First-principle lattice dynamics and thermodynamics of crystals

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Abstract. Recent first-principle phonon calculations make use of the standard DFT program, and the direct method. The procedure requires to optimize the structure, calculate the Hellmann-Feynman forces, construct the dynamical matrix, and hence all interesting phonon properties. The method has been already applied to a large number of crystal, crystal with defects, multilayers and surfaces to calculate the phonon dispersion curves, phonon density of states, and thermodynamical functions.

1. Introduction
A knowledge of phonon characteristics are required to describe mechanical, acoustic, dynamical, spectroscopical and thermodynamic properties of crystals at finite temperature. The easiest and most convenient way to calculate phonons from first-principles is to use existing and well-tested DFT softwares [1, 2, 3, 4], which can calculate crystalline structures, electronic bands, magnetic properties, and so called Hellmann-Feynman (HF) forces. To avoid the surface effects the DFT programs use supercells, on which three-dimensional periodic boundary conditions are imposed. The HF forces allow to find the forces of atomic response to a displacement of any other atom. To find harmonic phonons it is sufficient to convert the response HF forces to a force constants and then to use the basic equations of the dynamical lattice theory. This task has been coded in the PHONON [5] computer program.

2. Direct method
Traditionally, the ground state energy $E$ (at $T = 0$) as a function of atomic positions $\mathbf{R}(n, \mu)$, where $n$ is the primitive unit cell index and $\mu$ is the atomic index, is expanded over small displacements $\mathbf{U}(n, \mu)$ up to harmonic term. Any atomic displacement $\mathbf{U}(m, \nu)$ generates HF forces on all other atoms according to the relationship

$$F_i(n, \mu) = - \sum_{m, \nu, j} \Phi_{i,j}(n, \mu, m, \nu) U_j(m, \nu) \quad (1)$$

This relates the generated forces with the force constant matrices and atomic displacement. Knowing the displacements and arising HF forces one is able to determine the force constants $\Phi_{i,j}(n, \mu, m, \nu)$.
The dynamical matrix is defined as
\[ D(k; \mu, \nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_m \Phi(0, \mu; m, \nu) \exp\{-2\pi i k \cdot [R(0, \mu) - R(m, \nu)]\} \] (2)

Here, summation \( m \) runs over all atoms of the crystal, \( M_\mu, M_\nu \) are masses of atoms, and \( k \) is the wave vector. Eigenvalues of the dynamical matrix
\[ \omega^2(k, j)e(k, j) = D(k)e(k, j) \] (3)
give the phonon frequencies \( \omega^2(k, j) \) and polarization vectors \( e(k, j) \).

The calculations of vibrational properties start from minimizing the total energy of the crystal with respect to electronic part, lattice constants and atomic positions. At the minimized state all HF forces should vanish. Now, the HF forces should be calculated for configuration with single atom displaced from the equilibrium position. The HF forces are calculated in the supercell with a periodic boundary conditions, and that brings some modifications. Consider a supercell and displace an atom \( (m, \nu) \) by \( U(m, \nu) \). Due to periodic boundary conditions this displacement causes the same displacements of corresponding atoms \( (m + L, \nu) \) in all images of the supercell. Here, \( L = (L_a, L_b, L_c) \) are the indices of lattice constants of the supercell. Thus, according to Eq.(1), a displacement of a single atom \( (m, \nu) \) in original supercell generates a net force
\[ F_i(n, \mu) = -\sum_L \Phi_{i,j}(n, \mu, m + L, \nu)U_j(m, \nu). \] (4)

We may introduce the cumulant force constant defined as \( \Phi^{(Σ)}_{i,j}(n, \mu, m, \nu) = \sum_L \Phi_{i,j}(n, \mu, m + L, \nu) \) and the summation \( L \) runs over all supercell images. Thus, from the first-principle program one can only calculate the force constants \( \Phi^{(Σ)}_{i,j}(n, \mu, m, \nu) \). The solution of Eq.(4) is the essence of the direct method [6, 7].

