

# Thermal properties of materials from ab-initio quasi-harmonic phonons

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## 1 Introduction

Computer simulations allow for the investigation of many materials properties and processes that are not easily accessible in the laboratory. This is particularly true in the Earth sciences, where the relevant pressures and temperatures may be so extreme that no experimental techniques can operate at those conditions. Computer modeling is often the only source of information on the properties of materials that, combined with indirect evidence (such as *e.g.* seismic data), allows one to discriminate among competing planetary models. Many computer simulations are performed using effective inter-atomic potentials tailored to reproduce some experimentally observed properties of the materials being investigated. The remoteness of the physically interesting conditions from those achievable in the laboratory, as well as the huge variety of different atomic coordination and local chemical state occurring in the Earth interior, make the dependability of semi-empirical potentials questionable. First-principles techniques based on density-functional theory (DFT) (Hohenberg & Kohn 1964, Kohn & Sham 1965) are much more predictive, not being biased by any prior experimental input, and have demonstrated a considerable accuracy in a wide class of materials and variety of external conditions. The importance of thermal effects in the range of phenomena interesting to the Earth sciences makes a proper account of atomic

motion essential. Traditionally, this is achieved using molecular dynamics techniques which have been successfully combined with DFT in the first-principles molecular dynamics technique of Car and Parrinello (Car & Parrinello 1985). Well below the melting temperature, the numerical efficiency of molecular dynamics is limited by the lack of ergodicity, which would require long simulation times, and by the importance of long-wavelength collective motions (phonons), which would require large simulation cells. Both difficulties are successfully dealt with in the quasi-harmonic approximation (QHA) where the thermal properties of solid materials are traced back to those of a system of non-interacting phonons (whose frequencies are however allowed to depend on volume or on other thermodynamic constraints). An additional advantage of the QHA is that it accounts for quantum-mechanical zero-point effects, which would not be accessible to molecular dynamics with classical nuclear motion. The availability of suitable techniques to calculate the vibrational properties of extended materials using a combination of DFT and linear-response techniques (resulting in the so-called density-functional perturbation theory, DFPT (Baroni et al. 1987, Baroni et al. 2001)) makes it possible to combine the QHA with DFT. The resulting simulation methodology has shown to be remarkably accurate in a wide temperature range, extending up to not very far from the melting line and has been applied to a wide variety of systems, including many which are relevant to the Earth sciences. This paper gives a short overview of the calculation of thermal properties of materials in the framework of the QHA, using DFT. The paper is organized as follows: in Sec. 2 we introduce some of the thermal properties of interest and describe how they can be calculated in the framework of the QHA; in Sec. 3 we describe the DFPT approach to lattice dynamics; in Sec. 4 we briefly introduce some of the computer codes that can be used to perform this task; in Sec. 5 we review some of the application of the first-principles QHA to the study of the thermal properties of materials; finally, Sec. 6 contains our conclusions.

## 2 Thermal properties and the Quasi-Harmonic Approximation

The low-temperature specific heat of solids is experimentally found to vanish as the cube of the temperature, with a cubic coefficient that is system-specific (Kittel 1996, Wallace 1998). This is contrary to the predictions of classical statistical mechanics, according to which the heat capacity of a system of harmonic oscillators does not depend on temperature, nor on its spectrum. One of the landmarks of modern solid-state physics, that greatly contributed to the establishment of our present quantum-mechanical picture of matter, is the Debye model for the heat capacity of solids. This model naturally explains the low-temperature specific heat of solids in terms of the (quantum) statistical mechanics of an ensemble of harmonic oscillators, which can in turn be pictorially described as a gas of non-interacting quasi-particles obeying the Bose-Einstein statistics (*phonons*).

The internal energy of a single harmonic oscillator of angular frequency  $\omega$ ,

in thermal equilibrium at temperature  $T$ , is:

$$\langle E \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}, \quad (1)$$

where  $k_B$  is the Boltzmann constant. By differentiating with respect to temperature the sum over all the possible values of the phonon momentum in the Brillouin zone (BZ) of Eq. (1), the constant-volume specific heat of a crystal reads:

$$C_V(T) = \frac{1}{V} \sum_{\mathbf{q}\nu} \hbar\omega(\mathbf{q}, \nu) n'(\mathbf{q}, \nu), \quad (2)$$

where  $\omega(\mathbf{q}, \nu)$  is the frequency of the  $\nu$ -th mode (phonon) at point  $\mathbf{q}$  in the BZ,  $n'(\mathbf{q}, \nu) = \frac{\partial}{\partial T} \left( e^{\frac{\hbar\omega(\mathbf{q}, \nu)}{k_B T}} - 1 \right)^{-1}$ , and the sum is extended to the first BZ. By assuming that there are three degenerate modes at each point of the BZ, each one with frequency  $\omega(\mathbf{q}, \nu) = c|\mathbf{q}|$ ,  $c$  being the sound velocity, and converting the sum in Eq. (2) into an integral, the resulting expression for the heat capacity, valid in the low-temperature limit, reads:

$$C_V(T) = \frac{1}{\Omega} \frac{12\pi^4}{5} k_B \left( \frac{T}{\Theta_D} \right)^3, \quad (3)$$

where  $\Omega$  is the volume of the crystal unit cell and  $\Theta_D = \frac{2\pi\hbar}{k_B} c \left( \frac{3}{4\pi\Omega} \right)^{\frac{1}{3}}$  is the so-called Debye temperature.

In the Born-Oppenheimer approximation (Born & Oppenheimer 1927), the vibrational properties of molecules and solids are determined by their electronic structure through the dependence of the ground-state energy on the coordinates of the atomic nuclei (Martin 2004). At low temperature the amplitudes of atomic vibrations are much smaller than inter-atomic distances, and one can assume that the dependence of the ground-state energy on the deviation from equilibrium of the atomic positions is quadratic. In this, so called *harmonic*, approximation (HA) energy differences can be calculated from electronic-structure theory using static response functions (DeCicco & Johnson 1969, Pick et al. 1970) or perturbation theory (Baroni et al. 1987, Baroni et al. 2001) (See Sec. 3).

In the HA, vibrational frequencies do not depend on interatomic distances, so that the vibrational contribution to the crystal internal energy does not depend on volume. As a consequence, constant-pressure and constant-volume specific heats coincide in this approximation, and the equilibrium volume of a crystal does not depend on temperature. Other shortcomings of the HA include its prediction of an infinite thermal conductivity, infinite phonon lifetimes, and the independence of vibrational spectra (as well as related properties: elastic constants, sound velocities etc.) on temperature, to name but a few. A proper account of anharmonic effects on the static and dynamical properties of materials would require the calculation of phonon-phonon interaction coefficients for all modes in the BZ. Although the leading terms of such interactions can be computed even from first principles (Baroni & Debernardi 1994, Debernardi et al. 1995)—and the resulting vibrational linewidths have in fact been evaluated in some cases (Debernardi et al. 1995, Lazzeri et al. 2003, Bonini et al. 2007)—the extensive sampling of the phonon-phonon interactions over the BZ required

for free-energy evaluations remains a daunting task. The simplest generalization of the HA, which corrects for most of the above mentioned deficiencies, while not requiring any explicit calculation of anharmonic interaction coefficients, is the QHA.

