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Comparative study of quasiharmonic lattice dynamics, molecular dynamics and Debye model applied to $MgSiO_3$ perovskite☆

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Abstract

We consider three independent methodologies for calculating thermal equation of state (EOS) of the major earth-forming mineral, orthorhombic $MgSiO_3$ perovskite: molecular dynamics (MD), lattice dynamics (LD) and Debye model (DM). Using the most recent developments in the GULP code, we derive a new interatomic potential, which is demonstrated to be extremely robust at both high temperatures and high pressures. With this potential we construct a quasiharmonic self-consistent DM based on elastic properties of the crystal, and compare its results with results of more rigorous LD and MD simulations with the same potential model. We show that the DM reproduces quite accurately harmonic constant-volume heat capacity above 500 K, but gives thermal expansion and Grüneisen parameter (γ) that are too small. We conclude that $MgSiO_3$ perovskite is not a Debye-like solid, in contrast to what has often been assumed in geophysical literature. Acoustic γ, often used in geophysical studies, are a very crude approximation to the true γ. To obtain good accuracy, one needs to know the $\gamma(V)$ function more accurately than the DM can give. However, analytical functions, given by the Debye theory, are useful for fitting thermal expansion and related parameters at elevated temperatures. A common assumption that $q = \mathrm{d}\ln\gamma/\mathrm{d}\ln V$ is constant is found to be inadequate: in fact, q varies strongly with volume and can reach negative values towards the base of the lower mantle. This can be relevant for discussion of the anomalous properties of the core-mantle boundary (D″) layer. Comparison of results of LD and MD indicates importance of intrinsic anharmonic contributions in the thermal expansion and γ. Therefore, MD is the most suitable technique for simulating minerals at the Earth's mantle conditions.

Keywords: Equation of state; Grüneisen parameter; Thermal expansion; Anharmonicity; Interatomic potentials; Earth's lower mantle; D″ layer

1. Introduction

$MgSiO_3$ perovskite is currently believed to be the most abundant mineral on Earth, comprising about 70 vol.% of the lower mantle. The equation of state (EOS) of this phase at simultaneously high pressures and temperatures of the lower mantle (pressure between 24 and 136 GPa, temperature ca. 2000–4000 K) is crucial for interpreting seismological data and constructing reliable chemical, mineralogical, and thermal models of the lower mantle. Yet, accurate experimental EOS of $MgSiO_3$ perovskite are available only at the

☆ While this paper was under review, we found a paper, describing a quantum-mechanical study of phonons in $MgSiO_3$ perovskite (Parlinski K. and Kawazoe Y., 2000. Ab initio study of phonons and structural stabilities of the perovskite-type $MgSiO_3$. Eur. Phys. J., B 16, 49–58); total phonon spectrum of this phrase and its projections onto atomic species fully agree with our calculations.

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ambient temperature (e.g. Knittle and Jeanloz, 1987; Fiquet et al., 2000). Accurate experimental measurement of the temperature effects still poses a problem, e.g. thermal expansion coefficient of $MgSiO_3$ perovskite is very poorly known even at the ambient pressure. The difficulties in obtaining accurate thermoelastic parameters of this mineral from experiment were discussed in detail by Shim and Duffy (2000).

The highest experimentally reached hydrostatic pressure in experiments at the lower mantle temperatures is 94 GPa (Fiquet et al., 2000), which is still well below the core-mantle boundary pressure of 136 GPa. Moreover, experiments at such high pressures and temperatures can presently be performed only in laser-heated diamond anvil cells with very large uncertainties in temperature. To reproduce the extreme conditions of the lower mantle remains a major challenge for both theoreticians working at the ab initio level and experimentalists. Therefore, simplified models are still much in use.

