

HOMEWORK 9**Due Monday 4:30 pm, March 30, 2009****Phonon Calculations and Thermodynamic Properties****Problem 1: Aluminum**

In this homework, we will perform phonon calculations for aluminum using two methods: [the linear response method](#), and [the small displacement method](#). To do this, the Quantum Espresso package (in particular: pw.x, ph.x, q2r.x, and matdyn.x) and the PHON program by Dario Alfe need to be compiled and used. This homework closely follows a tutorial by Dario Alfe which can be found on his website (<http://chianti.geol.ucl.ac.uk/~dario/>)

Consider a crystal at a very low temperature and expand the potential energy function around the equilibrium position of the nuclei. The first term of the expansion will be the energy of the system in its equilibrium position, E_{perf} . If the crystal is near its equilibrium configuration then the linear term will be zero, and the first term will be a quadratic term in the atomic displacements:

$$U_{harm} = E_{perf} + \frac{1}{2} \sum_{l\alpha, l'\beta} \Phi_{ls\alpha, l't\beta} u_{ls\alpha} u_{l't\beta}$$

where u_{ls} denotes the displacement of atom s in a unit cell l , α and β are Cartesian components, and $\Phi_{ls\alpha, l't\beta}$ is known as the force constant matrix. The force constant matrix is given by the double derivative of energy with respect to atomic displacements: $-\partial^2 U / \partial u_{ls\alpha} \partial u_{l't\beta}$. The force constant matrix relates the forces, \mathbf{F}_{ls} with the displacements $u_{l't}$:

$$F_{ls\alpha} = \partial U / \partial u_{ls\alpha} = - \sum_{l't\beta} \Phi_{ls\alpha, l't\beta} u_{l't\beta}$$

Within the quasi-harmonic approximation, the potential energy function U_{harm} completely determines the physical properties of the system. The Helmholtz free energy is given as:

$$F(V, T) = E_{perf}(V) + F_{harm}(V, T)$$

$$F_{harm} = k_B T \sum_n \ln(2 \sinh(\hbar \omega_n / 2k_B T))$$

with ω_n being the frequency of the n th vibrational mode of the crystal. As discussed in class, in a periodic crystal, the vibrational modes can be characterized by a wave-vector \mathbf{q} . For each such wave-vector there are three vibrational modes for every atom in the primitive cell. If the frequency of the s th mode at \mathbf{q} is denoted by ω_{qs} then vibrational free energy is given as:

$$F_{harm} = k_B T \sum_{qs} \ln(2 \sinh(\hbar \omega_{qs} / 2k_B T))$$

Since we here discuss infinite crystals, we are really interested in the free energy per primitive cell:

$$F_{\text{harm}} = \frac{k_B T}{\Omega} \int_{\text{BZ}} dq \sum_s \ln(2 \sinh(\hbar \omega_{qs}) / 2k_B T)$$

where $\Omega = (2\pi)^3 / V$ is the volume of the Brillouin Zone. We can also calculate the above integral using the phonon density of states $g(\omega)$:

$$F_{\text{harm}} = k_B T \int_0^\infty d\omega g(\omega) \ln(2 \sinh(\hbar \omega) / 2k_B T)$$

where $g(\omega)d\omega$ is proportional to the number of phonons with frequency in the differential interval, and g is normalized so that the integral from 0 to ∞ is equal to the number of phonon branches (three times the number of atoms in the primitive cell).

The vibrational frequencies ω_{qs} are the eigenvalues of the dynamical matrix, $D_{s\alpha,t\beta}$:

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{l'} \Phi_{ls\alpha,l't\beta} \exp[i\mathbf{q} \cdot (\mathbf{R}_{l'} + \boldsymbol{\tau}_t - \mathbf{R}_l + \boldsymbol{\tau}_s)]$$

where $\mathbf{R}_l + \boldsymbol{\tau}_t$ represents the equilibrium position of atom t in primitive cell l , and the sum is in principle over the infinite number of primitive cells in the crystal. Translational invariance implies that the force constant matrix only depends on the differences in the distances between atoms in primitive cell l and l' . If the complete force-constant matrix is known, then $D_{s\alpha,t\beta}$ and so the frequencies ω_{qs} can be obtained at any \mathbf{q} . This

homework with go through two methods for finding the phonon frequencies using DFT.

One can quickly find a method for calculating phonons within our DFT framework by looking at our equation for the force constant matrix $\Phi_{ls\alpha,l't\beta}$. Since the force constant matrix relates displacements and forces, we can simply displace an atom t in cell l' in direction β , while keeping all other atoms fixed in equilibrium positions, and read in the forces $F_{ls\alpha}$ on all the other atoms. This directly gives the elements of the force constant matrix for the given $l't\beta$. Doing this for every $l't\beta$ gives our full force constant matrix. We assume displacements are small enough so that the relationship between displacements and forces is linear. Because of translational invariance and symmetry relationships, the number of separate calculations can be drastically reduced. This method is known as the small displacement method for phonon calculations.

