Nanoparticle Simulation Worksheet

Introduction

What Software is being used?

For these simulations, **Atomic Simulation Environment** (ASE) will be used. ASE is a set of tools and Python modules which allow the construction and manipulation of atomic structures along with being able to run simple calculations. Python itself is a programming language; programming languages are used to instruct the computer to run a set of instructions (a script) to produce outputs such as the nanoparticles seen in this project. ASE uses modules of code to produce models, which, in conjunction with an internal **graphical user interface** (GUI), allows the structures to be viewed, rotated and manipulated. All of this software will be run on a virtual machine with pre-installed software called Virtualbox, allowing "a computer within a computer" to be run.

What ASE modules are being used?

In this project two main ASE modules will be used, the first being the ase.nanocluster module, which includes the octahedron and wulff_construction scripts producing nanoparticle models as shown in Figure 1, left. Another module that will be used is the ase.molecule module; this allows for production of molecule models as shown in Figure 1, right.

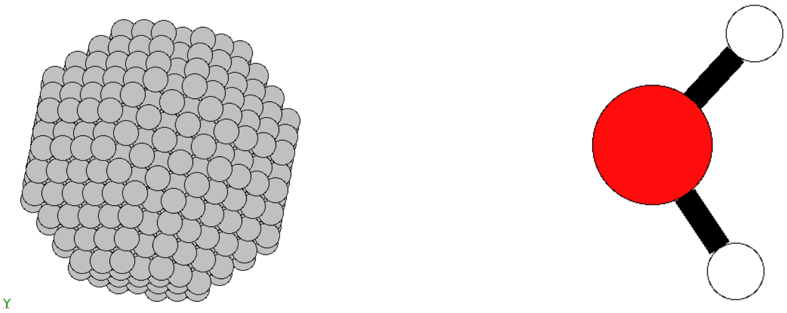


Figure 1: Left: A nanoparticle that can be created from the wulff_construction and the octahedron scripts. Right: A molecule model of water which can be created using the ase.molecule script.

How to start off

1. To log onto the VirtualBox first, click on the icon as shown in yellow in Figure 2.

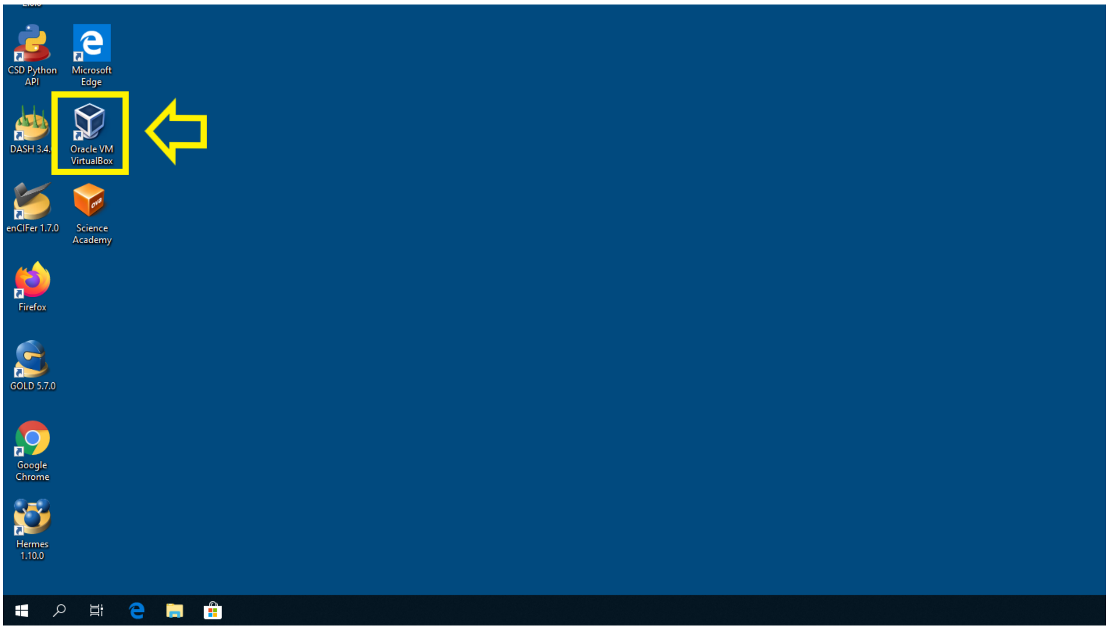
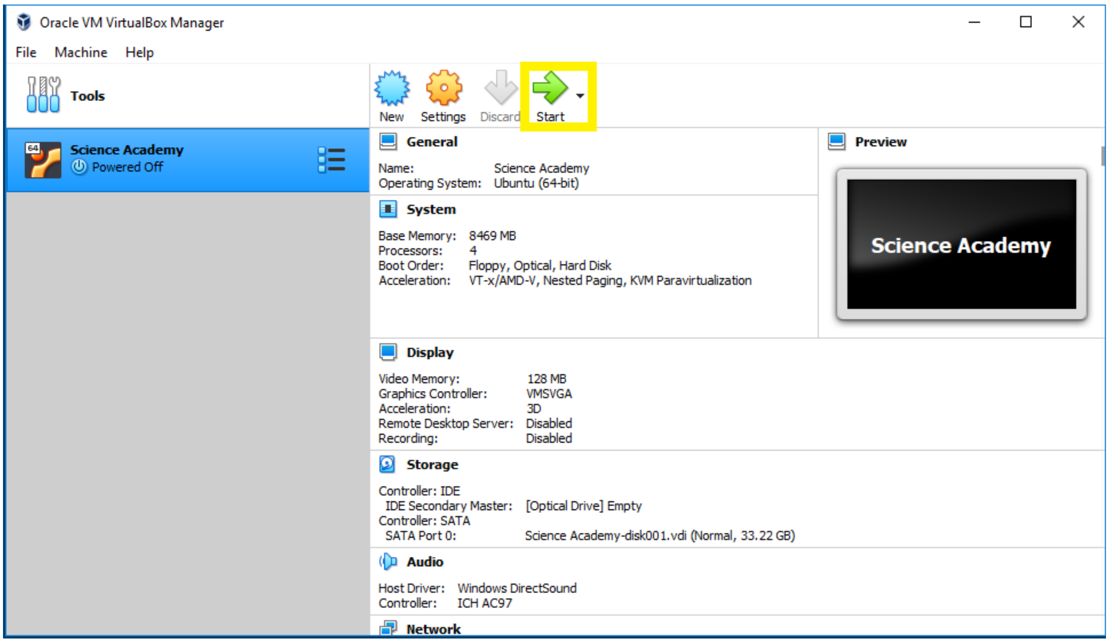


