orientation**. Change the **Applied** correction from **None** to **March-Dollase** and select the checkboxes for **a***, **b***, **c*** and **R0**.

Select the **Setup** tab and examine the proposed **Number of steps**.

Including the March-Dollase correction has increased the number of parameters from 7 to 10. The refinement of **a***, **b*** and **c*** (the components of the preferred orientation direction) adds only 2 parameters, since the length of this vector is meaningless. Because of the increased number of degrees of freedom, Powder Solve now suggests making 300,000 steps instead of 80,000.

All of the other settings, from the previous run, remain unchanged. You are now ready to start Powder Solve.

Select **File | Save Project** from the menu bar. Close all of the open documents apart from **cell.xsd**.

Click **Solve** on the Reflex Powder Solve dialog and close the dialog.

The Job Explorer informs you about the progress of the calculation. Depending on the specification of your computer, the calculation might take up to 1 hour.

When the calculation is complete, analyze the Powder Solve output.

In the **Project Explorer**, double-click the text document **MD PO correction Reflex PSolve\MD PO correction.txt** and examine its contents.

The lowest R_{wp} value is about 15.6%, probably obtained in several cycles. This indicates that the calculation located the global minimum for the given choice of variables. The best R_{wp} value obtained with the March-Dollase correction is significantly lower than the result obtained without a preferred orientation correction (35.3%). Therefore, it seems likely that the crystal structure is now solved.

Next, examine the comparison of the simulated and the experimental powder diffraction patterns.

In the **Project Explorer**, double-click the Chart Document **MD PO correction Reflex PSolve\MD PO correction Solution.xcd** and examine it.

Even though there are still some differences, this reproduces well the overall intensity distribution of the experimental powder diffraction pattern.

Finally, examine the crystal structure.

Reflex Plus: Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

In the **Project Explorer**, double-click the 3D Atomistic document **MD PO correction Reflex PSolve\MD PO correction Solution.xsd**.

Right-click the structure and choose **Display Style** from the shortcut menu. Select the **Lattice** tab and for the **Max** values for **A**, **B**, and **C** specify **2.00**.

Click **Calculate Close Contacts**  and then **Calculate Hydrogen Bonds** .

Switch off the display of motion groups.

There are no significant close contacts and a 1D hydrogen bonding scheme parallel to the b-axis is clearly recognizable. You can conclude that this solves the crystal structure.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

7. Rietveld refinement

This section describes how to perform Rietveld refinement of a limited number of parameters. Start by making a copy of the structure solution.

In the **Project Explorer**, double-click **MD PO correction Reflex PSolve\MD PO correction Solution.xsd** to make it active and select **Edit | Copy** from the menu bar.

Right-click the project name and choose **New | Folder** from the shortcut menu. Change the name of the new folder to **refinement**.

Right-click **refinement** and select **New | 3D Atomistic Document** from the shortcut menu. Change the filename of the new document to **refined structure**. Choose **Edit | Paste** from the menu bar and press **CTRL + D** to cancel selection of everything.

At the end of the structure solution procedure, this saves the preferred orientation parameters of the best solution in a parameter file. Now, you must restore these parameters.

In the **Project Explorer**, double-click **MD PO correction Reflex PSolve\MD PO correction - Powder Solve** to load the preferred orientation and other parameters used in the previous Powder Solve run.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, change the **Type** from Pawley to **Rietveld**.

Select the **Sample** tab and examine the preferred orientation parameters.

For the Rietveld refinement, this adds a global isotropic temperature factor and an additional flexible torsion to the parameters refined so far.

Open the **Display Style** dialog and reset the display range for **refined structure.xsd** so that only a single unit cell is visible.

Select the **Measure/Change** tool for torsions .

Choose one molecule in the 3D Viewer and click the double bond that links the acetamide fragment to the carbon ring system. A new torsion monitor appears.

Choose the **Selection** tool .

Select the **Structure** tab on the **Reflex Powder Refinement** dialog and ensure the selection of all the structural parameters for refinement.

On the **Sample** tab, scroll down to the **Temperature Factors** section and for **Applied** temperature factor choose **Global isotropic**. Select the checkbox to refine the **Global isotropic** temperature factor.

For Rietveld Refinement, use the full range of the powder diffraction pattern. In addition, you want the comparison between the calculated and the experimental patterns to be displayed in a new chart document.

On the **Setup** tab, click **More...** for **Convergence quality** to open the Refinement Convergence Options dialog. For the **Number of cycles** specify **5** and click **OK**.

On the **Setup** tab, change the **Max. 2-Theta** value to **50°**.

On the **Display** tab, in the **General** section, select the **Display simulation/experiment difference** checkbox. In the **View management** section, change the **Chart view** from **Replace** to **New**.

Click **Refine**.

The Rietveld refinement reduces the R_{wp} value to about 14.2%. Next, examine the crystal structure.

In the **Project Explorer**, double-click the 3D Atomistic document **refinement\refined structure.xsd**.

On the **Display Style** dialog, select the **Lattice** tab and for the **Max** values for **A**, **B**, and **C** specify **2.00**. Close the dialog.

Click **Calculate Close Contacts**  and then **Calculate Hydrogen Bonds** .

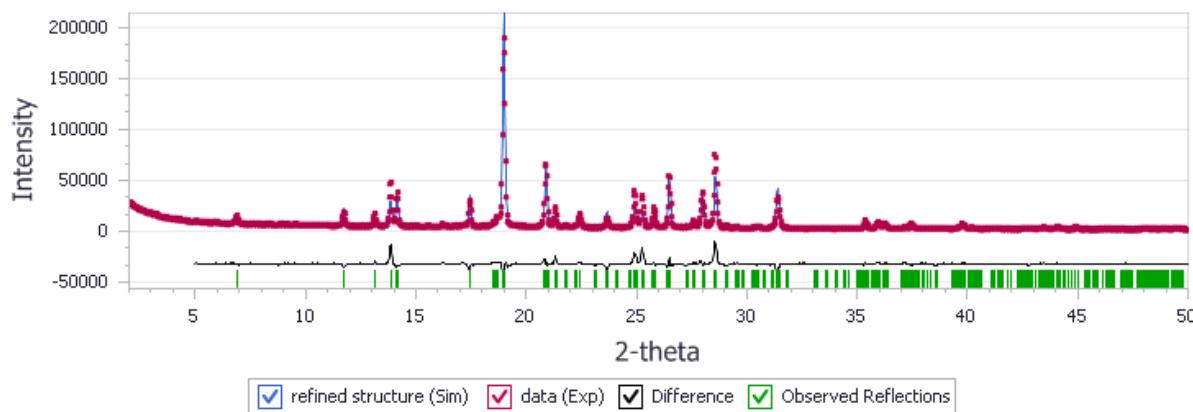
There are some minor close contacts. Next, examine the comparison of the simulated and the experimental powder diffraction pattern.

In the **Project Explorer**, double-click the Chart Document **refinement\refined structure.xcd** and examine it.

Reflex Plus: Structure solution in the presence of preferred orientation and energetic considerations in structure refinement

The calculation reproduces well the overall intensity distribution of the experimental powder diffraction pattern, although some regions show intensity differences as indicated in the difference plot in the chart document below.

Powder Refinement: $R_{wp} = 14.65\%$ $R_{wp(w/o bck)} = 25.65\%$
 $R_p = 10.62\%$



Comparison between the simulated powder pattern obtained by Rietveld refinement and experimental powder pattern.

Optionally you can generate an HTML document that summarizes the results of the Rietveld refinement.

Make **refinement\refined structure.xsd** the active document then select the **Display** tab of the Reflex Powder Refinement dialog. In the **View management** section, select the **Generate HTML report** checkbox. Click **Calculate**.

Examine the HTML report.

8. Rietveld refinement with energies and Pareto optimization

In this section, improve the structure solutions by including energy information into the Rietveld refinement process by optimizing a combined figure of merit.

Before performing a Rietveld refinement with energies calculation, you must select the energy weight factor determining the relative importance of the energy contribution. You can use the Pareto optimization automatically calculate some possible optimum refinement solutions, by performing a sequence of Rietveld refinement with energy calculations with varying energy weights.

Select **File | Save Project** from the menu bar and close all of the open documents, apart from **refined structure.xsd** in the **refinement** folder.

Select **File | Save As...** from the menu bar to open the Save As dialog. Type in **pareto** as the filename and click **Save**.

Next define each atom as an individual motion group for an all-atom Pareto optimization calculation. This means that each atom is described by three translational parameters. Start by deleting the motion groups and torsions defined previously.

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Right-click the document and select **Unhide**. Press **ALT** and double-click a motion group. This selects all motion groups. Press **DELETE**.

Repeat the same procedure to delete the torsions.

Select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu to select one entire molecule.

Open the **Reflex Powder Solve** dialog, select the **Structure Params** tab, and click **Create motion group(s) from selection as individual groups**. Ensure the selection of all the refinement checkboxes and of **Use hydrogens**. Close the Reflex Powder Solve dialog.

Press **CTRL + D** to cancel the selection everything.

Now use Pareto optimization to automatically calculate some possible optimal refinement solutions.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, for the **Refinement Type** select **Pareto optimization**. Click **More...** to open the Pareto Optimization Options dialog.

The number of points specify the total number of points to calculate on a Pareto curve. The energy window describes the tolerance window above the global minimum within which to expect realistic structure solutions. In this tutorial, use the default settings.

Close the **Pareto Optimization Options** dialog.

Specify the energy expression to apply during the refinement process. Select the same forcefield and charges that you used to optimize the molecular geometries.

On the **Energy** tab, change the **Forcefield** to **COMPASSIII** and select **Forcefield assigned** from the **Charges** dropdown list.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click **Refine** and close the **Reflex Powder Refinement** dialog.

Close **Pareto.xsd** and click **Yes** when asked if you want to save the changes.

Tip: Before you start a Pareto optimization, it is important that you choose an appropriate energy expression and forcefield. You must verify that it calculates the geometry and potential energy surface of the molecular fragments with sufficient accuracy.

Note: Pareto calculations run as remote jobs.

Once the calculation starts, this creates a new folder called **pareto** **Reflex** **Pareto** in the Project Explorer. The job automatically saves the parameter settings in a file called **pareto - Powder Diffraction**.

The Job Explorer informs you about the progress of the calculation. After some time, two new windows appear; a text document, **Status.txt**, and a chart document **pareto E vs Rwp.xcd**. As the job progresses, it regularly updates these documents.

Wait until the job finishes before proceeding.

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Note: The first step of a Pareto optimization is a minimization of the potential energy of the crystal with fixed lattice parameters. This energy minimum provides the reference for the energy contribution to the combined figure of merit.

Next analyze the pareto optimization results.

Select **File | Save Project** from the menu bar and then **Window | Close All**.

In the **Project Explorer**, double-click **pareto.txt** in the **pareto Reflex Pareto** folder.

The text file contains the values of all the settings used as input for the calculation, and a short summary of the calculation results.

Close **pareto.txt**.

In the **Project Explorer**, double-click **pareto.xtd** followed by **pareto E vs. Rwp.xcd** in the **pareto Reflex Pareto** folder.

Select **Window | Tile Vertically**.

Choose the **Selection** tool  and click any point in **pareto E vs. Rwp.xcd**.

You can see how the points on the chart relate to the trajectory frames. Alternatively, you can use the animation controls to select a trajectory frame and relate it to the corresponding graph point.

If the **Animation** toolbar is not displayed, select **View | Toolbars | Animation**.

Make **pareto.xtd** your active document. Click the **Animation Mode** arrow  and select **Options** from the dropdown list to open the Animation Options dialog. Type in **1** in the **Current frame** box and press **TAB**. Alternatively, use the spin controls to specify the frame number.

Next examine the optimized parameters for frame 1 and the weight of the energy contribution to the R_{comb} .

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, click **Load result settings**.

Click **More...** for **Rietveld with energies**. Examine the **Weight** and click **OK**.

Repeat the same procedure for other frames in **pareto.xtd**, loading the results settings for each frame.

The **Weight** is different for each frame.

Close the **Animation Options** dialog and the **Reflex Powder Refinement** dialog.

Select **Window | Close All** and click **No to All** when asked if you want to save the changes.

The Pareto optimization suggests a best solution that is closest to the absolute optimum (minimum R_{wp} , minimum E). In the energy versus R_{wp} chart **pareto E vs. Rwp.xcd**, this solution has the

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shortest distance from the origin. When the Pareto optimization completes, it automatically saves this in the project. Examine the crystal structure.

In the **Project Explorer**, double-click **pareto.xsd** in the **pareto Reflex Pareto** folder.

Open the **Display Style** dialog and select the **Lattice** tab, for the **Max** values for **A**, **B** and **C** specify **2.00**.

Click **Calculate Close Contacts**  and then **Calculate Hydrogen Bonds** . Switch off the display of motion groups.

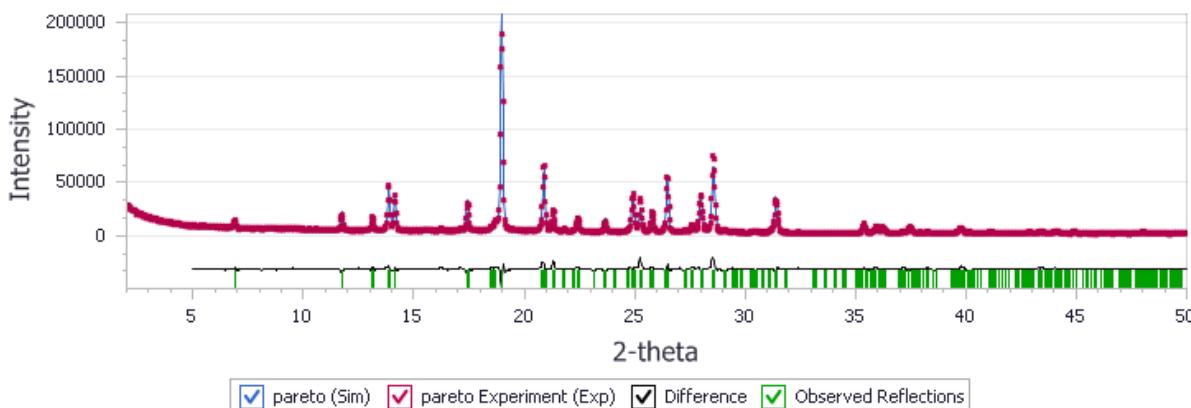
Close the **Display Style** dialog and the 3D Viewer for **pareto.xsd**, click **No** when asked if you want to save the changes.

Next, examine the comparison of the simulated and the experimental powder diffraction pattern.

In the **Project Explorer**, double-click the Chart Document **pareto Reflex Pareto\pareto.xcd** and examine it.

The R_{wp} reduce to around 11% compared to 14.2% obtained from regular Rietveld refinement. This reproduces well the overall intensity distribution of the experimental powder diffraction pattern. The inclusion of energy information into the Rietveld refinement process optimizing a R_{comb} allows for an improved structure solution.

Powder Refinement: $R_{wp} = 11.07\%$ $R_{wp}(w/o bck) = 19.31\%$
 $R_p = 8.34\%$



Comparison between the simulated powder pattern obtained by Rietveld refinement and experimental powder pattern.

Note: Pareto optimization only provides the optimum solutions. Although it suggests a "best solution", it by no means indicates that the solution indeed is the best solution. The decision on which of the optimum solutions to select cannot be automated and must be taken by the user according to specific criteria: is it more important in this particular case to have a good fit with the experimental pattern or is it critical that the energy is close to its minimum?

Compare the crystal structure obtained from Rietveld with energies with that obtained from Rietveld refinement by overlaying the two structures.

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Close **pareto.xcd**.

In the **Project Explorer**, double-click **pareto.xsd** in the **refinement\pareto Reflex Pareto** folder. Press **ALT** and double-click a motion group. This selects all motion groups. Press **DELETE**.

Click **Copy** .

In the **Project Explorer**, right-click project **preferred_orientation** and choose **New | 3D Atomistic Collection Document**. Click **Paste** .

In the **Project Explorer**, right-click **3D Atomistic Collection.xod** and change the name of the document to **overlay.xod**.

Open the **Display Style** dialog, on the **Atom** tab, for **Coloring** choose **Custom**. Click the color control to display the color chooser and select **red**. On the **Lattice** tab, for the **Color** select **red** as well.

Close **pareto.xsd** and click **No** when asked if you want to save the changes.

In the **Project Explorer**, double-click **refined structure.xsd** in the **refinement** folder. Right-click the document and select **Unhide**. Press **ALT** and double-click a motion group to select all motion groups. Press **DELETE**. Repeat this to delete all the torsions. **Copy** the entire document.

In the **Project Explorer**, double-click **overlay.xod** and **Paste**.

On the **Display Style** dialog, for the **Atom** and **Lattice** colors choose **white**.

Close **refined structure.xsd** and click **No** when asked if you want to save the changes.

Expand the **overlay.xod** 3D Viewer by clicking the **Maximize**  icon. Click once in the 3D Viewer to cancel selection of everything.

The two structures (**pareto .xsd** in red and **refined structure .xsd** in white) are indeed quite similar, with the differences mainly in the hydrogen positions. Examine the hydrogen bonding scheme and close contacts.

Right-click in the 3D Viewer and choose **Physical Systems** from the shortcut menu to open the Physical Systems dialog.

Click **pareto** to select the red structure. Click **Calculate Close Contacts** . Press **CTRL + D** to cancel selection of everything.

Repeat the same procedure for the white **refined structure**.

Next, examine the hydrogen bonding.

Press **ALT** and double-click a hydrogen bond to select all the hydrogen bonds. Press **DELETE**.

In the Physical Systems dialog, click **pareto** to select the red structure. Click **Calculate Hydrogen Bonds** . Press **CTRL + D** to cancel selection of everything.

Repeat the same procedure for the white **refined structure**.

Close the Physical Systems dialog.

The two structures have very similar hydrogen bonding schemes.

There are fewer close contacts for the structure solution obtained by Rietveld with energies. The inclusion of energy contribution in this case provides more accurate atomic positions, for example the hydrogen atoms.

9. To interpret preferred orientation parameters

As an additional test of the correctness of the structure solution, verify whether the observed preferred orientation parameters relate to the structural properties of the compound under investigation.

The powder diffraction pattern measurement used a flat plate sample holder. For this kind of experimental setup, there is in general a simple relationship between the particle shape and the preferred orientation parameters. For a compound forming plate-like crystals, R_0 is smaller than 1 and the preferred orientation direction is perpendicular to the plates. For a compound forming needles, R_0 is larger than 1 and the preferred orientation direction is parallel to the needle axis.

In a previous section, an examination of the solved crystal structure showed that there is 1D hydrogen bonding parallel to the b-axis. Strong bonding along the b-axis is likely to cause fast growth in this direction and so, the compound under investigation is expected to form needle-like crystals. Therefore, the direction of preferred orientation is parallel to the b-axis, with $R_0 > 1$.

Close **overlay.xod** and click **Yes** when asked if you want to save the file as part of the project.

In the **Project Explorer**, double-click **pareto.xsd** in the **refinement\pareto Reflex Pareto** folder.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, click **Load result settings**.

Select the **Sample** tab. Write down the preferred orientation parameters.

The strength of the preferred orientation is characterized by the parameter R_0 , which, in this case, is about 2.6. As expected, R_0 is larger than 1. The preferred orientation direction is expressed in fractional coordinates a^* , b^* , and c^* with respect to the reciprocal lattice. To interpret these values, you have to find out what the reciprocal lattice looks like.

Make sure that **pareto.xsd** is the active document. Click **Lattice Parameters**  to open the Lattice Parameters dialog. Examine the lattice parameters.

The lattice parameters are approximately $a = 14.3 \text{ \AA}$, $b = 5.1 \text{ \AA}$, $c = 15.1 \text{ \AA}$, and $\beta = 117^\circ$. As the b-axis is about three times shorter than the other two axes, the b^* -axis of the reciprocal unit cell is about three times longer than the a^* -axis and the c^* -axis. Since the b^* -axis is always perpendicular to the a-c-plane, it is parallel to the b-direction in this example.