Since our calculations in DFT use periodic boundary conditions for an infinite solid, we must make sure that our super cell is large enough so that the elements of the force constant matrix vanish at the edges. This is easily achieved for metals, but ionic materials may converge slowly.

Slow convergence in ionic materials is due to the limit towards zero wave-vector, the displacement of charges creates dipoles which interact with long range forces. These dipoles also produce a macroscopic electric field in the zero wave-vector limit, which is responsible for a splitting of the frequencies of the optical vibrational modes parallel and

perpendicular to the electric field (LO-TO splitting). The behavior of the dynamical matrix in the limit of small wave-vector is non analytical and has the following form:

$$D_{s\alpha,t\beta}^{na} = (M_s M_t)^{-1/2} \frac{4\pi e^2}{\Omega} \frac{(\mathbf{q} \cdot \mathbf{Z}_s^*)_\alpha (\mathbf{q} \cdot \mathbf{Z}_t^*)_\beta}{\mathbf{q} \cdot \epsilon^\infty \cdot \mathbf{q}}$$

where \mathbf{Z}_s^* is the Born effective charge tensor for atom s , ϵ is the high frequency static dielectric tensor and the M_s are the masses of the atoms. This non analytical part of the dynamical matrix is not defined at zero wave-vector, but provides the limiting values which help interpolating the dynamical matrix in the whole Brillouin zone.

Both the Born effective charge tensor, and the high frequency static dielectric tensor can be calculated using Density Functional Perturbation Theory (DFPT). This method is known as the linear response method. DFPT exploits the Hellmann-Feynman theorem to show that a linear order variation in the electric density upon application of a perturbation to the crystal is responsible for a variation in the energy up to second order of the perturbation. Using standard perturbation theory, this linear order variation of the electronic charge density can be calculated using only unperturbed wave-functions, which therefore only require calculations on the ground state crystal. This method also does not require the use of supercells.

The Small Displacement Method

We will now go through calculations for Aluminum using the small displacement method and the PHON codes. For detailed syntax of input files, please see the file manual.pdf, which is included (though the input should seem familiar to what we have been doing).

1. The first step is the construction of a primitive cell for the crystal, in this case an FCC crystal. For PHON, this is provided in a file called POSCAR. For this case it will look like this (given):

```
Al
3.9688275000
0.5000000000000000 0.5000000000000000 0.0000000000000000
0.0000000000000000 0.5000000000000000 0.5000000000000000
0.5000000000000000 0.0000000000000000 0.5000000000000000
1
Direct
0.0000000000000000 0.0000000000000000 0.0000000000000000
|
```

If you are familiar with the program VASP, this should look familiar. The lattice parameter is given as about 3.97 angstroms, which is close to the calculated DFT-LDA lattice parameter obtained with the pseudo potential used here. The first line is not read by the program. The second line gives the lattice parameter. The next three lines define the lattice vectors. The next line gives the number of atoms of each species (for us, just 1 Al). We then define the atomic basis in crystal coordinates.

2. We must now construct the super-cell, which is done using the following setting in the INPHON file:

```
# number of ions types and masses
NTYPES = 1;  MASS =26.98

# generate superlattice
LSUPER = .T.;  NDIM = 2 2 2;
DXSTART = 1 -1 1
```

LSUPER tells PHON that we are creating a supercell, with dimensions given in NDIM. Supercell generation with phon also gives a list of all the displacements needed to compute the force constant matrix with all the symmetries taken into account. DXSTART can be given if the first displacement wants to be specified.

Now run the PHON code by making sure your input files are set up correctly, and typing

```
phon
```

The program generates a file called SPOSCAR containing the super-cell (8 atoms for us). Now copy SPOSCAR to POSCAR either manually or by typing

```
cp SPOSCAR POSCAR
```

The displacements needed to compute the full force field are written in the file DISP. Because of all our symmetries, only one displacement is needed with a size of .04 angstroms (the default).

3. Now we need to displace the atom in the primitive cell according to the file DISP, and calculate the forces on all the atoms in the unit cell using pw.x. As always, we need check convergence with respect to cutoff energy and k-point sampling (there is much more to consider, as we have seen, but at the very least these two must be considered). We have set the plane-wave cutoff to 15 Ry, but you are welcome to play around with that parameter and report the results.