It has become an almost common practice (e.g. Stixrude et al., 1992; Anderson et al., 1995; Jackson and Rigden, 1996; Yagi and Funamori, 1996; Shim and Duffy, 2000; Stacey and Isaak, 2000; Hama et al., 2000) to use the Debye model (DM) in geophysical studies. This model is extensively used for fitting experimental thermal expansion or heat capacity data. It has also been often used as a convenient model for fitting experimental EOS. The DM does describe the general shape of the temperature dependences of thermodynamic functions of solids (with only one parameter!), and this is the reason why it can be used for their fitting even without the Debye theory being quantitatively accurate or even physically realistic. Recently, Anderson (1998) advocated that '$MgSiO_3$-perovskite is one of a small, select group of Debye-like minerals, for which thermoelastic properties and the EOS are calculable from acoustic data'. From the computational point of view, this model is very tempting, since it makes use of only zero-temperature elastic constants, and allows one to predict *all* thermoelastic properties at arbitrary *P–T* conditions based only on the easily evaluated static properties. Highly accurate ab initio calculations of athermal EOS and elastic constants of $MgSiO_3$ perovskite already exist in the literature (Wentzcovitch et al., 1995; Karki et al., 1997). Recently, Stacey and Isaak (2000) used acoustic Grüneisen parameters to construct EOS of the lower mantle minerals. Hama et al. (2000) used a self-consistent DM in order to obtain thermal EOS and seismic velocities of the major lower mantle minerals and construct a mineralogical and thermal model of the lower mantle. Below we show that such an approach can be used only as a first rough approximation.

1.1. Mie–Grüneisen thermal EOS

The Mie–Grüneisen EOS represents thermal effects via thermal pressure $P_{\rm th}$, which is a relatively small correction to the well-known static (or ambient temperature) EOS:

$$P(V,T) = P_{\rm stat}(V) + P_{\rm th}(V,T) = P_{\rm stat}(V) + \gamma(V,T)E_{\rm vib}(V,T)/V, \qquad (1)$$

where $P_{\rm stat}(V)$ is the athermal EOS, $E_{\rm vib}$ the vibrational energy, V the volume and γ the thermodynamic Grüneisen parameter. Using Eq. (1), the thermal expansion can be written as:

$$\alpha = \frac{\gamma C_V \beta_T}{V} \qquad (2)$$

where C_V is the constant-volume heat capacity and β_T isothermal compressibility. (Eq. (2) yields $\gamma = \alpha V/C_V\beta_T$, the definition of the thermodynamic Grüneisen parameter). Compressibility as a function of volume is rather well known from the low-temperature EOS, so all one needs to know to construct an accurate high-temperature EOS is C_V and γ as a function of temperature and volume. Vočadlo et al. (2000) have examined a number of approximate theories, correlating γ with $\boldsymbol{K}' = {\rm d}K/{\rm d}P$ (see Poirier, 2000), but none of those were found to be sufficiently accurate; a similar conclusion was earlier arrived at by Wallace (1972). It is possible to obtain both C_V and γ using lattice-dynamical models, of which the DM is the simplest. Thoroughly reviewed and criticised as inapplicable to most minerals (Kieffer, 1979), the DM in application to $MgSiO_3$ perovskite was rehabilitated by Anderson (1998), who has shown that it yields very accurate values of C_V at ambient pressure and $T > 400$ K. However, due to the absence of experimental data on elastic constants as a function of volume, he was not able to test ability

of the model to reproduce α and γ. We feel that such a test would be crucial for judging the DM.

Before discussing our results, we recap the main features of the DM and arguments used in its favour recently. For a thorough critical review of this model we address the reader to the paper by Kieffer (1979).

1.2. The Debye model (DM)

Debye model is the simplest lattice-dynamical model, applicable at least to some solids. Although never exact, it often performs well for structurally and chemically simple crystals, e.g. many metals.

The main point of the DM is the link between crystal's elasticity and its acoustic phonons at the Brillouin zone centre ($\boldsymbol{k} \to 0$): elastic constants determine the slopes of the acoustic dispersion curves $\varpi(\boldsymbol{k})$ at $\boldsymbol{k} \to 0$. *Monatomic* solids have only three vibrational modes, all of which are acoustic. For these solids, the model has only two approximations: (1) assumption that phonon dispersion curves $\varpi(\boldsymbol{k})$ are straight lines (with slopes given by elastic constants); (2) quasi-isotropic approximation (bulk and shear moduli, K and G, are used instead of the full elastic constant tensor; the shape of the Brillouin zone is assumed to be spherical). At this stage, one can define two Debye temperatures, one for one compressional, and one for two shear modes:

$$\theta_D = \frac{\hbar}{k}\left(\frac{6\pi^2}{V_{\mathrm{at}}}\right)^{1/3} v \tag{3}$$

where v is the sound velocity, V_{at} the volume per atom and $\hbar$, k and π fundamental constants. Average compressional (v_l) and shear (v_t) wave velocities, which yield the corresponding Debye temperatures, are

$$v_l = \sqrt{\frac{3K + 4G}{3\rho}} \quad \text{and } v_t = \sqrt{\frac{G}{\rho}} \tag{4}$$

where ρ is the density. A further approximation is introduced, giving one Debye temperature by using the average sound wave velocity $\langle v \rangle$ in Eq. (3):

$$\langle v \rangle = \left(\frac{1}{3v_l^3} + \frac{2}{3v_t^3}\right)^{-1/3} \tag{5}$$