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On the Sample tab, the absolute value of b^* is much larger than the absolute values of a^* and the c^* . In addition, the b^* axis is much longer than the a^* - and the c^* - axes. Therefore, it follows that the preferred orientation direction is basically parallel to the b -axis of the unit cell. The preferred orientation parameters are thus in good agreement with the crystal structure of (E)-2-(4,6-Difluoroindan-1-ylidene)acetamide.

Note that there is a twofold screw axis parallel to the b -direction in P 21/c. Therefore, the preferred orientation direction is either parallel or perpendicular to the b -direction. The slight deviation from a completely parallel alignment is probably because the March-Dollase correction does not describe the true nature of the preferred orientation accurately enough.

When using the March-Dollase correction, the intensity of reflections with k -vectors parallel to the preferred orientation direction are modified by a factor of R_0^{-3} . The intensity of reflections with k -vectors perpendicular to the preferred orientation direction changes by a factor of $R_0^{-3/2}$. In the present case, this corresponds to a reduction of the scattering intensity parallel to the preferred orientation direction by a factor of 14 and an increase of the intensity perpendicular to the preferred orientation direction by a factor of 4. Certain intensity ratios are modified by as much as a factor of 56.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

BIOVIA would like to thank P. G. Varlashkin, M. Sacchetti and J. Zhu from GlaxoSmithKline for supplying the experimental data.

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Structure solution of the inorganic compound FIN31

Purpose: Illustrates how the Powder Solve tool can be used to solve the crystal structures of inorganic compounds.

Modules: Materials Visualizer, Reflex Plus, VAMP

Time: 

Prerequisites: [Structure solution of 3-chloro-trans-cinnamic acid with Reflex Plus](#)

Introduction

In this tutorial, you will determine the crystal structure of the inorganic compound FIN31 ($\text{Ca}_5\text{F}(\text{PO}_4)_3$). FIN31 is one of several inorganic crystal structures that have been solved with Reflex Plus as part of a validation study.

This tutorial covers:

- [Getting started](#)
- [To index the diffraction pattern](#)
- [Pawley refinement](#)
- [To select the space group](#)
- [To prepare a starting model](#)
- [Structure solution](#)
- [Rietveld refinement](#)

Note: Later parts of this tutorial require the use of the VAMP module.

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **FIN31** as the project name, click the **OK** button.

The new project is created with *FIN31* listed in the Project Explorer. Now import the input file you will be studying.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the **Files of type** dropdown list. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click on **fin31.3cam**.

2. To index the diffraction pattern

In this section, you will process the diffraction pattern and pick diffraction peaks automatically. Using the selected peaks, you will then determine the unit cell parameters with the indexing algorithm

TREOR90.

The powder diffraction pattern has been measured using copper $K\alpha_1$ and $K\alpha_2$ radiation. To facilitate the automatic peak search, you first subtract the background, smooth the powder diffraction pattern and strip off the $K\alpha_2$ diffraction peaks.

Click the **Reflex** button  on the **Modules** toolbar and select **Pattern Processing** from the dropdown list to open the Reflex Pattern Processing dialog.

On the **Pattern Preparation** tab, in the **Background** section, click the **Calculate** button and then the **Subtract** button.

This opens a new chart document, called **fin31 (Background Removed).xcd**.

On the **Pattern Processing** tab, in the **Smoothing** section, set the **Gaussian width** to **0.05** and click the **Smooth** button.

This opens a new chart document, called **fin31 (Background Removed) (Smoothed).xcd**.

On the **K alpha 2** tab, in the **$K\alpha_2$ stripping** section, click the **Strip** button. **Close** the Reflex Pattern Processing dialog.

Three new chart documents have now been created. The active document is **FIN31 (Background Removed) (Smoothed) (Stripped).xcd**. You can now proceed to the automatic peak picking.

Choose **Modules | Reflex | Powder Indexing** from the menu bar to open the Reflex Powder Indexing dialog. On the **Peaks** tab change the **Low amplitude cutoff** to **2** and click the **Search** button.

You should always inspect the result of the automatic peak search visually. In cases where $K\alpha_2$ stripping has been carried out, you also need to ensure that no peak markers have been attributed to minor residual features belonging to the $K\alpha_2$ satellites of strong $K\alpha_1$ peaks.

Use the **Zoom**  and **Translation**  tools, on the Chart Viewer toolbar, to examine the powder diffraction pattern in the range 15° to 50° .

See the Chart mouse and keyboard actions topic for more information about how to manipulate charts.

If changes are necessary, you can add and move peaks using the *Chart Viewer Marker Mode*  tool. However, in this case, no changes are required.

Now you are ready to index the powder diffraction pattern.

In the **Project Explorer**, rename **FIN31 (Background Removed) (Smoothed) (Stripped).xcd** to **fin31_index**.

Select the **Setup** tab on the Reflex Powder Indexing dialog. Choose **TREOR90** as the indexing **Program** and check all checkboxes in the **Crystal systems to test** section.

The diffraction pattern has been measured using copper radiation so you do not have to change the default wavelength, in this case.

Click the **Index** button.

After TREOR90 has finished, a Study Table document containing the results of the indexing procedure is displayed. In the case of FIN31, the correct unit cell belongs to the hexagonal crystal system and has a volume of about 526 \AA^3 with $a = b \sim 9.4 \text{ \AA}$ and $c \sim 6.9 \text{ \AA}$.

Using the TREOR90 result, it is possible to generate a 3D model of an empty unit cell.

Click in the Study Table document with the indexing result to make it active. Click the **Create Cell** button on the Reflex Powder Indexing dialog and close the dialog.

A new 3D Atomistic document, called `fin31_index1.xsd` is created, containing an empty unit cell which matches the solution found by TREOR90.

In the **Project Explorer**, rename `fin31_index1.xsd` to `empty_cell`.

Choose **File | Save Project** from the menu bar.

3. Pawley refinement

The main purpose of Pawley refinement is to provide background parameters, profile parameters, cell parameters and the zero point shift for the structure solution step. In addition, it can be used to check the indexing results, since if the cell is incorrect there will usually be significant deviations between the simulated and the experimental powder patterns. The space group associated with the unit cell should be one with no systematic absences at this stage. So, by default, the lattice symmetry of this hexagonal unit cell is set to P3.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Setup** tab select **Pawley** from the refinement **Type** dropdown list.

The Pawley refinement proceeds in cycles. In each cycle, the peak intensities and background parameters are optimized first, while all other parameters remain fixed. In a second step, the peak intensities and background parameters are fixed and the remaining parameters are refined. By default, the number of cycles is set to 2. This value is usually too low to reach convergence in a single run so you should increase it.

On the **Setup** tab click the **More...** button for **Convergence quality** control to display the Refinement Convergence Options dialog. Change the **Number of cycles** from 2 to 5 and click the **OK** button.

The 2θ range has to be adjusted to match that of the powder diffraction pattern.

On the **Setup** tab, change the **2-Theta** range to **15°-85°**. When you have entered the new range, press **TAB**. Do not press **ENTER**, as this will start the Pawley refinement immediately.

On the **Exp. Data** tab select **Pattern 1** from the chart document `fin31.xcd`. Pattern 1 is the original data, Pattern 2 corresponds to the calculated background.

In general, the enhanced Pawley refinement method implemented in Reflex Plus is very stable and it is possible to refine all relevant parameters simultaneously. Using the Pseudo-Voigt profile function, you refine background parameters, the peak width parameters U, V, and W, the mixing parameters NA and NB, the zero point shift, and the lattice parameters.

On the **Pattern** tab, check the checkboxes for the refinement of the profile parameters **U**, **V**, **W** under FWHM, **NA** and **NB** under Profile parameters, and the **Zero point** under Line shift. The refinement of 20 background coefficients is switched on by default.

If `empty_cell.xsd` is not the active document, double-click on `empty_cell.xsd` in the Project Explorer.

On the **Lattice** tab, check the checkboxes for the refinement of all **cell parameters**.

Finally, you should modify the display options and start the Pawley refinement.

On the **Display** tab, check the **Display simulation/experiment difference** checkbox.

Click the **Refine** button on the Reflex Powder Refinement dialog.

As the Pawley refinement progresses, the cycle number and the current R_{wp} value are shown at the bottom of the Materials Visualizer window. After five cycles, the R_{wp} value should be about 7.8%. At the end of the calculation, a new chart document opens.

Examine the comparison of the simulated and the experimental powder patterns.

The agreement between the calculated and the experimental powder patterns should be quite good, confirming that the unit cell is correct. The final R_{wp} value is displayed at the top of the chart document. $R_{wp}(w/o bck)$ is the weighted Rietveld parameter calculated after background subtraction.

To make sure that the refinement has converged, you should carry out a second run.

In the **Project Explorer**, double-click on `empty_cell.xsd` to make it the active document.

Click the **Refine** button on the Reflex Powder Refinement dialog and close the dialog.

After the second set of 5 cycles, the R_{wp} value should be about 7.75%.

Note: By default, Pawley refinement or Rietveld refinement jobs are run synchronously on your Materials Studio client. However, the client-server architecture in Materials Studio allows all refinement jobs to be run on a remote computer server by switching off **Run synchronously** from the **Job Control** tab.

The Pawley refinement step is now finished and you should save the refined parameters.

Select **Modules | Reflex | Save Settings...** from the menu bar to open the Save Reflex Settings dialog. Enter `empty_cell` as the filename and click the **OK** button.

The settings document `empty_cell - Powder Diffraction` is added to the list of files in the Project Explorer. By double-clicking on this document, you can restore the refined parameters at a later stage.

Tip: If you right-click on `empty_cell - Powder Diffraction` in the Project Explorer and select *Powder Refinement* from the shortcut menu, the Reflex Powder Refinement dialog will be displayed with the settings used for this calculation.

Before you move on to the next section, you should save the project.

Choose **File | Save Project** from the menu bar.

4. To select the space group

You now have to identify the space group to which the crystal structure is likely to belong. Reflex provides functionality to estimate the likelihood for all space groups in a given crystal system, based on the intensities obtained by Pawley refinement ([Markvardsen et al., 2000](#)).

Make **empty_cell.xsd** the active document and open the **Reflex Powder Indexing** dialog. Select the **Space Groups** tab and click the **Search** button.

A study table document is generated in which all hexagonal and trigonal space groups are ranked according to their figure of merit. The highest figure of merit is shared by 3 space groups; P63/M, P63, and P6322. Under normal circumstances, it would be necessary to attempt structure solution for each space group until the crystal structure is solved. However, for the purposes of this tutorial you will only consider the correct space group, P63/M.

Now you should generate a 3D Atomistic document containing the unit cell with the correct space group settings.

Select the first row of the study table document **empty_cell.std**. Click the **Create Cell** button and close the dialog. Rename the new 3D Atomistic document **empty_cell_P63m_refined.xsd**.

You should repeat the Pawley refinement in the chosen space group.

Open the **Reflex Powder Refinement** dialog and click the **Refine** button. Close the dialog.

Finally, you should save the refined parameters and the project.

Select the **Reflex** button  , then select **Save Settings...** from the dropdown list to open the **Save Reflex Settings** dialog. Enter **empty_cell_P63m** as the filename and click the **OK** button.

Choose **File | Save Project** from the menu bar.

5. To prepare a starting model

In this section, you will build a starting model for structure solution. First, you have to decide how many atoms you expect to find in the asymmetric unit and how these atoms are distributed over general and special positions.

Tip: If you make a mistake while sketching, you can undo your changes by choosing *Edit / Undo* from the Materials Studio menu bar.

At the end of the last section, you set the space group symmetry to P63/M and carried out a Pawley refinement in this space group. Now, you should make a copy of the empty unit cell to use in the subsequent steps.

In the **Project Explorer**, double-click on **empty_cell_P63m_refined.xsd** to make it the active document. Choose **File | Save As...** from the menu bar and save the file as **empty_cell_P63m**. The extension **.xsd** will be added automatically.

The chemical composition of FIN31 is $\text{Ca}_5\text{F}(\text{PO}_4)_3$ and its density is approximately 3.2 g/cm^3 . To work out how many formula units to place in the asymmetric unit, you should begin by adding one formula unit, then comparing the calculated and the experimental density.

Start with the Ca ions. First, generate a model containing a single Ca ion.

In the **Project Explorer**, right-click on the project name **FIN31** and choose **New | 3D Atomistic Document** from the shortcut menu.

Rename the new document **Ca**.

Select the **Sketch Atom**  tool and click the **Element used to sketch** arrow . Choose **Periodic Table...** from the dropdown list to display the Periodic Table dialog, select **Ca** and click the **OK** button.

Left-click once in the middle of the 3D Viewer for **Ca.xsd**, then press **ESC**.

Now, make five copies of the Ca ion in the empty P63/M unit cell.

Select **Edit | Copy** from the menu bar.

In the **Project Explorer**, double-click on **empty_cell_P63m.xsd** to make it the active document.

Select **Edit | Paste** from the menu bar, 5 times.

In the next step, you add a single F ion to the asymmetric unit.

Create a 3D Atomistic document containing a F instead of a Ca. Copy and paste the F ion once into the P63/M unit cell.

Finally, place three PO₄ ions in the asymmetric unit. This step is a little more complicated, because you have to sketch the PO₄ ion before you can copy and paste it.

Create new **3D Atomistic** document called **PO4**.

Sketch a single **Phosphorus** atom. Change the **Sketch Atom to Use** from P to O. Click once in the 3D Viewer for **PO4.xsd** close to the P atom. Then click on the P atom. A bond is created between the P atom and the O atom. Repeat this three times.

On the Sketch toolbar, click the **Clean**  tool. Ensure that the PO₄ ion adopts a tetrahedral conformation.

To check the result of the sketching procedure, you should look at the PO₄ ion from different angles.

Use the **cursor keys** to rotate the model and ensure that **PO4.xsd** contains only a tetrahedral PO₄ ion. Now you will use VAMP to optimize the geometry.

Select **Modules | VAMP | Calculation** from the menu bar to open the VAMP Calculation dialog. On the **Setup** tab change the **Task** from **Energy** to **Geometry Optimization** and the **Hamiltonian** to **NDDO MNDO/d**. Set the **Charge** to **-3**. Click the **Run** button and close the dialog.

A new folder, called **PO4 VAMP GeomOpt**, opens in the Project Explorer. The progress of the job during the computation is presented in the form of chart and text documents. The optimized structure is located in the document **PO4 . xsd** in the new folder.

Having optimized the PO₄ ion, you should copy it into the P63/M unit cell.

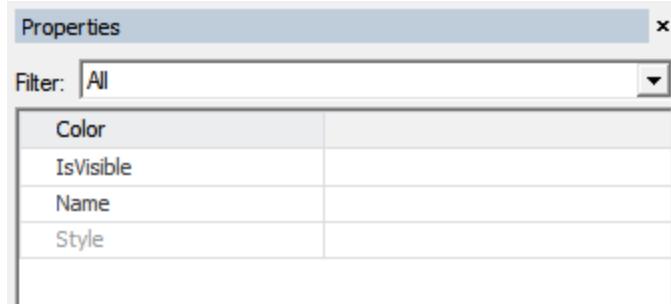
In the Project Explorer double-click on **PO4 VAMP GeomOpt/PO4.xsd** to make it the active document. Select **Edit | Copy** from the menu bar. Now double-click on **empty_cell_P63m.xsd** to make it the active document.

Select **Edit | Paste** from the menu bar, 3 times.

Note: In many cases, especially for small molecular fragments such as PO_4 , it is sufficient to attempt structure solution using molecular fragments that have been optimized with the *Clean* tool alone. However, if you have access to modules that allow you to geometry optimize molecular fragments using classical or quantum calculations, such as Forcite or VAMP, you can increase your chances of successful structure solution by performing the pre-optimization step as outlined above on each individual molecular fragment in the unit cell.

Now examine the calculated density.

If the **Properties Explorer** is not already open, choose **View | Explorers | Properties Explorer** from the menu bar.



Properties Explorer

Ensure that no atoms are selected in **empty_cell_P63m.xsd**. Choose the **Symmetry System** filter and scroll down the list of properties until you find the **Density**.

With one formula unit in the asymmetric unit, the density is 19.2 g/cm^3 . This value is 6 times larger than the experimental density of about 3.2 g/cm^3 . As a consequence, the content of the asymmetric unit is $1/6$ of the formula unit: $5/6 \text{ Ca}$, $1/6 \text{ F}$ and $1/2 \text{ PO}_4$. As all these numbers are smaller than one, all ions must occupy special positions.

Note: Throughout this tutorial, it is assumed that the crystal structure is entirely ordered.

According to the International Tables for Crystallography, special positions in P63/M have a multiplicity of 2, 4 or 6, while the general position has a multiplicity of 12. If an atom occupies a special position of multiplicity m_s , the fraction of the atom in the asymmetric unit is m_s/m_g , where m_g is the multiplicity of the general position. Therefore, the multiplicities of 2, 4 and 6 in P63/M correspond to fractions of $1/6$, $1/3$ and $1/2$ ions in the asymmetric unit. Using these fractions, there are several ways of building the asymmetric unit:

Ion	Total content	Decomposition
Ca	5/6	1/6,1/6,1/6,1/6,1/6 (2,2,2,2,2)
-	-	1/6,1/6,1/6,1/3 (2,2,2,4)
-	-	1/6,1/6,1/2 (2,2,6)
-	-	1/2,1/3 (6,4)
F	1/6	1/6 (2)
PO ₄	1/2	1/6,1/6,1/6 (2,2,2)
-	-	1/3,1/6 (4,2)
-	-	1/2 (6)

Since there are only 4 special positions of multiplicity 2 in P63/M, it is not possible for there to be 5×1/6 Ca ions in the asymmetric unit. Furthermore, the F ion must be located on a special position with a multiplicity of 2. However, this still leaves several options for the Ca and PO₄ ions.

If there is more than one possibility, it is usually a good idea to try structure solution for the least complex choice first and then work through the list of possibilities in order of increasing complexity. In this case, the least complex choice is to place a single PO₄ ion on a special position with a multiplicity of 6 and to put two Ca ions on special positions with a multiplicity of 4 and 6, respectively.

There are two ways to take special positions into account during the structure solution search using Reflex Plus. One method is to place the ions on special positions when the starting model is prepared. For ions on special positions, only those rotations and translations that do not remove the ions from their special positions are allowed. This approach can be quite cumbersome when there are several non-equivalent possibilities.

Alternatively, you can place the ions on general positions and adjust their occupancies so that the total unit cell content is the same as if the ions were placed on special positions with an occupancy of 1.0. During the structure search, the ions should be moved onto the special positions by the global search algorithm, so as to obtain good agreement with the experimental data. In the final structure solution several symmetry copies of the ions will be superimposed, so that the total occupancy of the occupied special positions is one.

In this tutorial, you will use the second approach. So, based on the discussion above, you have to introduce into the asymmetric unit two Ca ions with occupancies of 1/2 and 1/3, one F ion with an occupancy of 1/6 and one PO₄ ion with an occupancy of 1/2.

First, delete all atoms in the 3D Atomistic document **empty_cell_P63m.xsd**.

Make sure that **empty_cell_P63m.xsd** is the active document.

Select all of the atoms in the 3D Viewer and press **DELETE** to delete all of the atoms.

In the next step, you put the first of the two Ca ions into the asymmetric unit. In order to tell Reflex Plus that it should optimize the position of the Ca ion during the structure search, you must define the Ca ion as a motion group. In addition, you have to set the occupancy of the Ca ion.

In the **Project Explorer**, double-click on **Ca.xsd** to make it the active document. Press **CTRL + A** to select the Ca ion.

Open the **Reflex Powder Solve** dialog, on the **Structure Params** tab, in the **Motion groups** section, click the **Create** button.