In the QHA, the crystal free energy is assumed to be determined by the vibrational spectrum via the standard harmonic expression:

$$F(X, T) = U_0(X) + \frac{1}{2} \sum_{\mathbf{q}\nu} \hbar\omega(\mathbf{q}, \nu|X) + k_B T \sum_{\mathbf{q}\nu} \log \left( 1 - e^{-\frac{\hbar\omega(\mathbf{q}, \nu|X)}{k_B T}} \right), \quad (4)$$

where  $X$  indicates any global static constraint upon which vibrational frequencies may depend (most commonly just the volume  $V$ , but  $X$  may also include anisotropic components of the strain tensor, some externally applied fields, the internal distortions of the crystal unit cell, or other thermodynamic constraints that may be applied to the system), and  $U_0(X)$  is the zero-temperature energy of the crystal as a function of  $X$ . In the case  $X = V$ , differentiation of Eq. (4) with respect to volume gives the equation of state:

$$\begin{aligned} P &= -\frac{\partial F}{\partial V} \\ &= -\frac{\partial U_0}{\partial V} + \frac{1}{V} \sum_{\mathbf{q}\nu} \hbar\omega(\mathbf{q}, \nu) \gamma(\mathbf{q}, \nu) \left( \frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega(\mathbf{q}, \nu)}{k_B T}} - 1} \right), \end{aligned} \quad (5)$$

where

$$\gamma(\mathbf{q}, \nu) = -\frac{V}{\omega(\mathbf{q}, \nu)} \frac{\partial \omega(\mathbf{q}, \nu)}{\partial V} \quad (6)$$

are the so-called Grüneisen mode parameters. In a perfectly harmonic crystal, phonon frequencies do not depend on the interatomic distances, hence on volume. In such a harmonic crystal Eq. (5) implies that the temperature derivative of pressure at fixed volume vanish:  $(\partial P / \partial T)_V = 0$ . It follows that the thermal expansivity,  $\beta = V^{-1}(\partial V / \partial T)_P$ , which is given by the thermodynamical relation:

$$\beta = -\frac{(\partial P / \partial T)_V}{(\partial P / \partial V)_T} \quad (7)$$

$$= \frac{1}{B_T} \left( \frac{\partial P}{\partial T} \right)_V \quad (8)$$

$$= \frac{1}{B_T} \sum_{\mathbf{q}\nu} \hbar\omega(\mathbf{q}, \nu) \gamma(\mathbf{q}, \nu) n'(\mathbf{q}, \nu), \quad (9)$$

where  $B_T = V(\partial P / \partial V)_T$  is the crystal bulk modulus, would also vanish for perfectly harmonic crystals. Inspired by Eq. (2), let us define  $C_V(\mathbf{q}, \nu) = \hbar\omega(\mathbf{q}, \nu) n'(\mathbf{q}, \nu) / V$  as the contribution of the  $\nu$ -th normal mode at the  $\mathbf{q}$  point of the BZ to the total specific heat, and  $\gamma$  as the weighted average of the various Grüneisen parameters:

$$\gamma = \frac{\sum_{\mathbf{q}\nu} \gamma(\mathbf{q}, \nu) C_V(\mathbf{q}, \nu)}{\sum_{\mathbf{q}\nu} C_V(\mathbf{q}, \nu)}. \quad (10)$$

In terms of  $\gamma$ , the thermal expansivity simply reads:

$$\beta = \frac{\gamma C_V}{B_T}. \quad (11)$$

The vanishing of the thermal expansivity in the HA would also imply the equality of the constant-pressure and constant-volume specific heats. By imposing that the total differentials of the entropy as a function of pressure and temperature or of volume and temperature coincide, and by using the Maxwell identities, one can in fact show that (Wallace 1998):

$$C_P - C_V = -\frac{T}{V} \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \quad (12)$$

$$= TB_T \beta^2. \quad (13)$$

We conclude this brief introduction to the QHA by noticing that the ansatz given by Eq. (4) for the crystal free energy in terms of its (volume-dependent) vibrational frequencies gives immediate access to all the equilibrium thermal properties of the system. Whether this *implicit* account of anharmonic effects through the volume dependence of the vibrational frequency only is sufficient to describe the relevant thermal effects, or else an *explicit* account of the various phonon-phonon interactions is in order, instead, is a question that can only be settled by extensive numeric experience.

### 3 Ab-initio phonons

#### 3.1 Lattice dynamics from electronic-structure theory

Several simplified approaches exist that allow to calculate full (harmonic) phonon dispersions  $\omega(\mathbf{q}, \nu)$  from semi-empirical force fields or inter-atomic potentials (Brüesch 1982, Singh 1982). The accuracy of such semi-empirical models is however often limited to the physical conditions (pressure, atomic coordination, crystal structure, etc.) at which the inter-atomic potentials are fitted. Really predictive calculations, not biased by the experimental information used to describe inter-atomic interactions require a proper quantum-mechanical description of the chemical bonds that held matter together. This can be achieved in the framework of electronic-structure theory (Martin 2004), starting from the *adiabatic* or Born and Oppenheimer (BO) approximation, and using modern concepts from DFT (Hohenberg & Kohn 1964, Kohn & Sham 1965) and perturbation theory (Baroni et al. 2001).

Within the BO approximation, the lattice-dynamical properties of a system are determined by the eigenvalues  $E$  and eigenfunctions  $\Phi$  of the Schrödinger equation:

$$\left( -\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} + E_{BO}(\{\mathbf{R}\}) \right) \Phi(\{\mathbf{R}\}) = E \Phi(\{\mathbf{R}\}), \quad (14)$$

where  $\mathbf{R}_I$  is the coordinate of the  $I$ -th nucleus,  $M_I$  its mass,  $\{\mathbf{R}\}$  indicates the set of all the nuclear coordinates, and  $E_{BO}$  is the ground-state energy of a system of interacting electrons moving in the field of fixed nuclei, whose Hamiltonian—which acts onto the electronic variables and depends parametrically upon  $\{\mathbf{R}\}$ —reads:

$$H_{BO}(\{\mathbf{R}\}) = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{\{\mathbf{R}\}}(\mathbf{r}_i) + E_N(\{\mathbf{R}\}), \quad (15)$$