For *polyatomic* solids with the number n of atoms in the unit cell, DM assumes that optic modes behave in the same way as acoustic modes, i.e. have the same frequency distribution and Grüneisen parameter. This approximation is crude, and for complex solids, where optic phonons dominate and behave in a very different way, the DM breaks down. The phonon density of states (DOS) is:

$$g(\omega) = 9n\left(\frac{h}{k\theta_D}\right)^2 \omega^2, \quad \text{if } \omega < k\theta_D/\hbar \tag{6a}$$

$$g(\omega) = 0, \quad \text{if } \omega > k\theta_D/\hbar \tag{6b}$$

From the DOS, all thermodynamic properties can be calculated, e.g.:

$$E_{\mathrm{vib}} = \frac{9}{8}kn\theta_D + 3knTD\left(\frac{\theta_D}{T}\right) \tag{7}$$

$$C_V(T) = \left(\frac{\mathrm{d}E_{\mathrm{vib}}}{\mathrm{d}T}\right) v = 3kn\left[4D\left(\frac{\theta_D}{T}\right) - \frac{3(\theta_D/T)}{\mathrm{e}^{\theta_D/T} - 1}\right] \tag{8}$$

$$S(T) = \int_0^T \frac{C_p}{T}\mathrm{d}T = kn\left[4D\left(\frac{\theta_D}{T}\right) - 3\ln(1 - \mathrm{e}^{\theta_D/T})\right] \tag{9}$$

where $D(x) = (3/x^3)\int_0^x x^3 \mathrm{d}x/\mathrm{e}^x - 1, x = \theta_D/T$ (note that thermodynamic properties in Eqs. (7)–(9) are given per unit cell).

Within the quasiharmonic approximation, the DM leads to a simple expression for the Grüneisen parameter:

$$\gamma = -\frac{\mathrm{d}\ln\theta_D}{\mathrm{d}\ln V} \tag{10}$$

which is explicitly dependent only on the volume: its temperature dependence in this approximation is entirely due to thermal expansion.

1.3. Essential properties of a Debye-like solid

As we mentioned above, there are no strictly Debye-like solids. With regards to geophysical applications, we are mostly concerned with the high-P–T EOS and elastic properties, intimately related to the EOS and seismic velocities. Thermal expansion (Eq. (2)) becomes the key quantity of interest,

and therefore for a Debye-like solid the DM should closely reproduce:

1. heat capacity $C_V(T)$, at least at elevated temperatures and
2. Grüneisen parameter $\gamma(V)$.

Errors in any of these quantities will result in erroneous thermal EOS and, therefore, invalidate the model. We show that the second criterion is not accurately met for $MgSiO_3$ perovskite.

From the lattice-dynamical perspective, the orthorhombic $MgSiO_3$ perovskite has $n = 20$ atoms in the unit cell, what implies that there are $3n = 60$ vibrational modes, only three of which are acoustic. Due to structural relation to a hypothetical cubic phase ($n = 5$) nine optic modes are to a first approximation acoustic modes, folded back in the Brillouin zone. Still, the majority of phonons are not representable as acoustic modes. The only hope is that the average behaviour of all phonons altogether is somehow similar to the behaviour of the acoustic phonons alone.

Anderson (1998) gave a series of arguments in favour of the DM. First, he considered MgO periclase, and showed that this solid can be considered as a Debye-like one. This was shown on the basis of good agreement of calculated $C_V(T)$ with experiment, and near equality of the elastic θ_D and θ_D extracted from calorimetric data and atomic mean square thermal displacements (Debye–Waller factors) in the low-temperature and high-temperature limits. Anderson pointed out that a Debye-like solid should have: (a) no gap present in the DOS; (b) not many modes with frequencies higher than the maximum Debye frequency, $k\theta_D/\hbar$; (c) DOS, given by Eq. (6) at least in the limit of small ω. Other features of the DOS are not crucial.