In the **Properties Explorer**, select **Atom** from the **Filter** dropdown list. Double-click on **Occupancy** to open the Edit Occupancy dialog. Change the occupancy to **0.5** and click the **OK** button.

Copy the Ca atom and **paste** it into **empty_cell_P63m.xsd**.

Now add the second Ca ion.

In the **Project Explorer**, double-click on **Ca.xsd** to make it the active document.

In the **Properties Explorer**, change the **Occupancy** to **0.3333333**.

Copy the Ca atom and **paste** it into **empty_cell_P63m.xsd**.

You continue with the F ion.

In the **Project Explorer**, double-click on **F.xsd** to make it the active document.

Press **CTRL + A** to select the F ion.

Use the **Reflex Powder Solve** dialog to create a **Motion group**.

In the **Properties Explorer**, change the occupancy of the F ion to **0.1666666**.

Copy the F atom and **paste** it into **empty_cell_P63m.xsd**.

Finally, you add the PO₄ ion.

In the **Project Explorer**, double-click on **PO4 VAMP GeomOpt/PO4.xsd** to make it the active document.

Press **CTRL + A** to select the molecule.

Use the **Reflex Powder Solve** dialog to create a **Motion group**.

In the **Properties Explorer**, change the occupancy to **0.5**. The change automatically applies to all selected atoms.

Copy the PO₄ molecule and **paste** it into **empty_cell_P63m.xsd**.

Before you move on to the next section, you should verify that the density of the starting model is correct. You should also change the name of the starting model and save the project.

Ensure that **empty_cell_P63m.xsd** is the active document. Press **CTRL + D** to deselect everything. In the **Properties Explorer**, select the **Symmetry System** filter and examine the **Density**.

The density should be 3.2 g/cm³.

Change the name of the starting model from **empty_cell_P63m.xsd** to **FIN31.xsd**.

Select **File | Save Project** from the Materials Studio menu bar.

6. Structure solution

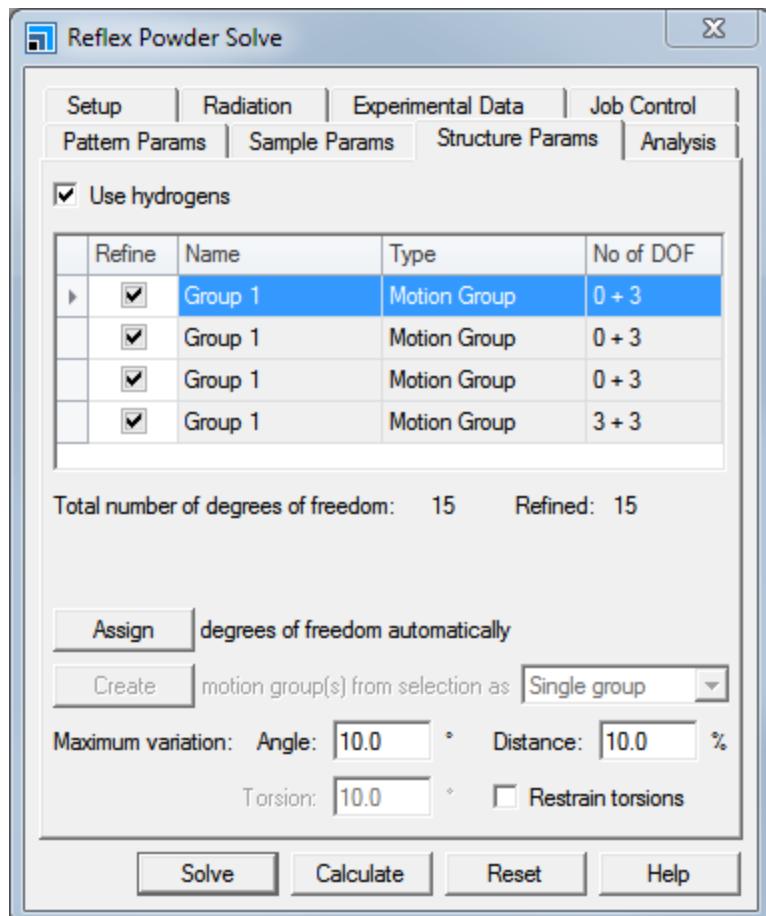
In this section, you will solve the crystal structure of FIN31.

To do this you must select the degrees of freedom that have to be optimized, decide on the global temperature factor, choose a computer to run your job on and select a global optimization algorithm.

First, make sure that all structural degrees of freedom are selected for optimization.

On the **Reflex Powder Solve** dialog, select the **Structure Params** tab and check all **Motion Groups** for refinement.

When you have done this, the *Structure Params* tab should look like the one shown below:



Reflex Powder Solve dialog, Structure Params tab with all of the Motion Groups selected for refinement.

Temperature factors are not optimized during the structure search. In general, it is a good idea to use a single global isotropic temperature factor for structure solution and to choose a value that is approximately right for the crystal structure under consideration. In the case of FIN31, the crystal structure has been measured at low temperature. So the average global isotropic temperature factor is quite small and can be neglected during structure solution.

On the **Sample Params** tab on the **Reflex Powder Solve** dialog, scroll down to the **Temperature factors** section. Set **Applied to None**.

Reflex Plus offers a choice of two global optimization algorithms, Monte Carlo simulated annealing and Monte Carlo parallel tempering.

Most simulation parameters are set automatically by default, but you have to decide on the number of cycles and the number of Monte Carlo steps.

As there is no guarantee that the crystal structure will be solved during the first cycle, you should always carry out several cycles. Only if the same solution is found in more than one cycle can you be reasonably sure that the global minimum has been reached.

By default, Reflex Plus estimates the required number of Monte Carlo steps based on the number of degrees of freedom. However, the estimate has been calibrated for organic compounds and tends to overestimate the number of steps required for the structure solution of inorganic compounds. So, for inorganic compounds, it is advisable to use a number of steps that is lower than the proposed number. However, if you choose a number that is too low, the structure will not be solved. It is therefore essential to check that the same solution is found in several cycles. If not, you should repeat the structure solution with a larger number of steps.

On the **Setup** tab on the Reflex Powder Solve dialog, in the **Solve** section, select **Simulated Annealing** from the **Method** dropdown list. Set the **Number of cycles** to **5**. Make sure that **Automatic** is checked and examine the proposed **Number of steps**.

Uncheck **Automatic** and set the **Number of steps** to **300000**.

You are now ready to start the Powder Solve run.

Click the **Solve** button and close the dialog.

The Job Explorer informs you about the progress of the calculation. After some time, two chart documents should appear. While the calculation is running, you may wish to rearrange the open documents and close some of them.

Choose **File | Save Project** from the menu bar. Close all of the open documents apart from those starting with **FIN31 Reflex PSolve**. Choose **Window | Tile Vertically** from the menu bar.

Examine the output in the two new chart documents.

The length of time this calculation takes to complete depends on the configuration of your computer. Before you continue, you should wait for the calculation to finish.

The best crystal structure obtained at the end of several Monte Carlo simulated annealing cycles is not necessarily the right structure solution. The true crystal structure may have been missed because there were an insufficient number of cycles or Monte Carlo steps, or because the search was not carried out in the right space group.

It is also possible that the solution obtained is unrealistic because the geometries of the rigid bodies were not estimated accurately enough prior to structure solution. To decide whether or not the crystal structure has been solved, the results of the structure solution procedure have to be examined carefully.

To start with, you should examine the text output. Among other information, the text output contains the best R_{wp} value found in each cycle. If the lowest R_{wp} value is obtained in several cycles, you can be fairly confident that the global minimum has been found for the given choice of space group and degrees of freedom.

In the **Project Explorer**, double-click on the text document **FIN31 Reflex PSolve\FIN31.txt** and examine it.

The lowest R_{wp} value of about 9.68 % has been found several times.

The R_{wp} value is only a number and you should always compare the simulated and the experimental powder patterns visually. For the solution with the lowest R_{wp} value, the comparison between the simulated and the experimental patterns is saved in the chart document **FIN31 Reflex PSolve\FIN31 Solution.xcd**.

In the **Project Explorer**, double-click on the chart document **FIN31 Reflex PSolve\FIN31 Solution.xcd**. Examine the comparison between the experimental and the simulated powder diffraction patterns.

Over the full range of the powder diffraction pattern, the calculated peak intensities are in good agreement with the experimental peak intensities.

Finally, you should examine the best structure solution closely.

In the **Project Explorer**, double-click on the 3D Atomistic document **FIN31 Reflex PSolve\FIN31 Solution.xsd**. Use the tools on the **3D Viewer** toolbar to inspect the structure solution.

You can see that several symmetry copies of each ion overlap, as you would expect for the correct crystal structure. The chance of this happening accidentally is very small, so there is no doubt, at this stage, that the crystal structure has been solved.

7. Rietveld refinement

In this section, you will use Rietveld refinement to obtain a more accurate crystal structure. To start with, you should make a copy of the structure solution and delete the motion groups.

In the **Project Explorer**, double-click on the 3D Atomistic document **FIN31 Reflex PSolve\FIN31 Solution.xsd**. Choose **File | Save As...** from the menu bar and save the file as **FIN31_intermediate.xsd** at the top level of the project directory.

Choose the **Selection**  tool. Press and hold **ALT**, then double-click on a motion group (represented by gray ellipsoids) in **FIN31_intermediate.xsd**. Press **DELETE** to delete all of the motion groups.

You should now place all of the atoms exactly on the corresponding special positions.

Choose **Build | Crystals | Rebuild Crystal...** from the menu bar to open the Rebuild Crystal dialog.

Select the **Options** tab and choose to **Check for atoms on special positions, within 1.0 Å**.

Click the **Rebuild** button.

All atoms have been positioned exactly on the corresponding special positions.

When atoms are snapped to special positions their occupancies are not automatically updated. Therefore, you have to reset the occupancy of all the atoms to 1.0 manually.

Press **CTRL + A** to select everything.

In the **Properties Explorer**, select the **Atom** filter, scroll down the list of properties until you find the **Occupancy** and set it to **1.0**.

Make sure that **FIN31_intermediate.xsd** is the active document. Choose **File | Save As...** from the menu bar and save the file as **FIN31_refinement.xsd**.

You can now start the Rietveld refinement of the crystal structure. First, you refine only the atomic positions. To refine atomic coordinates, every atom must be defined as a motion group.

Open the **Reflex Powder Refinement** dialog. On the **Setup** tab, in the **Refinement** section, set the **Type to Rietveld**.

Make sure that **FIN31_refinement.xsd** is the active document and press **CTRL + A** to select everything.

On the **Structure** tab select **Individual groups** from the dropdown list and click the **Create** button. Ensure that all 6 checkboxes are checked in the **Refine** column and examine the list of degrees of freedom.

Only 12 degrees of freedom are defined for the 7 inequivalent atoms in the asymmetric unit, so certain translations are symmetry forbidden for atoms on special positions.

Before you start the Rietveld refinement, you should make sure that no other parameters are refined. In addition, you want the comparison between the calculated and the experimental patterns to be displayed in a new chart document.

Select the **Pattern** tab and uncheck the checkboxes for the refinement of **U, V, W, NA, NB, Zero point** and **Background coefficients**.

Select the **Lattice** tab and make sure that the **lattice parameters** are not refined.

Select the **Display** tab, in the **View management** section, change **Chart view** from Replace to **New**.

Click the **Refine** button.

The resulting R_{wp} value should be about 8.81%.

Next you should refine some additional parameters, including a global isotropic temperature factor.

Make sure that **FIN31_refinement.xsd** is the active document.

On the **Pattern** tab, check the checkboxes for the refinement of **U**, **V**, **W**, **NA**, **NB**, **Zero point** and **Background coefficients**.

On the **Lattice** tab check on the refinement of **a**, **b**, and **c**. Check the **Keep fractional coordinates fixed during lattice changes** checkbox.

On the **Sample** tab, in the **Temperature factors** section, change **Applied** from **None** to **Global isotropic** and check the **Global isotropic** checkbox for refinement.

On the **Display** tab, in the **View management** section, change **Chart view** from **New** to **Replace**.

Click the **Refine** button.

Examine the value of the Global isotropic temperature factor after refinement.

The R_{wp} value and the global isotropic temperature factor should be about 8.57% and 0.0045, respectively.

Finally, you should refine individual isotropic temperature factors for all of the atoms.

Make sure that **FIN31_refinement.xsd** is the active document.

Press **CTRL + A** to select everything.

On the **Sample** tab, in the **Temperature factors** section set **Applied to Atomic**.

Select the **Atoms** tab. All of the rows in the table are highlighted in blue because all of the atoms are selected in the corresponding 3D Viewer. In the first row, click on **None** and change the value to **Isotropic**. Check the Refine checkboxes to the left of the Temperature Factor column to refine all the isotropic temperature factors.

In the **Properties Explorer**, select the **Atom** filter. Double-click on **TemperatureFactor** to open the Atomic Temperature Factors dialog. Set the value of the isotropic atomic temperature factor to **0.0045**. The change applies automatically to all selected atoms.

Click the **Refine** button on the Reflex Powder Refinement dialog.

Adding the isotropic atomic temperature factors has slightly reduced the R_{wp} value, which is now around 8.54%. This value is very close to the R_{wp} factor of 7.75% obtained by Pawley refinement and it is not necessary to refine any further parameters at this point.

In Pawley refinement, all peak intensities are independent adjustable parameters and the R_{wp} values obtained therefore represent the lower limit for the R_{wp} values obtained by Rietveld refinement.

Now generate an HTML document that summarizes the results of the Rietveld refinement. The HTML document contains error bars for all refined parameters.

On the **Display** tab, in the **View management** section, check the **Generate HTML report** checkbox.

Make sure that **FIN31_refinement.xsd** is the active document.

Click the **Refine** button and close the dialog.

In the **Project Explorer**, double-click on the document **FIN31_refinement.htm**. Examine the HTML report.

Finally, you should visualize the thermal ellipsoids.

Make sure that **FIN31_refinement.xsd** is the active document.

Press and hold down **ALT**, then **double-click** on a motion group to select all motion groups. To switch off the display of the motion groups, select *Visibility / Hide* from the **View** menu. Press **CTRL + D** to deselect the motion groups.

Open the Display Style dialog, select the **Temperature Factor** tab and click the **Add** button. Increase the **Scale factor** to **10** and close the dialog.

Make sure that **FIN31_refinement.xsd** is the active document. Press **CTRL + D** to deselect everything and examine the 3D Viewer.

Select **File | Save Project** from the menu bar.

You have successfully determined the crystal structure of FIN31.

This is the end of the tutorial.

References

Markvardsen, A. J., David, W. I. F., Johnson, J. C. and Shankland, K., "A probabilistic approach to space-group determination from powder diffraction data", *Acta Cryst.*, **A57**, 47-54, (2000).

Structure solution of 4-nitrophenylhexylurethane using a close-contact penalty

Purpose: Illustrates how to solve a crystal structure from a powder diffraction pattern using the close-contact penalty option in Reflex Plus.

Modules: Materials Visualizer, Reflex Plus, Forcite, COMPASS

Time:   

Prerequisites: Using the Crystal Builder, [Indexing of 4-nitrophenylhexylurethane using X-Cell](#)

Background

Occasionally, the available powder diffraction data do not contain enough information for a successful structure solution. In such cases, additional chemical knowledge may be needed to determine the correct crystal packing. Typical examples include:

- Low quality powder patterns with broad, overlapping peaks
- Structures with a large number of degrees of freedom
- Strong preferred orientation of crystallites that reduces information in certain spatial directions
- High symmetry structures with only a small number of peaks in the powder pattern

In these instances, trying to determine the structure using just the powder data will typically result in a large number of solutions with low R_{wp} values. Some of these solutions (often those with the lowest R_{wp} factors) will be chemically unreasonable. For example, they may contain a large number of undesirable close contacts between structural fragments. To overcome this problem, Powder Solve allows you to add a close-contact penalty to the figure of merit. Using this new combined figure of merit during structure optimization removes configurations with bad contacts from the set of possible solutions very effectively. As a result, it may be possible to solve crystal structures in cases when the powder data alone do not contain enough information to locate the correct solution.

Introduction

In this tutorial, the crystal structure of 4-nitrophenylhexylurethane will be solved from powder diffraction data using a close-contact penalty and preferred orientation correction.

This tutorial covers:

- [Getting started](#)
- [To build the unit cell](#)
- [Pawley refinement](#)
- [To determine the space group automatically](#)
- [To attempt structure solution without preferred orientation correction or a close-contact penalty](#)
- [To attempt structure solution with preferred orientation correction, but without a close-contact penalty](#)
- [Structure solution using a combined figure of merit](#)
- [To analyze the solution](#)
- [To refine the solution](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **NPHU_cc** as the project name, click the **OK** button.

The new project is created with **NPHU_cc** listed in the Project Explorer. Next import the powder diffraction pattern and molecular structure of 4-nitrophenylhexylurethane.

Click the **Import** button  to open the Import Document dialog. Choose **Chart Files** from the dropdown list to the right of the **File name** field. Navigate to the **Examples\Reflex\Experimental Data** folder and double-click on **NPHU.xcd**.

Open the **Import Document** dialog again and navigate to **Examples\Reflex\Structures**. Choose **All Files (*.*)** from the dropdown list to the right of the **File name** field. Select **NPHU.xsd** and click **Open**.

2. Building the unit cell

In the tutorial [Indexing of 4-nitrophenylhexylurethane using X-Cell](#), the powder diffraction pattern of 4-nitrophenylhexylurethane was indexed. If you have an empty unit cell from that indexing result, you can use the model. Otherwise, you need to build an empty unit cell using the indexing information. X-Cell proposed **P2₁** as the space group. You will confirm this later in the tutorial, but at this point, you should simply use the lowest symmetry monoclinic space group, **P2**.

Right-click on **NPHU_cc** in the Project Explorer and select **New | 3D Atomistic Document** from the shortcut menu. **Rename** the new document **cell.xsd**.

Select **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog. On the **Space Groups** tab, select space group number 3, **P2**. On the **Lattice Parameters** tab, enter the cell parameters obtained from the tutorial [Indexing of 4-nitrophenylhexylurethane using X-Cell](#): **a = 21.561 Å, b = 5.781 Å, c = 5.621 Å, β = 96.781°**. Click the **Build** button.

3. Pawley refinement

Now you should determine the appropriate space group. The space group proposed by X-Cell is $P2_1$. You can use the automatic space group determination tool to confirm that this is the most probable space group and to see what other possibilities should be considered. The automatic space group determination tool requires previous Pawley refinement.

Make the model **cell.xsd** the active document. Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog. On the **Exp. Data** tab, select **NPHU.xcd**.

The peaks at 38.8 and 44.5° in the powder diffraction pattern of 4-nitrophenylhexylurethane are due to the aluminum sample holder. So they will not be included in the calculations.

To fit the peaks in the low angle range, which are strongly asymmetric, you need to apply the Finger-Cox-Jephcoat asymmetry correction to the peak profile function. This will increase the time required for the Pawley refinement to converge, so you will limit the angular range of the asymmetry correction to the low 2θ range.

On the **Setup** tab click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **5** and click the **OK** button.

On the **Setup** tab, change the **Max. 2-Theta** value to **30°** .

On the **Pattern** tab, check the profile parameters **U**, **V**, **W**, **NA**, and **NB**, and the **Zero point** checkboxes. Select **Finger-Cox-Jephcoat** in the **Asymmetry Correction** dropdown field and set the **2-Theta limit to 20**. Check the **H/L** and **S/L** parameters checkboxes. The refinement of **20 Background coefficients** is switched on by default.

On the **Lattice** tab, check on the refinement of all the cell parameters by checking the appropriate checkboxes.

On the **Display** tab, check the **Display simulation/experiment difference** checkbox and select **New** from the **Chart view** dropdown list.

Ensure that **cell.xsd** is the active document and click the **Refine** button and close the dialog.

The R_{wp} value at the end of the refinement should be about 14.7% .

4. To determine the space group automatically

You can now determine which monoclinic space groups are the most probable.