$-e$  being the electron charge,  $V_{\{\mathbf{R}\}}(\mathbf{r}) = -\sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}$  is the electron-nucleus interaction, and  $E_N(\{\mathbf{R}\}) = \frac{e^2}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$  the inter-nuclear interaction energy. The equilibrium geometry of the system is determined by the condition that the forces acting on individual nuclei vanish:

$$\mathbf{F}_I \equiv -\frac{\partial E_{BO}(\{\mathbf{R}\})}{\partial \mathbf{R}_I} = 0, \quad (16)$$

whereas the vibrational frequencies,  $\omega$ , are determined by the eigenvalues of the Hessian of the BO energy, scaled by the nuclear masses:

$$\det \left| \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E_{BO}(\{\mathbf{R}\})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} - \omega^2 \right| = 0. \quad (17)$$

The calculation of the equilibrium geometry and vibrational properties of a system thus amounts to computing the first and second derivatives of its BO energy surface. The basic tool to accomplish this goal is the Hellmann-Feynman (HF) theorem (Hellmann 1937, Feynman 1939), which leads to the following expression for the forces:

$$\mathbf{F}_I = -\int n_{\{\mathbf{R}\}}(\mathbf{r}) \frac{\partial V_{\{\mathbf{R}\}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_N(\{\mathbf{R}\})}{\partial \mathbf{R}_I}, \quad (18)$$

where  $n_{\{\mathbf{R}\}}(\mathbf{r})$  is the ground-state electron charge density corresponding to the nuclear configuration  $\{\mathbf{R}\}$ . The Hessian of the BO energy surface appearing in Eq. (17) is obtained by differentiating the HF forces with respect to nuclear coordinates:

$$\frac{\partial^2 E_{BO}(\{\mathbf{R}\})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} \equiv -\frac{\partial \mathbf{F}_I}{\partial \mathbf{R}_J} \quad (19)$$

$$= \int \frac{\partial n_{\{\mathbf{R}\}}(\mathbf{r})}{\partial \mathbf{R}_J} \frac{\partial V_{\{\mathbf{R}\}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} \quad (20)$$

$$+ \int n_{\{\mathbf{R}\}}(\mathbf{r}) \frac{\partial^2 V_{\{\mathbf{R}\}}(\mathbf{r})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} d\mathbf{r} + \frac{\partial^2 E_N(\{\mathbf{R}\})}{\partial \mathbf{R}_I \partial \mathbf{R}_J}. \quad (21)$$

Eq. (21) states that the calculation of the Hessian of the BO energy surfaces requires the calculation of the ground-state electron charge density,  $n_{\{\mathbf{R}\}}(\mathbf{r})$ , as well as of its *linear response* to a distortion of the nuclear geometry,  $\partial n_{\{\mathbf{R}\}}(\mathbf{r})/\partial \mathbf{R}_I$ . This fundamental result was first stated in the late sixties by De Cicco and Johnson (DeCicco & Johnson 1969) and by Pick, Cohen, and Martin (Pick et al. 1970). The Hessian matrix is usually called the matrix of the *inter-atomic force constants* (IFC). For a crystal, we can write:

$$C_{ss'}^{\alpha\alpha'}(\mathbf{R} - \mathbf{R}') = \frac{\partial^2 E_{BO}(\{\mathbf{R}\})}{\partial u_s^\alpha(\mathbf{R}) \partial u_{s'}^{\alpha'}(\mathbf{R}')}, \quad (22)$$

where  $u_s^\alpha(\mathbf{R})$  is the  $\alpha$ -th Cartesian components of the displacement of the  $s$ -th atom of the crystal unit cell located at lattice site  $\mathbf{R}$ , and translational invariance shows manifestly in the dependence of the IFC matrix on  $\mathbf{R}$  and  $\mathbf{R}'$  through their difference only.

### 3.2 Density-functional perturbation theory

We have seen that the electron-density linear response of a system determines the matrix of its IFCs, Eq. (21). Let us see now how this response can be obtained from DFT. The procedure described in the following is usually referred to as density-functional perturbation theory (Baroni et al. 1987, Baroni et al. 2001).

In order to simplify the notation and make the argument more general, we assume that the external potential acting on the electrons is a differentiable function of a set of parameters,  $\boldsymbol{\lambda} \equiv \{\lambda_i\}$  ( $\lambda_i \equiv \mathbf{R}_I$  in the case of lattice dynamics). According to the HF theorem, the first and second derivatives of the ground-state energy read:

$$\frac{\partial E}{\partial \lambda_i} = \int \frac{\partial V^\lambda(\mathbf{r})}{\partial \lambda_i} n^\lambda(\mathbf{r}) d\mathbf{r}, \quad (23)$$

$$\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial^2 V^\lambda(\mathbf{r})}{\partial \lambda_i \partial \lambda_j} n^\lambda(\mathbf{r}) d\mathbf{r} + \int \frac{\partial n^\lambda(\mathbf{r})}{\partial \lambda_i} \frac{\partial V^\lambda(\mathbf{r})}{\partial \lambda_j} d\mathbf{r}. \quad (24)$$

In DFT the electron charge-density distribution,  $n^\lambda$ , is given by:

$$n^\lambda(\mathbf{r}) = 2 \sum_{n=1}^{N/2} |\psi_n^\lambda(\mathbf{r})|^2, \quad (25)$$

where  $N$  is the number of electrons in the system (double degeneracy with respect to spin degrees of freedom is assumed), the single-particle orbitals,  $\psi_n^\lambda(\mathbf{r})$ , satisfy the Kohn-Sham (KS) Schrödinger equation:

$$\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{SCF}^\lambda(\mathbf{r}) \right) \psi_n^\lambda(\mathbf{r}) = \epsilon_n^\lambda \psi_n^\lambda(\mathbf{r}), \quad (26)$$

and the *self-consistent* potential,  $V_{SCF}^\lambda$ , is given by:

$$V_{SCF}^\lambda = V^\lambda + e^2 \int \frac{n^\lambda(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{XC}[n^\lambda](\mathbf{r}), \quad (27)$$

where  $\mu_{XC}$  is the so-called *exchange-correlation* (XC) potential (Kohn & Sham 1965). The electron-density response,  $\partial n^\lambda(\mathbf{r})/\partial \lambda_i$ , appearing in Eq. (24) can be evaluated by linearizing Eqs. (25), (26), and (27) with respect to wave-function, density, and potential variations, respectively. Linearization of Eq. (25) leads to:

$$n'(\mathbf{r}) = 4\text{Re} \sum_{n=1}^{N/2} \psi_n^*(\mathbf{r}) \psi_n'(\mathbf{r}), \quad (28)$$

where the prime symbol (as in  $n'$ ) indicates differentiation with respect to one of the  $\lambda$ 's. The super-script  $\boldsymbol{\lambda}$  has been omitted in Eq. (28), as well as in any subsequent formulas where such an omission does not give rise to ambiguities. Since the external potential (both unperturbed and perturbed) is real, KS eigenfunctions can be chosen to be real, and the sign of complex conjugation, as well as the prescription to keep only the real part, can be dropped in Eq. (28).