Figure 2: VirtualBox icon.

2. After the Virtualbox opens, it will appear as shown in Figure 3.



General

Name: Science Academy
Operating System: Ubuntu (64-bit)

System

Base Memory: 8469 MB
Processors: 4
Boot Order: Floppy, Optical, Hard Disk
Acceleration: VT-x/AMD-V, Nested Paging, KVM Paravirtualization

Display

Video Memory: 128 MB
Graphics Controller: VMSVGA
Acceleration: 3D
Remote Desktop Server: Disabled
Recording: Disabled

Storage

Controller: IDE
IDE Secondary Master: [Optical Drive] Empty
Controller: SATA
SATA Port 0: Science Academy-disk001.vdi (Normal, 33.22 GB)

Audio

Host Driver: Windows DirectSound
Controller: ICH AC97

Network

Figure 3: VirtualBox first screen.

3. From this screen push the green start arrow (yellow box) which will start the VirtualBox.

4. A start screen will then appear which must be clicked and dragged up the screen, the login ‘CHEM390’ will now be displayed.
5. Type in the password ‘a1b2c3d4e5’ press enter and you will be logged in.
6. Open the Terminal which is the icon indicated by the yellow box in Figure 4.
7. Type ‘cd ase_nanoparticles/’ and press the enter key to access the correct folder.

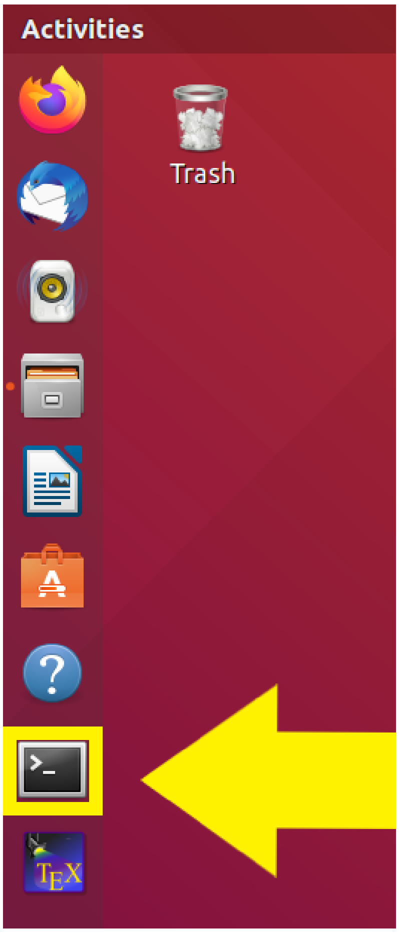
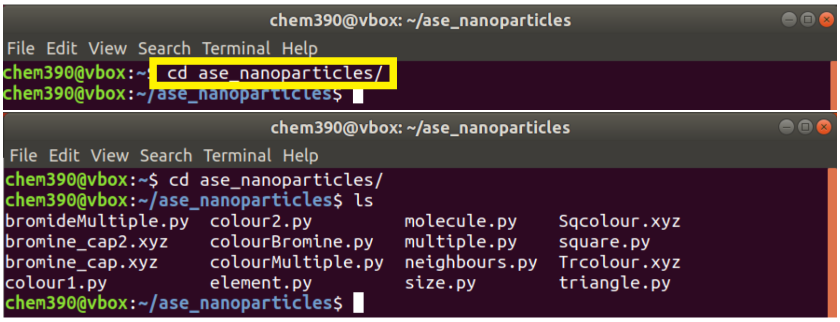


Figure 4: The terminal icon.

