Tutorial on calculating phonons: comparing the linear response and the small displacement methods

Dario Alfè

Department of Earth Sciences and Department of Physics and Astronomy,
University College London, Gower Street, WC1E 6BT, London, UK

1 Phonons in a crystal

Consider a crystal at very low temperature and expand the potential energy function around the equilibrium positions of the nuclei. The first term of the expansion is simply the energy of the system calculated with the ions in their equilibrium positions, E_{perf}. If the crystal is near its minimum energy configuration the linear term of the expansion is zero, and the first term is a quadratic term in the atomic displacements:

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

where $\mathbf{u}_{ls}$ denotes the displacement of atom s in unit cell l, α and β are Cartesian components, and $\Phi_{ls\alpha, l't\beta}$ is the force-constant matrix, given by the double derivative $\partial^2 U / \partial u_{ls\alpha} \partial u_{l't\beta}$ evaluated with all atoms at their equilibrium positions. This force constant matrix gives the relation between the forces $\mathbf{F}_{ls}$ and the displacements $\mathbf{u}_{l't}$, as can be seen by differentiating eqn (1) and ignoring the higher-order an-harmonic terms:

$$F_{ls\alpha} = -\partial U / \partial u_{ls\alpha} = - \sum_{l't\beta} \Phi_{ls\alpha, l't\beta} u_{l't\beta} \ . \tag{2}$$

Within this quasi-harmonic approximation (the prefix "quasi" is there to indicate that the force constant matrix may depend on volume), the potential energy function U_{harm} completely determines the physical properties of the system, and in particular the Helmholtz free energy, which takes the form:

$$F(V, T) = E_{\text{perf}}(V) + F_{\text{harm}}(V, T), \tag{3}$$

with the quasi-harmonic component of the free energy given by:

$$F_{\text{harm}} = k_{\text{B}} T \sum_n \ln(2 \sinh(\hbar \omega_n / 2 k_{\text{B}} T)) \ , \tag{4}$$

with ω_n the frequency of the nth vibrational mode of the crystal. In a periodic crystal, the vibrational modes can be characterised by a wave-vector $\mathbf{q}$, and for each such wave-vector there are three vibrational modes for every atom in the primitive cell. If the frequency of the sth mode at wave-vector $\mathbf{q}$ is denoted by $\omega_{\mathbf{q}s}$, then the vibrational free energy is:

$$F_{\text{harm}} = k_{\text{B}} T \sum_{\mathbf{q}s} \ln(2 \sinh(\hbar \omega_{\mathbf{q}s} / 2 k_{\text{B}} T)). \tag{5}$$

In an infinite crystal the meaningful quantity is the free energy per primitive cell, which is given by:

$$F_{\text{harm}} = \frac{k_{\text{B}} T}{\Omega} \int_{\text{BZ}} d\mathbf{q} \sum_s \ln(2 \sinh(\hbar \omega_{\mathbf{q}s} / 2 k_{\text{B}} T)), \tag{6}$$

where $\Omega = (2\pi)^3 / V$ is the volume of the Brillouin Zone (BZ). Here we will only be interested in crystals, and therefore we will use the symbol F_{harm} only to indicate the Helmholtz free energy of a perfect crystal per primitive cell.

An equivalent way to calculate the above integral is through the phonon density of states $g(\omega)$:

$$F_{\text{harm}} = k_B T \int_0^\infty d\omega g(\omega) \ln(2\sinh(\hbar\omega)/2k_B T), \qquad (7)$$

where $g(\omega)d\omega$ is proportional to the number of phonons with frequency between ω and $\omega + d\omega$, and $g(\omega)$ is normalised so that its integral from zero to $+\infty$ is equal to the number of phonon branches (three times the number of atoms in the primitive cell).

The vibrational frequencies $\omega_{\mathbf{q}s}$ are the eigenvalues of the dynamical matrix, $D_{s\alpha,t\beta}(\mathbf{q})$, defined as:

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l \Phi_{ls\alpha,l't\beta} \exp\left[i\mathbf{q}\cdot(\mathbf{R}_{l'} + \tau_t - \mathbf{R}_l - \tau_s)\right] . \qquad (8)$$

Where $\mathbf{R}_l + \tau_t$ 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 hence the frequencies $\omega_{\mathbf{q}s}$ can be obtained at any $\mathbf{q}$. The purpose of this practical is to explore two alternative techniques to calculate the phonon frequencies $\omega_{\mathbf{q}s}$, within the framework of density functional theory.