The variation of the KS orbitals,  $\psi_n'(\mathbf{r})$ , is obtained by standard first-order perturbation theory (Messiah 1962):

$$(H_{SCF}^\circ - \epsilon_n^\circ) |\psi_n'\rangle = -(V_{SCF}' - \epsilon_n') |\psi_n^\circ\rangle, \quad (29)$$

where  $H_{SCF}^{\circ} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2} + V_{SCF}^{\circ}(\mathbf{r})$  is the unperturbed KS Hamiltonian, ,

$$V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \kappa(\mathbf{r}, \mathbf{r}') n'(\mathbf{r}') d\mathbf{r}' \quad (30)$$

is the first-order correction to the self-consistent potential, Eq. (27),  $\kappa(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta\mu_{XC}(\mathbf{r})}{\delta n(\mathbf{r}')}$  is the *Hartree-plus-XC kernel*, and  $\epsilon'_n = \langle \psi_n^{\circ} | V'_{SCF} | \psi_n^{\circ} \rangle$  is the first order variation of the KS eigenvalue,  $\epsilon_n$ . Equations (28–30) form a set of self-consistent equations for the perturbed system completely analogous to the KS equations in the unperturbed case—Eqs. (25), (26), and (27)—with the KS eigenvalue equation, Eq. (26), being replaced by a linear system, Eq. (29). The computational cost of the determination of the density response to a single perturbation is of the same order as that needed for the calculation of the unperturbed ground-state density.

The above discussion applies to insulators, where there is a finite gap. In metals a finite density of states occurs at the Fermi energy, and a change in the orbital occupation number may occur upon the application of an infinitesimal perturbation. The modifications of DFPT needed to treat the linear response of metals are discussed in Refs. (de Gironcoli 1995, Baroni et al. 2001).

### 3.3 Interatomic force constants and phonon band interpolation

The above discussion indicates that the primary physical ingredient of a lattice-dynamical calculation is the IFC matrix, Eq. (21), from which vibrational frequencies can be obtained by solving the secular problem, Eq. (17). That phonon frequencies can be classified according to a well defined value of the crystal momentum  $\mathbf{q}$  follows from the translational invariance of the IFC matrix. Because of this, the IFC matrix can be Fourier analyzed to yield the so called *dynamical matrix*, prior to diagonalization:

$$\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) = \sum_{\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R}) e^{-i\mathbf{q}\cdot\mathbf{R}}, \quad (31)$$

and the squared vibrational frequencies,  $\omega(\mathbf{q}, \nu)^2$ , are the eigenvalues of the  $3n \times 3n$  dynamical matrix:

$$D_{st}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \tilde{C}_{st}^{\alpha\beta}(\mathbf{q}), \quad (32)$$

$n$  being the number of atoms in the unit cell. The direct computation of the IFCs is unwieldy because it requires the calculation of the crystal electronic linear response to a localized perturbation (the displacement of a single atom or atomic plane), which would in turn break the translational symmetry of the system, thus requiring the use of computationally expensive large unit cells (Martin 2004, Alfé n.d., Parlinski n.d.). The IFCs are instead more conveniently calculated in Fourier space, which gives direct access to the relevant  $\mathbf{q}$ -dependent dynamical matrices (Baroni et al. 2001). Because of translational invariance, the linear response to a *monochromatic* perturbation, i.e. one with a definite wave-vector  $\mathbf{q}$ , is also monochromatic, and all quantities entering the calculation can be expressed in terms of lattice-periodic quantities (Baroni et al. 2001). As a



consequence, vibrational frequencies can be calculated at any wave-vector in the BZ, without using any supercells, with a numerical effort that is independent of the phonon wave-length and comparable to that of a single ground-state calculation for the unperturbed system.

The accurate calculation of sums (integrals) of lattice-dynamical properties over the BZ (such as those appearing in the QHA formulation of the thermodynamics of crystals in Sec. 2) requires sampling the integrand over a fine grid of points. This may be impractical in many cases, and suitable interpolation techniques are therefore called for. The most accurate, and physically motivated, such technique consists in the calculation of real-space IFCs by inverse analyzing a limited number of dynamical matrices calculated on a coarse grid. Dynamical matrices at any arbitrary point in the BZ can then be inexpensively reconstructed by Fourier analysis of the IFC's thus obtained. According to the *sampling theorem* by Shannon (Shannon 1949), if the IFCs are strictly short-range, a finite number of dynamical matrices, sampled on a correspondingly coarse reciprocal-space grid, is sufficient to calculate them *exactly* by inverse Fourier analysis. The IFCs thus obtained can then be used to calculate exactly the dynamical matrices at any wave-vector not included in the original reciprocal-space grid. In the framework of lattice-dynamical and band-structure calculations this procedure is usually referred to as *Fourier interpolation*. Of course, IFCs are never strictly short-range, and Fourier interpolation is in general a numerical approximation, subject to so-called *aliasing* errors, whose magnitude and importance have to be checked on a case-by-case basis.

Let us specialize to the case of a crystal, in which lattice vectors  $\mathbf{R}$  are generated by primitive vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ :  $\mathbf{R}_{lmn} = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$ , with  $l, m, n$  integer numbers. The reciprocal lattice vectors  $\mathbf{G}$  are generated in an analogous way by vectors  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ , such that

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}. \quad (33)$$

Correspondingly we consider a symmetry-adapted uniform grid of  $\mathbf{q}$ -vectors:

$$\mathbf{q}_{pqr} = \frac{p}{N_1}\mathbf{b}_1 + \frac{q}{N_2}\mathbf{b}_2 + \frac{r}{N_3}\mathbf{b}_3, \quad (34)$$

where  $p, q, r$  are also integers. This grid spans the reciprocal lattice of a supercell of the original lattice, generated by primitive vectors  $N_1\mathbf{a}_1, N_2\mathbf{a}_2, N_3\mathbf{a}_3$ . Since wave-vectors differing by a reciprocal-lattice vector are equivalent, all values of  $p, q, r$  differing by a multiple of  $N_1, N_2, N_3$  respectively, are equivalent. We can then restrict our grid to  $p \in [0, N_1 - 1]$ ,  $q \in [0, N_2 - 1]$ , and  $r \in [0, N_3 - 1]$ . The  $\mathbf{q}_{pqr}$  grid thus contains  $N_1 \times N_2 \times N_3$  uniformly spaced points and spans the parallelepiped generated by  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ . It is often convenient to identify wave-vectors with integer labels spanning the  $[-\frac{N}{2}, \frac{N}{2} - 1]$  range, rather than  $[0, N - 1]$ . Negative indices can be folded to positive values using the periodicity of discrete Fourier transforms.