After pw.x has calculated forces, we should create a file called FORCES containing the information for the atom displaced, its displacement, and the forces of all the other atoms in the super cell. Also, pw.x reports forces in Ry/Bohr, and we should convert them to eV/angstrom.

The script runphon.pw performs all of these steps automatically. We just need to modify the script to provide the displacement. Look at runphon.pw. For now, it is good, so just run it:

```
runphon.pw
```

4. After the file has run, the FORCES file should be created. We will now compute phonon dispersions and compare them to experimental data (provided in EXPAL). To do this, modify the INPHON file:

With these settings PHON will calculate phonon frequencies at 51 points along three different special directions in the BZ, defined by the initial (QI) and the three final (QF) q-points. The first direction is Δ , the second is Σ , and the third is called Λ .

The phonon frequencies will be written in the file FREQ.cm. Run PHON and plot both the experimental and calculated frequencies to compare. What are some reasons the calculation is not exact?
5. What happens if you change the direction of the displacement but not its size? (Do this by changing DXSTART and seeing the results)
6. What happens if you change the size of the displacement? Try to increase it by a factor of 10 and rerun runphon.pw.
7. What happens if you reduce the size of the displacement?

Linear Response

We will now calculate the phonon dispersions of Al using linear response. With this method it is possible to calculate phonons at any \mathbf{q} -vector without generating a super cell, only calculations on the primitive cell will be needed. In order to obtain dispersions we will compute the dynamical matrix on a grid of \mathbf{q} -points, then Fourier transform it to obtain the force constant matrix, which will give us the dynamical matrix, and hence the phonon frequencies from its diagonalization, at any \mathbf{q} point.

In order to compare with the small displacement method, we should use the same grid of \mathbf{q} -points (a $2 \times 2 \times 2$ grid supercell was used previously).

1. We first need to perform a self consistent calculation on the primitive cell using pw.x. What grid of \mathbf{k} points do we need to do a comparable calculation, keeping in mind the supercell used previously? Run pw.x with the file al.scf.in and the appropriate \mathbf{k} point grid.
2. The next step is to calculate the dynamical matrix on a $2 \times 2 \times 2$ grid of \mathbf{q} points. This is done by running ph.x with the input as:

$$\text{ldisp} = \text{.true.}, \text{nq1} = 2, \text{nq2} = 2, \text{nq3} = 2$$
3. Run ph.x by typing: “ph.x <al.ph.in> al.ph.out” this generates the dynamical matrices on a $2 \times 2 \times 2$ grid of \mathbf{q} points.
4. We now need to Fourier transform this to get the force constant matrix. To do this, use q2r.x with the q2r.in input file provided.

- Now we want to calculate phonon dispersions along the same directions as done with the small displacement method. The points at which we want to calculate the dynamical matrix and its eigenvalues are given in the file `matdyn.in`. The executable `matdyn.x` calculates the phonon dispersions at the given points specified by the input. Run `matdyn.x` with the given input file. The phonon frequencies will be given in the file `al.freq`. To get the phonon frequencies in the same format as `FREQ.cm`, type: `f > ph24.cm`. Plot both `FREQ.cm` and `ph24.cm`, and see how close they are. Note that the two methods are essentially independent from each other. How well do the results agree?

Thermodynamics of Al

We will now calculate thermodynamic properties, in particular the Helmholtz free energy. To calculate thermodynamic properties with PHON you need to add the following settings to the `INPHON` file:

```
LFREE =.TRUE.
TEMPERATURE = 300
QA = 16; QB = 16; QC = 16
```

where QA, QB, and QC are the number of points which sample the BZ to calculate the integral. Notice that PHON has produced a file called `QPOINTS`, which contains the special points to calculate the integral. For subsequent calculations, for example if you want to calculate the free energy at a different temperature, you do not need to generate this file again, and you can simply comment out the line where QA, QB, and QC are set in the `INPHON` file. In the output of the PHON you can see the Helmholtz free energy, and, for example, the zero point energy.

- Find the thermodynamic properties of Al crystal using PHON. Print the output.
- Now, we can compare these to results using the linear response method. To do this use `matdyn.x` and `phdos.in`. Look at the `phdos.in` file, and make sure you understand what it means. Run `matdyn.x` by typing: “`matdyn.x <phdos.in> phdos.out`”. A file called `al.phdos` will be created which contains the phonon density of states. Now, apply this equation:

$$F_{\text{harm}} = k_B T \int_0^{\infty} d\omega g(\omega) \ln(2 \sinh(\hbar\omega) / 2k_B T)$$

by typing

```
awk '{e=e+2*1/2}END{print e/33.357*4.1357/1000}' al.phdos
```

into `cygwin`. What value do you get for the Helmholtz free energy or zero point energy? How does this compare the value PHON gives? How does this compare to experiment?