40th Anniversary Issue

PHON: A program to calculate phonons using the small displacement method ☆

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ABSTRACT

The program PHON calculates force constant matrices and phonon frequencies in crystals. From the frequencies it also calculates various thermodynamic quantities, like the Helmholtz free energy, the entropy, the specific heat and the internal energy of the harmonic crystal. The procedure is based on the small displacement method, and can be used in combination with any program capable to calculate forces on the atoms of the crystal. In order to examine the usability of the method, I present here two examples: metallic Al and insulating MgO. The phonons of these two materials are calculated using density functional theory. The small displacement method results are compared with those obtained using the linear response method. In the case of Al the method provides accurate phonon frequencies everywhere in the Brillouin Zone (BZ). In the case of MgO the longitudinal branch of the optical phonons near the centre of the BZ is incorrectly described as degenerate with the two transverse branches, because the non-analytical part of the dynamical matrix is ignored here; however, thermodynamic properties like the Helmholtz free are essentially unaffected.

Program summary

Program title: PHON
Catalogue identifier: AEDP_v1_0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AEDP_v1_0.html
Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland
Licensing provisions: Standard CPC licence, http://cpc.cs.qub.ac.uk/licence/licence.html
No. of lines in distributed program, including test data, etc.: 19 580
No. of bytes in distributed program, including test data, etc.: 612 193
Distribution format: tar.gz
Programming language: Fortran 90
Computer: Any Unix, Linux
Operating system: Unix
RAM: Depends on super-cell size, but usually negligible
Classification: 7.8
External routines: Subprograms ZHEEV and DSYEV (Lapack); needs BLAS. A tutorial is provided with the distribution which requires the installation of the quantum-espresso package (http://www.quantum-espresso.org)
Nature of problem: Stable crystals at low temperature can be well described by expanding the potential energy around the atomic equilibrium positions. The movements of the atoms around their equilibrium positions can then be described using harmonic theory, and is characterised by global vibrations called phonons, which can be identified by vectors in the Brillouin zone of the crystal, and there are 3 phonon branches for each atom in the primitive cell. The problem is to calculate the frequencies of these phonons for any arbitrary choice of **q**-vector in the Brillouin zone.
Solution method: The small displacement method: each atom in the primitive cell is displaced by a small amount, and the forces induced on all the other atoms in the crystal are calculated and used to construct the force constant matrix. Supercells of ∼100 atoms are usually large enough to describe the force constant matrix up to the range where its elements have fallen to negligibly small values. The force constant matrix is then used to compute the dynamical matrix at any chosen **q**-vector in the Brillouin zone, and the diagonalisation of the dynamical matrix provides the squares of the phonon frequencies.

The PHON code needs external programs to calculate these forces, and it can be used with any program capable of calculating forces in crystals. The most useful applications are obtained with codes based on density functional theory, but there is no restriction on what can be used.

Running time: Negligible, typically a few seconds (or at most a few minutes) on a PC. It can take longer if very dense meshes of **q**-points are needed, for example, to compute very accurate phonon density of states.

1. Theoretical overview

1.1. Phonons in a crystal

Consider a crystal at very low temperature and expand the potential energy function around the equilibrium positions of the nuclei [1]. 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 Eq. (1) and ignoring the higher-order anharmonic 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:

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

with ω_n the frequency of the nth vibrational mode of the crystal, k_B the Boltzmann constant, V the volume and T the temperature of the system. 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:

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

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

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

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 $g(\omega)$:

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

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 square root of eigenvalues of the dynamical matrix, $D_{s\alpha, t\beta}(\mathbf{q})$, defined as:

$$D_{s\alpha, t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l \Phi_{ls\alpha, 0t\beta} \exp\big[i\mathbf{q} \cdot (\mathbf{R}_0 + \boldsymbol{\tau}_t - \mathbf{R}_l - \boldsymbol{\tau}_s)\big], \tag{8}$$

where $\mathbf{R}_l + \boldsymbol{\tau}_s$ represents the equilibrium position of atom s with mass M_s in primitive cell l, and the sum runs over the infinite number of primitive cells in the crystal. 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 $\mathbf{q}$.

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 [2,3], is the one implemented in the PHON code, which I am describing here. 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 behaviour of the dynamical matrix in the limit of small wave-vector is non-analytical, and has the following form:

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

where $\mathbf{Z}^*_s$ is the Born effective charge tensor for atom s, ϵ^∞ the high frequency static dielectric tensor. 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 BZ. Note that in general these limiting values may be different for different directions (in the cubic crystal that I 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 [4–6] (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 [7]) 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 $\mathbf{q}$. This can be done for any arbitrary wave-vector, without the need for the construction of a super-cell.

The aim of this paper is to describe the PHON code, which uses the small displacement method. In order to assess the usability of the method I will present density functional theory calculations of phonons of two different materials: metallic aluminium and insulating MgO, and I will compare the small displacement method results to calculations performed with exactly the same density functional theory settings, but with the "linear response" method.

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, even if the non-analytical part of the dynamical matrix is ignored.

Before showing these specific examples, in the next section I will briefly review the main technical points of the small displacement method. A description of the method can also be found in the paper by Kresse et al. [2]. Since the linear response method is not the primary interest of this paper, I will not review this method, but the interested reader can find detailed information on this method in the recent review by Baroni et al. [6] for example.

2.1. Force constant matrix with the small displacement method

I now describe the technique used by PHON to compute the force constant matrix of crystals, $\Phi_{is\alpha,jt\beta} = \Phi_{\alpha,\beta}(\mathbf{R}_j + \boldsymbol{\tau}_t - \mathbf{R}_i - \boldsymbol{\tau}_s)$ where $\mathbf{R}_i$ is a vector of the lattice connecting different primitive cells, $\boldsymbol{\tau}_s$ is the position of the atom s in the primitive cell and α and β are Cartesian components. In principle, the elements of $\Phi_{is\alpha,jt\beta}$ are non-zero for arbitrarily large separations $|\mathbf{R}_j + \boldsymbol{\tau}_t - \mathbf{R}_i - \boldsymbol{\tau}_s|$, but in practice they decay rapidly with separation, so that a key issue in achieving a fixed target precision is the cut-off distance beyond which the elements can be neglected.