For $MgSiO_3$ perovskite, Anderson has shown that the DOS calculated for $MgSiO_3$ using semiclassical pair potentials (Choudhury et al., 1988; Winkler and Dove, 1992) meets conditions (a)–(c). He demonstrated that $C_V(T)$ at atmospheric pressure given by the DM agrees well with the experimental data above 400 K. Then, analysing several experimental sets of thermal expansion $\alpha(T)$, he chose the most plausible set, and used it in conjunction with other experiment-based thermoelastic parameters in all subsequent calculations of the Grüneisen parameter and thermal pressure. The Grüneisen parameter was not consistently calculated using Eq. (10), but essentially taken from experiment via experimental thermal expansion coefficient and compressibility.

Since currently limited experimental information does not allow one to use Eq. (10) to calculate γ, theoretical calculations present an ideal way of testing the DM within a whole self-consistent framework. First, we develop a new interatomic potential model for $MgSiO_3$ perovskite, which will be shown to reproduce accurately experimental crystal structure, elastic constants, EOS, heat capacity, entropy, and thermal expansion. Then, using the calculated elastic constants, we construct a self-consistent DM, and compare its results with results of more rigorous lattice dynamics (LD) and molecular dynamics (MD) simulations. Unlike the DM, the LD and MD calculations take into account all the phonons across the Brillouin zone and not just acoustic modes at $\mathbf{k} \to 0$, and intrinsic anharmonic effects are also accounted for by MD simulations. As we shall see, the DM does not reproduce the full-phonon calculations.

2. Theoretical calculations

2.1. Derivation of the new interatomic potential for $MgSiO_3$

Our interatomic potential was pairwise, and had the following form:

$$U_{ij}(R_{ij}) = \frac{z_i z_j}{R_{ij}} + b_{ij} \exp\left(-\frac{R_{ij}}{\rho_{ij}}\right) - \frac{c_{ij}}{R_{ij}^6} \qquad (11)$$

where R_{ij} is an interatomic distance. Atomic charges Z_i, and short-range potential parameters b_{ij}, ρ_{ij}, and c_{ij} for each pair of atoms were determined using the procedure described below.

Although there are a number of interatomic potentials available in literature (Lewis and Catlow, 1985; Matsui et al., 1987; Matsui, 1988; Wall, 1988; Leinenweber and Navrotski, 1988; Choudhury et al., 1988; Kubicki and Lasaga, 1991; Ghose et al., 1992; Stuart and Price, 1996), we preferred to derive our own potential. First of all, many previous potentials were derived from fitting calculated structure and properties at $T = 0$ K to experimental data at 300 K. Recent developments in the GULP code (Gale, 1996, 1997, 1998), which we used in this study, enabled for the first time to include quasiharmonically all thermal

and zero-point motion effects in the fitting procedure, which itself now involves complete structure optimisation for each set of trial potential parameters, making the whole procedure much more rigorous. Implementation of analytical free energy derivatives (Kantorovich, 1995; Gale, 1998) has speeded up free energy minimisation by orders of magnitude, thus enabling finite-temperature fitting even for relatively large systems. Some previous potentials, e.g. purely ionic transferable potential models (Lewis and Catlow, 1985), are known to have modest performance for $MgSiO_3$ perovskite. This can clearly be improved by adopting partial ionic charges (e.g. Matsui, 1988). Another problem is that some of the potential parameters in Eq. (11) are highly correlated (e.g. there are a number of combinations of ρ and b in the potential, which give nearly the same quality fits to the ambient-conditions crystal structure and properties. But many of these potentials will not perform well at high P–T parameters, or give reasonable predictions for properties that were not used in fitting). Statistical significance of the fitted potential parameters is often poor, because the number of observables used in fitting is usually comparable with the number of the fitted parameters. These problems can be solved by setting some of the parameters to values determined by physical considerations.