Handy Hints

1. After every command written in the terminal it must be followed by pressing the ‘enter key’ to execute the command.
2. To ensure that the correct folder has been opened, ‘ls’ (meaning list) can be typed resulting in a list of the contents. These steps can be seen in Figure 5. The folder should contain a number of python scripts (.py) to be used throughout the simulation.
3. When entering information into terminal the ‘’ are not needed, this is just to show what should be entered.


chem390@vbox: ~/ase_nanoparticles
File Edit View Search Terminal Help

```
chem390@vbox:~$ cd ase_nanoparticles/
chem390@vbox:~/ase_nanoparticles$
```

chem390@vbox: ~/ase_nanoparticles
File Edit View Search Terminal Help

```
chem390@vbox:~$ cd ase_nanoparticles/
chem390@vbox:~/ase_nanoparticles$ ls
bromideMultiple.py  colour2.py         molecule.py    Sqcolour.xyz
bromine_cap2.xyz    colourBromine.py   multiple.py    square.py
bromine_cap.xyz     colourMultiple.py  neighbours.py  Trcolour.xyz
colour1.py          element.py         size.py        triangle.py
chem390@vbox:~/ase_nanoparticles$
```

Figure 5: Visual instructions in order to get into the desired folder and list the folders contents.

What are nanoparticles?

Questions to consider

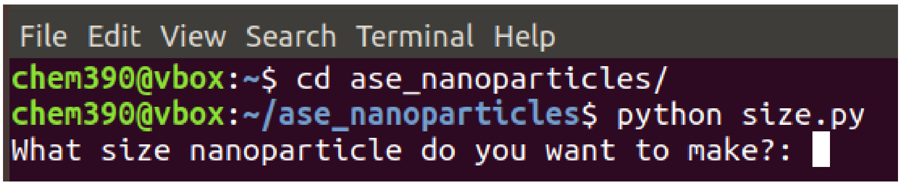
1. What shape are nanoparticles? Circular? Faceted?

2. What is a nanoparticle made up of?

3. What range of sizes can they have in this simulation? Range in number of atoms? Range in diameter of these nanoparticles?

Instructions

1. Use the instructions on how to start, from above.
2. Type 'python size.py' and execute the wulff construction script this will display as shown in Figure 6.



```
chem390@vbox:~$ cd ase_nanoparticles/
chem390@vbox:~/ase_nanoparticles$ python size.py
What size nanoparticle do you want to make?:
```

Figure 6: size.py script output

3. Type 500 into the terminal and hit enter.
4. This will give a structure as shown in the left of Figure 1 (on this worksheet) and can be rotated as described on the help sheet (page 1).
5. Measure the nanoparticles diameter as instructed on the help sheet (page 2) and write it below.

Nanoparticle diameter: ____________________Å

6. Edit the size of the nanoparticle by typing 'python size.py' again and typing a different size in the terminal. Try and find the largest and smallest nanoparticle the script will run with.
7. Record the number of atoms in the smallest and largest nanoparticles you find below. Instructions for how to count the number of atoms in each nanoparticle can be found at the bottom of page 2 in the helpsheet.

Number of atoms in the smallest nanoparticle: ____________________

Smallest nanoparticle diameter: ____________________Å

Number of atoms in the largest nanoparticle: ____________________

Largest nanoparticle diameter: ____________________Å

When a nanoparticle with a larger size is run particular care should be used when examining the structure. How many different 'faces' make up the nanoparticle? What shape are these? These will be further investigated shortly along with examining a few of the parameters seen within the python script.

It should be noted that a maximum size was set in order to maximise the computational performance. However modelling of larger sizes is possible on more advanced computers.

Answer the following questions below:

Focus Questions	
What shape are nanoparticles? Circular or faceted?	
What is a nanoparticle made up of?	
What range of sizes can they have in this simulation? Range in number of atoms? Range in diameter of these nanoparticles?	

How do nanoparticles and molecules differ?

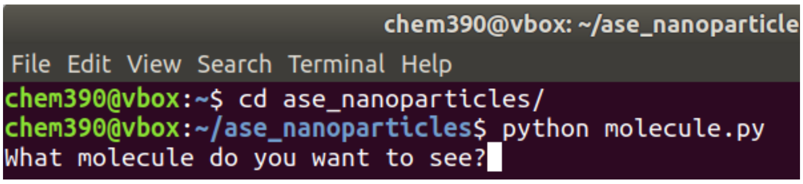
Questions to consider

1. What are the size differences between nanoparticles and molecules?

2. What are the structural differences between nanoparticles and molecules?

Instructions

1. Type 'python molecule.py' and execute the molecule script and the terminal will look as shown in Figure 7.



chem390@vbox: ~/ase_nanoparticle
File Edit View Search Terminal Help

```
chem390@vbox:~$ cd ase_nanoparticles/
chem390@vbox:~/ase_nanoparticles$ python molecule.py
What molecule do you want to see?
```

Figure 7: molecule.py script output.

2. Type 'H2O' into the terminal and execute this command, a water molecule will open which can be rotated and examined.
3. It will be noted that these molecules have no bonds present, therefore after each script is run press 'ctrl B' (with the ASE window selected) to show the bonds.
4. Measure the longest distance across the molecule and compare this to the previous nanoparticles.

Molecule size: ______________________Å

5. Water is a small molecule, so to compare to a larger molecule, type 'python molecule.py' and then type 'methylenecyclopropane' and examine its size.