The program PHONON solves Eq.(4) with respect to cumulant force constants which, in turn, are introduced to the dynamical matrix. For wave vectors, which are commensurate with the supercell, the summation over all atoms of the crystal in Eq.(2) leads to an exact dynamical matrix, and hence it provides exact phonon frequencies and polarization vectors. The phonon frequencies, which do not belong to the commensurate wave vectors, could bear some uncertainties. But if the supercell is so large that the force constants decay at half of supercell linear size (i.e. they are three order of magnitude smaller), then phonons at all wave vectors are correct. Program PHONON assures that the force constants have a correct symmetry required by the crystal space group. It is also able to impose the translational-rotational invariance conditions causing that the acoustic phonon modes start at zero frequencies from the Brillouin zone center.

Selection of the supercell shape is essential. It should have a form closest to a cube. Symmetry of the supercell should not break the crystal point group. Also it is necessary that all coordination shells defined within the supercell do have a complete list of atoms. Supercells of other shapes could reduce the crystal symmetry since the supercell acts as an external field. If it cannot be avoided to use supercell which breaks crystal symmetry, then a method described in [8] can recovered the full crystal symmetry. Elongated supercell shapes can help to supplement the list of exact phonon frequencies calculated with the direct method along a particular crystal direction. For polar crystals the macroscopic electric field splits the infrared active phonon modes to LO and TO components. This splitting can be satisfactorily handled when knowing the Born effective charges and the electronic dielectric constant. Moreover, the direct method allows to fit the computed phonon dispersion curves to a desirable selected frequencies. This option can be used to build most reliable phonon data basing on first-principle and experimental
methods. For surface phonon calculations [9], which use the slab supercell, it is easy to use the filling slab method, which allows to thicker the considered slab essentially. All mentioned option are included in PHONON program.

It is worth to mention the another phonon calculation method based on the density functional perturbation theory (DFPT) reviewed in Ref. [10]. This method could exactly handle phonons at incommensurate wavevectors, but due to its much larger computational demands it can be in practice applied to crystals with unit cells consisting of remarkably smaller number of atoms then unit cells used in direct method.

3. First-principle phonons

The VASP [1, 2] and PHONON [5] programs have been applied to a number of crystalline systems. Phonon dispersion curves have been successfully calculated for TiC [11], ZrC [12], MgO [13], BN [14], GaN [8], HgSe [15], ZnTe [16], FeBO$_3$ [17], AgGaS$_2$ [18], AgGaSe$_2$ [19], AgGaTe$_2$, CuInS$_2$ [21], CuInSe$_2$ [20] and ZnSnP$_2$ [22], AgGaSe$_2$ [23], CuInSe$_2$ [24], CuInSe$_2$ [25], Ba$_8$Si$_9$Gd$_6$ [26], Ba$_2$LaSi$_8$ [27] and UC$_3$Ga$_5$ [28]. Some systems exhibit phase transitions and they often manifest themselves as soft modes. To this class belongs crystals ZrO$_2$ [6], GeO$_2$ [30], SnO$_2$ [29], LiNbO$_3$ [31], MgSiO$_3$ [32] and CaTiO$_3$ [33]. Crystal with point defects can also be treated easily, like NiAl with Fe replacing Ni and Al [34]. Recent progress in handling the strong electron coupling systems allowed to calculate satisfactory phonons in such crystals as CoO [35], Fe$_3$O$_4$, having a Vervey phase transition [36], and 5f electron systems PuCoGa$_5$ [37, 38].

4. Thermodynamics

The first-principle phonon calculations are limited to $T = 0$K. Thermodynamic properties of the crystals are to large extent determined by phonons. Quasiharmonic approximation can describe such properties quite satisfactory. This approach replaces in some sense the temperature changes of the crystal properties by the pressure dependences at $T = 0$ K. In particular, a change of a crystal volume under increasing temperature is replaced by a similar change of a volume caused by a decrease of an ambient pressure. The approach to find the scaling factor between the pressure and temperature is the essence of the quasiharmonic approximation.