Once dynamical matrices have been calculated on the  $\mathbf{q}_{hkl}$  grid, IFCs are easily obtained by (discrete) fast-Fourier transform (FFT) techniques:

$$\begin{aligned} C_{st}^{\alpha\beta}(\mathbf{R}_{lmn}) &= \frac{1}{N_1 N_2 N_3} \sum_{pqr} \tilde{C}_{st}^{\alpha\beta}(\mathbf{q}_{pqr}) e^{i\mathbf{q}_{pqr} \cdot \mathbf{R}_{lmn}} \\ &= \frac{1}{N_1 N_2 N_3} \sum_{pqr} \tilde{C}_{st}^{\alpha\beta}(\mathbf{q}_{pqr}) e^{i2\pi \left( \frac{lp}{N_1} + \frac{mq}{N_2} + \frac{nr}{N_3} \right)}, \end{aligned}$$

where the bi-orthogonality of the real- and reciprocal-space primitive vectors, Eq. (33), is used to get  $\mathbf{q}_{pqr} \cdot \mathbf{R}_{lmn} = 2\pi \left( \frac{lp}{N_1} + \frac{mq}{N_2} + \frac{nr}{N_3} \right)$ . The IFCs thus obtained can be used to calculate dynamical matrices at wave-vectors not originally contained in the reciprocal-space grid. This can be done directly wave-vector by wave-vector, or by FFT techniques, by padding a conveniently large table of IFCs with zeroes beyond the range of those calculated from Fourier analyzing the original coarse reciprocal-space grid.

## 4 Computer codes

In order to implement the QHA from first principles, one needs to compute the complete phonon dispersion of a crystal for different values of the crystal volume. This can be done within DFT by the *direct* or *frozen phonon* method, or by the *linear response* method (Baroni et al. 2001, Martin 2004). The former does not require the use of specialized software beside that needed to perform standard ground-state DFT calculations, but is computationally more demanding. Some software tools that help analyze the output of standard DFT code to produce real-space IFC's and, from these, reciprocal-space dynamical matrices are available (Alfé n.d., Parlinski n.d.). As for the linear-response approach, two widely known general-purpose packages exist, QUANTUM ESPRESSO (Giannozzi et al. 2009) and ABINIT (Gonze et al. 2002). In the following we briefly describe the former, as well as another code, *QHA*, that can be used as a post-processing tool to perform QHA calculations starting from lattice-dynamical calculations performed with many different methods (semi-empirical as well as first-principles, frozen-phonon, as well as DFPT).

### 4.1 Quantum ESPRESSO

QUANTUM ESPRESSO (*opEn Source Package for Research in Electronic Structure, Simulation, and Optimization*) is an integrated suite of computer codes for electronic-structure calculations and materials modeling, based on DFT, plane waves, pseudopotentials (norm-conserving and ultrasoft) and all-electron Projector-Augmented-Wave potentials (Giannozzi et al. 2009). It is freely available under the terms of the GNU General Public License. QUANTUM ESPRESSO is organized into packages. For the purposes of lattice-dynamical calculations and QHA applications, the two most relevant ones are **PWscf** and **PHonon**. The former produces the self-consistent electronic structure and all related computations (forces, stresses, structural optimization, molecular dynamics). The latter solves the DFPT equations and calculates dynamical matrices for a single wave-vector or for a uniform grid of wave-vectors; Fourier interpolation can be applied to the results to produce IFCs up to a pre-determined range in real space. The effects of macroscopic electric field are separately dealt with using the known exact results valid in the long-wavelength limit (Born & Huang 1954). Both the electronic contribution to the dielectric tensor,  $\epsilon_\infty$ , and the effective charges  $Z^*$  are calculated by **PHonon** and taken into account in the calculation of interatomic force constants. Once these have been calculated, phonon modes at any wave-vector can be recalculated in a quick and economical way. Anharmonic force constants can be explicitly calculated using the **D3** code contained in the **PHonon** package. The volume dependence of the IFCs needed within the

QHA is simply obtained numerically by performing several phonon (harmonic) calculations at different volumes of the unit cell.

## 4.2 The *QHA* code

Once the IFC matrix (or, equivalently, the dynamical matrix over a uniform grid in reciprocal space) has been calculated, thermodynamical properties can be easily calculated using the *QHA* code (Isaev n.d.). *QHA* requires in input just a few data: basic information about the system (such as atomic masses, lattice type) and a file containing IFCs, stored in an appropriate format. *QHA* then calculates and several quantities such as the total phonon density of states (DOS), atom-projected DOS, the isochoric heat capacity, the Debye temperature, zero-point vibration energy, internal energy, entropy, mean square displacements for atoms, etc. The DOS is obtained via the tetrahedron method (Lehmann & Taut 1972), while integrals over the frequency are calculated using the Simpson’s “3/8 rule”.

# 5 Applications

The first investigations of the thermal properties of materials using *ab initio* phonons and the QHA date back to the early days of DFPT theory, when the thermal expansivity of tetrahedrally coordinated semiconductors and insulators was first addressed (Fleszar & Gonze 1990, Pavone 1991, Pavone et al. 1993). Many other applications have appeared ever since to metals, hydrides, inter-metallic compounds, surfaces, and to systems and properties of mineralogical and geophysical interest. Brief reviews of these applications can be found in Refs. (Baroni et al. 2001, Rickman & LeSar 2002); this section contains a more up-to-date review, with a special attention paid to those applications that are relevant to the Earth Sciences.

## 5.1 Semiconductors and insulators

One of the most unusual features of tetrahedrally coordinated elemental and binary semiconductors is that they display a negative thermal expansion coefficient (TEC) at very low temperature. This finding prompted the first applications of the QHA to semiconductors, using first a semi-empirical approach (Biernacki & Scheffler 1989), and first-principles techniques in the following (Fleszar & Gonze 1990, Pavone 1991, Pavone et al. 1993, Hamdi et al. 1993, Debernardi & Cardona 1996, Gaal-Nagy et al. 1999, Rignanese et al. 1996, Xie, Chen, Tse, de Gironcoli & Baroni 1999, Eckman et al. 2000, Mounet & Marzari 2005, Zimmermann et al. 2008). The detailed insight provided by the latter allowed one to trace back this behavior to the negative Grüneisen parameter in the lowest acoustic phonon branch and to its flatness that enhances its weight in the vibrational density of states at low frequency. This behavior is not observed in diamond at ambient conditions—which in fact does not display any negative TEC (Pavone et al. 1993, Xie, Chen, Tse, de Gironcoli & Baroni 1999)—whereas at pressures larger than  $\sim 700$  GPa the softening of the acoustic Grüneisen parameters determines a negative TEC. The TEC of diamond calculated in Ref. (Pavone et al. 1993) starts deviating from experimental points at  $T \gtrsim 600$  K

which was explained in terms of enhanced anharmonic effects at higher temperature. However, a recent calculation done with a different XC energy functional (GGA, rather than LDA) (Mounet & Marzari 2005) displayed a fairly good agreement with experiments up to  $T = 1200\text{K}$ , and with results of Monte-Carlo simulations (Herrero & Ramírez 2000) up to  $T = 3000\text{K}$ . Graphite shows negative in-plane TEC over a broad temperature range, up to  $600\text{K}$ , and the calculated TEC for graphene is negative up to  $2000\text{K}$  (Mounet & Marzari 2005). This is due to a negative Grüneisen parameter of the out-of-plane lattice vibrations along the  $\Gamma M$  and  $\Gamma K$  directions (the so called ZA modes, which plays an important role in the thermal properties of layered materials, due to the high phonon DOS displayed at low frequency because of a vanishing sound velocity (Lifshitz 1952, Zabel 2001)). Such an unusual thermal contraction for carbon fullerenes and nanotubes was confirmed by molecular dynamics simulations in Ref. (Kwon et al. 2004). The heat capacity of carbon nanotubes was calculated in Ref. (Zimmermann et al. 2008). The out-of-plane TEC calculated for graphite (Mounet & Marzari 2005) is in poor agreement with experiment. This is not unexpected because inter-layer binding is mostly due to dispersion forces which are poorly described by the (semi-) local XC functionals currently used in DFT calculations.