Molecule size: ______________________Å

6. Comparisons can be made for a number of molecules by typing any of the following: 'NaCl', 'CH3CH2OCH3' and 'CH3SiH3' using the same procedure as above.

Size of NaCl: ____________________Å

Size of CH3CH2OCH3: ____________________Å

Size of CH3SiH3: ____________________Å

Answer the following questions below:

Focus Questions	
What are the size differences between nanoparticles and molecules?	
What are the structural differences between nanoparticles and molecules?	

What are the faces on the surface of a nanoparticle?

Introduction

To understand a nanoparticle, it is crucial to understand that they are not circular and have different structures. The nanoparticles used here are octahedral in shape, these are bounded by both, square (purple) and triangle (green) faces seen in Figure 8. The structure of a nanoparticle includes two main sections, the surface (the faces) and the bulk. The bulk is the internal atoms whereas the surface (the faces) are on the outside of the nanoparticle. Both of these parts have different energies and properties depending on many factors such as element type.

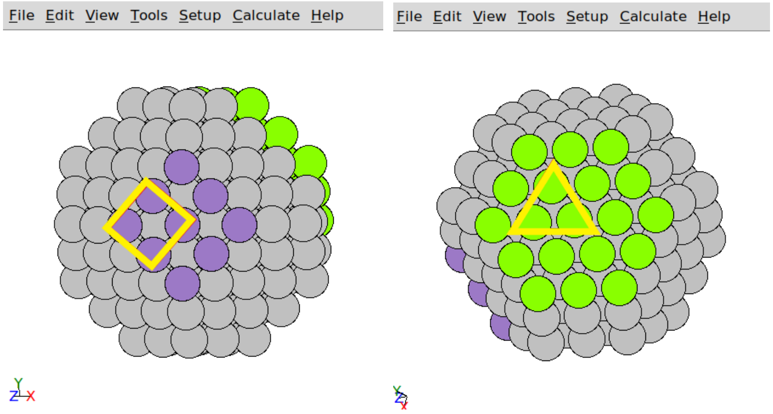

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Figure 8: The nanoparticle with coloured square (purple) and triangle (green) faces.

Questions to consider.

1. What faces are present on the nanoparticles?

2. How many neighbours does each atom have on each face? How many of these are close neighbours?

3. How many neighbours does each atom have in the bulk?

Instructions

1. Type ‘python colour1.py’ and execute the wulff construction script.
2. Rotate the output (as explained in the help sheet on page 1) and take care to examine the two different faces, taking note of the triangle and the square shapes.
3. Type ‘python colour2.py and execute the script which will give the same faces with neighbouring systems highlighted.

A neighbouring atom is demonstrated in Figure 9 for both faces. On the left the triangle face is shown with all of the centre atoms neighbours depicted in orange. This shows the neighbouring atoms of the triangle face are all equal distances apart. However, as seen on the right the square face has two neighbouring systems. There is the same close neighbours as depicted in orange, however also present is a neighbouring system which is slightly further away and is depicted in blue.

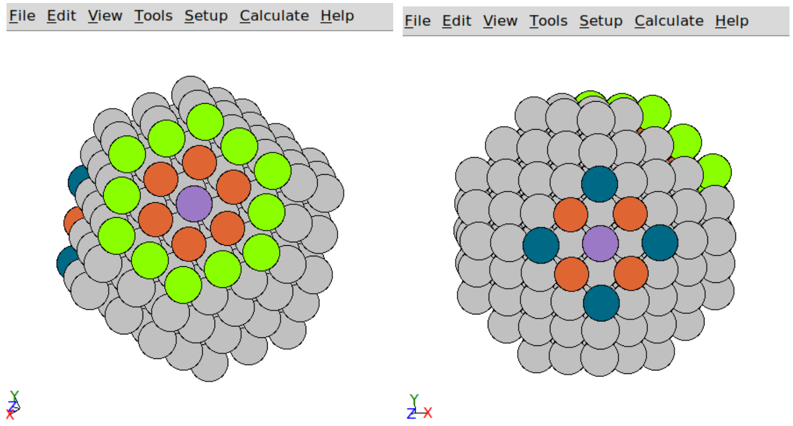
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Figure 9: The neighbouring system for both triangle (left) and square (right) face systems.

Triangle face

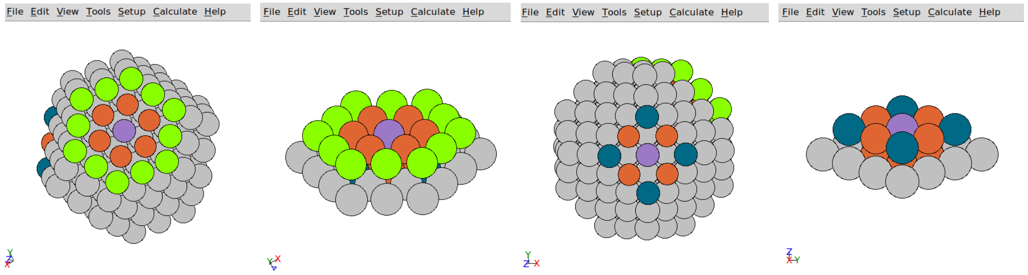
Neighbouring distance (purple - orange): ____________Å

Square face

Neighbouring distance 1 (purple - orange): ____________Å

Neighbouring distance 2 (purple - blue): ____________Å

Note: You may realise that these atoms have neighbours not just on the face but below the surface too. This can then be examined in terms of overall stability with all neighbouring systems considered. For ease of counting and viewing, all of the layers, except the two surface layers, have been stripped back for the square and triangle faces seen above. Again all of the atoms involved in each neighbouring system have been coloured. This can then be compared to the neighbouring system which an atom in the bulk (internal) has.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File Edit View Tools Setup Calculate Help

Figure 10: The neighbouring systems for both triangle (left) and square (right) face systems with the bulk model where every second image of the surfaces is the .xyz files which contain only two layers.