2   Calculation of phonon frequencies

The method that is easier to understand to calculate phonon frequencies is based on the fact that the force constant matrix expresses the proportionality between displacements and forces, when the displacements are small enough for this relationship to be linear (see Eq. 2). All that has to be done, in principle, is to displace a single atom t in cell l' in Cartesian direction β, all other atoms being held fixed at their equilibrium positions; the forces $F_{ls\alpha}$ on all the atoms give directly the elements of the force constant matrix $\Phi_{ls\alpha,l't\beta}$ for the given $(l't\beta)$. If this procedure is repeated for all other $(l't\beta)$, all the elements of the force-constant matrix can be obtained. Translational invariance implies that the number of separate calculations required to do this is at most three times the number of atoms in the primitive cell, but for most materials symmetry relations can be used to reduce this number substantially. This strategy, sometimes called the small displacement method [1, 2], is implemented for example in the PHON code [3], which will be used in this tutorial. Although the small displacement method is widely used, and can be very accurate, a word of caution is in order. Since calculations on condensed matter often use periodic boundary conditions, the repeating cell (the *super-cell*) must be large enough so that the elements $\Phi_{ls\alpha,l't\beta}$ have all fallen off to negligible values at the boundary of the super-cell. This is readily achieved for some materials, particularly metals. However, in ionic materials convergence can be slow. This is because in the limit of zero wave-vector the displacement of charges creates dipoles which interact with long range forces, and therefore the force constant elements fall off only as r^{-3}. These dipoles also produce a macroscopic electric field in the limit of zero wave-vector, which is responsible for a splitting of the frequencies of the optical vibrational modes parallel and perpendicular to the electric field (the so called LO-TO splitting). It turns out that the the behaviour of the dynamical matrix in the limit of small wave-vector is non-analytical, and has the following form:

$$D_{s\alpha,t\beta}^{\text{na}} = (M_s M_t)^{-1/2} \frac{4\pi e^2}{\Omega} \frac{(\mathbf{q}\cdot\mathbf{Z}_s^*)_\alpha (\mathbf{q}\cdot\mathbf{Z}_t^*)_\beta}{\mathbf{q}\cdot\epsilon^\infty\cdot\mathbf{q}}, \qquad (9)$$

where $\mathbf{Z}_s^*$ is the Born effective charge tensor for atom s, ϵ^∞ the high frequency static dielectric tensor and M_s, M_t the masses of the atoms. This non-analytical part of the dynamical matrix (which only affects the longitudinal phonons) is not defined at zero wave-vector, but provides the limiting values which, as we shall see, help interpolating the dynamical matrix in the whole Brillouin zone (BZ). Note that in general these limiting values may be different for different directions (in the cubic crystal that we will investigate here symmetry ensures that these limiting values do not depend on the direction along which the limit is taken).

The quantities $\mathbf{Z}_s^*$ and ϵ^∞ can be calculated in the framework of density functional perturbation theory [5, 6, 7] (DFPT), which also provides a second elegant strategy for the calculation of phonons in crystals (sometimes also known as the "linear response method"). The main idea in DFPT, pioneered by Baroni *et al.* [5] is to exploit the Hellmann-Feynman theorem to show that a linear order variation in the electron density upon application of a perturbation to the crystal is responsible for a variation in the energy up to second (in fact, third [8]) 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. If the perturbation is a phonon wave with wave-vector $\mathbf{q}$, calculation of the density change to linear

order in the perturbation can be used to determine the dynamical matrix at wave-vector **q**. This can be done for any arbitrary wave-vector, without the need for the construction of a super-cell.

In this tutorial we will calculate the phonons of two different materials, a metal and and insulator, using both the "small displacement" and the "linear response" methods. In both cases we will use the PWSCF code, which is density functional theory code based on plane-waves and pseudo-potentials. We will use the implementation of the exchange-correlation functional known as the local density approximation (LDA).

We shall see that in the case of a metal both methods can be efficiently used to provide phonons in the whole BZ. In the case of the insulator the long range forces make it more difficult to calculate phonons in the whole BZ using the small displacement method, while these difficulties are easily overcome with the linear response method. However, we shall see that if the interest is in calculating thermodynamic properties, the small displacement method can provide similar accuracy as the linear response method.

To install the tutorial untar the file 'tutorial_phonons.tar' inside the directory ~/espresso-3.2/examples. This will create two directories called 'Al' and 'Mg'.

3 Phonons of aluminium

Go inside the directory 'Al'.