The Gibbs free energy $G(T, P) = F(T, V) + PV$ consists of the free energy $F(T, V)$ and PV term. The free energy contains two contributions $F(T, V) = E(V) + F_{ph}(T, V)$, $E(V)$ which stand for the ground state energy and $F_{ph}(T, V)$ is the phonon free energy at a given unit cell volume $V$. The phonon free energy can be described by the following equation:

$$F_{ph}(V, T) = k_B T \int_0^\infty g(\omega) \ln \left(2 \sinh \left(\frac{\hbar \omega}{2 k_B T}\right) \right) d\omega,$$

(5)

where $\omega = \omega(V)$ denotes the volume dependent phonon frequencies and $g(\omega)$ is the phonon density of states.

To apply the quasiharmonic approximation one should proceed as follows: (i) The free energy $F(T, V)$ should be calculated for several volumes $V$ of the unit cell. Temperature $T$ appears in $F(T, V)$ via the phonon term. (ii) One should construct the Gibbs free energy $G(T, P)$ by adding to the free energy the term $PV$, where $P$ is the desired pressure, and $V$ is the volume for which $F(T, V)$ was calculated. (iii) The locus of the minima of $G(T, P)$ for a fixed pressure $P$ determines the stable states at a given temperature $T$. For a fixed pressure $P$ these minima of $G(T, V)$ should be presented as plots of a temperature dependences of the Gibbs free energy. Notice that the main contribution to a decrease of the Gibbs free energy as a function of temperature originates from the phonon free energy term. (iv) A state with the lower Gibbs free energy at a given temperature $T$ and pressure $P$ represent the stable phase. A crossing point of two curves representing different structures denotes the first order phase transition with coexistence temperature $T_c$ and pressure $P_c$. 


Combining \((T_c, P_c)\) the critical temperatures and pressures the P-T phase diagrams were established in the quasiharmonic approximation. In this way the \(P - T\) phase diagrams of \(MgSiO_3\) \([41]\) and \(AlN\) \([42]\) have been found. It is worth to remark that the strong first-order phase transition can be easier located on the P-T surface, than the phase transitions being close to the second order. Limiting the analysis to free energy temperature dependence only the phase transitions in \(ZrO_2\) \([39]\) and \(NiTi\) \([40]\) were confirmed.

5. Final remarks

The direct method has some advantages and disadvantages. A great advantage of the direct method is that it could use the data calculated by any standard DFT program, which is able to calculate the HF forces. For complex crystals for which the supercell is as big as the unit cell, and for which the interaction range is confined to the supercell, the phonon frequencies could be well reproduced. A disadvantage is that within direct method it is not easy to calculate the LO/TO splitting, and that the largest error of phonon frequencies is expected for the low-energy modes.

With a similar effort one may calculate phonons for surface, example being \(Fe(100), Fe(110)\) \([43]\), and \(MgO\) \([9]\) surfaces. Placing an atom on the surface one may find the vibration spectrum of the adsorbed atoms. These type of calculation require larger computer power, but the algorithm is well parallelized.

Acknowledgments

This work was partially supported by Marie Curie Research Training Network under Contract No. MRTN-CT-2006-035957 (c2c).