First of all, we fix ρ_{ij} at the values, calculated from the first ionisation potentials I_i of the atoms using the formula (Urusov, 1975):

$$\rho_{ij} = \frac{1.85}{\sqrt{I_i} + \sqrt{I_j}} \tag{12}$$

This formula can be derived given that long-range tails of atomic electron density fall off exponentially with the distance from the nucleus at large distances, and the exponent is related to $\sqrt{I}$ (the coefficient 1.85 in Eq. (12) comes from conversion of ionisation potentials to the conventionally used electron-volt units). This physical determination of the repulsion exponents ρ_{ij} ensures the best transferability of such a potential, and removes the problem of correlation between b_{ij} and ρ_{ij}. The O–O short-range potential ($b_{O–O} = 2023.8$ eV, $\rho_{O–O} = 0.2674$ Å and $c_{O–O} = 13.83$ eV Å^6) was taken from the study of Gavezzotti (1994), where it was extensively validated for organic compounds. Oxygen–oxygen short-range potential is very weak in most existing models, and therefore its details are not very important. We preferred Gavezzotti's potential, because it had the closest ρ_{ij} to the one given by Eq. (12) and a reasonable van der Waals parameter $c_{O–O}$.

We neglected cation–cation short-range interactions, because they are weak, and cation–anion dispersion interactions, because they may result in catastrophic behaviour in MD simulations at ultrahigh P/T. Both types of interactions can be safely neglected, because none of them is of crucial importance. As a result, only four independent parameters had to be fitted: atomic charges Z_{Si} and Z_{Mg} ($Z_O = -1/3(Z_{Mg} + Z_{Si})$), and pre-exponential repulsive parameters $b_{Mg–O}$ and $b_{Si–O}$. These parameters are virtually uncorrelated with each other and give a stable solution for the fitting problem. In this fitting procedure, we used experimental crystal structure at 1 atm and 300 K (Ross and Hazen, 1989) and full elastic constants tensor (Yeganeh-Haeri, 1994). Temperature was explicitly included via quasiharmonic LD treatment with analytical free energy derivatives. We used a $2 \times 2 \times 2$ Monkhorst and Pack (1976) grid for the Brillouin zone sampling in this finite-temperature fitting.

In summary, our potential parameters are: $Z_{Mg} = +1.9104$; $Z_{Si} = +2.9043$; $Z_O = -1.6049$; $b_{Mg–O} = 1041.435$ eV; $\rho_{Mg–O} = 0.2866$ Å; $b_{Si–O} = 1137.028$ eV; $\rho_{Si–O} = 0.2827$ Å; $b_{O–O} = 2023.8$ eV; $\rho_{O–O} = 0.2674$ Å; $c_{O–O} = 13.83$ eV Å^6. Note that a simple crystal potential fitting procedure has given us chemically reasonable atomic charges. Results, obtained with this potential, are given in Table 1. One can see that apart from describing well crystal structure and elastic properties, our potential gives excellent agreement for the thermal expansion coefficient, which was not used in the fitting of the potential. The calculated shear modulus is somewhat underestimated; this is probably responsible for overestimation of the entropy (Table 1) and can be improved by including many-body terms into our potential model. The calculated heat capacity and entropy at 300 K compare well with experimental estimates and are more accurate than those calculated with previous potentials (Stuart and Price, 1996). Room temperature Birch–Murnaghan EOS parameters are: $K_0 = 266$ and 269 GPa, $K' = 3.9$ and 4.04 in experiment (Knittle and Jeanloz, 1987) and theory (our LD calculations), respectively. These observations give us

Table 1
Crystal structure (space group *Pbnm*) and elastic properties of $MgSiO_3$ perovskite at 300 K and 1 atm[a]

Property	This work (GULP)	Experiment
a_0 (Å)	4.7822	4.7747
b_0 (Å)	4.8960	4.9319
c_0 (Å)	6.9322	6.8987
V_0 (Å^3)	162.31	162.45
Mg (x, y, z)	(0.5056, 0.5267, 1/4)	(0.5143, 0.5556, 1/4)
Si (x, y, z)	(0, 1/2, 0)	(0, 1/2, 0)
O_1 (x, y, z)	(0.1026, 0.4620, 1/4)	(0.1037, 0.4655, 1/4)
O_2 (x, y, z)	(0.1982, 0.2014, 0.5526)	(0.1974, 0.2011, 0.5538)
C_{11} GPa	500	482
C_{22} GPa	509	537
C_{33} GPa	398	485
C_{12} GPa	116	144
C_{13} GPa	210	147
C_{23} GPa	188	146
C_{44} GPa	174	204
C_{55} GPa	189	186
C_{66} GPa	102	147
K_{VRH}[b] GPa	270.4	264.0[c]
G_{VRH}[b] GPa	146.3	177.4[c]
θ_D (K)	984	1078[c]
α (1 atm, 300 K)	2.09[d]	1.57[e], 2.2[f]
C_V J (mol × K)$^{-1}$	80.88[d]	80.6[g]
S_V J (mol × K)$^{-1}$	61.81[d]	57.2[g]