5. Type ‘ase gui Sqcolour.xyz &’ and execute the script where the neighbouring system for the square face below the surface will appear. This script will show the surface with only two layers to easily examine the neighbours. For .xyz files the terminal input must be written in this format. This will show all of the neighbours an atom on the square surface will have in the colour code of close neighbours (orange) and further away neighbours (blue) as displayed in Figure 10.
6. Type ‘ase gui Trcolour.xyz &’ where the previous information will pop up for the neighbouring systems but now applied to the triangle surface which can once again be counted.

The amount of neighbours in the bulk can then be compared to the surfaces.

7. Type ‘python neighbours.py’ and execute the script where a traditional nanoparticle will appear with the same colour coding as the previous scripts.

8. These models should be rotated and the number of close neighbours (purple - orange) and further away neighbours (purple - blue) counted and compared to the orange and blue atoms of the surfaces. This reinforces why triangle face should be changed to have purple centre atom for consistency.

Use the second colour and the neighbouring script to answer the following:

Triangle surface

Amount of close neighbours (purple - orange): ____________

Amount of further away neighbours (purple - blue): ____________

Square surface

Amount of close neighbours (purple - orange): ____________

Amount of further away neighbours (purple - blue): ____________

Bulk

Amount of close neighbours (purple - orange): ____________

Amount of further away neighbours (purple - blue): ____________

Answer the following questions below:

Focus Questions	
What faces are present on the nanoparticles?	
How many neighbours does each atom have on each face? How many of these are close neighbours?	
How many neighbours does each atom have in the bulk? *(This will help make the energy argument more clear later on.)*	

How can these faces be related to energetics and stability?

Questions to consider.

1. What does more neighbours mean in terms of stability?

2. What surface is higher in energy?

3. What does energy means in terms of nanoparticle stability?

Introduction

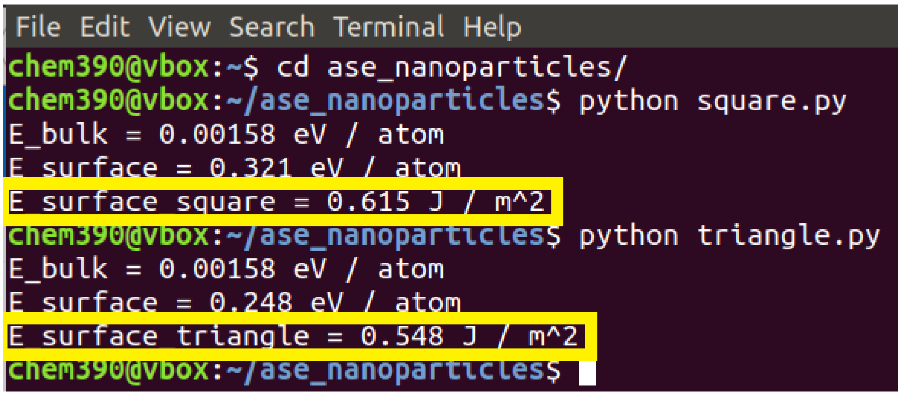
The stability in these nanoparticles can be related to the macroscopic world by thinking of how a person could be lifted. Having more people can stabilise the person making it easier for them to be picked up. In contrast, when people are further away, this compromises some stability, which raises the energy of the system.

This can be related to bonding behaviour of carbon, carbon wants four bonds, hence CH_4 is more 'stable' than CH_3. Since CH_4 is more stable, this means that the molecule has an overall lower energy, making it the more favourable form. This is similar to how the metals are working in these simulations.

The metals in this simulation want to have eight neighbours, complete octet. When a complete octet is formed, the energy of the system is decreased. Therefore, the more neighbours an atom has the closer it is to having a full octet, making it lower in energy. When we look at these neighbour models, it is seen that the triangle motif has more neighbours and therefore is lower in energy.

Instructions

1. Type 'python square.py' and execute this script and follow up with executing 'python triangle.py.'
2. This script will give a print out as shown in Figure 11.



```
chem390@vbox:~$ cd ase_nanoparticles/
chem390@vbox:~/ase_nanoparticles$ python square.py
E_bulk = 0.00158 eV / atom
E_surface = 0.321 eV / atom
E_surface_square = 0.615 J / m^2
chem390@vbox:~/ase_nanoparticles$ python triangle.py
E_bulk = 0.00158 eV / atom
E_surface = 0.248 eV / atom
E_surface_triangle = 0.548 J / m^2
chem390@vbox:~/ase_nanoparticles$
```

Figure 11: The results of the surface energy calculations.