References

[1] Kresse G and Hafner J 1993 Phys. Rev. B 47 558; ibid 1994 49 14251
[2] Kresse G and Furhtmüller J 1996 Phys. Rev. B 54 11169; 2002 Software VASP Vienna
  http://cns.mpi.univie.ac.at/vasp/vasp.html
[3] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J Software WIEN2k http://www.wien2k.at/
[4] Artacho E, Gale J, García A, Junquera J, Ordejón P, Sánchez-Portal D and Soler J M 2001 Software SIESTA
  http://www.uam.es/siesta/
[5] Parlinski K 2007 Software PHONON Cracow http://wolf.ifj.edu.pl/phonon/
[6] Parlinski K, Z Q Li Z Q and Kawazoe Y 1997 Phys. Rev. Lett. 78 4063
[7] K.Parlinski, 1999 Conference Proceedings 479, "Neutrons and Numerical Methods - N\(_2\)M edited by
  M.R.Johnson, G.J.Kearley and H.G.Böttner, Am.Inst.Phys. p121
[8] Parlinski K and Kawazoe Y 1999 Phys. Rev. B 60 15511
[9] Parlinski K 2006 Phys. Rev. B 74 184309
[10] Baroni S, de Gironcoli S, Dal Corso A and Giannozzi P 2001 Rev. Mod. Phys. 73 515
[11] Jochym P T, Parlinski K and Sternik M 1999 Europ. Phys. J. B 10 9
[12] Jochym P T and Parlinski K 2000 Euro. Phys. J. B 15 265
[13] K.Parlinski, Łażewski J and Kawazoe Y 1999 J. Phys. Chem. Solids 61 87
[14] K.Parlinski 2001 J. Alloys and Compounds 328 97
[15] Łażewski J, Parlinski K, Szuśkiewicz W and Hennion B 2003 Phys. Rev. B 67 134300
[16] Camacho J, Parlinski K, Cantarero A and Syassen K 2004 Phys. Rev. B 70 033205
[17] Parlinski K, Łażewski J, Jochym P T, Chumakov A, Rüffer R and Kresse G 2001 Europhysics Lett. 56 2
[18] Łażewski J and Parlinski K 2001 J. Phys. Chem. 328 162
[19] Łażewski J and Parlinski K 1999 J. Phys.: Condens. Matter 11 9673
[20] Łażewski J, Parlinski K, Hennion B and Couret R 1999 J. Phys.: Condens. Matter 11 9665
[21] Łażewski J, Jochym P T and Parlinski K 2002 J. Chem. Phys. 117 2726
[22] Łażewski J and Parlinski K 2001 J. Alloys and Compounds 114 6734
[23] Fouret R, Derollez P, Laamym A, Hennion B and Gonzalez J 1997 J. Phys.: Condens. Matter 9 6579
[24] Derollez P, Fouret R, Laamym A, Hennion B and Gonzalez J 1999 J. Phys.: Condens. Matter 11 3987
[25] Łażewski J, Neumann H, Parlinski K, Lippold G and Stanbery B J 2003 Phys. Rev. B 68 144108
[26] Tse J S, Iitaka T, Kume T, Shimizu H, Fukuoka H and Tamanak S 2005 Phys. Rev. B 72 155441
[27] Tse J S, Iitaka T and Parlinski K 2006 Phys. Rev. B 75 153
[28] Metoki U, Kaneko K, Raymond S, Sanchez J-P, Piekarz P, Parlinski K, Oleś A M, Ikeda S, Matsuda T D, Haga Y, Onuki Y and Lander G H 2006 Physics B 378-380 1003
[29] Parlinski K and Kawazoe Y 2000 Europ. Phys. J. B 13 679
[30] Lodziana Z, Parlinski K and Hafner J 2001 Phys. Rev. B 63 134106
[31] Parlinski K, Li Z Q and Kawazoe Y 2000 Phys. Rev. B 61 272
[32] Parlinski K and Kawazoe Y 2000 Europ. Phys. J. B 16 49
[33] Parlinski K and Kawazoe Y 2001 J. Chem. Phys. 114 2395
[34] Parlinski K, Jochym P T, Leupold O, Chumakov A I, Rüffer R, Chofer H, Jiano A, Dutkiewicz J and Maziarz W 2004 Phys. Rev. B 70 224304
[35] Wdowik U D and Parlinski K 2007 Phys. Rev. B 75 104306
[36] Piekarz P, Parlinski K and Oleś A M 2006 Phys. Rev. Lett. 97 156402
[37] Piekarz P, Parlinski K, Jochym P T, Oleś A M, Sanchez J-P and Rebizant J 2005 Phys. Rev. B 72 014521
[38] Raymond S, Piekarz P, Sanchez J-P, Serrano J, Krisch M, Janousova B, Rebizant J, Metoki N, Kaneko K, Jochym P T, Oleś A M and Parlinski K 2006 Phys. Rev. Lett. 96 237003
[39] Sternik M and Parlinski K 2005 J. Chem. Phys. 122 064707
[40] Parlinski K and Parlinska-Wojtan M 2002 Phys. Rev. B 66 064307
[41] Sternik M and Parlinski K 2006 J. Phys. Chem. Solids 67 796
[42] Siegel A, Parlinski K and Wdowik U D 2006 Phys. Rev. B 74 104116
[43] Łazewski J, Korecki J and Parlinski K 2007 Phys. Rev. Lett. 75 054303