3.1 The small displacement method

We will now calculate the phonons of Al using the small displacement method as implemented in the PHON code.

3.1.1 Primitive cell

The first step is the construction of a primitive cell for the crystal, in this case a face-centred-cubic (FCC) crystal. This has to be provided in a file called POSCAR, which has the same format as in the program VASP [4]. In this particular case it will be:

```
Al
3.9688275
0.5    0.5    0.0
0.0    0.5    0.5
0.5    0.0    0.5
1
Direct
0.0    0.0    0.0
```

The value of the lattice parameter 3.97 Å is close to the calculated DFT-LDA lattice parameter obtained with the pseudo-potential to be used here (compare this with the experimental lattice parameter 4.04 Å)

3.1.2 Super-cell generation

The next step is to construct a super-cell, this can be done using the following setting in the INPHON file:

```
LSUPER =.TRUE. (default)
NDIM = NX NY NZ (default: 1 1 1)
NTYPES = 1 (no default)
```

where NX, NY and NZ are positive integer numbers. NTYPES is the number of different atomic species (1 in this example). We shall start with a small super-cell, so set NX = NY = NZ = 2. Now run the PHON code:

> phon

The program has generated a file called SPOSCAR which contains the super-cell (8 atoms in this case). Now copy SPOSCAR to POSCAR.

```
> cp SPOSCAR POSCAR
```

The program also prints out a guess for the displacements needed to construct the full force field. These are written on the stout and in the file DISP. Because of the symmetries present in the fcc crystal, in this particular case only one displacement is needed. The size of the displacement is 0.04 Å by default.

Now we need to displace the atom in the primitive cell according to the suggested displacement and calculate the forces on all the atoms in the unit cell using PWSCF. As usual, when performing a DFT calculation we need to check convergence of the results with respect to a number of technical parameters, like plane-wave cutoff energy and **k**-point sampling. The plane-wave cutoff has been set to 15 Ry to start with, but you are welcome to explore the convergence of the results by trying to increase it or decrease it. The convergence with respect to **k**-point sampling will be explicitly tested during the practical. Note that we are using a smearing of the occupation numbers according to the scheme of Methfessel and Paxton, with a smearing energy of 0.04 Ry (this will also affect the convergence of the results).

After PWSCF has calculated the forces we need to create the file FORCES which contains the informations on the atom displaced, its displacement, and the forces on all the atoms in the super-cell. PWSCF provides forces in units of Ry/Bohr, PHON needs them in units of eV/A, so we need to convert them.

All the above steps are automatically performed by the script *runphon.pw*. All we need to do is to modify the script to provide the displacement. To start with, the script already contains a good displacement, so now just run it:

```
> runphon.pw
```

After the script has run you will find a newly created FORCES file, which now can be used by PHON to calculate phonons. The first thing we are going to do is to calculate phonons dispersions, and compare them with the experimental data (provided in the file EXPAL). To do this, we have to set the following in the INPHON file:

MASS = 26.98   the mass of the Al atom in amu units
LSUPER = .FALSE.
LRECIP = .F.   special q-points in Cartesian coordinates
ND = 3   3 different special directions in the BZ
NPOINTS = 51   51 points between any two special q-points
QI = 0.0 0.0 0.0   1.0 1.0 0.0   0.0 0.0 0.0   the 3 initial special q-points
QF = 1.0 0.0 0.0   0.0 0.0 0.0   0.5 0.5 0.5   the 3 final special q-points

with these setting PHON will calculate phonon frequencies at 51 points along three different special directions in the BZ, defined by the three initial (QI) and the three final (QF) **q**-points. The first direction is defined by QI=(0.0,0.0,0.0) (called Γ) and QF=(1.0,0.0,0.0) (called X), and is called Δ. The second direction is defined by QI=(1.0,1.0,0.0) and QF=(0.0,0.0,0.0) and is called Σ. Note that (1.0,1.0,0.0) is equivalent to (1.0,0.0,0.0), so the initial and the final points of this second direction are the same as those of the previous direction, with the QI and QF swapped, however, the direction is different, as this second one also goes through the point K = (0.75,0.75,0.0). The third and final direction has QI=(0.0,0.0,0.0) and QF=(0.5,0.5,0.5) (called L), and is called Λ.