In the above calculation, the only important parts to understand is the final E_surfaces which are highlighted in yellow. These show the ratio of the energy in the bulk vs the energy in the surface, giving the overall value in J m^{-2}. Look at which one is higher in energy, and why this might this be in context of neighbouring atoms from the previous exercise?

Square
Amount of close neighbours: ______________Atoms
Surface energy: ______________Jm^{-2}

Triangle
Amount of close neighbours: ______________Atoms
Surface energy: ______________Jm^{-2}

Answer the following questions below:

Focus Questions	
What does more neighbours mean in terms of stability?	
What surface is higher in energy?	
What does energy mean in terms of nanoparticle stability?	

What effect does metal type have on nanoparticles?

Questions to consider.

1. Do different metal nanoparticles look different? How?

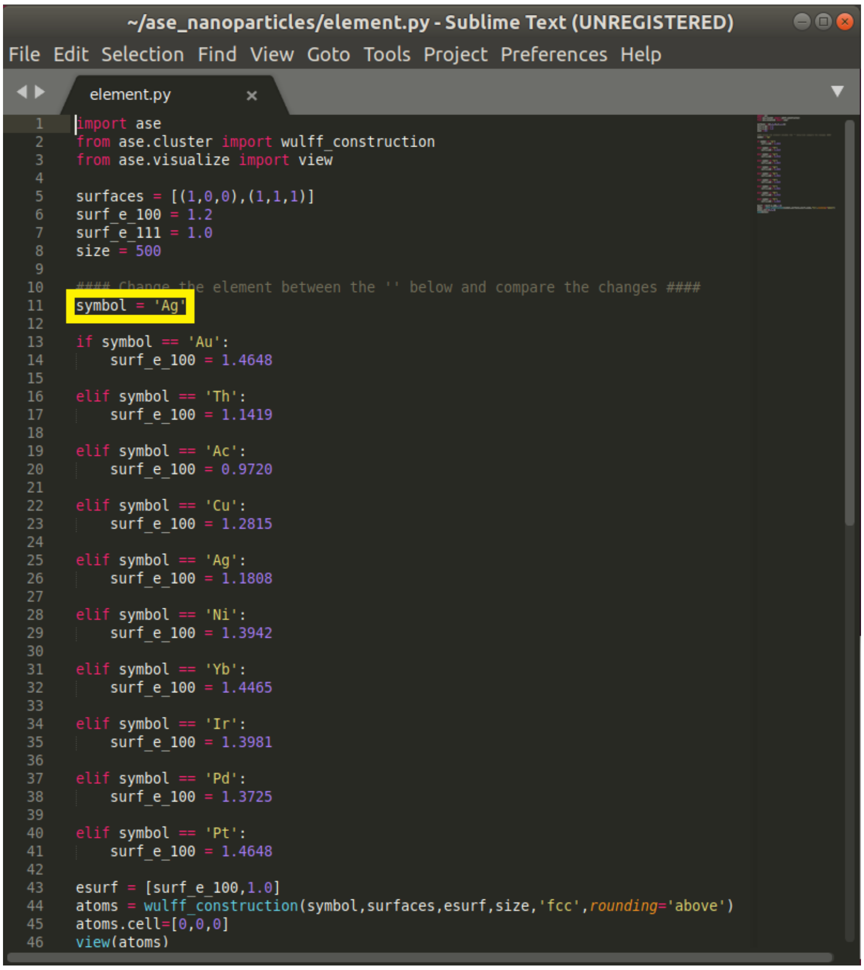
2. What might this mean for the surfaces energies for each face?

Introduction

All metals have different ratios for their surface and bulk energies which can alter the appearance of the nanoparticle. When there is a higher energy surface (compared to the other) the nanoparticle will arranges so that there is less of that face exposed, giving different shapes.

Instructions

1. Type ‘python element.py’ and execute the script, which will give a similar nanoparticle as the very first simulation.
2. The script can then be edited by typing ‘subl element.py’ and executing this. Instructions can be seen on the help sheet (page 3) The script is seen in Figure 12, the line of interest is shown in yellow.
3. The symbol can be changed to any of the following; Gold (Au), Thorium (Th), Copper (Cu), Silver (Ag), Nickel (Ni), Ytterbium (Yb), Iridium (Ir), Palladium (Pd), Platinum (Pt). Just remember to use the text editor Sublime (subl) to change the element each time and to save the change before using python on this script.


~/ase_nanoparticles/element.py - Sublime Text (UNREGISTERED)
File Edit Selection Find View Goto Tools Project Preferences Help
element.py

```python
import ase
from ase.cluster import wulff_construction
from ase.visualize import view

surfaces = [(1,0,0),(1,1,1)]
surf_e_100 = 1.2
surf_e_111 = 1.0
size = 500

#### Change the element between the '' below and compare the changes ####
symbol = 'Ag'

if symbol == 'Au':
    surf_e_100 = 1.4648

elif symbol == 'Th':
    surf_e_100 = 1.1419

elif symbol == 'Ac':
    surf_e_100 = 0.9720

elif symbol == 'Cu':
    surf_e_100 = 1.2815

elif symbol == 'Ag':
    surf_e_100 = 1.1808

elif symbol == 'Ni':
    surf_e_100 = 1.3942

elif symbol == 'Yb':
    surf_e_100 = 1.4465

elif symbol == 'Ir':
    surf_e_100 = 1.3981

elif symbol == 'Pd':
    surf_e_100 = 1.3725

elif symbol == 'Pt':
    surf_e_100 = 1.4648

esurf = [surf_e_100,1.0]
atoms = wulff_construction(symbol,surfaces,esurf,size,'fcc',rounding='above')
atoms.cell=[0,0,0]
view(atoms)
```

Figure 12: The element.py python script.