2.1.1. Calculation of the force constant matrix

The program PHON calculates $\Phi_{is\alpha,jt\beta}$ using the small-displacement method as described in Ref. [3], and in a similar way as described in Ref. [2]. I recall here the main ideas. In the harmonic approximation, the α Cartesian component of the force exerted on the atom at position $\mathbf{R}_i + \boldsymbol{\tau}_s$ is:

$$F_{is\alpha} = -\sum_{jt\beta} \Phi_{is\alpha,jt\beta} u_{jt\beta}, \tag{10}$$

where $u_{js\beta}$ is the displacement of the atom in $\mathbf{R}_j + \boldsymbol{\tau}_t$ along the direction β. The force constant matrix can be calculated by

$$\Phi_{is\alpha,jt\beta} = -\frac{F_{is\alpha,jt\beta}}{u_{jt\beta}} \tag{11}$$

by displacing once at a time all the atoms of the lattice along the three Cartesian components by $u_{jt\beta}$, and calculating the forces $F_{is\alpha,jt\beta}$ induced on the atoms in $\mathbf{R}_i + \boldsymbol{\tau}_s$ by displacing an atom in $\mathbf{R}_j + \boldsymbol{\tau}_t$. Since the crystal is invariant under translations of any lattice vector, it is only necessary to displace the atoms in one primitive cell ($j = 0$) and calculate the forces induced on all the other atoms of the crystal.

It is important to appreciate that the $\Phi_{ls\alpha,l't\beta}$ in the formula for $D_{s\alpha,t\beta}(\mathbf{q})$ is the force-constant matrix in the infinite lattice, with no restriction on the wave-vector $\mathbf{q}$, whereas the calculations of $\Phi_{ls\alpha,l't\beta}$ can only be done in super-cell geometry. Without a further assumption, it is strictly impossible to extract the infinite-lattice $\Phi_{ls\alpha,l't\beta}$ from super-cell calculations, since the latter deliver information only at wave-vectors that are reciprocal lattice vectors of the super-lattice. The further assumption needed is that the infinite-lattice $\Phi_{ls\alpha,l't\beta}$ vanishes when the separation $\mathbf{R}_{l't} - \mathbf{R}_{ls}$ is such that the positions $\mathbf{R}_{ls}$ and $\mathbf{R}_{l't}$ lie in different Wigner–Seitz (WS) cells of the chosen super-lattice. More precisely, if we take the WS cell centred on $\mathbf{R}_{l't}$, then the infinite-lattice value of $\Phi_{ls\alpha,l't\beta}$ vanishes if $\mathbf{R}_{ls}$ is in a different WS cell; it is equal to the super-cell value if $\mathbf{R}_{ls}$ is wholly within the same WS cell; and it is equal to the super-cell value divided by an integer P if $\mathbf{R}_{ls}$ lies on the boundary of the same WS cell, where P is the number of WS cells having $\mathbf{R}_{ls}$ on their boundary. With this assumption, the $\Phi_{ls\alpha,l't\beta}$ elements will converge to the correct infinite-lattice values as the dimensions of the super-cell are systematically increased [3].

It is not always necessary to displace all the atoms in the primitive cell, since the use of symmetries can reduce the amount of work needed. This is done as follows. We displace atom *one* in the primitive cell, and we calculate the forces induced by the displacement on all the other atoms of the super-cell. Then we take the second atom of the list, atom *two*, and we look for a symmetry operation S such that, when S is applied to the crystal atom *two* is sent into atom *one* and the whole crystal is invariant under such transformation. If we find this symmetry, then it is not necessary to displace atom *two*, and the part of the force constant matrix associated with its displacement can be calculated using

$$\boldsymbol{\Phi}_{is,02} = \mathbf{B}(S)\boldsymbol{\Phi}_{\lambda_{is}(S),01}\mathbf{B}(S^{-1}), \tag{12}$$

where $\mathbf{B}(S)$ is the 3×3 matrix representing the point group part of S in Cartesian coordinates, and $\lambda_{is}(S)$ indicates the atom of the crystal where the atom in $\mathbf{R}_i + \boldsymbol{\tau}_s$ is brought because of the action of the symmetry operation S. If there is no symmetry operation connecting atom *two* to atom *one* then atom *two* is displaced and all the induced force field is calculated. The procedure is repeated for all the atoms inside the primitive cell.

In principle each atom has to be displaced along the three Cartesian directions. It is sometimes convenient to displace the atoms along some special directions so as to maximise the number of symmetry operations still present in the *excited* super-cell, in this way the calculations of the forces in a first-principles based scheme are less expensive, as the number of $\mathbf{k}$-points in the calculations is reduced to the minimum. This can always be done, as long as one displaces the atoms along three linearly independent directions. The forces induced by the displacements along the three Cartesian directions is easily reconstructed by the linear combination [2]:

$$\mathbf{F}_{is,0t\alpha} = \sum_l \mathbf{A}_{l\alpha}\tilde{\mathbf{F}}_{is,0tk}, \tag{13}$$

where $\tilde{\mathbf{F}}_{is,0tk}$ is the force induced on the atom in $\mathbf{R}_i + \boldsymbol{\tau}_s$ due to a displacement of the atom in $\boldsymbol{\tau}_t$ along the direction $\mathbf{u}_k$, and $\mathbf{A} = (\frac{\mathbf{u}_1}{|\mathbf{u}_1|}, \frac{\mathbf{u}_2}{|\mathbf{u}_2|}, \frac{\mathbf{u}_3}{|\mathbf{u}_3|})^{-1}$ is the inverse of the 3×3 matrix whose columns are the normalised displacements in Cartesian coordinates.