[a] Experimental crystal structure from Ross and Hazen (1989), elastic constants from Yeganeh-Haeri (1994).
[b] Voigt-Reuss-Hill averages (e.g., Belikov et al., 1970).
[c] Calculated using data of Yeganeh-Haeri (1994).
[d] Lattice-dynamical calculations (see Section 2.2).
[e] Fiquet et al. (1998).
[f] Ross and Hazen (1989). Experimental data on the volume thermal expansion coefficient of $MgSiO_3$ perovskite are still highly uncertain. The most plausible range is 1.5–1.9 × 10^{-5} K^{-1} at 300 K and 1 atm.
[g] C_p and S from Akaogi and Ito (1993).

confidence in our potential, which perhaps is as good as a simple pairwise rigid-ion model can be.

2.2. Computational methods

In order to construct a self-consistent DM, we performed static calculations of the athermal EOS and elastic constants,[1] which were derived from stress–strain relations (Barron and Klein, 1965; Wallace, 1972) using the GULP code (Gale, 1997).

Our state-of-the-art LD calculations based on the newly implemented analytical free energy derivatives were also performed using GULP. This new approach allows one to perform calculations of unprecedented precision with large Brillouin zone sampling grids, and without conventional 'ZSISA' (zero static internal stress approximation, in which only the unit cell parameters are determined by the free energy minimisation, while all atomic coordinates are calculated by minimising the *internal* energy). Free energy minimisation was performed with 6 × 6 × 6 grids for the Brillouin zone integration. This grid showed very good convergence for all properties. For calculations of the DOS and its projections and heat capacity (C_V) we

[1] Within the quasiharmonic approximation (T.H.K. Barron, personal communication) acoustic velocities and θ_D at finite temperatures should be determined from elastic constants corresponding to a static lattice of the same volume. In the athermal limit adiabatic and isothermal elastic moduli are equal; at finite temperatures adiabatic moduli are to be used for calculations of θ_D and γ. Adiabatic elastic constants (at least for simple crystals), unlike isothermal ones, explicitly depend only on the volume, and make θ_D and γ explicitly dependent only on the volume, but not temperature.

used even denser grids, $12 \times 12 \times 12$ and $20 \times 20 \times 20$, respectively.

For MD (Allen and Tildesley, 1987) calculations we used the Moldy code (Refson, 1988–2000). The NPT-ensemble in conjunction with Nose–Hoover (Hoover, 1985) thermostat and Parrinello–Rahman (Parrinello and Rahman, 1981) constant-pressure algorithm was used throughout. The computational box contained 540 atoms ($3 \times 3 \times 3$ supercell), which was sufficient for high accuracy of results. The system was allowed to evolve for 10 ps, of which first 5 ps were used for equilibration and not included in calculation of thermodynamic averages. Timestep of 1 fs was used for integrating equations of motion.

It should be noted that in the high-temperature limit (closely approached at the lower mantle temperatures, roughly between 2000 and 4000 K), where atomic motion is classical, MD (based on the classical approximation) becomes exact. Quasiharmonic LD, on the other hand, breaks down at high temperatures. Divergence of the LD and MD results at high temperatures indicates degradation of the quasiharmonic LD.

3. Properties of $MgSiO_3$ perovskite and predictions of the Debye model

Here we discuss the following properties: vibrational DOS, heat capacity C_V, Grüneisen parameter γ and thermal expansion α. Harmonic properties (DOS and C_V) were calculated for a fixed volume, corresponding to the athermal energy minimum ($V_0 = 160.46\,\text{Å}^3$). Anharmonic properties (γ and α) were studied as a function of both volume (or pressure) and temperature.

3.1. Vibrational DOS and its projections

The vibrational DOS calculated with our interatomic potential is shown in Fig. 1a in comparison to the Debye DOS. Fig. 1b shows projections of the total DOS onto atomic contributions. One can see that although the shape of the DOS is different from the Debye spectrum, it does satisfy the main criteria, formulated by Anderson (1998): no gap, and parabolic shape in the low-frequency limit. This suggests that harmonic properties (C_V, S_V, zero-point energy and heat contents) of the DM should be reasonable. This was one of the arguments of Anderson (1998).