One of the early achievements of DFT that greatly contributed to its establishment in the condensed-matter and materials-science communities was the prediction of the relative stability of different crystal structures as a function of the applied pressure (Gaal-Nagy et al. 1999, Eckman et al. 2000, Correa et al. 2006, Liu et al. 1999, Isaev et al. 2007, Mikhaylushkin et al. 2007, Dubrovinsky et al. 2007). Thanks to the QHA, vibrational effects can be easily included in the evaluation of the crystal free energy, thus allowing for the exploration of the phase diagram of crystalline solids at finite temperature. In Refs. (Gaal-Nagy et al. 1999, Eckman et al. 2000), for instance, the  $P - T$  phase diagram for Si and Ge was studied in correspondence to the diamond  $\rightarrow \beta\text{-Sn}$  transition. Noticeable changes in the EOS of ZnSe at finite temperature were shown in (Hamdi et al. 1993). The phase boundary between cubic and hexagonal BN has been studied in Ref. (Kern et al. 1999) using the QHA with an empirical correction to account for the leading (explicit) anharmonic effects. Other applications of the QHA in this area include the low-temperature portion of the  $P - T$  phase diagram for the diamond  $\rightarrow \text{BC8}$  phase transition (Correa et al. 2006) and the sequence of Rhombohedral ( $223\text{K}$ )  $\rightarrow$  Orthorhombic ( $378\text{K}$ )  $\rightarrow$  Tetragonal ( $778\text{K}$ )  $\rightarrow$  Cubic phase transitions in  $\text{BaTiO}_3$  (Zhang et al. 2006) at ambient pressure.

## 5.2 Simple metals

The QHA has been widely used to investigate the thermal properties of BCC (Quong & Liu 1997, Liu et al. 1999, Debernardi et al. 2001), FCC (Debernardi et al. 2001, Li & Tse 2000, Grabowski et al. 2009, Xie et al. 2000, Narasimhan & de Gironcoli 2002, Xie, de Gironcoli, Baroni & Scheffler 1999a, Tsuchiya 2003, Sun et al. 2008), and HCP (Ismail et al. 2001, Althoff et al. 1993) metals. These works generally report a good agreement with experiments as concerns the calculated lattice volume, bulk modulus, TEC, Grüneisen parameter, and high-pressure/high-temperature phase diagram. Some discrepancies in the temperature dependence of  $C_P$  and TEC might be connected to the neglect of ex-

implicit anharmonic effects at high temperatures, as well as due to overestimated cell volumes when using GGA XC functionals. In Ref. (Grabowski et al. 2009) it was stressed that implicit quasi-harmonic effects dominate the thermal properties, being almost two orders of magnitude larger than explicit anharmonic ones, irrespective of the XC functional adopted.

The QHA has also been an important ingredient in the calculation of the melting curve of some metals, such as Al (Vocadlo & Alfe 2002), Si (Alfe & Gillan 2002), and Ta (Gülseren & Cohen 2002, Taioli et al. 2007), performed via thermodynamic integration. The vibrational contribution to the low-temperature free energy of the crystal phase was shown to be important for lighter elements (such as Al), whereas it is negligible for heavier ones, such as Ta. The  $P - T$  phase diagram for HCP-BCC Mg has been obtained in Ref. (Althoff et al. 1993), where it was shown that a proper account of lattice vibrations improves the prediction of the transition pressure at room temperature. Interestingly, in Ref. (Xie, de Gironcoli, Baroni & Scheffler 1999a) it was noticed that in the QHA equation of state (EOS) of Ag there exists a critical temperature beyond which no volume would correspond to a vanishing pressure—thus signaling a thermodynamic instability of the system—and that this temperature is actually rather close to the experimental melting temperature of Ag. Narasimhan *et al.* (Narasimhan & de Gironcoli 2002) studied the influence of different (LDA and GGA) functionals on the thermal properties of Cu. The contribution of lattice vibrations to the phase stability of Li and Sn has been studied in Refs. (Liu et al. 1999, Pavone et al. 1998, Pavone 2001): a proper account of vibrational effects considerably improves the predictions of the low-temperature structural properties of a light element such as Li, which is strongly affected by zero-point vibrations (Liu et al. 1999). The large vibrational entropy associated with low-frequency modes stabilizes the BCC structure of Li (Liu et al. 1999) and  $\beta$ -Sn (Pavone et al. 1998, Pavone 2001) just above room temperature.

### 5.3 Hydrides

One of the best illustrations of the ability of the QHA to account for the effects of lattice vibrations on the relative stability of different crystalline phases is provided by iron and palladium hydrides, FeH and PdH. FeH was synthesized by different experimental groups (Antonov et al. 1980, Badding et al. 1992, Hirao et al. 2004) and its crystalline structure was found to be a double hexagonal hexagonal structure (DHCP), contrary to the results of *ab initio* calculations (Elsasser et al. 1998) that, neglecting vibrational effects, would rather predict a simple HCP structure. The puzzle remained unsolved until free-energy calculations for FCC, HCP, and DHCP FeH (Isaev et al. 2007) showed that the hydrogen vibrational contribution to the free energy actually favors the DHCP structure. This is a consequence of the linear ordering of H atoms in HCP FeH, which shifts to higher frequencies the mostly H-like optical band of the system, with respect to the FCC and DHCP phases. The corresponding increase in the zero-point energy makes the DHCP structure—which is the next most favored, neglecting lattice vibrations—the stablest structure at low pressure. The quantum nature of hydrogen vibrations and its influence on the phase stability of hydrides was also clearly demonstrated in (Caputo & Alavi 2003, Hu et al. 2007). First-principles pseudopotential calculations for PdH have shown that tetrahe-

drally coordinated H (B3-type PdH) is energetically favored with respect to octahedrally coordinated H (B1-type PdH), at variance with experimental findings (Rowe et al. 1972, Nelin 1971). The quantum-mechanical behavior of hydrogen vibrations dramatically affects on the stability of PdH phases at low temperature, favoring the octahedral coordination of hydrogen atoms in PdH (Caputo & Alavi 2003). As another example, the QHA does not predict any  $\alpha \rightarrow \beta$  (monoclinic to orthorhombic) phase transition in  $\text{Na}_2\text{BeH}_4$  (Hu et al. 2007), contrary to the conclusions that were reached from static total-energy calculations. Overall, the structural parameters of most alkaline hydrides calculated using the QHA turned out to be substantially improved by a proper account of zero-point vibrations, both using LDA and GGA XC functionals (more so in the latter case) (Roma et al. 1996, Barrera et al. 2005, Lebègue et al. 2003, Zhang et al. 2007).