Using symmetries it is possible to reduce the number of displacements even further: if applying a point group symmetry operation U to the displacement vector $\mathbf{u}_1$ one obtains a vector $\mathbf{u}_2$ which is linearly independent from $\mathbf{u}_1$, then the force field that would be induced by the displacement $\mathbf{u}_2$ can be calculated by

$$\mathbf{F}_{is,0t2} = \mathbf{B}(U)\mathbf{F}_{\lambda_{is}(U^{-1}),0t1}. \tag{14}$$

If a linearly independent direction cannot be found one has to displace the atom along a chosen independent direction and perform an other calculation. This is done until a set of three independent directions is found [2].

The force constant matrix is invariant under the point group symmetry operations of the crystal. This is not automatically guaranteed by the procedure just described, because in general the crystal is not harmonic, and therefore Eq. (11) is only an approximation. So, the force constant matrix must be symmetrised with respect to the point group operations of the crystal:

$$\boldsymbol{\Phi}_{is,0t} = \frac{1}{N_G}\sum_U \mathbf{B}(U)\boldsymbol{\Phi}_{\lambda_{is}(U),0t}\mathbf{B}(U^{-1}). \tag{15}$$

The symmetrisation of the force constant matrix also removes all lowest-order anharmonicities [2]. The harmonic approximation becomes better and better as the displacement are made smaller and smaller. However, if the displacements are small, also the induced forces are small, and the numerical error can become dominant for forces that are too small, so one cannot make too small displacements. Usually a fraction of a % of the nearest-neighbour distance is a good compromise, and as a rule of thumb one may adjust the displacements so that the forces on the atoms are no larger than $\simeq 0.5$ eV/Å.

As an example of the procedure just described let us consider the hexagonal closed packed (hcp) crystal. There are two atoms in the primitive cell, so in principles we would need six independent calculations. However, one can easily recognise that only one atom needs to be displaced: if we translate the crystal from one atom to the other and we perform a spatial inversion the crystal remains unchanged. Displacing the atom along one random direction would be enough to construct the whole force constant matrix. Alternatively, in order to maximise the number of symmetry operations in the crystal with the displacement, one could make one displacement along, say, the x-direction. Then, by applying a clockwise rotation of 120 degrees, for example, one obtains an independent displacement. So only one additional displacement along the z-direction is needed. So, the force constant matrix of an hcp crystal can either be obtained by performing *one* off-symmetry displacement, or *two* displacements along directions of high symmetry.

2.1.2. Translational invariance

When all the atoms are moved by the same amount, i.e. the crystal is rigidly shifted, the force *on each atom* must be zero. This is a stronger constraint than the one in which it is the *sum* of the forces on each atom to be zero. The latter is expressed by:

$$\sum_{s,t,i} \Phi_{is\alpha,0t\beta} = 0, \tag{16}$$

where s and t run over the number of atoms N in the primitive cell and i over the M lattice vectors included in the calculation. If this constraint is not satisfied, it is straightforward to impose it by subtracting from the calculated force on each atom the value $\mathbf{F}/(MN)$, where $\mathbf{F} = \sum_{s,i} \mathbf{F}_{si}$, and $\mathbf{F}_{si}$ is the force acting on atom s in primitive cell i.

The former condition is:

$$\sum_{s,i} \Phi_{is\alpha,0t\beta} = 0; \quad \text{for each } t = 1, N. \tag{17}$$

Clearly, Eq. (16) implies Eq. (17), but the opposite is not true in general. However, it is Eq. (17) to imply that at $\mathbf{q} = (0, 0, 0)$ the three acoustic branches have identically zero frequencies.

The constraint in Eq. (17) has to be imposed in such a way that the force constant matrix remains symmetric: $\Phi_{\alpha,\beta}(\mathbf{R}_j + \boldsymbol{\tau}_t - \mathbf{R}_i - \boldsymbol{\tau}_s) = \Phi_{\beta,\alpha}(-[\mathbf{R}_j + \boldsymbol{\tau}_t - \mathbf{R}_i - \boldsymbol{\tau}_s])$. In the PHON code this is done iteratively, in a number of steps in which the symmetry is re-imposed at each step.

3. Description of the program and input/output files

The program reads the following files:

- INPHON: contains the input parameters
- POSCAR: contains the crystal parameters and atomic positions, the format is the same as in the program VASP [16], and is the following:

```
SiO2
−47.88
4.2212779176   0.0000000000   0.0000000000
0.0000000000   4.2212779176   0.0000000000
0.0000000000   0.0000000000   2.6869912363
2   4
Direct
0.00000000   0.00000000   0.00000000
0.50000000   0.50000000   0.50000000
0.30657944   0.30657944   0.00000000
0.69342056   0.69342056   0.00000000
0.19342056   0.80657944   0.50000000
0.80657944   0.19342056   0.50000000
```

This example is the Stishovite structure of SiO_2. The first line is a comment, the second line is a scale factor, if negative is interpreted as the volume of the system (like in this case). Then the three lattice vectors, followed by the number of atoms for each specie (here 2 silicons and 4 oxygens). The next line precedes the atomic coordinates, and tells if these are in unit of the lattice vectors of in Cartesian coordinates (here they are in unit of crystal coordinates). Finally the atomic coordinates. Note that the crystal must be in its ground state. It is important to relax the primitive cell very accurately before starting any phonon calculation.

