Introduction

The aim of these hands-on is to calculate phonons! First, we are going to compute the phonon spectrum of fcc Al using the DFPT, which is the most accurate method. Then, we're going to use the results of an *ab initio* molecular dynamics calculation (that has been performed elsewhere) in order to plot the phonon spectrum of fcc Al at two different temperatures using a method called TDEP, and compare the results with those obtained by DFPT.

Phonons of fcc Al at 0K with DFPT

1. You should have a number of files available in the shared directory that you need to copy in your work folder. These are abinit.in, abinit.files, mrgddb.in, anaddb.in, and anaddb.files.

   As phonon calculations are not the easiest to prepare, we provide you with these files, but you should read them carefully in order to understand what's happening.

2. Open the abinit.in file for reading and, well, read it!

3. Run abinit! You are strongly advised to use a few MPI processes to fasten the calculation, because it can take up to 1 hour on a single process. Beware though, since the number of k-points differ in each dataset, abinit may or may not crash :)

4. What is abinit doing?

   - In the first dataset, it calculates and prints the GS wavefunctions with a great accuracy.
   - In the second dataset, it reads the GS wavefunctions and determines at which q-point it will compute the phonon frequencies, depending on the q-point grid provided. In our case, the Γ point.
   - It uses the q-point symmetries in order to reduce the number of atomic displacements (that is, perturbations) to be made.
   - It solves the Sternheimer equation and computes the frequencies, which are printed in the _DDB (as in "database") file.
   - Repeat for all q-points.

5. Type grep Perturbation abinit.out. It will return a nice overview of what happened during the calculation. You can see all q-points and all perturbations. Note that abinit did not compute all directions because of symmetries.

6. Unfortunately, we cannot get the phonon spectrum yet. How can we be sure that everything has gone well? Open the output file and look for the string "Fourteen". This will lead you to a summary of all the energy components that were computed during one DFPT dataset. **There is one of these summaries for each q-point**.

   Compare the two following energies: **2DEtotal** and **non-var. 2DEtotal**. If they are similar (to the 4th digit, at least), then it's a good sign that the calculation went well.

7. Now we want the phonon spectrum! Because abinit prints separately the results of each q-point, the first thing to do is to merge them back. For this we use the mrgddb tool, which is provided with abinit. There should be a mrgddb.in file in your directory. There's little interest in reading it but you can if you are curious. Then just type mrgddb < mrgddb.in. This will merge all DBB files and output a mrgddb.out file, that you still cannot use!

8. One last step (and not the least...) is to use the anaddb tool, which will **analyse** the merged DDB. Open the anaddb.in file and read it carefully, in order to understand what it does. Basically it takes the frequencies calculated with abinit and **extrapolates** them to other q-points, that are specified at the end of the file.

   I know, it is quite a hassle to have to specify all the q-points but hey, no rest for the wicked!

9. Run anaddb by typing anaddb < anaddb.files. It will output a number of files, but the ones you want most are anaddb.out_PHFRQ (phonon spectrum!) and anaddb.out_PHDOS (phonon DOS!)

10. Plot the phonon spectrum using xmgrace -nxy anaddb.out_PHFRQ. Let's make this spectrum beautiful!

    - First you can see that the units are lousy (don't ask me why...). Go to Data>Transformations>Geometric Transforms. Select All Sets and in the Scale Y case, just put **27211**. This will convert the Ha into meV. Click on Accept, then on AS (Auto-Scale) to rescale the plot. We have now meV.

    - Now we want to specify the high symmetry q-points on the x-axis. Double-click on the x-axis and that should open a window called Grace: Axes. Click on the Tick marks tab and check the Draw grid lines box under the Major ticks group box. You should now have ugly grid lines on your plot. Let's arrange this.

    - Keep the same window open and go in the Special tab. Set Special ticks to **Tick marks and labels** then decrease the Number of user ticks to use to 5 (this is the number of q-points that we will show).

    - Now we will fill the first 5 cases below that. The first number is the coordinate on the x-axis of the plot and the second is the q-point label. Set them as follows: **(0, G) (100, X) (200, X) (338, G)** and **(425, L)**. Now the line should match the high-symmetry q-points.

    - One last thing: on the top of this same window, set the Stop to **425** instead of **500** and click on Accept.

