ISIS Neutron Training Course 2014

Tutorial: PHONON PROPERTIES OF SODIUM HYDRIDE

Start Materials Studio

- You should see a complex application, and (depending on previous use) a prompt panel enquiring whether to open a new or existing project.

Create a new project. Unless you were presented with a prompt window for this you can do this by the menu "File"->"New Project"

- A pop-up window will ask you to choose a suitable name.

Choose any suitable name. This tutorial will assume "NaH-Phonon"

- You will see a "Project Explorer" on the left with the new project and a blank canvas on the right.

SETTING UP THE STRUCTURE

Now you must create a crystal structure model of NaH. There are various options for doing this

A) Create a crystal structure from lattice parameters and co-ordinates. We will not do this here, but there is a Materials Studio tutorial to explain how to do this.

B) Import an existing crystal structure

Menu "File->Import" will pop up a navigation menu. If you had a "cif" or other structure file you could import it from here. But Materials Studio also possesses a database of crystal structures, which can be found under "Structures".

NaH is not present in the database, but you will find NaCl. Locate and select NaCl.

- You will now see a cubic crystal structure of NaCl.

Bring up the "display style" menu using a right mouse click (or find it as one of the toolbar icons) and select Ball and Stick. Experiment with the mouse to rotate and scale the structure.

Now transform NaCl into NaH. First bring up the "Properties Explorer" using the menu "View"->"Explorers"->"Properties Explorer".

- You will see a long list of atomic attributes on the left below the "Project Explorer".

Finally you should change the name of the crystal from NaCl to NaH in the Project Explorer.

Click to select one of the Cl atoms. You can now change this into H by double-clicking "Element Symbol" in the properties explorer.

-You will be presented with a periodic table to choose the new element. Choose H of course.

Now change *all* of the Cl into H. Hint - use the right mouse menu to find all of the symmetry images.

- You ought now to have an NaH structure but with the lattice parameters of NaCl.

For calculation purposes it is best to work with the primitive cell. You can change to this using the "Build"->"Symmetry" menu.

- The cubic conventional cell view should be replaced by a primitive cell one.

We could now edit the lattice parameters, but instead let CASTEP to the work. Start the CASTEP setup driver - the "wavy lines" icon on the tool bar.

- You will see a window appear labelled "CASTEP Calculation"

Choose the settings
Under "Setup"

Task: Geometry Optimization
Click "More" and choose "Optimize cell"
Quality: Fine - this chooses the "quality" and size of the basis set.
Metal: You should uncheck this box (otherwise LO/TO splitting will not be calculated in the subsequent phonon calculation).

Under "Electronic"

Pseudopotentials: "Norm Conserving"
k-point set: "Medium" (For speed)

Job Control

Gateway Location: ui1.scarf.rl.ac.uk - this chooses which computer to run the (computationally expensive) CASTEP calculation. SCARF is the STFC compute facility.

Now you are ready to run the calculation. Click "Run"

- If you did not already choose it, you will be asked to choose whether to convert to use a primitive cell for this calculation. This is quicker so check "Yes"

The job will be submitted to SCARF but should run and complete quickly - around 30s.

- You will be presented with a window containing the CASTEP output file. This contains several geometry optimization steps (BFGS iterations) for a constant-pressure optimisation.

- Near the end of the file you will find the "BFGS: Final Configuration" and a description of the final lattice parameters.

What is the cubic lattice parameter of NaH? Hint - you will need some arithmetic
to work this out. How does it compare with the experimental value of 4.89

Now you need to get the optimised structure back into Materials Studio. Under

the "Wavy lines" tool icon select " CASTEP Analysis".

 - The analysis window will pop up giving a list of things to analyse.

From the list choose "Structure". For the next part you MUST click the crystal structure display window. Click the "Update" button.

At this point you can also import the electron density if you like.

 - You should see an electron density isosurface displayed.

RUNNING THE PHONON CALCULATION

In the project explorer select the NaH crystal structure which should contain the
updated structure.

As before, start the CASTEP setup tool.

Choose the settings
Under "Setup"

 Task: Properties   (This will enable phonons and much more)
 Quality: Fine - this chooses the "quality" and size of the basis set.
 Metal: You should uncheck this box otherwise LO/TO splitting will not be calculated

Under "Electronic"

 Pseudopotentials: "Norm Conserving"
 k-point set: "Coarse" or "Medium" (For speed)

Under "Properties"

Check "Phonons".

  - You should be presented with a choice of DOS, dispersion or both. Why not do
    both?

Click the "More" button. Then click the dispersion "Path" button to define the Q-space path through the Brillouin Zone.

  - A labelled Brillouin Zone should appear on top of your structure. Materials
    Studio sets up a good default path and there is no need to choose it.

Theory note: The calculation does not compute the frequencies at each wavevector independently. Instead it computes the full force constant matrix of Lattice Dynamics theory using a regular grid of q-points, and uses Fourier methods to compute the DOS and dispersion. For this first run you should set the ""q-vector
grid spacing for interpolation" to around 0.08. ** Warning - you can make the calculation arbitrarily expensive using this control!

Now you are finally in a position to run the calculation. Choose the scarf gateway, select 16 processors and optimise for speed, and click the "Run" button.

 - The job will be submitted to the SCARF queue and should take a minute or two

to run.

Analysing the results

As before, under the "Wavy lines" toolbar item icon select " CASTEP Analysis".

- You will see a list of possible analyses. Select "Phonon density of states"

To enable the reading in of the data you must first select the CASTEP output "NaH_PhonDOS" in the Project Explorer in the left-hand panel.

- When you have done the correct selections, the "Results File" box in the Analysis window should read "NaH_PhonDOS.castep"

You will then be able to click the "View" button

- You should see a plot of the DFT calculated phonon density of states of sodium hydride.

Repeat the procedure but for phonon dispersion, being sure to select the correct output file.

- You should see a plot of the phonon dispersion of sodium hydride.

What happens if you attempt to analyse the "NaH_PhonDisp" calculation as if a density of states.

- Can you explain what you see?

You can also calculated some thermochemical properties by performing the "Thermodynamic Properties" analysis of the DOS results.

- The result will be plots of energy, heat capacity entropy and Debye temperature as a function of T.

If there is time, you could attempt to repeat the DOS calculation using a finer grid of points. The setting can be found under "Quality" in the "Phonon Properties Setup" window.