- FORCES: contains the displacements and the force field for each displacement, the format is the following:

```
4
1    0.005    0.000    0.000
−0.61854500   0.18897800    0.00000000
0.30803200    −0.00013900    0.00000000
0.01746700    0.01833500   0.00000000
−0.01926700   −0.01606600    0.00000000
0.14414800    −0.08517300   0.00000000
0.16816400    −0.10593400    0.00000000
1    0.000    0.000    0.005
0.00000000    0.00000000    −0.29116700
0.00000000    0.00000000    −0.00207200
0.01356000    0.01356000   0.01857500
−0.01356000    −0.01356000    0.01857500
−0.00997600    0.00997600    0.12804500
0.00997600    −0.00997600    0.12804500
3    0.005    0.000    0.000
−0.00548400    −0.00305700    0.00000000
0.15831200    0.09934800    0.00000000
```

```
−0.42565500   −0.18284700    0.00000000
 0.08338600    0.08818100    0.00000000
−0.01075400    0.01564000    0.00000000
 0.20019500   −0.01726600    0.00000000
 3   0.000   0.000   0.005
−0.00001000   −0.00001000    0.01963200
 0.00388400    0.00388400    0.12906300
 0.01036900    0.01036900   −0.25656500
−0.01400200   −0.01400200   −0.00218800
−0.01406100    0.01382000    0.05502900
 0.01382000   −0.01406100    0.05502900
```

The first line is the number of displacements, then, for each displacement, a line containing a number which indicates the position of the atom in the super-cell which has been moved, followed by the displacement (in crystal coordinates), followed by the forces on all the atoms in the super-cell (in units of eV/A).

In this example the super-cell is a primitive cell (to economise on space), in general you need to construct a super-cell, displace the atoms in the primitive cell appropriately and calculate the induced forces. The procedure is explained below.

3.1. Super-cell generation

The first step to calculate phonons in a crystal is to construct the super-cell, this can be done using the following setting:

LSUPER =.TRUE. (default)
NDIM = NX NY NZ (default: 1 1 1)
NTYPES = 2 (no default)

where NX, NY and NZ are positive integer numbers. NTYPES is the number of different atomic species (2 in the Stishovite example). PHON reads the file POSCAR which must contain a super-cell $(n_x\mathbf{a}_1, n_y\mathbf{a}_2, n_z\mathbf{a}_3)$ (possibly $n_x = n_y = n_z = 1$) and generates the file SPOSCAR which contains the super-cell whose lattice vectors are (NX$\mathbf{a}_1$, NY$\mathbf{a}_2$, NZ$\mathbf{a}_3$), where $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ are the lattice vectors of the primitive cell. Do not use NX $\neq$ NY if the crystal has a symmetry operation which connects $\mathbf{a}_1$ with $\mathbf{a}_2$. For face-centred-cubic (FCC) and body-centred-cubic (BCC) crystals do not use simple-cubic lattice vectors with 4 and 2 atoms in the primitive cell respectively, use proper FCC and BCC lattice vectors and one atom per primitive cell.

The program 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. The size of the displacement can be changed setting the variable DISP:

DISP = 25 (default, corresponding to displacements of 0.04 Å).

In principle, a single off symmetry displacement could be enough to generate the full force field, as three linearly independent displacement may be generated from this using the symmetry operations of the crystal (this may not be true if the crystal has low symmetry). In practice, however, one would like to use displacements that alter as little as possible the symmetry of the crystal, because this minimises the computational effort in *ab-initio* calculations (maximising the number of symmetry operations in general reduces the number of **k**-points needed). For this reason, the displacements suggested by the program work on the assumption that the first displacement will be along the *x*-axis, and appropriate additional displacements along *y* and/or *z* are suggested if they are needed. The user may suggest his own first displacement using the variable: DXSTART:

DXSTART = xstart ystart zstart

3.2. Calculating forces

Now we need to calculate the forces on all the atoms in the super-cell for each displacement in the list and construct the file FORCES as described above. This calculation involves the use of some external program, so I will not describe how to do this any further. However, I will later point to a tutorial which is attached to the present distribution of the program, and this tutorial also contains scripts to use in conjunction with the code PWSCF to obtain these forces.

3.3. Phonon dispersions

To calculate the dispersions we need to add the following settings in the INPHON file:

LRECIP =.T.
ND = 4; NPOINTS = 50
QI = 0.5   0.5   0.0 0.0   0.0   0.0 0.5   0.0   0.0 0.5   0.5   0.5
QF = 0.0   0.0   0.0 0.5   0.0   0.0 0.5   0.5   0.5 0.0   0.0   0.0

MASS = 28.085   16.0.

LRECIP =.T. means that the coordinates of the initial (QI) and final (QF) **q**-points are in units of reciprocal space lattice vectors. Set LRECIP=.F. if you want to give these numbers in Cartesian coordinates. ND is the number of initial and final points (usually high

symmetry points in the BZ), and NPOINTS is the number of points between them. MASS is the mass of the ions. We also need to add:

LSUPER=.F.

which will tell PHON to go beyond the generation of the super-cell (and not generating one). These settings will make PHON generate the file FREQ containing the frequencies in THz, and the file FREQ.cm with the frequencies in cm^{-1}. PHON also produces a number of files FREQ1.... FREQn, where n is the number of atoms in the primitive cell, each of these files contains only three phonon branches in THz. By setting the variable:

LFORCEOUT=.TRUE. (default =.FALSE.)

The program writes the file HARMONIC which contains the force constant matrix.

3.4. Density of states and thermodynamic quantities

The program also calculates the density of states, writing the file DOS. The input variables:

DOSIN = 0; DOSEND = 25; DOSSTEP = 0.1; DOSSMEAR = 0.02

specify the starting and the ending frequency (in THz), the step and the smear. The smear is the width of the Gaussian which is convoluted with the dos spectrum. The density of states will be calculated using the available frequencies, which in this case are those coming from the dispersion curves. This is not the best way to do this, because the DOS is the integral over the whole BZ of the phonon frequencies, and the dispersions along some special directions do not usually provide a good sampling of the BZ.