The phonon frequencies are written in the file FREQ.cm, which we can now plot (for example using gnuplot) together with the experimental frequencies contained in the file EXPAL. You can use the file f.g for convenience, edit this appropriately and then type:

```
> gnuplot
gnuplot> lo 'f.g
```

You can see that the agreement with the experimental phonons is only fair. There are at least three reasons for this. The first reason is of course that density functional theory with the present pseudo-potential is not exact quantum mechanics, and therefore might be not good enough, however, we expect DFT to do much better than this in the present case. The second reason is that the calculated phonons are only exact at **q**-vectors compatible with the super-cell, and the rest represent only an interpolation in the BZ.

Exercise 1: prove this. **Hint**: note that for a calculation in p.b.c. displacing one atom implies displacing also all its images, and therefore the calculated force constant matrix is the sum of the exact force constant

matrix evaluated at all periodic images of the displaced atom.

However, although the relatively small 2x2x2 super-cell may be responsible for some of the disagreement between the calculated and the experimental phonon dispersions in some parts of the BZ, this cannot be the reason for the disagreement at the point (1.0,0.0,0.0) (the M point), because this point is indeed compatible with the 2x2x2 cell. The third reason is related to the first one, and it is that DFT may be ok, but the way we are applying it is not good enough .... (can you think why?) We will come back to this later.

Now we want to try a few things which may affect the calculations:

Question 1: What happens if you change the direction of the displacement (but not its size)? Try to do this by setting DXSTART to some random direction in the INPHON file.

Question 2: What happens if you change the size of the displacement? Try to increase it by a factor of 10 and re-run runphon.pw.

Question 3: What happens if you reduce the size of the displacement ?

3.2   Linear response

We will now calculate the same phonon dispersions of Al using linear response. With this method it is possible to calculate phonons at any **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 **q**-points, then Fourier transform it using the inverse of Eq. 8 to obtain the force constant matrix, which we will use again with Eq. 8 to obtain the dynamical matrix (and hence the phonon frequencies from its diagonalisation) at any **q**-vector.

In order to compare the calculations with those performed earlier with the small displacement method we need to use the same grid of **q**-points. Since we used a 2x2x2 super-cell earlier, here we need to calculate the dynamical matrix on a 2x2x2 grid of **q**-points. The first step is to perform a self-consistent calculation on the primitive cell, which means running pw.x on a primitive cell (containing a single Al atom).

Question 4: What grid of **k**-points do we need to use to do comparable calculations?

Now run:

> pw.x < al.scf.in

Which generates the self-consistent wave-functions. The next step is to calculate the dynamical matrix on a 2x2x2 grid of **q**-points. This is done by running the ph.x program after setting in its input:

ldisp = .true., nq1 = 2, nq2 = 2, nq3 = 2

Now type:

> ph.x < al.ph.in

this generates the dynamical matrices on a 2x2x2 grid of **q**-points. We now want to Fourier transform this to obtain the force constant matrix, so type:

> q2r.x < q2r.in

Now we are ready to calculate the phonon dispersions along the same directions as done earlier with the small displacement method. The points at which we want to calculate the dynamical matrix (and its eigenvalues) are defined in the file matdyn.in, so now type:

> matdyn.x < matdyn.in

5

and we now have the phonon frequencies in the file al.freq. For convenience of plotting, now run:

> f > ph24.cm

and now the file ph24.cm should contain the phonon frequencies in the same format as the file FREQ.cm. We can now compare the two methods by plotting both FREQ.cm and ph24.cm, and we observe that the two calculations produce essentially identical results. Note that these two methods to calculate phonons are completely independent from each other, a part of course for being both based on the same implementation of density functional theory. The fact that they agree closely represents a good check on the correctness of the results.

3.3 Phonons of Al, improving the calculations

Now that we have proven that the linear response and the small displacement methods provide the same answer for the phonons of Al, if applied consistently, we want to see how we can improve the calculations in order to obtain better agreement with the experimental phonons. We mentioned earlier that one reason for the disagreement could be the size of the super-cell in the small displacement method (or equivalently the finess of the chosen **q**-points grid in the linear response method), and we will explore this a bit later. Before doing this however, we notice that the **k**-point sampling of the BZ was rather coarse (a 4x4x4 grid for the BZ of the primitive cell) for a system like Al, which is a metal. This suggests that a first improvement of the phonon dispersions might be obtained by increasing the number of **k**-points.

3.3.1 Convergence with respect to k-point sampling

Edit runphon.pw, change the grid of **k**-points from 2 2 2 to 4 4 4, and run the script again. Before running phon again copy FREQ.cm to FREQ22.cm, in order to store it. It is also useful to store the FORCES file, which is all you will need to recalculate the frequencies. After that run PHON. Repeat also the steps described in the previous section and calculate the phonon dispersions using the linear response method.