Select **File | Save Project** from the menu bar and **close** all the Viewers except **cell.xsd**.

Select **Modules | Reflex | Powder Indexing** from the menu bar to open the Reflex Powder Indexing dialog. Click the **Search space groups** button on the **Space Groups** tab.

A study table document, **cell.std**, containing all the monoclinic space groups ranked according to the figure of merit (FOM) is generated. Space groups with systematic absences not compatible with the experimental data have negative FOMs. Those without systematic absences have $FOM = 0$ and the most probable space groups have positive FOMs. In this case, the most likely ones are $P2_1$ and $P2_1/m$. The general position multiplicity is different for the two space groups. It is possible to eliminate one of them

Reflex Plus: Structure solution of 4-nitrophenylhexylurethane using a close-contact penalty

based on density considerations. The molecular weight of 4-nitrophenylhexylurethane is 266.296 g/mol and, according to the tutorial [Indexing of 4-nitrophenylhexylurethane using X-Cell](#), the cell volume is 700.630 Å³. A P2₁ cell, with two molecules in the unit cell, would have a density of 1.26 g/cm³. A P2₁/m cell, with 4 molecules in the unit cell, would have an unrealistic density of 2.52 g/cm³. So Powder Solve should be run on the P2₁ cell.

Select the row in the study table document **cell.std** that contains details of the P2₁ unit cell. Click the **Create Cell** button and close the dialog.

A new 3D Atomistic document containing the empty P2₁ cell is created.

Right-click on this document in the Project Explorer and rename it **P21_cell.xsd**.

Select **Modules | Reflex | Powder Refinement** from the menu bar to open the Reflex Powder Refinement dialog.

On the **Setup** tab, click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **3** and click the **OK** button. Click the **Refine** button.

The R_{wp} value at the end of the refinement should be about 14.6%.

Close the Reflex Powder Refinement dialog. Select **File | Save Project** from the menu bar and then **Window | Close All**.

5. To attempt structure solution without preferred orientation correction or a close-contact penalty

Initially, you should try to solve the structure using the diffraction data alone. Begin by attempting to solve the structure without refining the preferred orientation parameters.

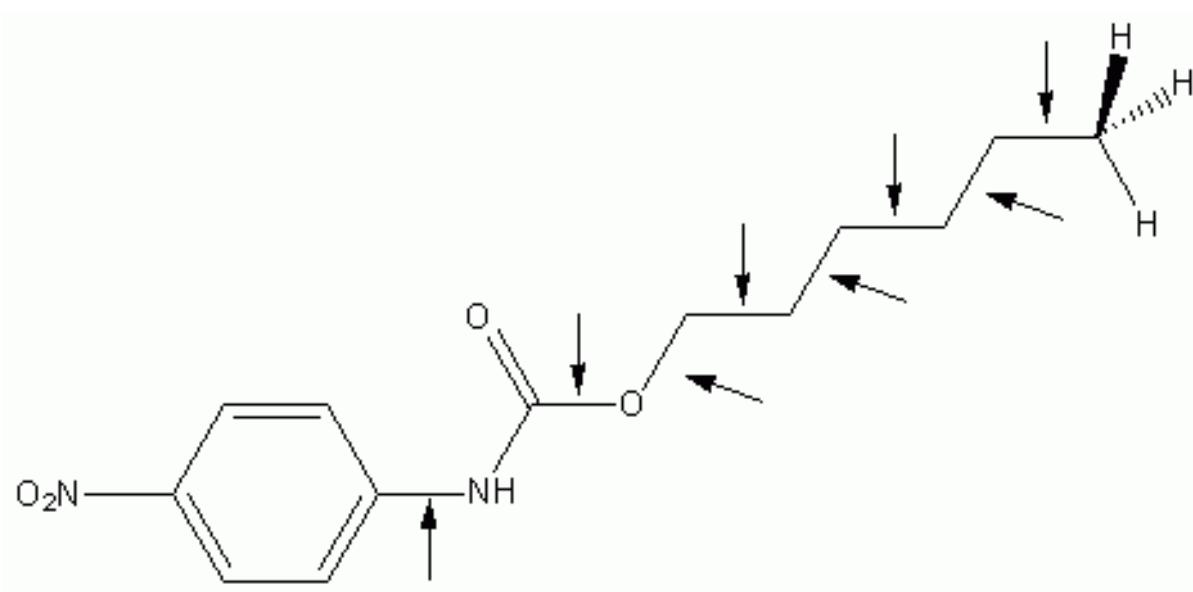
In the Project Explorer, double-click **NPHU.xsd** in the Project Explorer. Click the **Copy** button .

Open **P21_cell.xsd** and click the **Paste** button  to insert the optimized 4-nitrophenylhexylurethane molecular structure.

Because of the symmetry of the P2₁ space group, two copies of the molecule are automatically placed in the unit cell.

Magnify the structure using the **Zoom** tool , until you have a good view of one of the molecules in the unit cell. Click the **Measure/Change** arrow  and select **Torsion** from the dropdown list.

A number of flexible single bonds are identified in the figure below. Click on them in turn, starting from one end of the chain and working your way to the other.



Flexible single bonds in 4-nitrophenylhexylurethane

Now that the unit cell is set up, you can use Powder Solve to attempt to solve the crystal structure of 4-nitrophenylhexylurethane from the powder diffraction data.

Click the **3D Viewer Selection Mode** button and select one of the atoms. Right-click and choose **Select Fragment** from the shortcut menu.

Open the **Reflex Powder Solve** dialog. On the **Structure Params** tab, click the **Create motion group (s) from selection as Single group** button to construct a motion group from the selected atoms. Click in **P21_cell.xsd** to deselect the structure.

Check all the checkboxes in the **Refine** column of the list except for that for C-C-H, enabling refinement of all the parameters except for the terminal bond to the methyl group, and ensure that the **Use hydrogens** checkbox is checked.

The C-C-H torsion is not included in the refinement at this stage because it can only influence the position of the methyl hydrogens. The position of the methyl hydrogens becomes important when intermolecular interactions are taken into account in the refinement. Since you will be attempting to solve the structure of 4-nitrophenylhexylurethane by applying a close-contact penalty in a subsequent section of this tutorial, the C-C-H torsion is being included, but not refined, at this stage simply for convenience.

On the **Setup** tab, change the **Number of cycles** to **5** and the global search **Method** to **Parallel Tempering**.

On the **Experimental Data** tab, select **NPHU.xcd**.

On the **Job Control** tab, choose **My Computer** as the **Gateway location**. Turn off the **Automatic Job description** option by unchecking the checkbox and enter **NPHUnoCCnoPO** as the **Job description**.

Select **File | Save Project** and **close** all the open documents. Open **NPHU.xcd** and then **P21_cell.xsd**. Click the **Solve** button and **close** the Reflex Powder Solve dialog.

Details of the new job will appear in the Job Explorer, informing you about the progress of the calculation. Two chart documents and a view of the unit cell are opened when the job starts and are periodically updated as it progresses. If you wish, you can close some or all of these documents while the calculation is running.

When the calculation is complete, details of the solutions are written to the file **NPHUnoCCnoPO.txt**.

In the Project Explorer, double-click **NPHUnoCCnoPO Reflex PSolve\NPHUnoCCnoPO.txt** to open it.

The lowest R_{wp} value reported is about 28%. Now examine the packing arrangement of the best solution, paying particular attention to the hydrogen bond patterns (if any) and close contacts.

Using the Project Explorer, open **NPHUnoCCnoPO Reflex PSolve\NPHUnoCCnoPO Solution.xsd**.

Right-click on the structure and choose **Display Style** from the shortcut menu to open the Display Style dialog. On the **Lattice** tab, set the **Max** values for **A**, **B**, and **C** to **2.00** and close the dialog.

Now search the crystal structure for close contacts.

Choose **Build | Close Contacts** from the menu bar to open the Close Contact Calculation dialog. Click the **Calculate** button and close the dialog.

To make the crystal structure easier to view, you can switch off the display of the motion groups.

Hold down **ALT** and double-click on a motion group. All the motion groups are selected. To switch off the display of the motion groups, select **Visibility | Hide** from the **View** menu. Press **CTRL + D** to deselect the motion groups.

The best solution has a number of close contacts and voids.

6. To attempt structure solution with preferred orientation correction, but without a close-contact penalty

Now try to refine preferred orientation parameters during the global search.

Select **File | Save Project** from the menu bar and **Close** all the open documents apart from **P21_cell.xsd** and **NPHU.xcd**.

Open the **Reflex Powder Solve** dialog and make **P21_cell.xsd** the active document.

On the **Sample Params** tab, select **March-Dollase** from the dropdown list for **Preferred orientation** in the **Value** column. Check the boxes to refine all the preferred orientation parameters, **a***, **b***, **c***, and **RO**.

On the **Experimental Data** tab, select **NPHU.xcd**.

On the **Job Control** tab, ensure **My Computer** is the **Gateway location** and change the **Job description** to **NPHUnoCC**.

Click the **Solve** button and **close** the Reflex Powder Solve dialog.

As before, the new job will appear in the Job Explorer, where you can monitor the progress of the calculation. Various documents will be generated automatically and updated as the job progresses.

When the calculation is complete, **open** the folder **NPHUnoCC Reflex PSolve** in the Project Explorer and double-click on the text document **NPHUnoCC.txt**.

The lowest R_{wp} value reported should be about 19%. You should now examine the packing arrangement of the best solution, particularly any close contacts.

In the Project Explorer, double-click on **NPHUnoCC Reflex PSolve\NPHUnoCC Solution.xsd**. Open the **Display Style** dialog, on the **Lattice** tab, set the **Max** values for **A**, **B**, and **C** to **2.00** and close the dialog.

Click the **Calculate Close Contacts** button .

Switch off the display of the motion groups.

Once again, the structure exhibits several close contacts and voids. Therefore, it can be concluded that there is not enough information in the powder diffraction pattern to determine the correct crystal packing. In order to arrive at the correct structure, it will be necessary to introduce an additional chemical requirement in the form of a close-contact penalty.

7. Structure solution using a combined figure of merit

Obviously, the crystal structure of 4-nitrophenylhexylurethane will not contain overlapping atoms and this requirement can be incorporated into the optimization process by applying a close-contact penalty. This may allow the correct structure to be determined, even though the powder pattern alone does not contain enough information to distinguish it from other solutions.

Select **File | Save Project** from the menu bar and **close** all the open documents apart from **P21_cell.xsd** and **NPHU.xcd**.

Open the **Reflex Powder Solve** dialog and make **P21_cell.xsd** the active document.

On the **Sample Params** tab the preferred orientation parameters shown here are the best values found in the previous run. Change them back to the default values, **a* = 0, b* = 0, c* = 1, R0 = 1**.

On the **Structure Params** tab, check the appropriate checkbox in the **Refine** column of the list of parameters to include the previously neglected C-C-C-H torsion of the methyl group in the refinement.

On the **Setup** tab, check the **Apply close contact penalty** checkbox. Click the **More...** button to open the Powder Solve Options dialog. Change the **Radius scale factor** to **0.95** and click the **OK** button.

On the **Experimental Data** tab, select **NPHU.xcd**.

On the **Job Control** tab, ensure **My Computer** is the **Gateway location**. Enter **NPHUCC** as the **Job description**.

Click the **Solve** button and **close** the Reflex Powder Solve dialog.

The progress of the calculation can be followed using the Job Explorer.

When the calculation is complete, **Open** the folder **NPHUCC Reflex PSolve** in the Project Explorer and double-click on the text document **NPHUCC.txt**.

The lowest R_{wp} value of the best solution (lowest R_{comb}) should be about 19.5%

In the Project Explorer, double-click on **NPHUCC Reflex PSolve\NPHUCC Solution.xsd**. Open the **Display Style** dialog, on the **Lattice** tab, set the **Max** values for **A, B, and C** to **2.00** and close the dialog.

Click the **Calculate Close Contacts** button .

Switch off the display of the motion groups.

Looking at the best solution from the calculation using a close-contact penalty reveals that there are still too many close contacts for this structure to be viable.

Next investigate some of the other solutions that were found in the calculation. Each time a new structure is arrived at in the cycle of refinement, it is written to a trajectory file. The best solutions from each cycle of refinement can be extracted from this trajectory file.

Select **File | Save Project** from the menu bar and **close** all the open documents. Open the trajectory file **NPHUCC Reflex PSolve\NPHUCC.xtd**.

Open the **Reflex Powder Solve** dialog. On the **Analysis** tab, set the **X-axis property** to **Frame Number**, the **Y-axis property** to **Rwp**, and the **Graph style** to **Line**. Click the **Analyze** button and close the dialog.

This produces a plot of R_{wp} against frame number for all the solutions recorded in the trajectory file.

Make **NPHUCC.xtd** the active document and click the **Animation Mode** arrow , select **Options** from the dropdown list to open the Animation Options dialog. Check the **Recalculate atom visibility every frame** checkbox and close the dialog.

Make **NPHUCC.xcd** the active document and select the **Chart Viewer Selection Mode** tool  from the Chart Viewer toolbar. Examine the chart document to find the frame with the next lowest R_{wp} after the best solution. Click on the point representing this frame in the plot.

The trajectory document is updated with the structure found in this frame. You can now examine the structure for close contacts as you did previously for the best solution. Check the five frames with the lowest R_{wp} values and find the one with the fewest close contacts.

Now examine the hydrogen bonding in the selected structure.

Click the **Calculate Hydrogen Bonds** button .

The hydrogen bonds in the crystal are drawn as pale blue dotted lines. You should find that the hydrogen bonds overlay the close contacts, showing that the only close contacts in the structure are due to hydrogen bonds. You should also find that the alkyl chain adopts a low energy all-trans conformation. However, before you conclude that you have solved the crystal structure, you should perform some additional reality checks. This is always advisable and especially important in cases where the structure has been solved using a preferred orientation correction, which modifies the intensity ratios.

8. To analyze the solution

A straightforward way to check that a structure is chemically sensible is to verify that it is energetically stable. The simplest way to do this is to perform a forcefield minimization, while keeping the lattice parameters constrained to their experimentally confirmed values.

Make **NPHUCC.xtd** the active document and select **File | Export...** from the menu bar to open the Export dialog. Select **Materials Studio 3D Atomistic Files** from the **Save as type** dropdown list, name the new file **best_solution_to_verify.xsd**, and navigate to the **Documents** folder, at the same level as **P21_cell.xsd**. Click the **Save** button.

Select **File | Save Project** from the menu bar and then **Window | Close All**. Open **best_solution_to_verify.xsd**.

Click the **Forcite** button  and choose **Calculation** from the dropdown list to open the Forcite Calculation dialog.

Select **Geometry Optimization** from the **Task** dropdown list and click the **More...** button to open the Forcite Geometry Optimization dialog. Make sure that the **Optimize cell** checkbox is unchecked, so that the experimental lattice is preserved, and close the dialog.

On the **Energy** tab, select **COMPASSIII** from the **Forcefield** dropdown list. Ensure that **Ewald** is selected for both the **Electrostatic** and **van der Waals** summation methods.

On the **Job Control** tab, select **My Computer** as the **Gateway location**. Click the **Run** button and close the dialog.

A new folder called **best_solution_to_verify** Forcite GeomOpt is created in the Project Explorer. When the job is complete, the minimized structure is saved in the document **best_solution_to_verify.xsd** and the results of the calculation are contained in the text file **best_solution_to_verify.txt**, both of which are in the new folder. If you inspect the optimized structure you will find that it is basically the same as what you started with, except that the alkyl chain is closer to a perfect all-trans conformation. By visual inspection or by superposition you can verify that the optimized structure is very close to the Powder Solve solution. Therefore, it can be concluded that the packing arrangement found by Powder Solve is stable.

Now check that the observed preferred orientation parameters are consistent with the structural properties of the solution.

The lattice parameters are approximately $a = 21.6 \text{ \AA}$, $b = 5.8 \text{ \AA}$, $c = 5.6 \text{ \AA}$, and $\beta = 96.8^\circ$. With one axis four times longer than the other two, a plate-like morphology can be expected with the smallest crystal dimension being more or less parallel to the a -axis. The preferred orientation correction for compounds forming plate-like crystals is expected to have $R0 < 1$ in a direction perpendicular to the plates.

In the Project Explorer, double-click on **NPHUCC - Powder Solve** in the **NPHUCC Reflex PSolve** folder. Select the **Sample Params** tab and verify that the preferred orientation parameters are in good agreement with the crystal structure.

9. To refine the solution

It has been established that the amount of information contained in the powder pattern is insufficient to find the right packing arrangement. Therefore, it can be expected that a Rietveld refinement alone will not be sufficient to refine the crystal structure. In this case, you have verified that COMPASSIII is suitable to optimize the crystal structure. Consequently, COMPASSIII can also be used to refine it. To do this, you should start by optimizing the molecular conformation in the crystal environment while continuing to keep the cell parameters fixed.

Select **File | Save Project** from the menu bar and **close** all the open documents.

In the Project Explorer, double-click on **best_solution_to_verify.xsd** in the **best_solution_to_verify Forcite GeomOpt** folder. This is the forcefield-minimized structure produced by Forcite. Make a copy of it by selecting **File | Save As...** from the menu bar. Rename the copy **best_solution_refining.xsd** and **Save** it in the **Documents** folder.

You can now use Rietveld refinement to further refine the structure. After optimization with the COMPASSIII forcefield, you can assume that the molecular conformation is close to its final structure. Thus, you can keep it fixed during the Rietveld refinement. Begin by loading the Pawley refinement parameters.

In the Project Explorer, right-click on **NPHUCC - Powder Solve** in the **NPHUCC Reflex PSolve** folder and select **Powder Refinement** to open the Reflex Powder Refinement dialog. Click the **Calculate** button.

The Pawley R_{wp} factor should be 14.6%, as it was at the beginning of the calculation.

On the **Setup** tab, change the **Type** from Pawley to **Rietveld**. Click the **More...** button for **Convergence quality** to open the Refinement Convergence Options dialog. Set the **Number of cycles** to **10** and click the **OK** button.

On the **Pattern** tab, uncheck the refinement parameters **H/L** and **S/L**.

Select the **Lattice** tab and make sure that all the cell parameters checkboxes are checked. Check the **Keep fractional coordinates fixed during lattice changes** checkbox.

On the **Sample** tab, change the **Temperature factors** to **Global isotropic** and check the appropriate checkbox to refine them.

On the **Display** tab, select **New** from the **Chart view** dropdown list.

On the **Structure** tab, deselect all the torsions, leaving only the refinement of the motion group position switched on, so that all the checkboxes except the first one are unchecked. Click the **Refine** button and close the dialog.

The final R_{wp} factor should be around 26%. The structure is in good agreement with the reported single crystal structure ([Yakimanski et al., 1997](#)).

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Yakimanski, A. V.; Kolb, U.; Matveeva, G. N.; Voigt-Martin, I. G.; Tenkova, A. V. "The Use of Structure Analysis Methods in Combination with Semi-Empirical Quantum-Chemical Calculations for the Estimation of Quadratic Nonlinear Optical Coefficients of Organic Crystals", *Acta Crystallogr., Sect. A*, **53**, 603-614 (1997).

Reflex Plus: Structure solution of 4-nitrophenylhexylurethane using a close-contact penalty

BIOVIA would like to thank Dr Ute Kolb of the University of Mainz, Germany, for supplying the experimental powder diffraction pattern for NPHU.

Chapter 23: Sorption tutorials

The following tutorials illustrate how to utilize Sorption's capabilities.

- [Predicting the loading of CH₄ in zeolite MFI with Sorption](#)
- [Predicting the loading of ions in Al-substituted zeolite MFI](#)

Predicting the loading of CH₄ in zeolite MFI with Sorption

Purpose: Illustrates how to use Sorption to compute a loading curve for a molecule in a zeolite framework.