The correct way to calculate the density of states is to generate a set of points which accurately sample the BZ, and calculate the frequencies at these points. This can be done with the following settings:

LFREE =.TRUE.; TEMPERATURE = 1000
LGAMMA =.FALSE.
QA = 11; QB = 11; QC = 11

QA, QB and QC are the divisions for a Monkhorst and Pack (MP) [15] special points grid generation, LGAMMA = .TRUE. means that the grid will pass through Γ. With the setting LFREE =.TRUE. the program will also calculate zero-point energy, Helmholtz free energy, internal energy, specific heat and entropy, at the temperature given by the variable TEMPERATURE in degrees Kelvin. The MP special points are written in the file QPOINTS, which can be used for subsequent calculations without generating the points again (dense meshes can take time to be generated) by setting QA to a negative number (default).

A convenient way to generate a set of thermodynamic properties as function of temperature is to set the variable:

PTEMP= 10 90

This will create a file called THERMO, which contains the internal energy, the free energy, the free energy in the classical limit, the entropy and the constant volume specific heat, as function of temperature, in the example above starting from a temperature equal to the value of the input variable TEMPERATURE, in steps of 10 K, for 90 steps.

3.4.1. Partial density of states

In some experiments the measured density of states can be due to the vibrational frequencies of only some of the atoms of the material investigated. For example, this is the case when inelastic X-ray spectroscopy is used to exploit the Mössbauer effect, in which only the atoms having a nuclear energy level which resonate with the incoming X-ray radiation can interact with the radiation. The result is that only the vibrations of these atoms are sampled in these experiment [9].

In order to calculate the partial density of states in a system in which, for example, there are two different atoms, the following setting:

USETHIS =.F..T.

will calculate the partial density of states due to the second atom only.

3.5. Translational invariance

To impose translational invariance as described in Section 2.1.2, set with the variable:

NTI = 20

Translational invariance is imposed iteratively, and ~ 20 iterations are usually enough.

The amount of output printed by the PHON is controlled by the variable IPRINT. IPRINT=0 will produce a minimal output, IPRINT=3 a verbose output, which also includes the dynamical matrix and its eigenvectors.

A full list of input variables is reported in Table 1, and a list of the input/output files needed/generated by PHON is reported in Table 2.

Table 1
Input variables.

Input variable	Meaning	Variable type	Default
NTYPES	Number of atomic types	Integer	No default
MASS	Mass of atoms	Real*NTYPES	1.0
LSUPER	Generate supercell	Logical	.T.
NDIM	Supercell dimensions	Integer*3	(1, 1, 1)
LFREE	Thermodynamic properties	Logical	.F.
TEMPERATURE	Temperature	Real	No default
PTEMP	Temperature increment, number of increments	Real*2	(0.0, 1.0)
LFORCEOUT	Writes force constant matrix file	Logical	.F.
LSYMM	Symmetrises force constant matrix	Logical	.F.
DXSTART	Initial displacement	Real*3	(1.0, 0.0, 0.0)
DISP	One over size of displacement (in Å^{-1})	Integer	25 (0.04 Å)
QA, QB, QC	Number of divisions for q-points grid	Integers	No defaults
LGAMMA	**q**-points grid through Γ	Logical	.F.
DOSIN, DOSEND, DOSSTEP	Density of states parameters	Reals	0.0, 25.0, 0.1 (THz)
DOSSMEAR	Width of Gaussian convoluted with DOS	Real	0.02 (THz)
USETHIS	Partial density of states	Logic*NTYPES	.T. (total DOS)
ND	Number of **q**-points in dispersion segments	Integer	0
QI, QF	Initial and final points for dispersion segments	Real*3	(0.0, 0.0.0.0), (0.0, 0.0, 0.0)
LRECIP	**q**-points in reciprocal lattice coordinates	Logical	.T.
NTI	Imposes translational invariance	Integer	1 (no TI imposed)
IPRINT	Controls verbosity of output	Integer	0 (little output)

Table 2
Input/output files.

| File name	Input/output	Description of data
INPHON	Input	Input variables
POSCAR	Input	Supercell
FORCES	Input	Forces on all atoms (eV/Å), for each displacement
QPOINTS	Input/output	**q**-points for thermodynamics
DISP	Output	Suggestions for displacements
SPOSCAR	Output	File containing supercell
FREQ, FREQ.cm	Output	Phonon dispersions (THz and cm^{-1})
FREQi, i=1,number of atoms in primitive cell	Output	Phonon dispersions in groups of three (THz)
DOS, DOS.cm, DOS.meV	Output	Density of states (THz, cm^{-1}, meV)
THERMO	Output	Thermodynamic properties
HARMONIC	Output	Force constant matrix

4. Test case

I now describe one of the three examples distributed with the program. This is located in the subdirectory "examples/Al". The example is Al in the FCC structure. The POSCAR contains already a $4 \times 4 \times 4$ super-cell (64 atoms), and the file FORCES has been already constructed using forces calculated with a density functional theory code. The INPHON file is set to calculate phonon density of states and thermodynamic properties in the range of temperature 1000–1890 K. Running PHON with this INPHON file will produce the files DOS, DOS.meV and DOS.cm, containing the density of states in units of number of frequencies/THz, or number of frequencies/meV or number of frequencies/cm^{-1} respectively, and the file THERMO which contains the internal energy, the free energy, the free energy in the classical limit, the entropy and the constant volume specific heat. The following are the first lines of the file THERMO:

```
# T(K)    E(eV/cell)  F(eV/cell)   Fc(eV/cell)   S(kB/cell)   Cv(kB/cell)
1000.00   0.26047710  −0.33379199  −0.33477073   6.89616445   2.97739731
1010.00   0.26304303  −0.33974746  −0.34071653   6.92579274   2.97784007
1020.00   0.26560934  −0.34572835  −0.34668793   6.95513343   2.97826997
1030.00   0.26817601  −0.35173440  −0.35268468   6.98419200   2.97868750
1040.00   0.27074303  −0.35776537  −0.35870653   7.01297378   2.97909314
.........................................................
```