Question 5: How do you need to modify the al.scf.in file in order to do comparable calculations?

After you have done save the frequencies in, for example, ph28.cm, modify the f.g file appropriately and plot again the results. You should observe that now the frequencies agree better with the experiments, though there still are significant differences.

You can now keep increasing the **k**-point sampling until the phonon dispersions stop changing, you should see that once you use an 8x8x8 grid on the 2x2x2 super-cell (or, equivalently, the 16x16x16 grid in the primitive cell used with the linear response method) the phonon dispersions are essentially converged.

3.3.2 Convergence with respect to the size of the super-cell

We mentioned that a possible reason for the disagreement with the experiments is the relative small size of the super-cell used in the calculations. Now we want to test this by increasing the size of the super-cell. To do this, go back to Sec. 3.1 and repeat the steps to generate a super-cell, for example to a 4x4x4. In order to make comparable calculations, modify the runphon.pw script by halving the size of the displacement (in order to still have a displacement with a length of 0.04 Å). To start with, modify also the **k**-point sampling to:
K_POINTS gamma

This setting will only use the $\Gamma = (0.0, 0.0, 0.0)$ point, and PWSCF will exploit the special symmetry of the Γ point to run twice as fast as it would otherwise. This **k**-point sampling is equivalent to a 2x2x2 grid on a 2x2x2 super-cell, so the present results can be compared with the very first calculations we performed (hopefully stored in FREQ22.cm). Now run runphon.pw and phon and plot FREQ.cm together with FREQ22.cm.

Question 6: What do you observe by making this comparison?

Now do the linear response calculations. For this you need to modify the al.ph.in input file as follows:

ldisp = .true., nq1 = 4, nq2 = 4, nq3 = 4

and of course the al.scf.in input file as follows:

```
K_POINTS automatic
4 4 4 0 0 0
```

Now save the frequencies in ph44.cm and plot them together with those obtained with the small displacement method. Again, you will see that the two methods agree in predicting the same phonon dispersions.

Here it is even more evident that the **k**-point sampling is insufficient, as the phonon dispersions are poor. In the previous section we found that a 8x8x8 **k**-point grid on a 2x2x2 super-cell produced converged results, so let's try now to keep this sampling of the Brillouin Zone also for the calculation on the 4x4x4 super-cell. This means using a 4x4x4 **k**-point sampling in runphon.pw.

Now the calculations start to be expensive, so if you have the possibly of running the code on a parallel machine modify the call to pw.x in runphon.pw to something like mpirun -np 4 pw.x, or even more processors if you can. This calculation may take approximately 20 minutes on 4 processor, so we may need to leave it running for later. The equivalent linear response calculation will be faster, although when run on a parallel machine it will be slightly more difficult to exploit parallelism because ph.x only runs on a primitive cell. To make things easier, a FORCES.444_444 file containing the forces calculated with the above **k**-point settings has been provided, so if you don't want to wait 20 minutes just copy this file into FORCES and run PHON.

3.4   Thermodynamics of Al

We will now calculate thermodynamic quantities, and in particular the Helmholtz free energy, defined in Eqs. 5, 6, 7. To calculate thermodynamic properties with PHON you need to add the following setting to the INPHON file:

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

where QA, QB and QC are Monkhorst & Pack points which sample the BZ to calculate the integral in Eq. 6. You will notice that PHON has produced a file called QPOINTS, which contains the special MP points to be used to calculate the integral in in Eq. 6. 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 in the INPHON file the line where QA, QB and QC are set. In the output of PHON you can see the Helmholtz free energy and, for example, the zero point energy.

Similarly, we can calculate these quantities using the results obtained with the linear response method. For this run:

> matdyn.x < phdos.in

and this will produce a file called 'al.phdos' which contains the phonon density of states. Now apply Eq. 7, for example by typing:

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

and you should see that the Helmholtz free energy or the zero point energy are the same as those computed using PHON.

4   Phonons of MgO

The techniques described so far should be enough to calculate the main physical quantities, namely phonon dispersions and thermodynamic quantities in the quasi-harmonic approximation. These techniques are the same for any material, and in particular for the Earth's mantle relevant material MgO, which are going to investigate now. We will see that, since MgO is a polar material, for the reasons described in Sec. 2 convergence of the force constant matrix with respect to the size of the super-cell is going to be slow, and this will presents us with some problems for the interpolation of the phonon frequencies in the BZ. We shall see how these problems can be overcome, and also when do we really have to worry about them.