Modules: Materials Visualizer, Sorption

Time: 

Prerequisites: Project management Visualizer Tutorial

Background

You can use Sorption to simulate sorption of small molecules, called sorbates (guest molecules), into porous 3D frameworks (hosts). The frameworks are typically microporous inorganic structures such as zeolites and aluminophosphates. Characterizing the behavior of these materials has important applications in the fields of catalysis and separations technology.

The Sorption module is designed for use by experimental scientists, as well as computational chemists. Output-analysis features, such as automatic calculation and display of isotherms, make it easy to directly compare Sorption data with bench results.

Introduction

In this tutorial, you learn how to use Sorption to calculate a loading curve for a small molecule, CH₄, in a framework, zeolite MFI. A loading curve is a series of fixed pressure (grand canonical ensemble) calculations performed over a series of fugacities.

This tutorial covers:

- [Getting started](#)
- [To set up the calculation](#)
- [To run the calculation](#)
- [To analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CH4_MFI** as the project name.

This creates a new project with **CH4_MFI** listed in the Project Explorer. Begin by importing the structures you need.

Sorption: Predicting the loading of CH₄ in zeolite MFI with Sorption

Select **File | Import...** from the menu bar or click **Import**  to open the Import Document dialog. Navigate to **Structures/orgamics** and select **methane.xsd**, then click **Open**.

Open the **Import Document** dialog again and navigate to **Structures/zeolites**, select **MFI.xsd**, and click **Open**.

Sorption calculations require P1 crystal structures (those without any symmetry) as inserting the guest molecules breaks any symmetry that is present. Change the symmetry of MFI to P1.

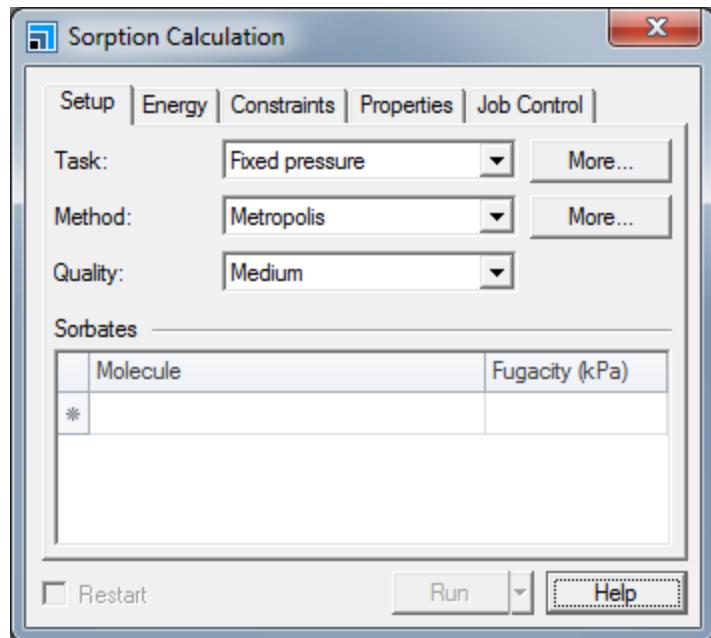
Ensure that **MFI.xsd** is the active document and select **Build | Symmetry | Make P1** from the menu bar.

2. To set up the calculation

Now you are ready to specify the parameters for the calculation.

Click **Sorption Tools**  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the Sorption Calculation dialog.



Sorption Calculation dialog, Setup tab

Select **Adsorption isotherm** as the **Task** and **Metropolis** for the **Method**. For the **Quality**, choose **Coarse**.

In the **Sorbates** section, click first cell in the **Molecule** column and select **methane.xsd** from the dropdown list.

Note: Use the **Coarse** option so that this tutorial runs quickly. A realistic statistical analysis requires the **Medium** or **Fine** setting.

You need to specify the upper and lower fugacities at which to perform calculations and the number of intervals between them. In this example, use a lower fugacity of 1 atm (101.325 kPa) and an upper fugacity of 10 atm (1013.25 kPa).

Click in the cell for the **Start** column of the **Sorbates** grid and enter a value of **101.33** kPa, enter a value of **1013** kPa in the **End** column.

Click **More...** for the **Task** to open the Sorption Isotherm dialog. For the **Fugacity steps**, specify **9** and select the **Logarithmic** checkbox. For the **Temperature** specify **298** K.

Close the Sorption Isotherm dialog.

Next select the forcefield options to use in the calculation.

On the **Energy** tab of the Sorption Calculation dialog, choose **COMPASSIII** as the **Forcefield** and for the **Charges** choose **Forcefield assigned**.

For the **Quality** of the energy calculation, choose **Medium**. For the **Electrostatic** summation method, select **Ewald & Group** and for the **van der Waals** summation method choose **Atom based**.

Finally, make sure that you request the appropriate properties calculations.

On the **Properties** tab of the Sorption Calculation dialog, ensure selection of the checkboxes for **Energy distribution**, **Density field**, and **Energy field**.

For the **Sample interval**, specify **50**.

For the **Grid resolution**, select **Medium**, this automatically defines the **Grid interval** as **0.4 Å**.

3. To run the calculation

Now define the job control options and start the calculations.

On the **Job Control** tab of the Sorption Calculation dialog, select an appropriate server for the **Gateway location**.

Click **Run** and **close** the dialog.

This creates a new folder in the Project Explorer, called **MFI Sorption Isotherm**. As the job progresses, updates are presented in both chart and text documents. The calculation completes quickly.

Sorption performs a fixed pressure calculation at 10 different values of fugacity ranging from 101 kPa to 1013 kPa. Sorption returns the following graphs for each fugacity, you can use these to monitor the status of the calculation.

- **MFI_Etotal.xcd** displays the value of energy at each Monte Carlo move, showing the total energy and various components.
- **MFI_Energy.xcd** displays an energy distribution histogram.
- **MFI_Loading.xcd** displays the instantaneous and average loading (number of molecules per unit cell) at each step.

Sorption: Predicting the loading of CH₄ in zeolite MFI with Sorption

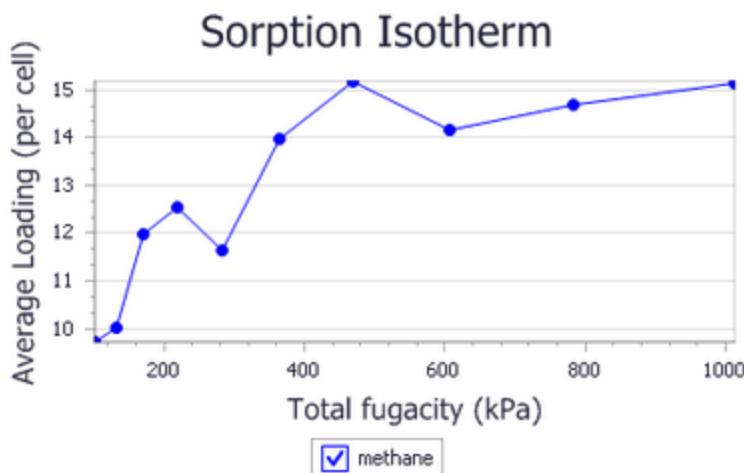
When sufficient Monte-Carlo steps accumulate, each of the graphs listed above converges on a final value. When the calculation completes the requested number of steps, the program restarts at the next value of fugacity.

Note: The temporary documents, **Status.txt**, **MFI_Energy.xcd**, **MFI_Etotal.xcd**, **MFI_Loading.xcd**, and **MFI.xsd**, are only relevant at run time and you can disregard these once the job completes. The output documents, **MFI.txt**, **MFI.std** and **MFI_Isotherm.xcd** contain the final results of the Sorption job.

4. To analyze the results

Click **OK** to close the Job Completed dialog.

Locate the output folder for the Sorption job, **MFI Sorption Isotherm**, in the Project Explorer and open the adsorption isotherm results file, **MFI Isotherm.xcd**.



Adsorption isotherm for CH₄ in MFI computed by Sorption

The adsorption isotherm generated in this tutorial is not very smooth because its generation used coarse settings. You can obtain a smoother and more realistic curve with finer grained settings.

Note: Your results may not look exactly like the images in the tutorial because of the random nature of Monte-Carlo calculations, but they are qualitatively similar.

The adsorption isotherm displays the adsorption in molecules per cell at each fugacity. In a typical case, the curve rises toward a saturation point value beyond which no more molecules can be adsorbed.

Tip: The calculation returns field values for every fugacity. The **MFI.xsd** 3D Atomistic document in the *Project Explorer* contains the results from the final fugacity.

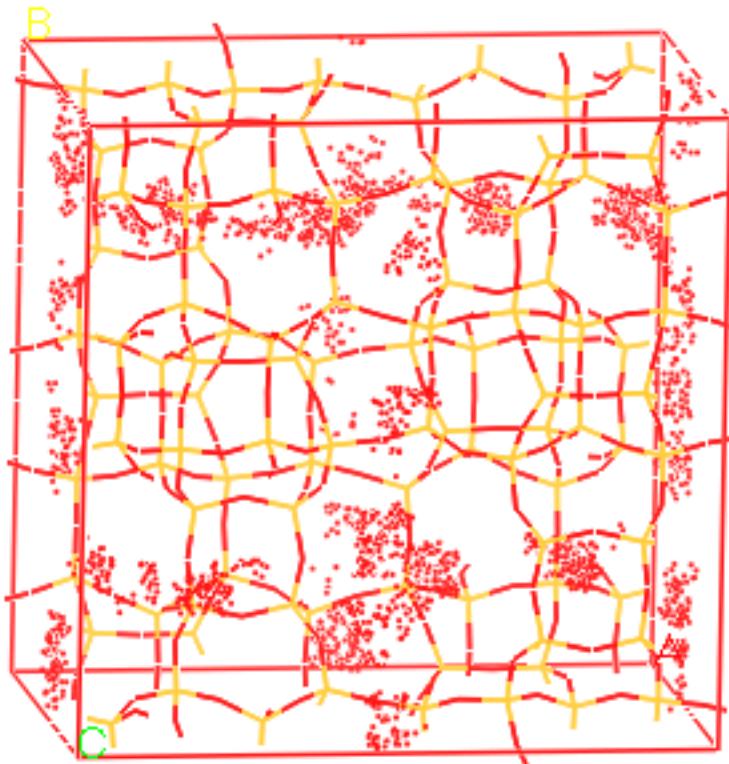
Next examine the density and energy fields returned by Sorption.

Double-click the **MFI.std** study table document in the Project Explorer.

The study table includes the total energy, fugacity, and energy components for each interval on the loading curve.

Locate the entry in the third row of the study table and double-click the structure **MFI_structure_3**.

This displays a *Detail View* similar to that below.



Density field for CH₄ in MFI computed by Sorption

The red output field represents a density distribution of CH₄ molecules in the MFI lattice framework. This grid representation of the density distribution has a resolution 0.4 Å. Results from the Monte-Carlo calculation are binned onto this grid. Regardless of the number of steps in the calculation, the amount of data displayed is constant.

Tip: You can change the resolution of the grid at run time by using a different sample interval on the *Properties* tab.

Now change the volumetric representation of the results to get a better insight into the location of energy "hot spots" in the cell.

Select **View | Toolbars | Volume Visualization** from the menu bar to display the Volume Visualization toolbar.

There are two fields in the *Detail View*, a density field and an energy field. Begin by selecting the density field.

Click **Volumetric Selection** on the Volume Visualization toolbar to open the Volumetric Selection dialog. Ensure selection of the **methane-Density** checkbox.

Now change the display of the field.

Sorption: Predicting the loading of CH₄ in zeolite MFI with Sorption

Right-click in the Detail View of **MFI_structure_3** and choose **Display Style** from the shortcut menu to open the Display Style dialog.

On the **Field** tab, choose **Color by field values** in the **Coloring** section.

The field changes from a uniform red to a range of colors that represent the different density values.

Tip: To see the values associated with each color, click *Color Maps*  on the **Volume Visualization** toolbar.

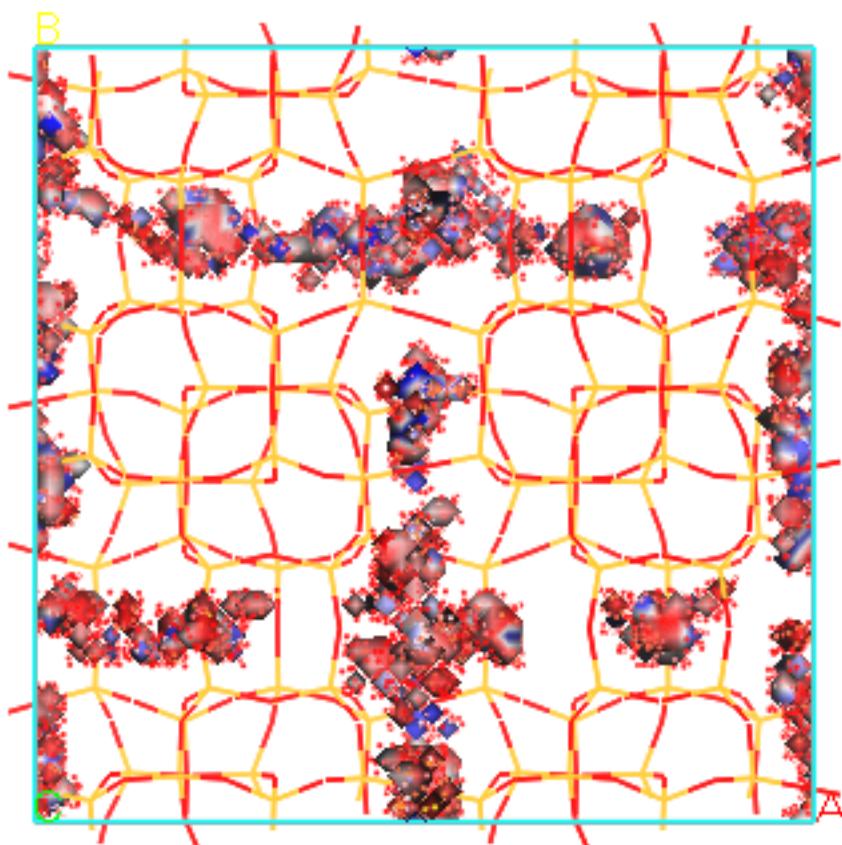
Now generate a display that combines the energy and density distribution information.

Select a display style of **Empty** on the **Field** tab of the Display Style dialog. Click **Create Isosurfaces**  on the **Volume Visualization** toolbar to open the Choose Fields To Isosurface dialog. Select **methane-Density of MFI** and click **OK** to generate an isodensity surface.

When the isosurface appears, click it once to select it.

On the **Isosurface** tab of the Display Style dialog, for the **Isovalue** specify **0.002**. Select **methane-Potential of MFI** from the **Mapped field** dropdown list.

You have created a surface of constant density and colored it by the potential energy. In this display, dark blue areas have the lowest energy and dark red the highest energy. You can use this analysis to look for favorable binding sites in the lattice framework.



Isodensity surface colored by potential for CH₄ in MFI

This is the end of the tutorial.

Predicting the loading of ions in Al-substituted zeolite MFI

Purpose: Illustrates how to use Sorption to locate the positions of extra-framework cations in a zeolite.

Modules: Materials Visualizer, Sorption

Time:  

Prerequisites: [Predicting the loading of CH₄ in zeolite MFI with Sorption](#)

Background

Sorption is used to simulate sorption of small molecules, called sorbates (guest molecules), into porous 3D frameworks (hosts). The frameworks are typically microporous inorganic structures such as zeolites and aluminophosphates. In most active forms of zeolites some Si atoms have been replaced by Al anions. There must be enough extra-framework cations to balance the charge of the Al ions.

The Sorption module can perform calculations on ionic systems, and this can be used to predict the locations of the cations. However, assigning charges to the system can be problematic.

Introduction

In this tutorial, you will learn how to use Sorption to calculate the positions of Na cations in zeolite MFI.

This tutorial covers:

- [Getting started](#)
- [To prepare the structures](#)
- [To set up the calculation](#)
- [To run the calculation](#)
- [To analyze the results](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Al_MFI** as the project name.

The new project is created with **Al_MFI** listed in the Project Explorer. You will begin by importing the structures you will need.

Select **File | Import...** from the menu bar or click the **Import** button  to open the Import Document dialog. Navigate to **Structures/zeolites**, select **MFI.xsd** and click the **Open** button.

Sorption calculations require P1 crystal structures (those without any symmetry) as inserting the guest molecules will break any symmetry that is present. You will change the symmetry of MFI to P1.

Select **Build | Symmetry | Make P1** from the menu bar.

2. To prepare the structures

You need to replace five of the Si atoms with Al, for purposes of the tutorial, you can select any 5 at random. In a realistic zeolite, however, no two Al atoms should be bonded to the same oxygen atom.

From the menu bar, select **Tools | Materials Studio Scripts | Utilities | Substitutional Disorder**. In the Substitutional Disorder dialog, enter **5** for **Percent_Atoms**, and click **OK**.

The selected Si atoms will be changed to Al atoms, colored pink in the 3D Viewer.

Tip: It is easier to select individual atoms if you change the display style to *Ball and Stick*.

Finally, you will need to create a document that contains the extra-framework Na cation that will be used to balance the charges on the Al.

Select **File | New...** from the menu bar to open the New Document dialog. Select **3D Atomistic** and click the **OK** button.

You will add a single sodium atom to this document.

Click the **Sketch Atom** button  on the **Sketch** toolbar and then the **Element used to sketch** button. Select **Periodic Table...**, choose **Na** and click the **OK** button.

Click anywhere in the 3D Viewer to add a new Na atom. Click the **3D Viewer Selection Mode** button  on the **3D Viewer** toolbar to exit sketch mode.

The new document with the Na atom has a default name of **3D_Atomistic.xsd**, you will rename this document to **Na atom**.

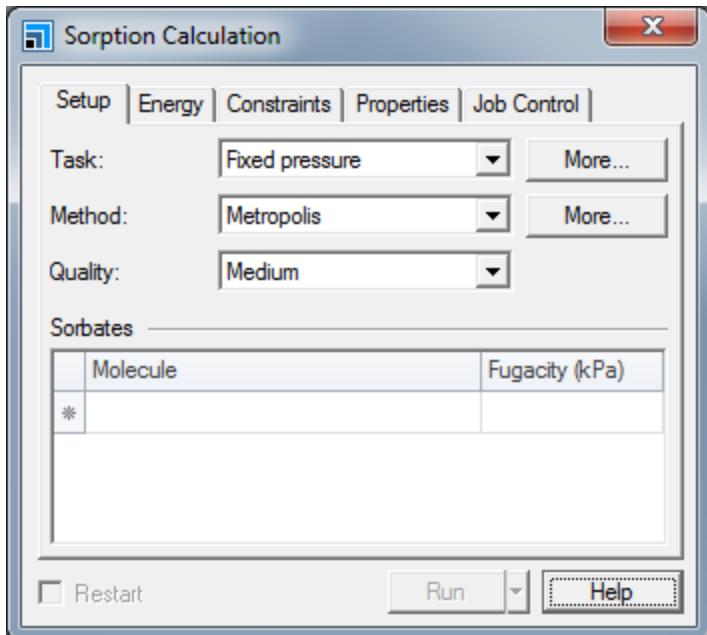
Rename the new document **Na atom.xsd**.

3. To set up the calculation

Now you are ready to set the parameters for the calculation.

Ensure that **MFI.xsd** is the active document. Click the **Sorption** button  on the **Modules** toolbar and choose **Calculation** from the dropdown list.

This opens the Sorption Calculation dialog.



Sorption Calculation dialog, Setup tab

Select **Locate** as the **Task** and **Metropolis** for the **Method**, set the **Quality** to **Coarse**.

Click the **More...** button for the task, to open the Sorption Locate dialog. Ensure that the **Automated temperature control** and **Adjust step sizes** checkboxes are checked. Select **Return lowest energy frames**, and set the **Number of frames** to **10**. Close the Sorption Locate dialog.