Note: You will observe that for these some of these elements they appear different in structure, showcasing that not all elements have the same properties giving different nanoparticles. For this task only the square faces will be counted as they are easier to observe, compare and count.

Palladium (Pd)

How many atoms is on a square face: ____________Atoms

Gold (Au)

How many atoms is on a square face: ____________Atoms

Answer the following questions below:

Focus Questions	
Do different metal nanoparticles look different? How?	
What might this mean for their surfaces energies for each face?	

Silver nanoprisms

What do the silver nanoprisms look like?

Questions to consider.

1. What shape are they?

2. What do the solutions look like?

3. What do you notice about the colour spectrum?

As you might know the experiment involved the sodium borohydride reduction of a silver salt, which is then re-oxidised by hydrogen peroxide (H_2O_2) to form silver nanoprisms as shown in Figure 13. A range of volumes of potassium bromide (KBr) were then added to the solutions, giving different sized particles and coloured solutions such as demonstrated in Figure 13. These simulations all aim to help the understand the observations of the silver nanoprism experiment.

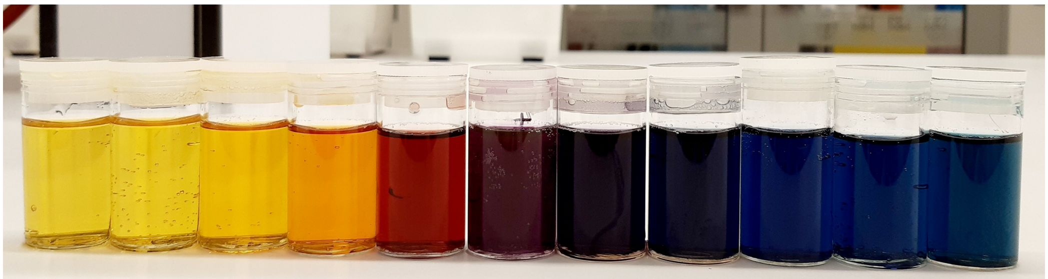


Figure 13: Possible coloured solutions made in the silver nanoprism experiment.

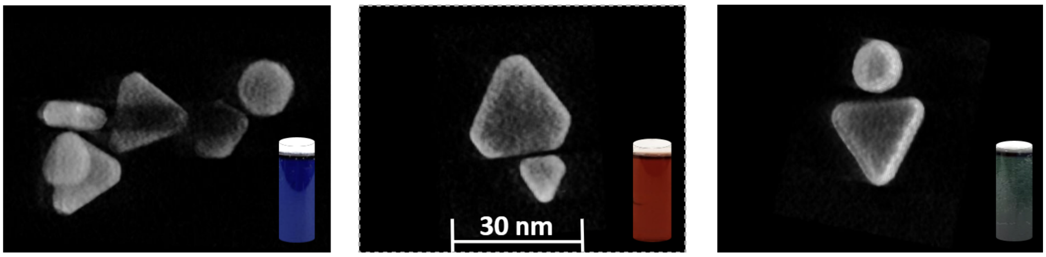


Figure 14: TEM imaging made of the silver nanoprisms showing their shape and size.

In the silver nanoprism experiment different coloured solutions are made (Figure 13) and these depended on the shape and size of the nanoprism which can be seen in transmission electron microscopy (TEM) imaging (Figure 14). TEM gives a two-dimensional (2D) representation of a structure which can then be transformed into a three-dimensional (3D) structure through the use of electron tomography. These images are the ones displayed in Figure 14 and can be used in order to confirm the shape of the silver nanoprisms formed.

Answer the following questions below:

Focus Questions	
What shape are they?	
What do the solutions look like?	
What do you notice about the colour spectrum?	

Why are the different sizes of nanoprisms different colours?

Questions to consider.

1. Why does the size of the nanoprism impact the colour?

2. How does the nanoprism stop growing?

Instructions

1. Type python colourMultiple.py and execute the octahedral script which is a mini movie script.
2. Instructions on how to set up to view the ‘mini movie’ are detailed on the help sheet page 4.
3. If play is pushed, the ‘mini movie’ will play which shows a nanoparticle of the same shape getting bigger.
4. These sizes can be related to colour. Draw a single wavelength of light, (∼) across the outlines of the different sized nanoprisms below. Make sure to adjust to the height and size of the nanoparticle.
   Ensure to compare these wavelengths to the spectrum on page 21.