In the previous sections we exploited the fact that by knowing the exact phonon frequencies at a number of special points in the BZ we could extrapolate the frequencies at any **q**-vector in the BZ using Eq. 8. This strategy will also work for a slowly converging force constant matrix, provided that a sufficient number of special points are known. The additional problem present in polar materials has to do with the frequencies of longitudinal optical (LO) phonons, and their values in the limit of small wave-vector. Because of the induction of an electrical dipole moment which creates a macroscopic electric field, the frequencies of the LO phonons are different from those of the transverse optical (TO) modes. Moreover, at the Γ point the frequency of the LO mode is not uniquely defined. What is defined is the limiting value of this frequency as Γ is approached from a selected direction (see Eq. 9). This limiting value is very difficult to obtain within the small displacement method, because at the Γ point a super-cell calculation only provides the analytical part of the dynamical matrix, which results in no difference between the frequencies of the TO and the LO modes. Therefore one needs large super-cells in order to obtain the exact values of the LO frequencies for a series of small enough values of **q**, in order to perform a reliable extrapolation to zero wave-vector. If one uses only the analytical part of the dynamical matrix to interpolate the frequencies in the whole BZ, the incorrectness of the LO frequency at Γ results in a poor interpolation.

We will now calculate the phonons of MgO, and see in more details the appearance of this problem and how to overcome it. However, we will also see that, in fact, the poor interpolation of LO frequencies in the BZ is not a serious problem for the calculation of thermodynamic properties.

Again, here we will compare the small displacement and the linear response method for the calculation of the phonon dispersions and the thermodynamic properties of MgO.

Go inside the directory 'Mg'.

4.1 The small displacement method

We have to repeat now the procedure described in Sec. 3.1, modified appropriately to take into account the fact that now there are two different atoms in the primitive cell, and therefore the POSCAR will be:

MgO
4.1910818
0.5   0.5   0.0
0.0   0.5   0.5
0.5   0.0   0.5
1 1
Direct
0.0   0.0   0.0
0.5   0.5   0.5

where the value of the lattice parameter 4.19 Å is the DFT-LDA calculated one, and it is very close to the experimental value 4.21 Å.

Now generate a 2x2x2 super-cell with the settings:

LSUPER = .TRUE.
NDIM = 2 2 2
NTYPES = 2
MASS = 24.304 16.0

and notice that now the DISP file contains two displacements, one for the Mg atom and a second one for the O atom. The reason for this extra displacement here is that there are no symmetry operations that allow the swapping of the Mg and the O atoms. The calculations will therefore require to run pw.x twice, one for each displacement. Again, this is set up already in the provided runphon.pw file.

The **k**-point sampling are set to 2x2x2 to start with, and also notice that there is no smearing of the occupation numbers because MgO is an insulator. We will need to check convergence with respect to **k**-points just as we did previously in the Al case, but we will find here that since we are dealing with an insulator with a large band gap, the results converge much quicker.

Now copy SPOSCAR to POSCAR and run runphon.pw. Then modify INPHON by setting LSUPER = .FALSE. and re-run phon to generate the phonon dispersions. Since there are two atoms in the primitive cell now you have 6 phonon branches instead of 3 as in the Al case. The first three are the *acoustic* phonons, and the other three the *optical* phonons.

If you plot the phonon dispersions now you will notice that at Γ the three optical phonons are degenerate, while the LO frequency should really be different from the two TO frequencies. This is a limitation of the small displacement method, and we will come back to this when we will do the calculations with the linear response method.

Now check convergence with respect to **k**-point sampling by repeating the calculations with a denser grid, for example a 4x4x4. You will see that the phonon dispersions are essentially the same as those obtained with the 2x2x2 grid.

Now increase the size of the super-cell to a 4x4x4 and re-run the calculations. Remember to udate the size of the displacements in the runphon.pw file, and note that in this particular case the position of the second atom to be displaced changes as you change the size of the cell. Clearly, in order to keep the same 2x2x2 **k**-point sampling of the 2x2x2 super-cell we need to use a 1x1x1 grid, or in other words just the electronic Γ point.