In the **Sorbates** section of the Sorption Calculation dialog, click in the top cell in the **Molecule** column and select **Na atom.xsd** from the dropdown list. Enter **5** for the **Loading**.

Note: The **Coarse** option is used so that this tutorial is not time consuming. A realistic statistical analysis would require the **Medium** or the **Fine** setting.

Next you will select the forcefield options that will be used in the calculation. At this stage you will also assign atomic charges to the atoms in the system. There are several ways that you can assign charges to atoms, but in this tutorial you will assign charges by hand to each atom type.

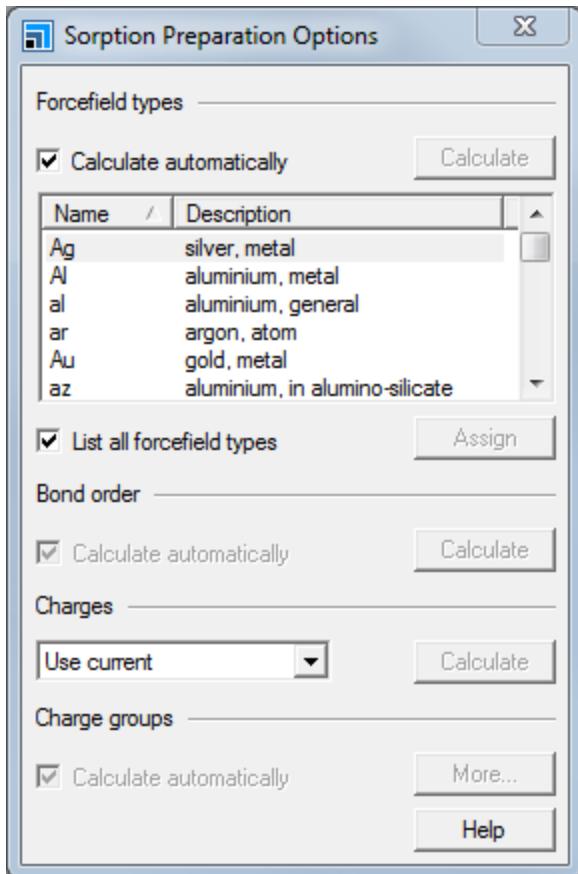
On the **Energy** tab of the Sorption Calculation dialog, select **cvff** from the **Forcefield** dropdown list.

Select **Use current** from the **Charges** dropdown list and set the **Quality** to **Medium**.

Select **Ewald** from the **Electrostatic** dropdown list.

Note: The **Electrostatic** option must be set to **Ewald** for systems where the framework and sorbates are charged.

Click the **More...** button for the **Forcefield** to open the Sorption Preparation Options dialog.



Sorption Preparation Options tab

Before you can assign charges, you need to assign forcefield types.

Ensure that **MFI.xsd** is the active document. On the Sorption Preparation Options dialog **unchecked** the **Calculate automatically** checkbox and click the **Calculate** button.

Make **Na atom.xsd** the active document and click the **Calculate** button again. **Close** the Sorption Preparation Options dialog.

Tip: You can see which forcefield types were assigned by using the Label dialog.

Make **MFI.xsd** the active document. Hold down **ALT** and **double-click** one of the Si atoms.

All the Si atoms are selected.

Select **Modify | Charges** from the menu bar to open the Charges dialog. On the **Edit** tab select the **Set all charges to** radio button and enter **2.4**. Click the **Assign** button.

Repeat this procedure to assign charges of **1.4** to all **Al** atoms and charges of **-1.2** to all **O** atoms.

Make **Na atom.xsd** the active document and assign the Na atom a charge of **1.0**. **Close** the Charges dialog.

Sorption: Predicting the loading of ions in Al-substituted zeolite MFI

The charges you assigned are the ones used by the cvff_aug forcefield. They have been optimized for simulations of silicates, aluminosilicates, clays and aluminophosphates.

As a result of using these charges, note that the total charge for all the Si atoms is +218.4, for all O atoms it is -230.4 and for all the Al atoms the total charge is +7. The zeolite, therefore, has a total -5 charge. You have specified a loading of five Na atoms, each with a +1 charge, which will neutralize the total charge on the zeolite when they are added to the structure during the Sorption calculation.

4. To run the calculation

Now you will set the job control options and start the calculation.

On the **Job Control** tab of the Sorption Calculation dialog, select an appropriate server for the **Gateway location**.

Make sure that **MFI.xsd** is the active document.

Click the **Run** button and close the Sorption Calculation dialog.

A new folder, called **MFI Sorption Locate**, is created in the Project Explorer. As the job progresses, updates are presented in both chart and text documents.

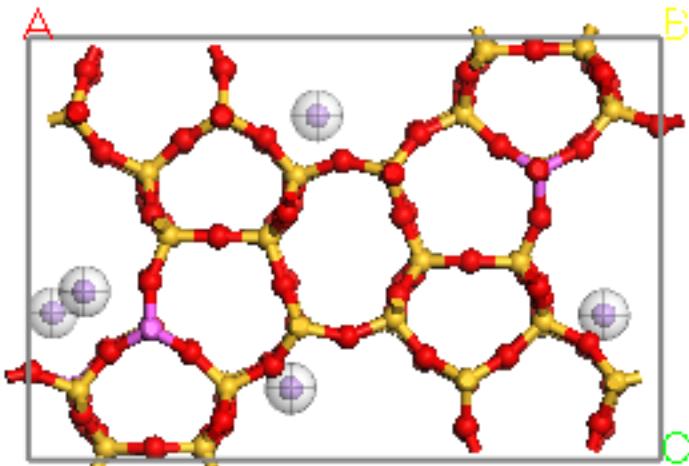
The following files are produced:

- **MFI.xsd** contains the minimum energy configuration of the sorbates and the framework.
- **MFI.txt** is the output file from the calculation. It contains information on the number and type of Monte Carlo moves.
- **MFI Low energy.xtd** is a trajectory file containing the lowest few configurations. The number of configurations can be specified as an input parameter to the Locate job.

Note: The file **MFI Low energy.xtd** is only produced when you select *Return lowest energy frames* on the *Sorption Locate* options dialog.

5. To analyze the results

Double-click on **MFI.xsd** in the **MFI Sorption Locate** folder in the Project Explorer.



Minimum energy configuration of Na in MFI computed by Sorption

The results of your job will be different depending up the location of the Al ions and on the random nature of the Monte-Carlo calculation. Note that the sorbates are displayed within a Motion Group to highlight their locations.

Double-click on **MFI_Etotal.xcd** in the Project Explorer.

The total energy and energy components are plotted as a function of step. In a converged calculation, the total will converge to an asymptotic value. Because you used coarse settings for this tutorial, the energy may not have converged.

Examine again the final structure in **MFI.xsd**. As part of a scientific investigation, you would normally use this to perform subsequent calculations within Materials Studio. You could, for example, use this model to perform calculations of the loading of CH₄ as in the tutorial [Predicting the loading of CH₄ in zeolite MFI with Sorption](#). What effect do you think the presence of the Na cations will have on the loading?

You could also perform a geometry optimization with DMol³ or CASTEP to obtain a more accurate structure and energy.

This is the end of the tutorial.

Chapter 24: Synthia tutorials

The following tutorial illustrates how to utilize Synthia's capabilities.

Predicting the properties of two random copolymers

Purpose: Illustrates how to use Synthia to predict properties for random copolymers.

Modules: Materials Visualizer, Synthia

Time: 

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

The weight average molecular weight (M_w), the number average molecular weight (M_n), and the polydispersity of the system are important properties for characterizing a polymer. In dilute solutions of polymers, light-scattering experiments are one of several methods used to measure M_w . For dilute solutions of polymers, the rate of change of the refractive index with the concentration of the polymer, known as the specific refractive index increment (dn/dc), can be used to predict the optical constant, K_c . When K_c is divided by the excess Rayleigh ratio, ΔR , this gives a concentration-dependent function that can be extrapolated to a concentration of 0. When the concentration is 0, $K_c/\Delta R = I/M_w$, thus giving the value of M_w ([Young et al., 1991](#)). The specific refractive index increments can be defined as:

$$\frac{dn}{dc} = \frac{n_p - n_s}{\rho_p}$$

where n_p is the refractive index of the polymer, n_s is the refractive index of the solvent, and ρ_p is the density of the polymer.

Synthia enables you to predict many properties of repeat units. Among these are the refractive index and the density, which you can then use to predict the specific refractive index increments.

Introduction

In this tutorial, you will build two copolymers, poly(*N*-benzyl methacrylamide-*co*-acrylamide) and poly(*N*-methyl methacrylamide-*co*-acrylamide). You will use Synthia to predict the density and refractive index for a range of concentrations from pure acrylamide to pure *N*-benzyl methacrylamide or pure *N*-methyl methacrylamide. Once you have these data, you will define a new function in the study table to predict dn/dc and plot this for the two copolymers. This work is based on results from a study by Bicerano ([1994](#)).

This tutorial covers:

- [Getting started](#)
- [To sketch the repeat units](#)
- [To define the structures as repeat units](#)
- [To define the copolymer](#)
- [To work with the study table](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

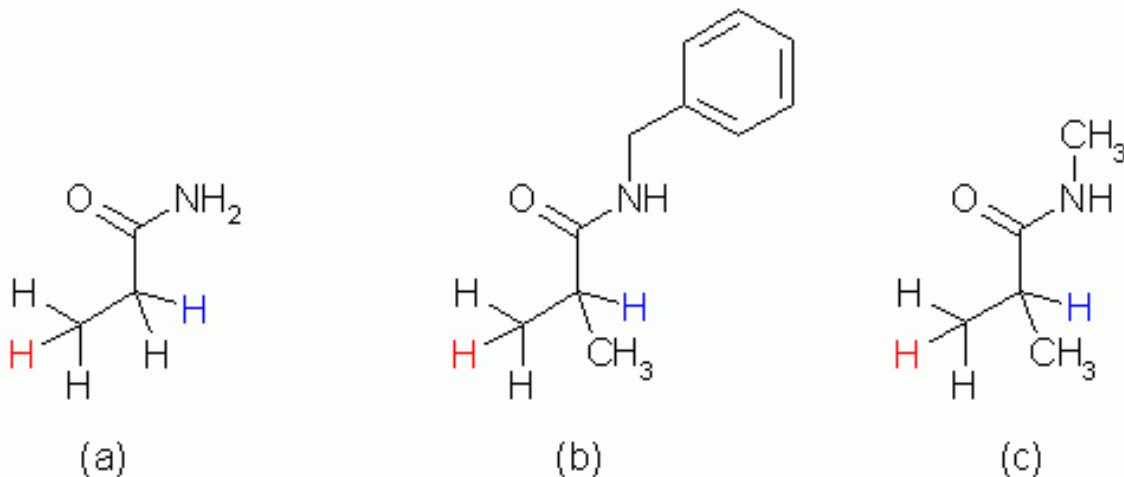
Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **Copolymer** as the project name, click the **OK** button.

The new project is created with *Copolymer* listed in the Project Explorer.

2. To sketch the repeat units

The first stage in this tutorial is to sketch the three repeat units that will be used to generate the copolymers.



Repeat units used to generate the copolymers: (a) acrylamide; (b) *N*-benzyl methacrylamide; (c) *N*-methyl methacrylamide

Start by sketching acrylamide.

Click the **New** arrow on the toolbar and select **3D Atomistic Document** from the dropdown list. **Rename** the new document **acrylamide.xsd**.

Use the tools on the **Sketch** toolbar to construct acrylamide, as above.

Click the **Adjust Hydrogen** button then the **Clean** button .

Next sketch the other two fragments.

Open two more 3D Atomistic documents. Sketch *N*-benzyl methacrylamide and *N*-methyl methacrylamide, adjust the number of hydrogen atoms, and clean the structures. Rename the documents **N-benzyl.xsd** and **N-methyl.xsd**.

You should now have three 3D Atomistic documents containing the structures of the three monomers.

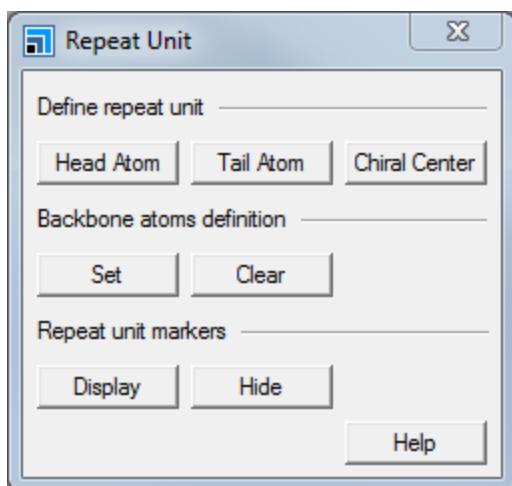
Tip: Calculations of the mechanical properties - bulk, shear, and Young's modulus, Poisson's ratio, shear yield stress, or brittle fracture stress - use the length of the repeat unit as a descriptor. Therefore, you should optimize the geometry of the repeat units using Forcite prior to performing Synthia calculations of these properties. All the calculations of other properties do not use the geometry of the structure and so optimization is not required.

3. To define the structures as repeat units

For Synthia to recognize the structures as repeat units, head and tail atoms must be defined. This is achieved using the Repeat Unit tool in the Polymer Builder functionality.

Ensure that **acrylamide.xsd** is the active document. Select **Build | Build Polymers | Repeat Unit** from the menu bar.

This opens the Repeat Unit dialog.



Repeat Unit dialog

The head/tail atoms are defined as hydrogen atoms attached to the two carbon atoms in the ethyl group (see the structures above).

Click the **3D Viewer Selection Mode** button  on the toolbar. Select the hydrogen shown in red in the figure above and click the **Head Atom** button on the Repeat Unit dialog. Select the hydrogen shown in blue as the tail atom and click the **Tail Atom** button. Repeat this process for the other two structures and close the Repeat Unit dialog.

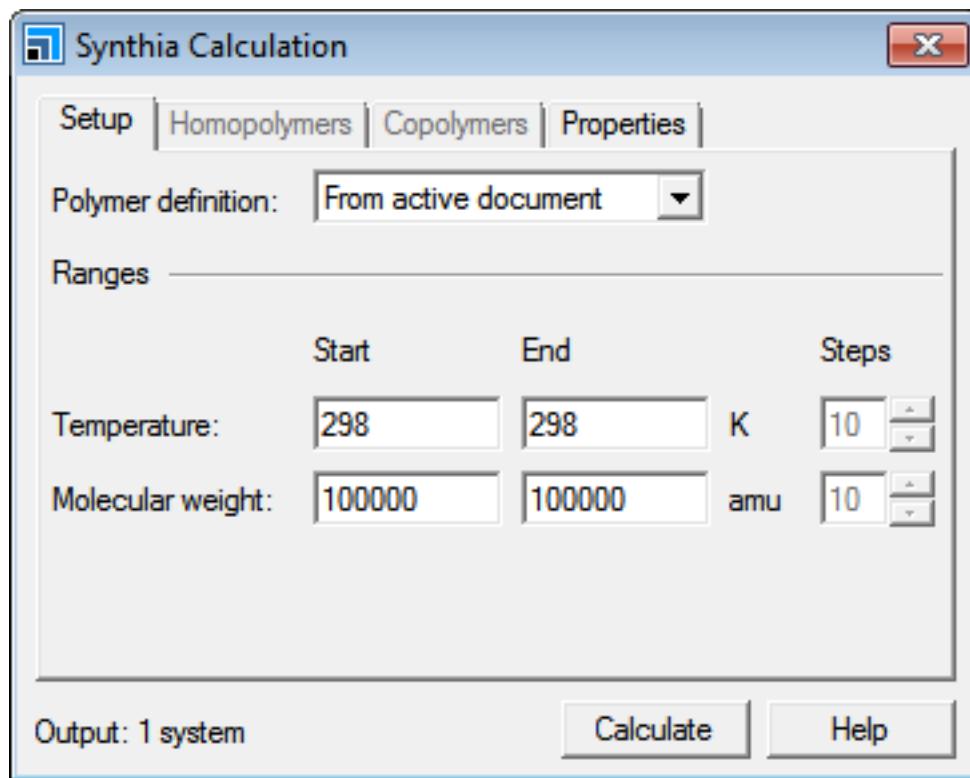
Select **File | Save Project** from the menu bar.

All of the structures are now identified as repeat units and can be used in a Synthia calculation.

4. To define the copolymer

Click the **Synthia** button  on the **Modules** toolbar and choose **Calculation** or select **Modules | Synthia | Calculation** from the menu bar.

This opens the Synthia Calculation dialog.



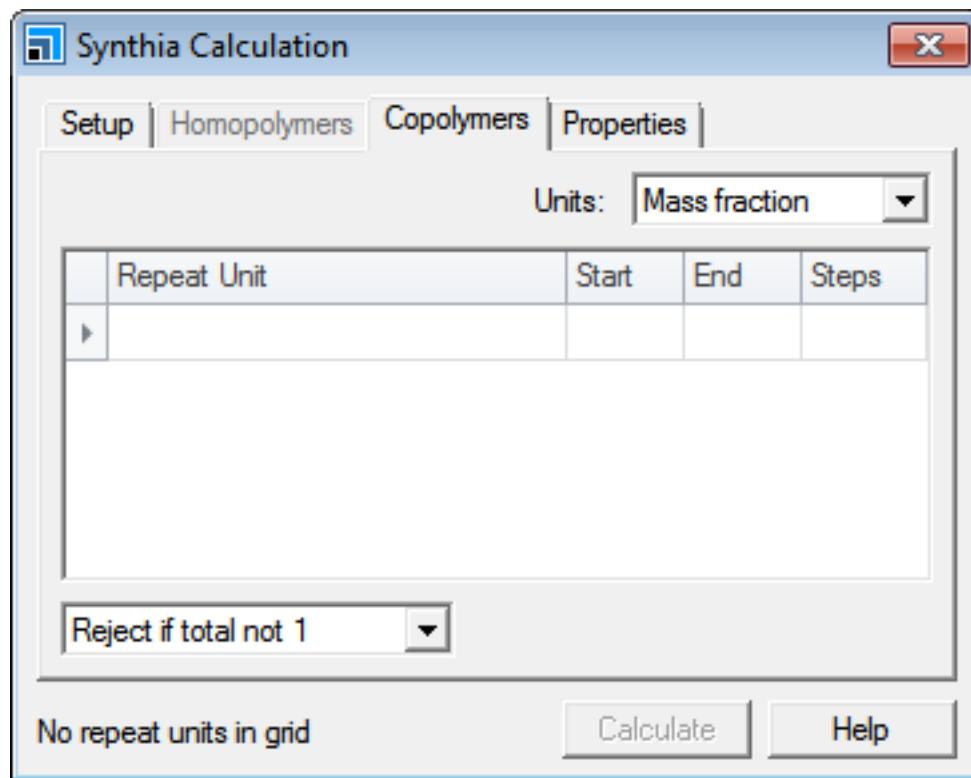
Synthia Calculation dialog, Setup tab

You have the option to calculate properties for the current repeat unit, select multiple homopolymers and calculate their properties, or generate one or more copolymers.

On the **Setup** tab, select **Random copolymers** from the **Polymer definition** dropdown list.

You are going to calculate the properties at 298 K and a constant molecular weight so you can move on to specify the copolymer.

Select the **Copolymers** tab.



Synthia Calculation dialog, Copolymers tab

You are going to define two copolymers. The first copolymer is acrylamide and *N*-benzyl methacrylamide. The second copolymer is acrylamide and *N*-methyl methacrylamide. You could define two separate copolymers and run two calculations but, as they share acrylamide as a repeat unit, it is easier to define them all in one calculation.

The first step is to add the common repeat unit.

Click in the Repeat Unit column on the first (empty) row. Click again to drop down the list of repeat unit libraries. Open the **Current project** item at the bottom of the list and check the box for **acrylamide**. Click outside the list area to close the drop down list.

The **Current project** filter shows all the structures in the current project. However, only structures defined as repeat units will activate the **OK** button.