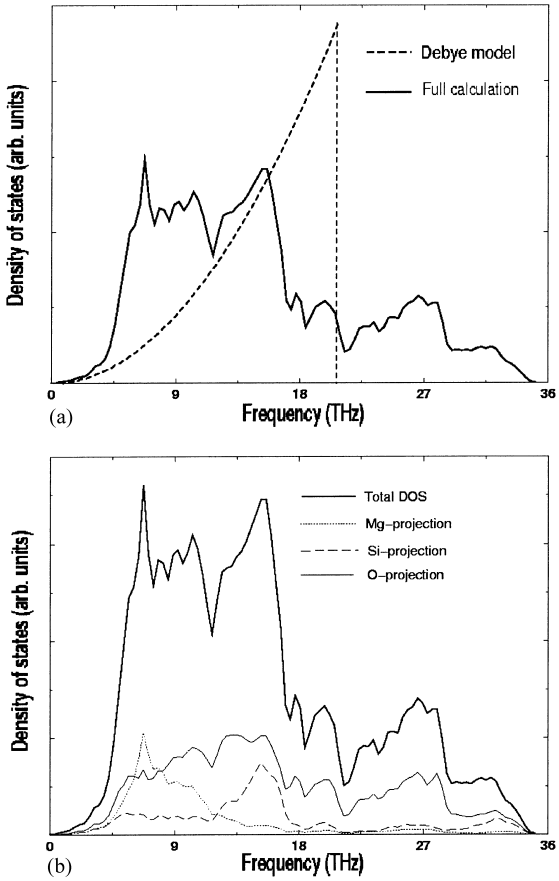

Fig. 1. Phonon DOS of $MgSiO_3$ perovskite: (a) full harmonic calculation vs. DM; (b) projections of the total DOS onto atomic species.

However, projections of the DOS already show significant deviations from the 'acoustic' behaviour. For a Debye solid, at each frequency, all atoms have a constant proportion of the total DOS, determined by relative masses and numbers of atoms of each sort. LD calculations show that this is far from reality: atomic contributions to the DOS tend to localise in certain parts of the spectrum: Mg contribution clearly tends to the low-frequency part, while Si projection leans to the high-frequency region of the DOS. This is a direct consequence of the different bond strengths: Si–O bonds are much stiffer than Mg–O. A consequence is that atomic thermal mean square

displacements (U_j) will differ significantly from the predictions of the DM. The latter becomes obvious if we write the high-temperature U_j (see Dove, 1993) in the following way:

$$U_j = \sqrt{\int g_j(\omega)\mathrm{d}\omega \frac{3kT}{m_j\omega^2}} \tag{13}$$

where $g_j(\omega)$ are atomic projections of the total DOS.

3.2. Specific heat C_V

In Fig. 2 we compare C_V, given by the DM in Eq. (6) and the full lattice-dynamical treatment, based on the harmonic formula:

$$C_V(T) = k\int g(\omega)\left(\frac{h\omega}{kT}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{kT}\right)}{\left(\exp\left(\frac{\hbar\omega}{kT}\right)-1\right)^2}\mathrm{d}\omega \tag{14}$$

with the DOS integrated over a 20 × 20 × 20 Monkhorst–Pack grid. The DM is exact for the heat capacity in the low-temperature limit, although at temperatures about 100 K it already gives serious errors, which practically disappear at 500 K. As can be seen in Fig. 1, the average mode frequencies of the DM and of the full harmonic spectrum and consequently, their zero-point vibrational energies ($E_{zp} = 3n\langle\hbar\omega_{ik}/2\rangle$) are close. The same follows from the $C_V(T)$ plot (Fig. 2), because $E_{zp} = \lim_{T\to\infty}(3RT - \int_0^\infty C_V\mathrm{d}T)$