## 5.4 Intermetallics

The QHA has been also successfully applied to the thermal properties of intermetallics and alloys. For example, the Grüneisen parameters, isothermal bulk modulus, TEC, and constant-pressure specific heat for  $\text{Al}_3\text{Li}$  have been calculated in (Li & Tse 2000). The TEC temperature dependence of the technologically important superalloys B2 NiAl and  $\text{L}_{12}$   $\text{Ni}_3\text{Al}$ , as well as  $\text{L}_{12}$   $\text{Ir}_3\text{Nb}$ , have been studied in Refs. (Wang et al. 2004, Arroyave et al. 2005, Lozovoi & Mishin 2003, Gornostyrev et al. 2007). This is a very significant achievement of QHA, as it makes it possible very accurate temperature-dependent calculations of the misfit between lattice parameters of low-temperature FCC/BCC alloy and high-temperature  $\text{L}_{12}$ /B2 phases, which plays a considerable role in the shape formation of precipitates. It has been found that zero-point vibrations do not affect the type of structural defects in B2 NiAl, nor do they change qualitatively the statistics of thermal defects in B2 NiAl (Lozovoi & Mishin 2003). Ozolins *et al.* (Ozolins et al. 1998) and Persson *et al.* (Persson et al. 1999) have studied the influence of vibrational energies on the phase stability in Cu-Au and Re-W alloys, using a combination of the QHA and of the cluster-variation method. It turns out that lattice vibrations considerably enhance to the stability of CuAu intermetallic compounds and Cu-Au alloys with respect to phase separation (Ozolins et al. 1998), as well as to the relative stability of the ordered vs. disordered phases at high temperature (Persson et al. 1999).

## 5.5 Surfaces

*Ab initio* calculations for surfaces coupled with the QHA have been done for the past 10 years. For example, an anomalous surface thermal expansion, the so called *surface pre-melting*, has been studied for a few metallic surfaces, such as Al(001) (Hansen et al. 1999), Al(111) (Narasimhan & Scheffler 1997), Ag(111) (Xie, de Gironcoli, Baroni & Scheffler 1999b, Narasimhan & Scheffler 1997, Al-Rawi et al. 2001), Rh(001), Rh(110) (Xie & Scheffler 1998), Mg(10 $\bar{1}$ 0) (Ismail et al. 2001), Be(10 $\bar{1}$ 0) (Lazzeri & de Gironcoli 2002) and Be(0001) (Pohl et al. 1998). Hansen *et al.* (Hansen et al. 1999) noticed that the QHA is fairly accurate up to the Debye temperature, above which *explicit* anharmonic effects, not accounted for in this approximation, become important. While no peculiar effects for the surface inter-layer spacing were found for



Al(111) (Narasimhan & Scheffler 1997), for Ag and Rh surfaces it was found that the outermost interlayer distance,  $d_{12}$ , is reduced at room temperature, with respect to its bulk value, whereas it is expanded at high temperatures (Narasimhan & Scheffler 1997, Xie, de Gironcoli, Baroni & Scheffler 1999*b*, Al-Rawi et al. 2001, Xie & Scheffler 1998). The expansion of  $d_{12}$  in the Ag and Rh surfaces, as well as in Be(0001) (Pohl et al. 1998), is related to the softening of some in-plane vibrational modes with a corresponding enhancement of their contribution to the surface free energy. Free energy calculations for Be(10 $\bar{1}$ 0) (Lazzeri & de Gironcoli 2002) and Mg(10 $\bar{1}$ 0) (Ismail et al. 2001) successfully account for the experimentally observed oscillatory behavior of the interatomic distances. The large contraction of  $d_{12}$  in Be(10 $\bar{1}$ 0) was explained in terms of a strong anharmonicity in the second layer in comparison with the surface layer (see also (Marzari et al. 1999)). For Be(0001) no oscillatory behavior in inter-layer spacings was observed in (Pohl et al. 1998), but an anomalously large surface thermal expansion does occur.

## 5.6 Earth Materials

The extreme temperature and pressure conditions occurring in the Earth interior make many geophysically relevant materials properties and processes difficult, if not impossible, to observe in the laboratory. Because of this, computer simulation is often a premier, if not unique, source of information in the Earth sciences. By increasing the pressure, the melting temperature also increases, so that the temperature range over which a material behaves as a harmonic solid is correspondingly expanded, thus making the QHA a very useful tool to investigate materials properties at Earth-science conditions.

Iron, the fourth most abundant element on Earth and the main constituent of the Earth core, plays an outstanding role in human life and civilization. In Refs. (Körmann et al. 2008, Sha & Cohen 2006*b*, Sha & Cohen 2006*a*) the thermodynamics and thermoelastic properties of BCC Fe have been treated by means of the QHA and finite-temperature DFT. The temperature dependence of the calculated constant-pressure heat capacity deviates from experiment at room temperature, but a proper inclusion of magnetic effects dramatically improves the agreement up to the Curie temperature (Körmann et al. 2008). The calculated Debye temperature and low-temperature isochoric heat capacity  $C_V$  are in good agreement with available experimental data. The magnitude and temperature dependence of the calculated  $C_{12}$ ,  $C_{44}$  elastic constants (Sha & Cohen 2006*a*) are consistent with experiment (Leese & Lord Jr. 1968, Dever 1972, Isaak & Masuda 1995) in the temperature range from 0K to 1200K at ambient pressure, while  $C_{11}$  is overestimated (Sha & Cohen 2006*a*), likely because of an underestimated equilibrium volume. The ambient-pressure shear and compressional sound velocities are consistent with available ultrasonic measurements. The  $c/a$  ratio of  $\epsilon$ -Fe has been studied in (Sha & Cohen 2006*c*) up to temperatures of 6000 K and pressures of 400 GPa by using the QHA, resulting in good agreement with previous calculations (Gannarelli et al. 2003) and X-Ray diffraction experiment (Ma et al. 2004). A combination of experiments and calculations performed within the QHA was used to show that the FCC and HCP phases of nonmagnetic Fe (Mikhaylushkin et al. 2007) can co-exist at very high temperatures and pressures ( $\sim 6600$  K and 400 GPa), due to quite small free-energy differences.