Repeat units can be defined as sets and a set is displayed in braces, {}. If a set is defined, separate calculations will be performed for each unit in the set. This means you can generate more than one copolymer in the same calculation.

Click in the **Repeat Unit** column on the next row and open the drop down list. Open the **Current project** item and select both **N-benzyl** and **N-methyl**. Click outside the list area to close the drop down list.

The two repeat units are specified on the same line enclosed in braces, {}, meaning they are defined as a set.

For this example, you will vary the composition from pure acrylamide to pure *N*-benzyl methacrylamide or pure *N*-methyl methacrylamide. Therefore, the composition matrix should be edited to reflect this.

On the **Copolymers** tab, change the **Start** value from **1.0** to **0.0** in both rows.

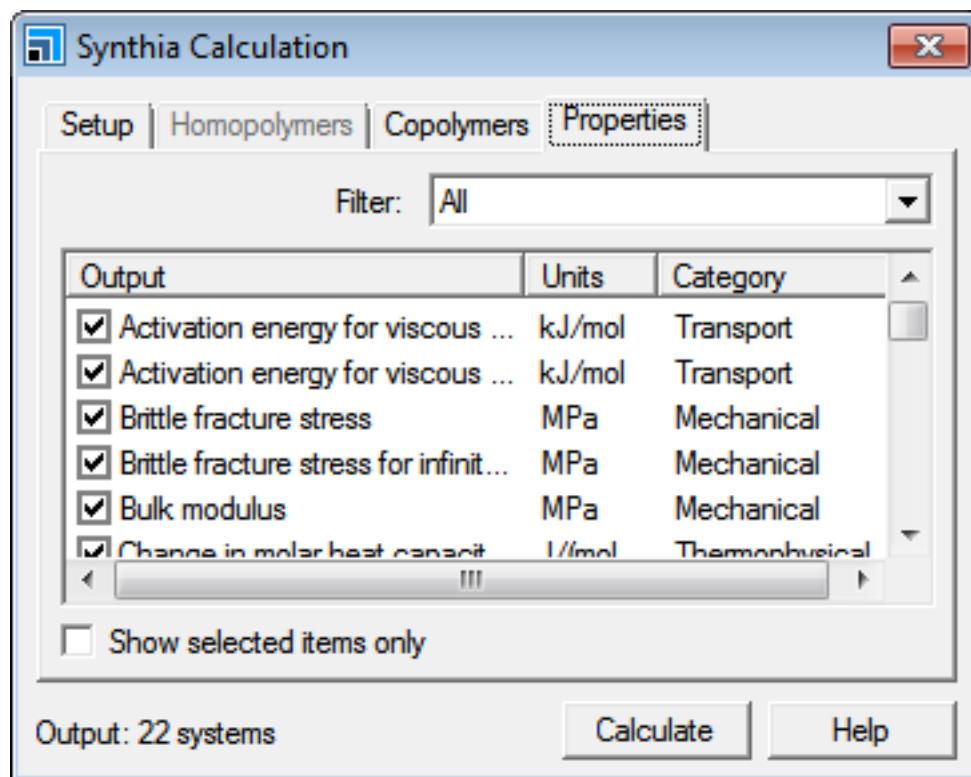
Finally, change the units from mass fraction to mole fraction.

Select **Mole fraction** from the **Units** dropdown list.

The number of calculations is shown at the bottom of the dialog and should now read *Output: 22 systems*.

You have now set up the copolymer calculation. The next step is to select the properties you wish to predict.

Select the **Properties** tab.



Synthia Calculation dialog, Properties tab

Initially, all the properties are selected. As the Synthia method uses underlying correlations to predict the properties, calculating all the properties does not take much more time than calculating only one. However, for this tutorial, you only need to calculate the refractive index and the density.

Select a row in the list and press **CTRL + A** to select all rows. Uncheck any of the checkboxes to uncheck all.

This will deselect all the currently selected properties.

Check the **Density** (not *Density at 298K*) checkbox and check the **Refractive index** (not *Refractive index at 298K*) checkbox.

Synthia: Predicting properties of two random copolymers

Tip: Click on any heading in the list of properties to sort the entries alphanumerically on that heading. Click again to toggle the sort order between descending and ascending.

The results of the calculation will be written to the currently selected folder; therefore, you should ensure that the root project folder is selected.

In the Project Explorer, click the project name (**Copolymer**). On the Synthia Calculation dialog, click the **Calculate** button and close the dialog.

The results of the calculation are displayed in a study table document called **Synthia.std**, which contains the results for both copolymers.

5. To work with the study table

The study table document contains different columns for the repeat units, their concentrations, the temperature, and the molecular weight. These are all the input variables into the Synthia calculation and are displayed in black text. The predicted properties, density and refractive index, are displayed in blue.

The two monomer units are currently displayed alternately in the study table. You can use the study table sorting tools to separate them into blocks.

Select column **C** and click the **Sort Ascending** button .

The results for *N*-benzyl methacrylamide are now displayed first and the results for *N*-methyl methacrylamide second.

Tip: If you wanted to separate the results entirely, you could select all the *N*-benzyl methacrylamide rows and use the *Filter* tool  to separate them into two worksheets on the same study table.

You can plot the properties directly from the study table.

Select column **D**. Hold down **CTRL** and select column **H**. Click the **Quick Plot** button .

A chart document called **Synthia Scatter plot.xcd** is displayed, which plots the refractive index against the mole fraction of *N*-benzyl and *N*-methyl methacrylamide.

Close all the open documents, except **Synthia.std** and **Synthia Scatter plot.xcd**. Select **Window | Tile Horizontally** from the menu bar to view the study table and the scatter plot simultaneously. Click on any point in the scatter plot.

Selecting points on the chart document highlights the corresponding rows in the study table.

To calculate the specific refractive index increment (dn/dc), you need to use both the refractive index and the density. The relationship being:

$$\frac{dn}{dc} = \frac{n_p - n_s}{\rho_p}$$

In this case, the refractive index of the solvent, water, is 1.33.

Ensure that **Synthia.std** is the active document. Click the **Define Function** button  on the toolbar to open the Define Function dialog.

In the **Expression** field, enter $(H-1.33)/G$. In the **Name** field, enter **Specific Refractive Index Increment**. In the **Description** field, enter **dn/dc** . Click the **OK** button.

A new column, column *I*, is automatically created and populated with the results of the calculation. You can now plot these against the comonomer mole fraction.

Select column **D** and column **I**. Click the **Quick Plot** button .

The following chart is displayed.

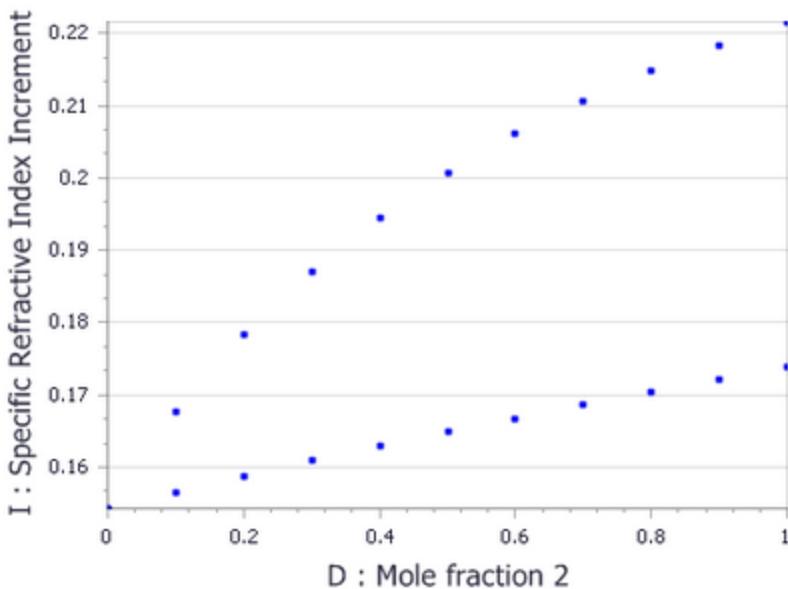


Chart of specific refractive index increment against mole fraction for *N*-benzyl methacrylamide (top line) and *N*-methyl methacrylamide (bottom line).

This is the end of the tutorial.

References

Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd Edition, Chapman and Hall: London (1991).

Bicerano, J. *Soil Sci.*, **158**, 255-266 (1994).

Chapter 25: VAMP tutorials

The following tutorials illustrate how to utilize VAMP's capabilities.

- [Geometry Optimization and Transition State Calculation with VAMP](#)
- [Predicting the UV spectrum of cinnamate](#)

Geometry optimization and transition state calculation with VAMP

Purpose: Introduces the use of VAMP for predicting molecular structures, properties, and transition states of chemical reactions.

Modules: Materials Visualizer, VAMP

Time:  

Prerequisites: None

Background

VAMP is a semiempirical molecular orbital program that has been optimized to be highly numerically stable and fast so that most calculations can be run interactively on workstations and personal computers. It contains many enhancements in comparison with normal geometry optimization methods so that it optimizes even problematic systems successfully.

Other features of VAMP are transition state optimization, solvent models, and the calculation of many electronic properties.

Introduction

In this tutorial, you will learn how to use VAMP to optimize molecules, analyze the results, calculate molecular properties, and determine transition states of chemical reactions.

In the first part, you will optimize the structure of indigo, a classic pigment, and you will analyze several of its properties, derived from the calculated wavefunction.

In the second part of the tutorial, you will calculate the transition state of a chemical reaction leading to a heterocyclic organic compound.

This tutorial covers:

- [Getting started](#)
- [Optimizing the structure of indigo](#)
 - To prepare the structure for the optimization
 - To optimize the indigo structure
 - To analyze the VAMP output file and display electronic properties
- [Finding a transition state for the reaction of nitrone and ethylene to form isoxazolidine](#)
 - To prepare the structures for the calculation
 - To find and confirm the transition state

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **indigo_VAMP** as the project name, click the **OK** button.

VAMP: Geometry optimization and transition state calculation with VAMP

The new project is created with *indigo_VAMP* listed in the Project Explorer. You should create two folders for the different parts of the tutorial.

In the Project Explorer, right-click on the project root and select **New | Folder** from the shortcut menu. Right-click on the new folder and select **Rename** from the shortcut menu. Change the name of the folder to **Indigo**. Repeat these steps to create a second folder called **TS**.

Optimizing the structure of indigo

1. To prepare the structure for the optimization

In this section of the tutorial, you will build a single indigo molecule from the indigo crystal structure provided in the Materials Studio database.

In the Project Explorer, select the **Indigo** folder. Select **File | Import** from the menu bar to open the Import Document dialog. Navigate to the **Structures/molecular-crystals/pigments** folder and import the crystal structure of indigo, **indigo_1.xsd**.

You have now imported the crystal structure of an indigo polymorph. From this crystal structure, you can obtain the structure of a single indigo molecule.

Select **Build | Symmetry | Unbuild Crystal** from the menu bar. Click the **Recenter** button .

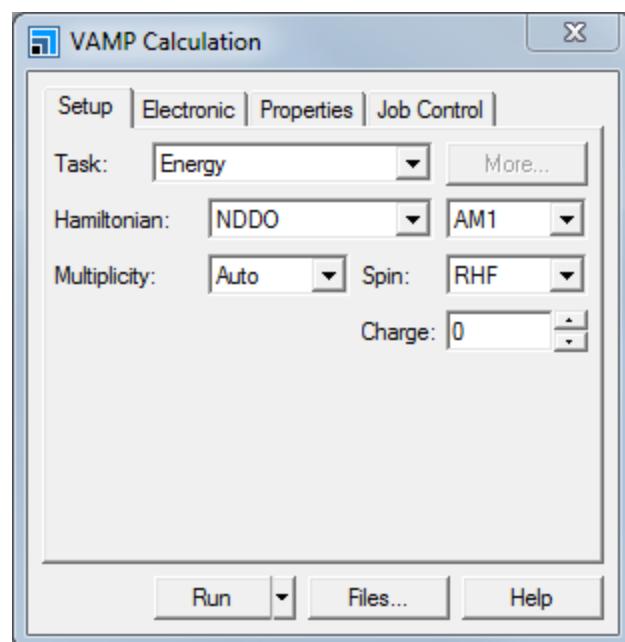
There should now be one indigo molecule centered in the 3D Viewer.

2. To optimize the indigo structure

Next, use the semiempirical VAMP program to optimize the geometry of the molecule.

Click the **VAMP** button  on the **Modules** toolbar, then select **Calculation** from the dropdown list or select **Modules | VAMP | Calculation** from the menu bar.

This opens the VAMP calculation dialog.



VAMP Calculation dialog, Setup tab

On the **Setup** tab, change the **Task** from Energy to **Geometry Optimization**. Make sure the **Hamiltonian** is set to **AM1**.

You have specified the calculation task and the semiempirical approximation to the Hamiltonian used in this calculation.

Click the **Run** button and close the dialog.

A new folder called `indigo_1` VAMP GeomOpt opens in the Project Explorer. The progress of the job during computation is presented in the form of chart and text documents. The entire calculation takes about 30 seconds, depending on the speed of the processor in your computer.

3. To analyze the VAMP output file and display electronic properties

The optimized indigo structure is located in `indigo_1.xsd` in the new folder, while the VAMP text output of the computation is in the `indigo_1.out` document. In this section, you will examine the text output document and use the VAMP analysis tool to display isosurfaces.

VAMP calculates many properties, such as heats of formation, dipole moments, static polarizabilities, and ¹³C chemical shifts, by default. The results for these properties can be viewed in the text output file.

Double-click on `indigo_1.out` in the **indigo_1 VAMP GeomOpt** folder. Press **CTRL + F** and search for **Heat**. Click the **Find Next** button until you reach the part of the document that looks like this:

```
* Heat of formation      =      38.942625 Kcal/mol

* Electronic energy     =      -20000.056110 ev
* Core-core repulsion   =      16761.585834 ev
* Total energy          =      -3238.470275 ev

* Gradient norm         =      0.332340
* RMS force              =      0.035032

* Ionization potential  =      8.365898 ev
*                               48 filled levels
* Molecular weight       =      262.267
```

The heat of formation for indigo, as calculated by VAMP, is approximately 39 kcal mol⁻¹. Examples of other properties displayed are the total electronic and the total nuclear repulsion energies. The sum of these two energies gives the total energy.

The next two lines contain two convergence criteria, the gradient norm, and the root-mean-square force on the atoms. Default convergence criterion for the gradient norm is 0.4 kcal/mol/Å. The output shows that the convergence criterion is satisfied. Finally the ionization potential, the number of filled molecular orbitals and the molecular weight of indigo are listed.

Press **CTRL + F** and search for **Mulliken**. Click the **Find Next** button until you reach **Mulliken atomic charges**.

Below this line the net atomic charges resulting from a Mulliken analysis are displayed. If you scroll down further in the output file you find other properties displayed such as dipole moments, static polarizabilities, bond orders, electron populations, and ¹³C chemical shifts. The last two lines of the output report the successful completion of the calculation and the total run time.

Now you will make use of the VAMP Analysis tool to display several properties on the screen.

Double-click on **indigo_1.xsd** in the **indigo_1 VAMP GeomOpt** folder. Click the **VAMP** button  on the **Modules** toolbar and select **Analysis** from the dropdown list.

This opens the VAMP Analysis dialog. There are several different properties you can display using the VAMP Analysis tool. Initially, you are going to view the electron density as an isosurface.

Click the **Import** button.

Tip: You can improve the quality of the isosurface by changing the grid settings from the Analysis dialog. However, increasing the grid quality will affect the speed with which graphical objects are manipulated.

The total charge density is displayed. The Materials Visualizer has different tools for controlling how you view objects such as isosurfaces and these are located on the Display Style dialog. One of these tools allows you to control the transparency of isosurfaces.

Right-click in the 3D Viewer and select **Display Style** from the shortcut menu to open the Display Style dialog. Select the **Isosurface** tab and drag the **Transparency** slider to the right.

The isosurface becomes more transparent, revealing the molecule.

On the **Atom** tab change the display style to **Ball and stick**.

The atoms and bonds of the molecule are now displayed as balls and sticks. Once you have an isosurface displayed, you can map different properties onto it, such as the electrostatic potential. To do this, you must add the electrostatic potential field data to the 3D Atomistic document.

On the VAMP Analysis dialog select **Potentials** and click the **Import** button.

On the **Isosurface** tab of the Display Style dialog, change the mapped field from <none> to **VAMP electrostatic potential of indigo_1**.

The electrostatic potential is mapped onto the total charge density isosurface using color to represent the variation. Mapping the electrostatic potential in this manner gives you an insight into the charge distribution over the molecule.

You can remove the isosurface by either selecting it and pressing **DELETE** or by using the Volumetric Selection tool.

Click the **Volumetric Selection** button  on the **Volume Visualization** toolbar. Expand the **VAMP total electron density** node and select **Isosurface1**. Press **DELETE** and close the dialog.

The isosurface is removed, but the field data remains. You can also use VAMP to examine the orbitals of indigo.

On the **VAMP Analysis** dialog select **Orbitals**.

A list of all the calculated orbitals and their respective energy eigenvalues is displayed in the grid.

Change the **Filter** from All to **Minimal**.

Now only the three nearest eigenvalues on both sides of the highest occupied molecular orbital (HOMO) are listed. If you had performed a spin-polarized calculation, you could also list all spin-up or all spin-down orbitals.

Select **HOMO** from the orbital list and click the **Import** button.

The HOMO of indigo is displayed on the screen.

Click on the isosurface and press **DELETE** to remove it.

You can also apply the charges that VAMP calculates to the structure in the 3D Atomistic document.

Select **Population analysis** on the VAMP Analysis dialog and click the **Assign Coulson charges to structure** button. Right-click in the 3D Viewer and select **Label** from the shortcut menu to open the Label dialog. Set the **Object type** to **Atom**, select **Charge** from the **Properties**, and click the **Apply** button.

Now the partial atomic charges as calculated by the Coulson method are displayed on the molecule. You can also choose to display the Mulliken charges by changing the charge type to **Mulliken** on the VAMP Analysis dialog and pressing the *Assign chosen charges to structure* button.

On the Label dialog, click the **Remove** button.

Click the **Assign Mayer bond orders to structure** button on the VAMP Analysis dialog and close the dialog.

On the Label dialog, change the **Object type** to **Bond** and select **BondOrder** from the list of **Properties**. Click the **Apply** button and close the dialog.

The bonds in the molecule are updated from the VAMP calculation. Before you continue to the second part of this tutorial, you should save the project and close all the documents.

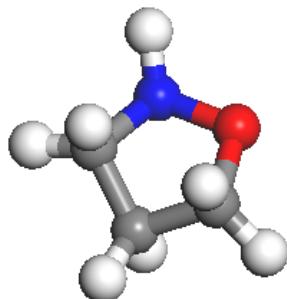
Select **File | Save Project**, then **Window | Close All** from the menu bar.

Finding a transition state for the reaction of nitrone and ethylene to form isoxazolidine

In the second part of the tutorial, you are going to use VAMP to find a transition state for a 1,3-dipolar cycloaddition reaction of nitrone and ethylene, which forms the heterocyclic compound isoxazolidine. 1,3-Dipolar cycloadditions provide an important synthetic route to functionalized five-membered heterocyclic systems, including those commonly found in natural products. A detailed understanding of the transition state is essential for predicting the regiochemistry of the reaction products.

1. To prepare the structures for the calculation

In this section you will prepare the structures for the transition state optimization starting from the product, isoxazolidine.



Structure of isoxazolidine

In the Project Explorer, right-click on the **TS** folder and select **New | 3D Atomistic Document** from the shortcut menu.

Click the **Sketch Ring** arrow and select **5 Member**. Click once in the 3D Viewer.

A five-membered carbon ring is displayed in the new 3D Atomistic document.

Change the appropriate atoms to **Nitrogen** and **Oxygen**. Click the **Adjust Hydrogen** button and the **Clean** button .