Now set LFREE=.F. in the INPHON file and run the code again. The files FREQ, FREQ1 and FREQq.cm will appear, which contain the phonon frequencies along three special directions in the Brillouin zone. The files FREQ and FREQ1 are identical in this particular case, because there is only one atom in the primitive cell, and they both contains the frequencies in units of THz. The file FREQ.cm contains the frequencies in units of cm^{-1}. The following are the first lines of the file FREQ:

```
0.00000000   −0.00000   −0.00000    −0.00000
0.01428499   0.11682    0.12905     0.22737
0.02856997   0.23376    0.25796     0.45456
0.04285496   0.35096    0.38659     0.68141
0.05713994   0.46853    0.51481     0.90775
...........................................
```
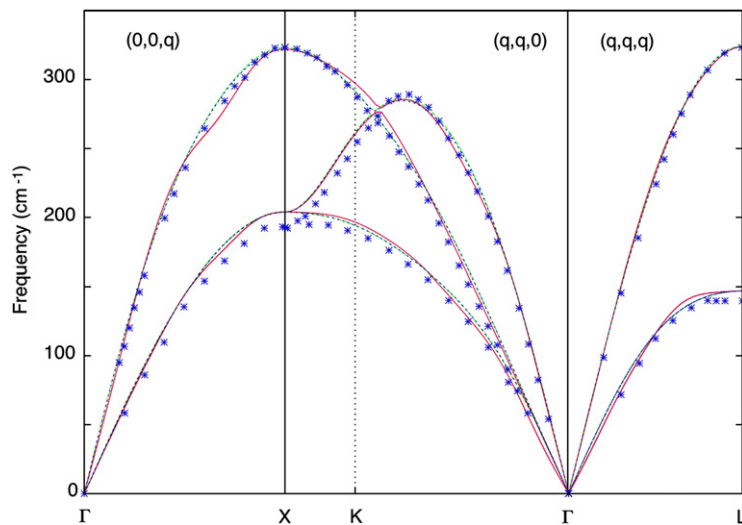
Fig. 1. Phonon dispersions of Al calculated with the small displacement method and with linear response. Green and blue dashed lines (indistinguishable) correspond to calculations with a $4 \times 4 \times 4$ super-cell (small displacement) and a $4 \times 4 \times 4$ equispaced grid of **q**-points (linear response). Red and purple lines (indistinguishable) correspond to calculations with a $8 \times 8 \times 8$ super-cell and a $8 \times 8 \times 8$ grid of **q**-points with the two methods respectively. A small difference can be noticed between the $4 \times 4 \times 4$ and the $8 \times 8 \times 8$ sets, but no difference can be observed between the small displacement and the linear response methods. Experimental data are displayed with blue crosses, and are taken from Ref. [10]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A more useful tutorial on how to calculate phonons is described in the attached file "tutorial_phonons.tar", in which the steps described in the previous sections are carried out using the external code PWSCF [8]. The tutorial describes in detail how to do a phonon calculation, and also compares the direct method used by PHON with the linear response method implemented in PWSCF.

In the following section I now present a detailed comparison between the direct method and linear response, for two limiting cases: a metal and an insulator. I will show that the two methods are essentially identical for the description of the thermodynamical properties of the two systems, and also for the description of the phonon frequencies everywhere in the Brillouin zone in the case of the metal.

5. Two examples: phonons of Al and MgO

I will now present two examples. In the first I will show the phonon dispersions, the free energy F and the constant volume specific heat C_v as function of temperature of the metal Al, and in the second example the dispersions, F and C_v of the insulator MgO.

5.1. Phonons of Al

The phonons of Al have been computed using density functional theory with the local density approximation, using the PWSCF code [8]. The pseudo-potential used in the calculations is available from http://www.pwscf.org/pseudo/1.3/UPF/Al.pz-vbc.UPF. I used a plane-wave cutoff of 15 Ry, and a Methfessel–Paxton smearing function of order 1 (product of a Gaussian times a fist order Hermite polynomial) with an amplitude of 0.04 Ry. I used a $4 \times 4 \times 4$ FCC super-cell (64 atoms) with a $4 \times 4 \times 4$ Monkhorst–Pack [15] **k**-point grid. For an FCC crystal a single displacement along the x-direction is sufficient to generate the full force constant matrix, and I chose the displacement to have an amplitude of 0.04 Å. A calculation performed with a displacement amplitude of 0.02 Å gives essentially indistinguishable results. Once the approximate force constant matrix is constructed, I can use Eq. (8) to calculate phonons at any **q**-vector in the BZ. In particular, the phonon dispersions along some special directions in the BZ are plotted in Fig. 1, together with the experimental results of Ref. [10]. Since the super-cell is a $4 \times 4 \times 4$, the phonon frequencies are only exact on a correspondingly $4 \times 4 \times 4$ grid of **q**-points in the BZ, everywhere else they only represent an interpolation.

To test the quality of the interpolation, or, which is the same, the convergence of the force constant matrix with respect to the size of the simulation cell, I have repeated the calculations using an $8 \times 8 \times 8$ super-cell (512 atoms), still with a displacement of 0.04 Å and a $2 \times 2 \times 2$ **k**-point grid, which guarantees an equivalent sampling of the BZ. The dispersions obtained with this larger super-cell are also plotted in Fig. 1, and we see that they are very similar to those obtained with the smaller cell. Such a fast convergence of the force constant matrix with respect to the distance between the atoms is expected in metals.

I then used linear response as implemented in the quantum-expresso distribution [8] to calculate the phonon frequencies on the same $4 \times 4 \times 4$ grid of **q**-points in the BZ, of course using the same pseudo-potential, equivalent **k**-point sampling ($16 \times 16 \times 16$ grid for the fcc primitive cell) and the same smearing function. Using the calculated $4 \times 4 \times 4$ grid of **q**-points I have then constructed the approximate force constant matrix using Eq. (8), which I have then used to interpolate the phonon frequencies along the chosen special directions in the BZ. The dispersion are plotted in Fig. 1, and they are essentially identical to those obtained with the small displacement method and the $4 \times 4 \times 4$ super-cell, as expected. Finally, I have repeated he procedure using a $8 \times 8 \times 8$ grid of **q**-points. The results are also plotted in Fig. 1, and again, within the thickness of the lines in the figure, they are indistinguishable from those obtained with the small displacement method.

