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

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:

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.

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.

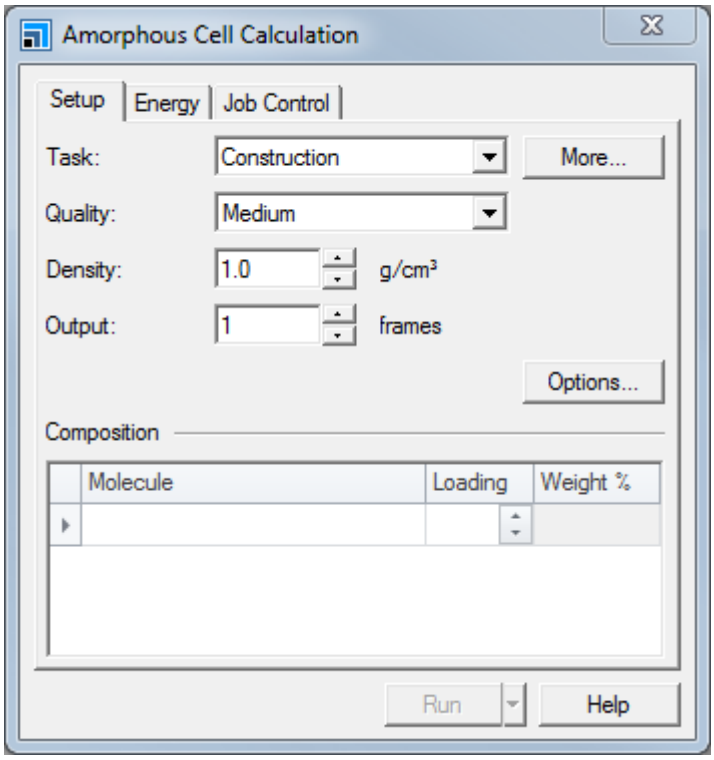
Select **File | Save Project** from the menu bar, followed by **Window | Close All**.

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 0.95 g/cm^3.

Set the **Density** to **0.95** g/cm^3.

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.

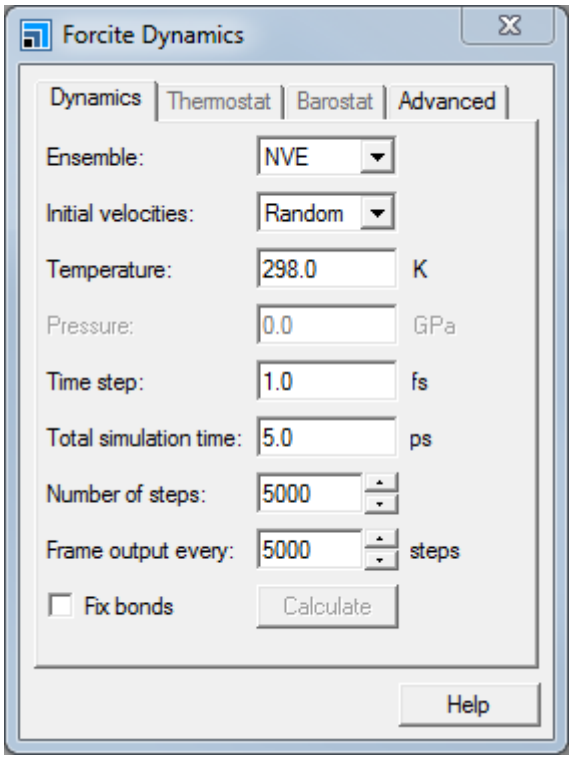
Set the number of **Annealing cycles** to **1**, the **Initial temperature** to **300** K, and the **Mid-cycle temperature** to **500** K. Close the dialog.

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 `cell.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 0.95 g/cm^3. Since this is also the average density of this system at 300 K and 1 atm, with the selected forcefield, 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.

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 the **CTRL** key and **double-click** on each molecule in turn.

> **Tip:** To automatically select all molecules of a kind you can use the Find Patterns tool.

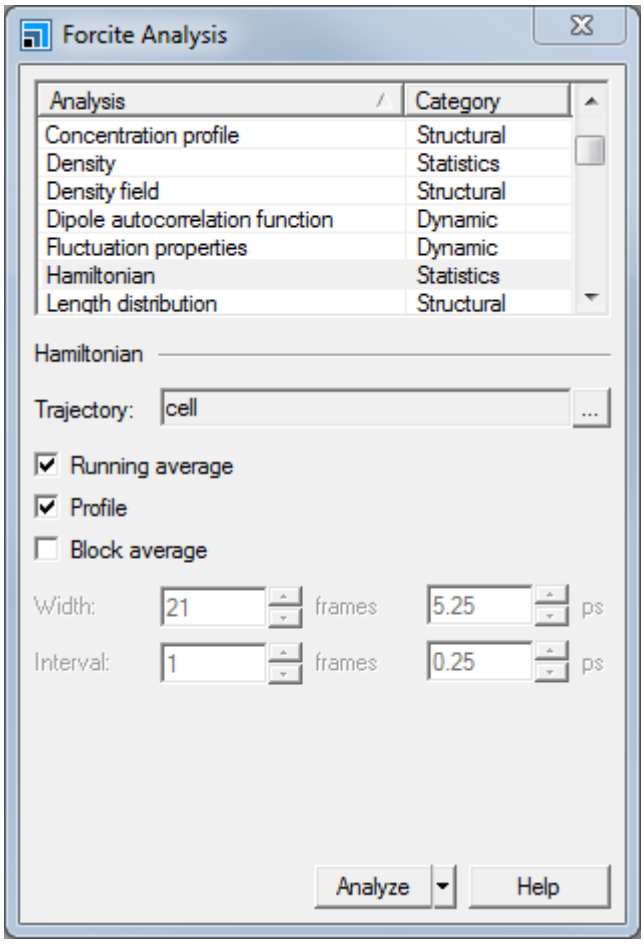
Now you can use the Edit Sets tool to create a set of the selected atoms.

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:

$$D = \frac{1}{6N_\alpha} \lim_{t\to\infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \left\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \right\rangle$$

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 Å^2/ps. To convert to the more commonly used unit cm^2/s, the resulting value must be divided by 1e4.

Calculated values for the diffusion of methane in PBD have been reported in the range between 2.25×10^{-6} cm^2 s^{-1} and 7.5×10^{-6} cm^2 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 **0.95**.
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 **Run via 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.

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).