B1-type MgO and CaO, MgSiO<sub>3</sub> perovskite, the aragonite and calcite phases of CaCO<sub>3</sub>, the various polymorphs of aluminum silicate, Al<sub>2</sub>SiO<sub>5</sub>, silica, SiO<sub>2</sub> and alumina, Al<sub>2</sub>O<sub>3</sub> are very important constituents of the Earth's crust and lower mantle. Besides, it is believed that the Earth's  $D''$  layer is mostly composed of post-perovskite MgSiO<sub>3</sub>, while  $\gamma$ -spinel Mg<sub>2</sub>SiO<sub>4</sub> is the dominant mineral for the lower part of Earth's transition zone. Note that Mg-based minerals do contain some amount of Fe substituting Mg. The high-pressure crystalline structure and stability of these phases are discussed in (Oganov 2004, Oganov, Price & Scandolo 2005). Lattice dynamics and related thermal and elastic properties of B1 MgO have been studied in Refs. (Strachan et al. 1999, Drummond & Ackland 2002, Oganov et al. 2003, Oganov & Dorogokupets 2003, Karki et al. 2000, Karki et al. 1999, Wu et al. 2008, Wu & Wentzcovitch 2009). Wentzcovitch and *et al.* have introduced a *semi-empirical ansatz* that allows for an account of explicit anharmonic contributions to the QHA estimate of various quantities, such as the TEC and  $C_p$  (Wu et al. 2008, Wu & Wentzcovitch 2009), resulting in a much improved agreement with experiments. The temperature and pressure dependence of elastic constants of B1 MgO (Karki et al. 2000, Karki et al. 1999, Isaak et al. 1990) calculated within QHA show very good agreement with experimental data (Isaak et al. 1989). Besides, pressure dependence of *ab initio* compressional and shear sound velocities is in consistent with seismic observations for the Earth's lower mantle (Karki et al. 1999). In contrast with these successes, the calculated thermal properties of the B1 and B2 phases of CaO (Karki & Wentzcovitch 2003) are inconsistent with experimental data, and this is most likely due to the too small lattice parameter predicted by the LDA, as later investigations based on a GGA XC functional seem to indicate (Zhang & lai Kuo 2009).

The thermal properties of MgSiO<sub>3</sub> and Mg<sub>2</sub>SiO<sub>4</sub> and the phase transition boundary in these minerals (perovskite→post-perovskite MgSiO<sub>3</sub> and spinel→post-spinel Mg<sub>2</sub>SiO<sub>4</sub>) have been extensively studied (Wentzcovitch et al. 2006, Oganov & Ono 2004, Oganov & Price 2005, Wu & Wentzcovitch 2009, Yu et al. 2007, Wu et al. 2008, Yu et al. 2008, Ono & Oganov 2005) due to their great importance for the Earth's  $D''$  layer and lower mantle, respectively. Improved EOS of B1 MgO (Wu et al. 2008), obtained by means of *renormalized* phonons and QHA, has been used as a new pressure calibration to re-evaluate the high pressure – high temperature phase boundary in MgSiO<sub>3</sub> and Mg<sub>2</sub>SiO<sub>4</sub> minerals using experimental data from (Fei et al. 2004, Hirose et al. 2006, Speziale et al. 2001).

Alumina, Al<sub>2</sub>O<sub>3</sub>, plays an important role in high-pressure experiments: for example, it serves as a window material for shock-wave experiments. Cr-doped alumina, ruby, is used as a pressure calibration material in diamond-anvil-cell experiments. Besides, it is a component of solid solutions with MgSiO<sub>3</sub> polymorphs that have significantly different thermal properties from pure MgSiO<sub>3</sub> minerals. Corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) is the most stable phase of alumina at ambient conditions, preceded by the  $\theta$  phase at lower temperature. The energy difference between the  $\theta$  and  $\alpha$  phases of alumina is rather small, and this raised a question as to whether  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is stabilized by phonons. Zero-point vibrations stabilize the corundum phase at low temperatures (Lodziana & Parlinski 2003), whereas free-energy calculations show that the  $\alpha$  phase can not be stabilized by phonons only at room temperature. QHA calculations revealed that at high pressures alumina transforms to CaIrO<sub>3</sub>- (Oganov & Ono 2005) and U<sub>2</sub>S<sub>3</sub>-type (Umemoto & Wentzcovitch 2008) polymorphs.



The  $P - T$  phase diagram for  $\text{Al}_2\text{SiO}_5$  polymorphs (andalusite, sillimanite, and kyanite) (Winkler et al. 1991) and the thermal properties of  $\text{CaCO}_3$  polymorphs (calcite and aragonite) (Catti et al. 1993, Pavese et al. 1996) have been studied within the QHA using model inter-atomic potentials. The effect of zero-point vibrations on the equilibrium volume in the calcite phase was found to be quite important and actually larger than the thermal expansion at relatively high temperature (Catti et al. 1993). These calculations (Pavese et al. 1996) were not able to account for the experimentally observed (Rao et al. 1968) negative in-plane TEC in calcite. The heat capacity and entropy calculated for the aragonite phase substantially deviate from experiment. All these problems can be possibly traced back to the poor transferability of model inter-atomic potentials.

The thermal properties of the  $\alpha$ -quartz and stishovite phases of  $\text{SiO}_2$  have been studied in (Lee & Gonze 1995). The heat capacities of both phases were found to be in good agreement with experimental data (Lord & Morrow 1957, Holm et al. 1967), with the stishovite phase having a lower capacity below 480K. Interestingly, zero-point vibration energy of the stishovite phase affects on thermodynamical properties stronger than in the  $\alpha$ -quartz phase (Lee & Gonze 1995). The  $P - T$  phase diagram of  $\text{SiO}_2$  has been examined in Refs. (Oganov, Gillan & Price 2005, Oganov & Price 2005), with emphasis on the stishovite  $\rightarrow$  CaCl<sub>2</sub>  $\rightarrow$   $\alpha$ -PbO<sub>2</sub>  $\rightarrow$  pyrite structural changes, resulting in a sequence of transitions that do not correspond to any observed seismic discontinuities within the Earth. Further investigations at ultrahigh temperature and pressure show that  $\text{SiO}_2$  exhibits a pyrite  $\rightarrow$  cotunnite phase transition at conditions that are appropriate for the core of gas giants and terrestrial exoplanets (Umemoto et al. 2006).

## 6 Conclusions

The QHA is a powerful conceptual and practical tool that complements molecular dynamics in the prediction of the thermal properties of materials not too close to the melting line. In the specific case of the Earth Sciences, the QHA can provide information on the behavior of geophysically relevant materials at those geophysically relevant pressure and temperature conditions that are not (easily) achieved in the laboratory. Large-scale calculations using the QHA for geophysical research will require the deployment of a large number of repeated structure and lattice-dynamical calculations, as well as the analysis of the massive data generated therefrom. We believe that this will require the use of dedicated infrastructures that combine some of the features of massively parallel machines with those of a distributed network of computing nodes, in the spirit of the grid computing paradigm. The QUANTUM ESPRESSO distribution of computer codes is geared for exploitation on massively parallel machines up to several thousands of closely coupled processors and is being equipped with specific tools to distribute lattice-dynamical calculation over the grid (Di Meo et al. n.d.).

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