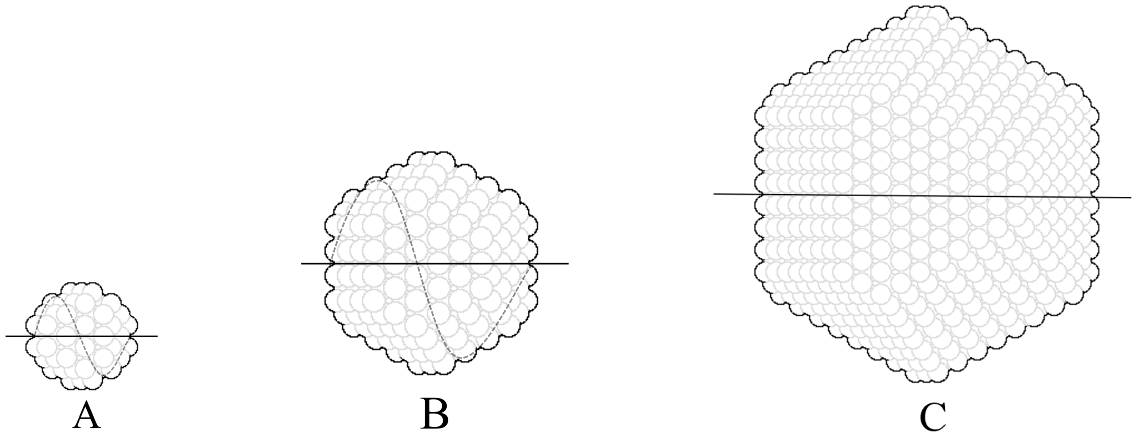
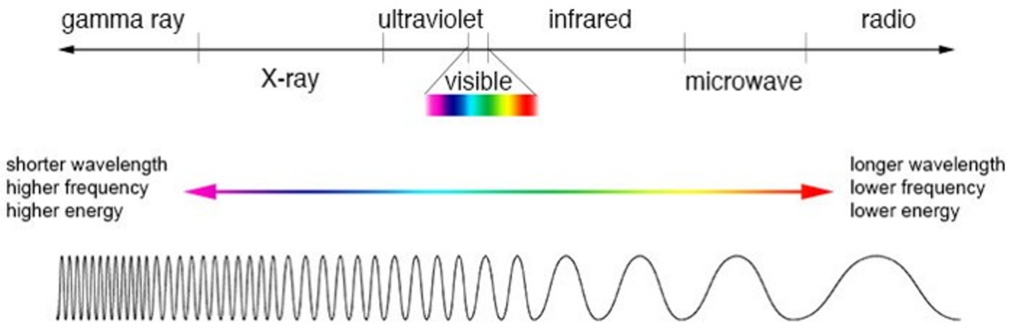


Figure 15: The outlines of the smallest (left), medium (middle) and biggest (right) nanoprisms.

5. The wavelengths drawn for these shapes can then be used alongside the spectrum in Figure 16 to compare the shape of the wavelength and what colour may be associated with a smaller/bigger nanoparticle.



Colour Absorbed.
The observed coloured solution is found on the opposite end of this spectrum.

Figure 16: Wavelength and colour spectrum.

These nanoprisms (in this case) grow by complete shells from the charged silver particles in the solution adhering to the surface. When this experiment was done, varying amounts of bromine (in the form of KBr) were added to the solution which resulted in different coloured solutions. Therefore, if there was something else in the solution such as the bromide which can adhere instead, it can cause the growth to be stopped the different size nanoprisms are formed. The more bromide there is around in the solution, the more likely the nanoprisms will be capped earlier.

6. Type ‘python colourBromine.py’ and execute the octahedral script. Another ‘mini movie’ will play where the nanoprism shows normal growth until some bromide attaches to its outer shell which stops the growing process giving different sized nanoprisms with different colours.

Which particle has the longest wavelength? ______________
Which particle has the shortest wavelength? ______________

Which colour solutions therefore relate to the largest particles? ______________
Which colour solutions therefore relate to the smallest particles? ______________

Answer the following questions below:

Focus Questions	
Why does the size of the nanoprism impact the colour?	
How does the nanoprism stop growing?	

Why are the different shapes of nanoprisms made?

Questions to consider.

1. How do the nanoprisms grow?

2. How are the prismatic shapes formed and capped?

Introduction

The shape and growth of these prismatic structures is related to the square and triangle faces discussed earlier. When these nanoprisms grow, the adhering silver orients itself around the silver nanoprism in a way to reduce the amount of 'exposed high energy surfaces', therefore the square (higher energy) surface is covered faster than the triangle face. In this growth simulation each layer becomes more and more prismatic as the high energy square faces are being 'covered up' faster than the triangle faces, which essentially produce more stable nanoparticles.

Instructions

1. Type 'python multiple.py' and execute the octahedral script which is a 'mini movie' script.
2. Instructions on how to set up to view the 'mini movie' are detailed on the help sheet.
3. If play is pushed, the 'mini movie' will play which shows a nanoparticle of the same shape getting bigger and more prismatic.
4. These sizes can be related to the prismatic structures seen in TEM images.

Answer the following questions below:

Focus Questions	
How do the nanoprisms grow?	
How are the prismatic shapes formed and capped?	

Summary of the silver nanoprisms experiment.

1. Type 'python bromideMultiple.py' and execute the octahedral script which is the final mini movie script.
2. If play is pushed, the 'mini movie' will play which shows a nanoparticle of the same shape getting bigger and more prismatic and then being capped by bromide.
3. These different sized and different shaped nanoparticles are then capped by the bromide halting its growth when done so.