5.1.1. Thermodynamics of Al

The thermodynamic properties of Al in the harmonic approximation can be obtained from the Helmholtz free energy, which I calculated using Eq. (5) summing over a $16 \times 16 \times 16$ grid of **q**-points. The Helmholtz free energy is plotted in the left panel of Fig. 2 in the range
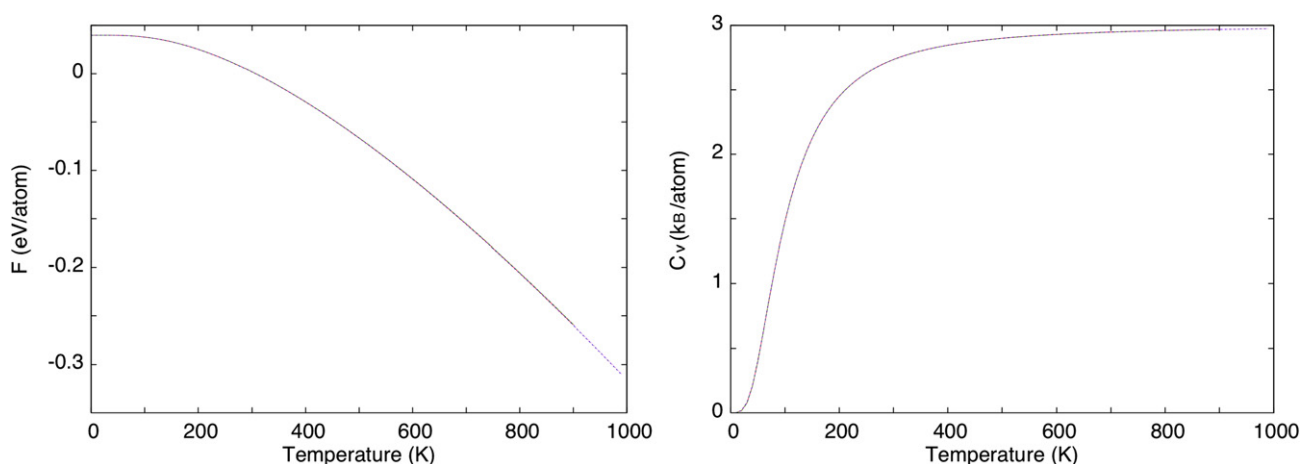
Fig. 2. Quasi-harmonic free energy (left panel) and constant volume specific heat (right panel) of Al. Results are shown for both the small displacement and the linear response methods, using $4 \times 4 \times 4$ and $8 \times 8 \times 8$ super-cells (small displacement) or grid of **q**-points (linear response), respectively. The four sets of results are indistinguishable within the thickness of the lines.

$T = 0$–1000 K, using force constant matrices obtained with both the $4 \times 4 \times 4$ and the $8 \times 8 \times 8$ super-cells. The two sets of data are on top of each other, showing that the free energy is converged to a fraction of a meV in the whole range of temperature. On the same figure I show also the results obtained with the linear response method, but once again it is impossible to distinguish them from those obtained with the small displacement method. In the right panel of Fig. 2 I show the constant volume specific heat.

5.2. Phonons of MgO

I now turn to the polar material MgO. For the reasons described in Section 2 convergence of the force constant matrix with respect to the size of the super-cell is expected to be slower, 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 can interpolate 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 longitudinal optical (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 for the LO branch.

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.

As for the previous Al case, the phonons have been computed using density functional theory with the local density approximation, using the PWSCF code [8]. The pseudo-potentials used in the calculations are available from http://www.pwscf.org/pseudo/1.3/UPF/Mg.pz-n-vbc.UPF and http://www.pwscf.org/pseudo/1.3/UPF/O.pz-rrkjus.UPF for Mg and O respectively. I used a plane-wave cutoff of 30 Ry, and a charge density cutoff of 240 Ry. The cutoff on the charge density is large because the O pseudo-potential is ultra-soft [14]. I used a $4 \times 4 \times 4$ face-centred-cubic (FCC) super-cell (128 atoms) with a $2 \times 2 \times 2$ Monkhorst–Pack [15] **k**-point grid, and a $8 \times 8 \times 8$ FCC super-cell (1024 atoms) with just the Γ-point to investigate size effects. Two displacements are needed in this case, one for the Mg atom and a second one for the O atom, and I chose also in this case displacements with an amplitude of 0.04 Å, which give fully converged results.

The phonon dispersions are plotted in Fig. 3. The difference between the dispersions obtained with the $8 \times 8 \times 8$ and the $4 \times 4 \times 4$ super-cells are due to the fact that the LO frequency at Γ is wrongly described as degenerate with the two TO frequencies, and therefore the Fourier interpolation of the frequencies is wrong. Note, however, that the phonons frequencies are still correct at the points of the Brillouin zone compatible with th dimension of the super-cell in real space, as expected. A linear response calculation using $4 \times 4 \times 4$ and $8 \times 8 \times 8$ grids show how the inclusion of the non-analytical part of the dynamical matrix can describe well the phonon dispersions even with the relatively coarse $4 \times 4 \times 4$ grid.

5.3. Thermodynamics of MgO

We now calculate the thermodynamic properties of MgO using both the small displacement method, which ignores LO-TO splitting and the linear response method, which fully includes it.