In the Project Explorer, right-click on the **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Enter the name **isoxazolidine**.

Now you can use VAMP to optimize the structure of the isoxazolidine product.

Open the **VAMP Calculation** dialog.

On the **Setup** tab, change the **Task** to **Geometry Optimization** and ensure that the **Hamiltonian** selected is **AM1**.

Click the **Run** button and close the dialog.

A new folder, called **isoxazolidine VAMP GeomOpt**, is created in the Project Explorer. Examine the text output file.

Double-click on **isoxazolidine.out** in the **isoxazolidine VAMP GeomOpt** folder. Press **CTRL + F** and search for **Heat**. Click the **Find Next** button until you reach the part of the document that looks like this:

* Heat of formation	=	-8.894573 Kcal/mol
* Electronic energy	=	-3533.525022 ev
* Core-core repulsion	=	2526.879750 ev
* Total energy	=	-1006.645272 ev
* Gradient norm	=	0.348646
* RMS force	=	0.058108

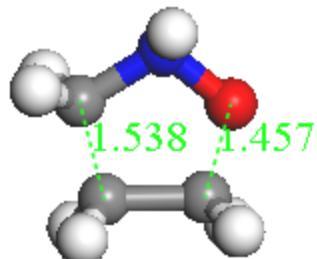
* Ionization potential = 9.816158 eV
 * 15 filled Levels
 * Molecular weight = 73.094

Now that you have built the isoxazolidine product, you can break two bonds to form the two reactant structures.

Ensure that the original (unoptimized) **isoxazolidine.xsd** structure is the active document. Select the CH₂-CH₂ bond adjacent to the CH₂-N bond. Hold down **SHIFT** and select the C-O bond. Press **DELETE**.

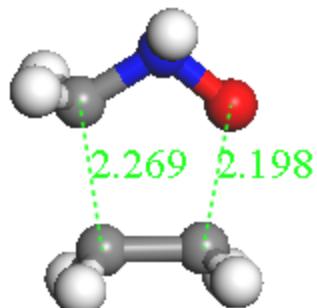
Now you are going to use the *Measure/Change* tool to calculate the lengths of the bonds you have just removed.

Click the **Measure/Change** arrow  and select **Distance** from the dropdown list. Select the atoms that were connected by the bonds you just deleted.



Distance monitors are displayed in green and both distances should be about 1.5 Å. To set up the starting structure for the calculation, you need to separate the two fragments.

Choose the **Selection Mode** tool. Select the oxygen atom, right-click, and choose **Select Fragment** from the shortcut menu. Hold down the **SHIFT** and **ALT** keys and use the right mouse button to separate the fragments until they are approximately 2.2 Å apart.



Tip: If you have a three-button mouse or a mouse with a wheel, you can use the middle mouse button and SHIFT to translate selected objects.

2. To calculate and confirm the transition state

Next, use the VAMP Calculation dialog to optimize the transition state and the vibrational modes of the structure.

Open the **VAMP Calculation** dialog.

Change the **Task** to **TS Optimization** and the **Hamiltonian** to **AM1**. Click the **More...** button to open the VAMP TS Optimization dialog. Change the **Method** to **Powell** and close the dialog.

On the **Properties** tab check the **Frequency** checkbox.

You have specified the approximate Hamiltonian and the calculation task. In this example, you will use the Powell algorithm for the transition state search. On the *Properties* tab, you selected *Frequency*, so that a normal mode analysis will be performed. This means that you can verify the transition state by animating the imaginary normal mode associated with the reaction coordinate.

Click the **Run** button and close the dialog.

The result of the transition state search is returned. Values of $r_{C-C} = 2.15 \text{ \AA}$ and $r_{O-C} = 2.04 \text{ \AA}$ are obtained. These are very close to earlier Hartree-Fock results ($r_{C-C} = 2.19$, $r_{O-C} = 2.04 \text{ \AA}$) obtained by Sosa et al. (1994). However, the same authors, obtained another transition state ($r_{C-C} = 2.34$, $r_{O-C} = 2.24 \text{ \AA}$) using local density functional theory, in accordance with earlier MCSCF calculations (Hehre et al., 1969).

Finally, calculate the normal modes at the transition state and animate the reaction mode.

Ensure that the **isoxazolidine VAMP TSOpt/isoxazolidine.xsd** optimized transition state structure is the active document. Select **Tools | Vibrational Analysis** from the menu bar to open the Vibrational Analysis dialog. Click the **Calculate** button.

A list of frequencies, or eigenvalues, is displayed in the *Analysis* tab, one of which is negative. The presence of a large single negative eigenvalue indicates that this is the transition state.

Highlight the negative mode and click the **Animation** button and close the dialog.

The normal mode associated with this negative frequency is animated. This is the reaction mode.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

References

Hehre, W. J.; Stewart, R. F.; Pople, J. J. *J. Chem. Phys.*, **51**, 2657 (1969).

Sosa, C.; Andzelm, J. *Int. J. Quantum Chem.*, **49**, 511 (1994).

Predicting the UV spectrum of cinnamate

Purpose: Illustrates how to use VAMP to perform geometry optimization and to calculate optical spectra.

Modules: Materials Visualizer, VAMP

Time:  

Prerequisites: Sketching simple molecules Visualizer Tutorial

Background

VAMP is a semiempirical molecular orbital program that has been optimized to be highly numerically stable and fast, so that most calculations can be run interactively on workstations and personal computers. It contains many enhancements in comparison to normal geometry optimization methods so that it even optimizes problematic systems successfully. Other features of VAMP include transition state optimization, solvent models, the calculation of many electronic properties, and the prediction of optical spectra.

Introduction

In this tutorial, you will learn how to use VAMP to calculate UV/vis optical spectra.

First you will optimize the structure of 2-ethylhexyl-p-methoxycinnamate (cinnamate), a classic sunscreen molecule, and then you will calculate its UV spectrum.

This tutorial covers:

- [Getting started](#)
- [Optimizing the structure of cinnamate](#)
 - To prepare the structure for optimization
 - To perform the optimization
- [Calculating the UV spectrum of cinnamate](#)
 - To prepare the input file for the calculation
 - To calculate the UV spectrum and analyze the output

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **cinnamate** as the project name, click the **OK** button.

The new project is created with *cinnamate* listed in the Project Explorer.

Optimizing the structure of cinnamate

1. To prepare the structure for optimization

In this section of the tutorial, you will build a single cinnamate molecule (shown below) using the tools provided in the Materials Visualizer.

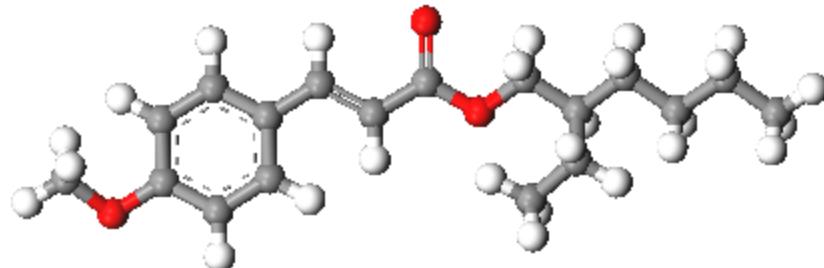


Figure 1. Structure of cinnamate

Begin by creating a new 3D Atomistic document.

Select **File | New...** from the menu bar to open the New Document dialog. Select **3D Atomistic** and click the **OK** button.

In the **Project Explorer**, right-click on **3D Atomistic.xsd** and select **Rename** from the shortcut menu. Rename the document to **cinnamate** and press **ENTER**.

Now sketch the cinnamate structure, starting with the aromatic ring.

Click the **Sketch Ring** arrow button  on the **Sketch** toolbar and select **6 Member** from the dropdown list. Hold down **ALT** and click once in the **cinnamate.xsd** 3D Viewer.

A 6 membered aromatic ring appears in the document. Now, sketch the oxymethane substituent.

Add the side-chains as shown in [Figure 1](#), ensure that you change the appropriate atoms to **Oxygen** to form the ester and methoxy groups. Make sure that you place the double bonds correctly.

When the basic structure of the cinnamate molecule is complete, finish off by adding the hydrogen atoms and cleaning the structure.

Click the **Adjust Hydrogen** button  and the **Clean** button  on the **Sketch** toolbar.

Before continuing you should save the project.

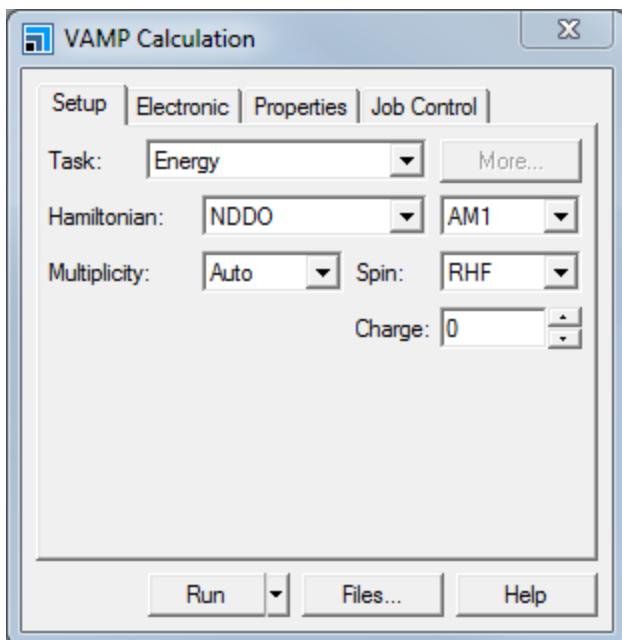
Select **File | Save Project** from the menu bar.

2. To perform the optimization

In this step, you will use the semiempirical VAMP program to optimize the geometry of the cinnamate molecule.

Click the **VAMP** button  on the **Modules** toolbar and select **Calculation** from the dropdown list.

This opens the VAMP calculation dialog.



VAMP Calculation dialog, Setup tab

First, specify the task you wish to perform and the semiempirical approximation to the Hamiltonian that will be used in the calculation.

On the **Setup** tab, select **Geometry Optimization** from the **Task** dropdown list.

Click the **More...** button to display the VAMP Geometry Optimization dialog. Select **Fine** from the **Quality** dropdown list and close the dialog.

On the **Electronic** tab of the VAMP Calculation dialog select **Fine** from the **SCF quality** dropdown list.

Click the **More...** button to display the VAMP Electronic Options dialog. Set the **Max. SCF cycles** to **500** and close the dialog.

Now start the geometry optimization.

Click the **Run** button on the VAMP Calculation dialog.

A new folder, called **cinnamate VAMP GeomOpt**, is created in the *Project Explorer*. As the job progresses, updates are presented in both chart and text documents. The calculation should take a few minutes, depending on the speed of the processor in your computer.

When the job is complete, the optimized cinnamate structure can be found in **cinnamate.xsd** in the new folder and textual output from the run is contained in the file, **cinnamate.out**.

Click the **OK** button to close the Job Completed dialog.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

To calculate the UV spectrum of cinnamate

This section of the tutorial illustrates how to use VAMP to calculate the UV spectrum of cinnamate.

VAMP: Predicting the UV spectrum of cinnamate

1. To set up the UV spectrum calculation

Ensure that the optimized cinnamate structure is active.

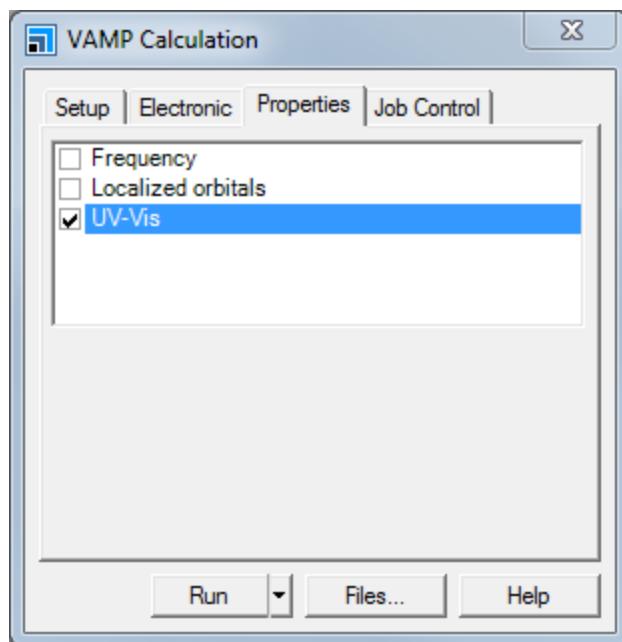
In the **Project Explorer**, double-click on **cinnamate.xsd** in the **cinnamate VAMP GeomOpt** folder.

Now you can prepare the VAMP input file required for the calculation.

On the **Setup** tab of the VAMP Calculation dialog, select **Energy** from the **Task** dropdown list.

On the **Electronic** tab select **Full** from the **CI type** dropdown list. Click the **More...** button to open the VAMP Electronic Options dialog and set the **Total CI orbitals** to **6**. Check the **Ignore degenerate orbitals** checkbox and close the dialog.

On the **Properties** tab check the **UV-Vis** checkbox.



VAMP Calculation dialog, Properties tab

Now the input file is ready, you can start the calculation.

Click the **Run** button on the VAMP Calculation dialog and close the dialog.

The calculation begins. It should take around a minute, depending on the speed of the processor in your computer.

Click the **OK** button to close the Job Completed dialog.

2. To analyze the UV spectrum

The output from the calculation is written to the file **cinnamate.out** in the **cinnamate VAMP Energy** folder.

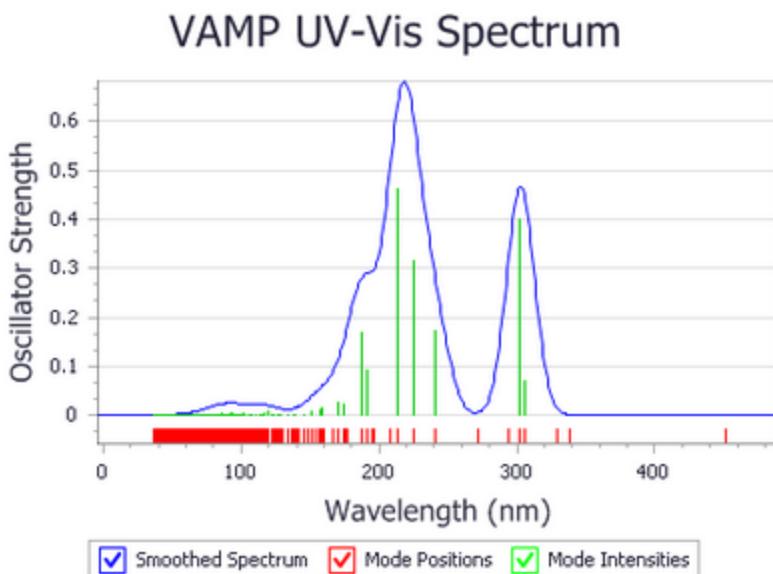
Click the **VAMP** button  on the **Modules** toolbar and select **Analysis** from the dropdown list to open the VAMP Analysis dialog.

Double-click on **cinnamate.xsd** in the **cinnamate VAMP Energy** folder in the **Project Explorer**.

Note: The results you obtain may vary slightly from those shown because of minor differences in the structure of the starting model.

Select **Electronic levels** in the VAMP Analysis dialog and click the **View spectrum** button.

A graph is displayed in a new Chart Viewer.



VAMP simulated spectrum for cinnamate

The green lines on the graph represent the positions and non-zero intensities of the absorption frequencies computed by VAMP. The short red lines show the positions of all computed transitions, even forbidden transitions. Notice that there is a significant number of forbidden transitions. The smooth blue line indicates a simulated spectrum based on the computed frequencies and intensities. This is achieved by broadening the computed results with a Gaussian or Lorentzian function.

Double-click on **cinnamate.xsd** in the **cinnamate VAMP Energy** folder in the **Project Explorer**.

On the VAMP Analysis dialog, select **Electronic levels** and click the **View electronic energy levels** button.

A table is displayed in a new Study Table Viewer

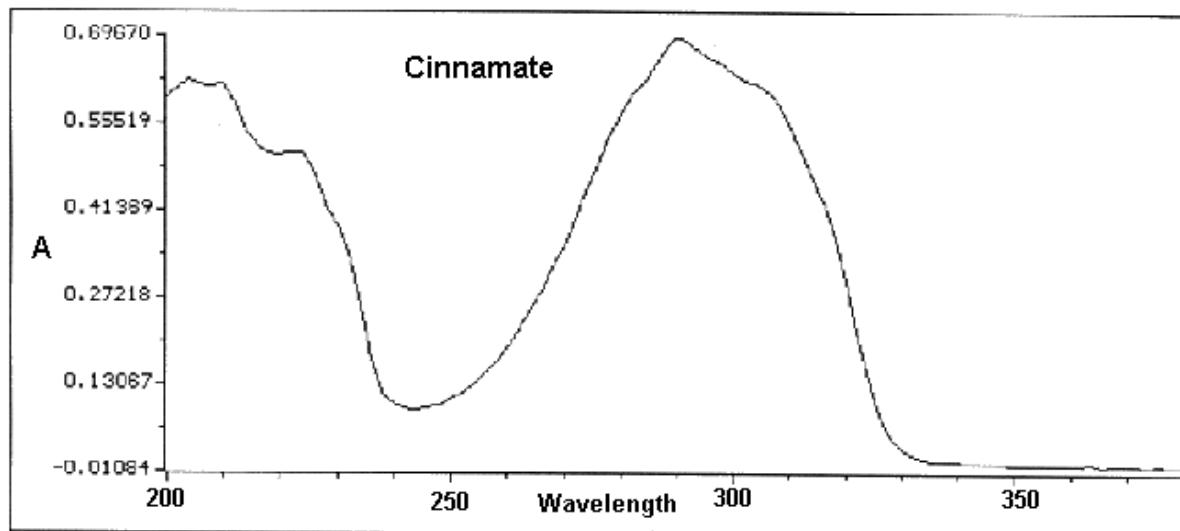
VAMP: Predicting the UV spectrum of cinnamate

	A	B	C	D	
	Level Energy (eV)	Excitation wavelength (nm)	Oscillator Strength	Multiplicity	
1	-0.56567200	0.00000000	Ground State	Singlet	
2	2.70172700	458.89159300	Forbidden	Triplet	
3	3.64493400	340.14330100	Forbidden	Triplet	
4	3.73524300	331.91947400	Forbidden	Triplet	
5	4.01644400	308.68101200	0.02501300	Singlet	
6	4.08373200	303.59486000	0.44910300	Singlet	
7	4.20481000	294.85281900	Forbidden	Triplet	
8	4.33294800	286.13315600	Forbidden	Triplet	
9	5.08321200	243.90089200	0.13738400	Singlet	
10	5.45588500	227.24168700	0.25750800	Singlet	

Computed VAMP frequencies and intensities

The table provides values for the energy (in eV), the excitation wavelength (in nm), the multiplicity (spin arrangement), and the oscillator strength (transition dipole moment) of each electronic state.

The spectrum contains two maxima, at about 210 nm and 300 nm. Compare this with the experimentally derived spectrum shown below:



Experimental spectrum of cinnamate

The theoretical peaks agree with the experimental ones, to within 20 nm. Optical spectra depend strongly on the structure of the system as well as solvent effects and this probably accounts for the discrepancies. A better starting geometry could be obtained by performing ab initio calculations using DMol³. Solvent effects can be simulated by setting the solvation scheme to COSMO or SCRF on the *Electronic* tab of the VAMP Calculation dialog.

Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

This is the end of the tutorial.

Dassault Systèmes Support Resources

For additional resources or to contact Dassault Systèmes Customer Support, visit the Support portal:

<https://www.3ds.com/support/>

From this portal, you can:

- Call or email Dassault Systèmes Customer Support
- Submit a request
- Download installers
- Access hardware and software requirements
- Access Knowledge Base
- Access Communities and Twitter feeds