Once more, this is going to be a relatively long calculation, so run it in parallel if you can. If you don't want to wait for the results the file FORCES.444_111 has been already provided, and you can use this to generate phonon dispersions. If you now plot the dispersions obtained with the 4x4x4 super-cell and those obtained with the 2x2x2 super-cell you notice a few interesting things. First, the phonons obtained in the two calculations are identical at Γ and at zone boundary, as they should be. However, in the 4x4x4 super-cell now the phonons are also correct at points corresponding to one half of the distance between Γ and zone boundary. In particular, the LO phonon branch is correct at these extra points in the middle of the BZ. Since the interpolated dispersions must go through these points, you can notice that the LO branches in particular look very different when obtained from the two different super-cells. This is a signature of the slow convergence of the force constant matrix in this system.

It would be useful to know what the limiting value of the LO frequency is at Γ, because this would allow us to perform a better interpolation (in the particular case of cubic symmetry the limiting values of the LO frequencies do not depend on the direction of approach to Γ, and therefore this is uniquely defined. This is not true for a general crystal). We can do this using the linear response method.

4.2   The linear response method

We mentioned in Sec. 2 that in the limit of small wave-vector the dynamical matrix is non-analytic, as expressed in Eq. 9. The quantities needed to calculate this non-analytical behaviour are the Born effective charge tensors $\mathbf{Z}_s^*$ and the high frequency static dielectric tensor ϵ^∞. These two quantities can be both calculated within the framework of the linear response method. Once these are known, one can calculate the values of the frequencies at Γ (or the limiting values of frequencies for small wave-vectors). This non-analytic part of the dynamical matrix only affects the LO frequencies, and therefore determines the so called LO-TO splitting. Once the correct LO frequencies are known it is possible to Fourier transform these using Eq. 8 to interpolate the frequency everywhere in the BZ.

This can be done by repeating all the steps described in Sec 3.2, with the additional setting epsil=.true. in the input to ph.x. The input files for pw.x, ph.x, q2r.x, matdyn.x are mgo.scf.in, mgo.ph.in, q2r.in, matdyn.in respectively, and they have already been prepared to calculate phonons on a 4x4x4 grid of **q**-points, using the converged 4x4x4 grid of **k**-points.

It turns out that in the out of the box version of espresso-3.2 epsil=.true. is enforced of the code when ldisp=.true.. Here for pedagogical reasons we have commented out the line in the code in which this enforcement is done, so that you can run ph.x with epsil=.false. too. If you do that, this will give you the same phonon dispersions as those obtained with the small displacement method, as we observed previously when we calculated the phonon dispersions of Al.

4.3   Thermodynamics of MgO

We conclude the tutorial by calculating the thermodynamic properties of MgO. Again, we will do this both with the small displacement method and with the linear response method. The main difference between the two methods here is that the thermodynamic quantities calculated with PHON will be wrong because at Γ instead of having two TO modes plus one LO mode we have three degenerate TO modes. However, as we shall see, the error that we make on thermodynamic quantities, like the zero point energy for example, are extremely small already using a 4x4x4 super-cell (they obviously converge to the right result in the limit of a large enough super-cell).

So, refer to Sec. 3.4 and calculate the Helmholtz free energy of MgO at 300 K and its zero point energy using PHON. You will find that the zero point energy is equal to 0.15053 eV/cell.

Now construct a phonon density of states using the results obtained with the linear response method. For this run:

```
> matdyn.x < phdos.in
```

where in phdos.in you can use the force constant matrix obtained with the calculation in which epsil=.true.. If you now calculate the zero point energy from the phonon density of states, which can be done by typing the following:

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

you will see that the zero point energy is 0.15035 eV/cell, which is essentially identical to that obtained with phon.

5   Conclusions

In this tutorial we have examined two alternative methods to calculate phonons in crystals within the framework of density functional theory. The two methods are generally known as the *small displacement* and the *linear response* method. We have seen that when applied consistently the two methods deliver the same results. We have used these methods to calculate the phonon dispersions and the thermodynamic properties of Al and MgO. We have pointed out a difficulty of the small displacement method to describe the phonons of MgO, due to the polar nature of this material. However, we have seen that if one is interested in integrated quantities like the Helmholtz free energy, or the zero point energy, the error made by the incorrect treatment of the longitudinal optical frequencies at the Γ is very small, and can be neglected for all practical purposes.

One advantage of the linear response method over the small displacement one is that one does not need to create super-cells, which can be in some cases computationally more efficient. Moreover, in systems where the phonon dispersions behave in an anomalous way (like systems with Kohn anomalies) the linear response method is more suitable, because it is capable of calculating the exact phonons at the requested points. Finally, the linear response method provides a natural way of dealing with the LO-TO splitting of the phonon frequencies in polar materials.