The Helmholtz free energy has been calculated using Eq. (5) summing over a $16 \times 16 \times 16$ grid of **q**-points, and is plotted in Fig. 4 in the range $T = 0$–3000 K, using force constant matrices obtained with both the $4 \times 4 \times 4$ and the $8 \times 8 \times 8$ super-cells. The two sets of data
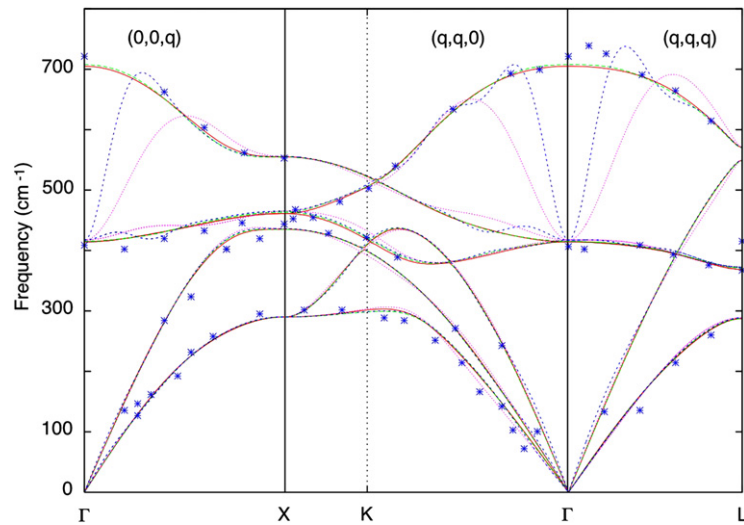
Fig. 3. Phonon dispersions of MgO calculated with the small displacement method and with linear response. Pink dotted and greed dashed lines correspond to calculations with a $4 \times 4 \times 4$ super-cell (small displacement) and a $4 \times 4 \times 4$ equispaced grid of **q**-points (linear response). Blue dashed and red solid lines correspond to calculations with a $8 \times 8 \times 8$ super-cell and a $8 \times 8 \times 8$ grid of **q**-points with the two methods, respectively. Experimental data are displayed with blue crosses, and are taken from Refs. [11–13]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
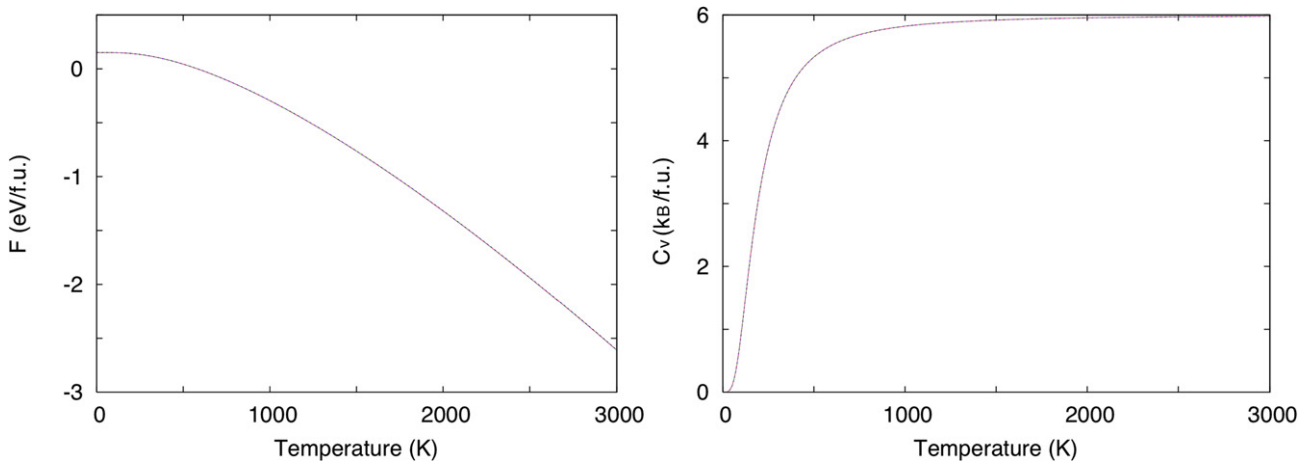
Fig. 4. Quasi-harmonic free energy (left panel) and constant volume specific heat (right panel) of MgO per formula unit (f.u.). Results are shown for both the small displacement and the linear response methods, using $4 \times 4 \times 4$ and $8 \times 8 \times 8$ super-cells (small displacement) or grid of **q**-points (linear response) respectively. The four sets of results are indistinguishable within the thickness of the lines.

are essentially on top of each other, showing that the free energy is converged to a fraction of a meV in the whole range of temperatures. In the same figure I show also the results obtained with the linear response method, but once again it is impossible to distinguish them from those obtained with the small displacement method. In the right panel of Fig. 4 I show the constant volume specific heat.

This shows that despite the apparent poor description of the LO phonons in the absence of the non-analytical part of the dynamical matrix the thermodynamic properties of the system are essentially exact, and even with super-cells of modest size like a $4 \times 4 \times 4$ the free energy is converged to within 1.5 meV/atom at worse in the whole temperature range 0–3000 K. In fact, even $2 \times 2 \times 2$ super-cells give quite respectable results, with errors no bigger of 10 meV/atom at the highest temperature of 3000 K, and a zero-point energy only wrong by $\sim$1 meV/atom.

6. Conclusions

I have described here the PHON code, which adopts the so-called *small displacement* strategy to compute force constant matrices in crystals, and to obtain phonon frequencies and thermodynamic properties with them.

I have compared the small displacement method with the *linear response* method, and shown that when applied consistently the two methods deliver the same results. I have used these methods to calculate the phonon dispersions and the thermodynamic properties of Al and MgO. I 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, 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.

There are many advantages of the linear response method over the small displacement method, like the absence of the 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 (at the time of writing, codes like VASP [16] and WIEN2K [17] for example do not include an implementation of the linear response method, but the small displacement method implemented in PHON can easily be used in conjunction with these codes).

Acknowledgements

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