11. Save your work! We will need it. Click on File>Save and save it as Phonons_DFPT.agr

Phonons of fcc Al at 50K and 1000K with TDEP

This section is much easier than the previous one because the largest part of the work has already been done. In order to calculate phonons with TDEP, you just need a file containing the result of a molecular dynamics calculation. It can be done with **empirical potential** (classical MD) or with **DFT** (*ab initio* MD).

1. In your shared folder, there should be two _HIST.nc files, which have been output from two separate AIMD calculations. output_0050K_HIST.nc and output_1000K_HIST.nc are results from a AIMD at 50K and 1000K, respectively. Copy these files into a new working directory.

2. Let's start with the MD @ 1000K. Open it with QAgate: qagate output_1000K_HIST.nc. You can see that this is a 32-atom supercell of fcc-Al. This corresponds to a 2x2x2 expansion of the **conventional** unitcell. When computing phonons with TDEP, **you need large supercells of at least 100+ atoms** in order to get accurate phonons. So we do not expect to have a great accuracy here.

   Let's see what more we can get out of this:

   - Play the dynamics. You see that atoms are significantly moving off their ideal positions. It's kind of normal given the high temperature.

   - Plot the pressure wrt the number of steps. You see that it takes around 200 steps for the pressure to stabilise (that is, to have regular oscillations). This is called **equilibration**.

   - Plot the energy wrt to the number of steps. Here again, you see that equilibration takes around 200 steps.

   - Plot the Pair Distribution Function (PDF). This shows us that the supercell is actually too small for an accurate phonon calculation, because very few neighbors are plotted. Still, it will give interesting results.

   - Plot the stress tensor (σ) wrt to the number of steps. **This is a very important thing to do with TDEP** because it can be an indication of **dynamical instability**. You should have 6 stresses, the first three are stresses along the x, y and z axis and the other three are sheer constraints. The sheer constraints must oscillate around zero. As for the other three, they must have the same values on average. If one of the stresses is far from the two others, it means that the stresses are not **isotropic**, hence **dynamical instability**. Here, all is well!

     Keep in mind to always check the stresses. Very often, the phonons do not show a dynamical instability whereas the stresses do!

   - Finally, click on TDEP! QAgate starts by searching the primitive unit cell of your system, then maps the supercell on this primitive unitcell and calculate phonons. You should end up with the primitive cell shown on QAgate. Exit the program.

   - QAgate has output several files that begin with the temperature of the MD. Plot the phonon spectrum by typing xmgrace -nxy 957.855Komega.dat. The phonons look a bit steep, compared to those from DFPT. Let's compare them.

   - Close xmgrace and go back to the previous work directory where you saved your Phonons_DFPT.agr file. Open it with xmgrace: xmgrace Phonons_DFPT.agr.

   - Go to Data>Import>ASCII and navigate through your directories to find the 957.855Komega.dat files output by QAgate. **DO NOT ACCEPT YET!** Set the Load as entry to **NXY** and, more importantly, set Autoscale on read to **None** and click OK.

- Now the two spectra are on the same plot and you see major differences, in particular with the high frequency phonon modes. However, these differences could be due to:
    - The massive increase in temperature from 0 to 1000K.
    - The supercell size that is too small.
    - The number of steps in the dynamics.
- To check whether it is a temperature effect, let's compute the phonon spectrum from the AIMD @ 50K. Just do exactly the same thing as with 1000K. Note that you should do the computation on a separate folder. What do you get?
- If you have some time left, just raise your hand if you're interested in learning how to check convergence wrt to the number of steps!

What would a real AIMD calculation look like?

In these hands-on, our AIMD calculation was a bit short on accuracy. If you wish to compute a real phonon spectrum at finite temperature, you would need to:

- Have a sufficiently large supercell. It's actually not about the size of the supercell, but rather about the number of neighbors. In α-uranium for instance, there are 16 atoms in the primitive unit cell, so that with only this you get a real nice number of neighbors. For fcc and bcc crystal, however, more than a hundreds atoms are required.

- The cut off energy should be a bit larger. We used 10 Ha for computational costs reduction but you should always check for convergence wrt the cutoff anyway.

- You also need to always check the convergence of the phonon spectrum wrt the number of steps in the dynamics. TDEP is known to converge quickly but sometimes 8000 steps are necessary (usually at very high temperatures).

That is all! Not much is needed for a phonon calculation. The major drawback lies in the huge number of atoms that are required :) For instance, a single phonon calculation on a 108-atom plutonium supercell takes 10 millions cpu hours!!

And remember, the DFPT calculation is always right :)