One advantage of the small displacement method is that it is an *add on* that can work with any code, also non-density functional theory codes. All is needed is the ability of the external code to compute forces (codes like VASP and WIEN2K for example do not include an implementation of the linear response method, but the small displacement method implemented in PHON can be used in conjunction with these codes).

6   Answers to questions

Proof of exercise 1 : In practical calculations one usually uses super-cells with periodically boundary conditions. So moving one atom also means moving all its periodic images. As a consequence of this one does not have the exact force constant matrix $\Phi^{ex}_{ls,l't}$ but the linear combination

$$\Phi_{ls,l't} = \sum_L \Phi^{ex}_{L+ls,l't} \tag{10}$$

where L labels all possible images of the super-cell and l labels primitive cells contained in the super-cell. We can convince ourselves that this is true by looking at Eq. 2, which in a periodic crystal reads:

$$F_{ls\alpha} = -\sum_L \partial U/\partial u_{L+ls\alpha} = -\sum_L \sum_{l't\beta} \Phi^{ex}_{L+ls\alpha,l't\beta} u_{L+l't\beta} = -\sum_L \sum_{l't\beta} \Phi^{ex}_{L+ls\alpha,l't\beta} u_{l't\beta} \ . \tag{11}$$

where the last equality comes from the fact that the displacements $\mathbf{u}_{l'+Lt}$ are all identical to $\mathbf{u}_{l't}$. If we now insert Eq. 10 into Eq. 8 we obtain:

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l \Phi_{ls\alpha,l't\beta} \exp\left[i\mathbf{q} \cdot (\mathbf{R}_l + \tau_t - \mathbf{R}_{l'} - \tau_s)\right] = \tag{12}$$

$$= \frac{1}{\sqrt{M_s M_t}} \sum_l \sum_L \Phi^{ex}_{l+Ls\alpha,l't\beta} \exp\left[i\mathbf{q} \cdot (\mathbf{R}_l + \tau_t - \mathbf{R}_{l'} - \tau_s)\right] \tag{13}$$

$$= \frac{1}{\sqrt{M_s M_t}} \sum_{l+L} \exp\left[-i\mathbf{q} \cdot \mathbf{R}_L\right] \Phi^{ex}_{l+Ls\alpha,l't\beta} \exp\left[i\mathbf{q} \cdot (\mathbf{R}_{l+L} + \tau_t - \mathbf{R}_{l'} - \tau_s)\right] = \tag{14}$$

$$\tag{15}$$

where $\mathbf{R}_L$ is a vector connecting two super-cells, and $\mathbf{R}_{l+L} = \mathbf{R}_l + \mathbf{R}_L$. Recognising that the sum over $l + L$ is the same as the sum of any vector in the system connecting different primitive cells, this has the same form of Eq. 8, but with the additional term $\exp[-i\mathbf{q} \cdot \mathbf{R}_L]$. Therefore, it is clear that the dynamical matrix is exact only if $\mathbf{q} \cdot \mathbf{R}_L = 2n\pi$, with n nd integer number, and for all the other values of $\mathbf{q}$ it represents only an interpolation.

Answer 1: The phonon dispersions are exactly the same, but the calculations take longer because if the displacement is towards a low symmetry direction PWSCF will not be able to fully exploit symmetries and will need to run with more $\mathbf{k}$-points.

Answer 2: With this displacement size (0.4 Å) the linear relation between forces and displacement is no longer valid, and therefore the phonons will be incorrect.

Answer 3: If the displacement is reduced a little bit the phonons will still look the same, provided we were in the harmonic limit already. However, since the forces are now smaller, numerical noise may become more important, and therefore we need to calculate them more accurately. Usually a good compromise is obtained with a displacement size of the order of 0.02-0.04 Å, but this may depend on the system, so it needs to be accurately checked.

Answer 4: In the calculations with the small displacement method we used (see the input file pw.d):

K_POINTS automatic
2 2 2 0 0 0

so here we need to use:

K_POINTS automatic
4 4 4 0 0 0

with this choice the $\mathbf{k}$-points sampling is exactly the same in the two sets of calculations.

Answer 5: The $\mathbf{k}$-point sampling in al.scf.in needs to be modified as follows:

K_POINTS automatic
8 8 8 0 0 0

Answer 6: The phonon dispersions in FREQ.cm are different from those in FREQ22.cm, as expected, but they are exactly the same at the points X=(1.0,0.0,0.0) and L=(0.5,0.5,0.5). This is because these two points are compatible with both the 2x2x2 and the 4x4x4 super-cells.

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