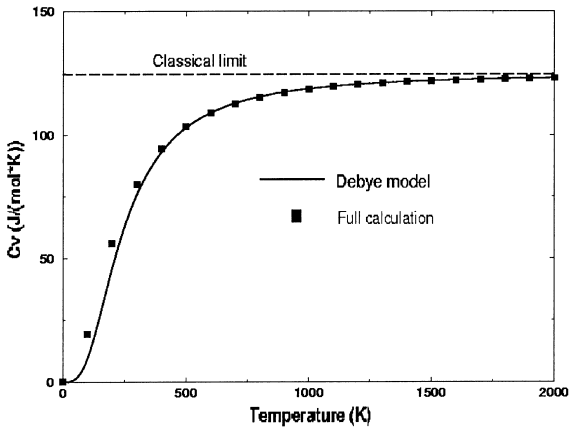

Fig. 2. Heat capacity C_V of $MgSiO_3$ perovskite from the full harmonic calculation (filled squares) and DM (line).

and areas below the $C_V(T)$ curves of the DM and full harmonic calculation are very close. According to LD and DM calculations, the classical limit is nearly reached at 1000 K and higher temperatures.

3.3. Grüneisen parameter $\gamma(V)$

We are mostly interested in the properties at high temperatures, where quantum effects are very small, and all phonons are practically fully excited. At high temperatures partial heat capacities C_{ik} of all the phonon modes at all *k*-points of the Brillouion zone are very close to their high-temperature limit, and the usual quasiharmonic formula for the thermodynamic Grüneisen parameter:

$$\gamma = \frac{\sum_{i,k} C_{ik}\gamma_{ik}}{\sum_{i,k} C_{ik}} = \frac{\sum_{i,k} C_{ik}\gamma_{ik}}{C_V} \tag{15}$$

reduces to a constant high-temperature limit, which is just an arithmetic mean over all the *i*th mode Grüneisen parameters γ_{ik} throughout the Brillouion zone:

$$\gamma = \langle\gamma_{ik}\rangle \tag{16}$$

Unlike the situation at low temperatures, where acoustic modes are of crucial importance, in the average of Eq. (16) these modes have the same weight as optic modes, but the latter comprise the overwhelming majority of vibrations. Therefore, the acoustic Grüneisen parameter (Eq. (10)) can be a very crude approximation beyond the low-temperature limit.

This point is illustrated in Fig. 3a, where we depict the temperature dependence of the Grüneisen parameter at 50 GPa. In both LD and MD we determined the Grüneisen parameter from Eq. (2), using the calculated α, β_T and C_V (C_V was given by Eq. (14) in LD calculations, or by the classical limit value, $3nR$, in MD simulations). The high-temperature constant value is virtually reached in LD calculations at 500 K, and a small linear increase of γ is due to the change of volume with temperature. MD, based on the classical approximation, always gives the high-temperature limit value. Below 500 K, LD gives noticeable non-monotonic temperature variation of γ. A sudden rise and anomalously high values of γ, found in LD-calculations at $T > 2000$ K, are artifacts of the quasiharmonic approximation and indicate its breakdown in this temperature range, where MD is

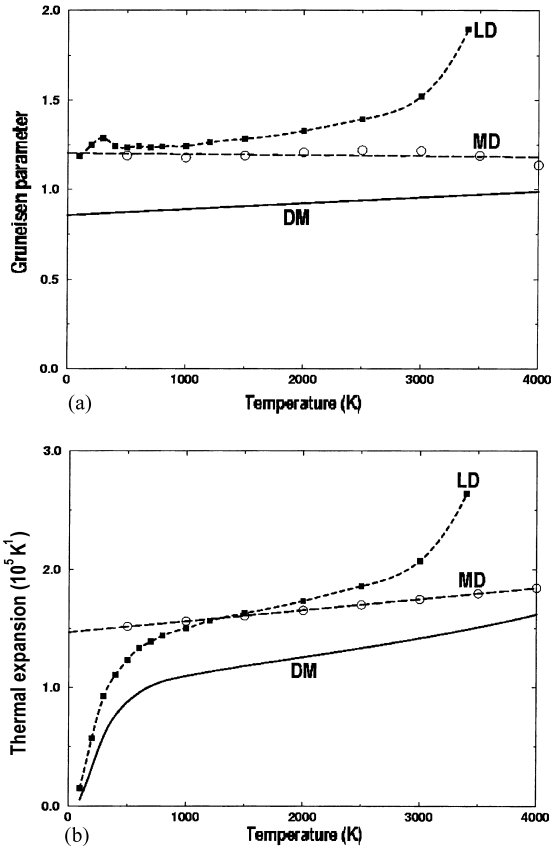

Fig. 3. Grüneisen parameter (a) and thermal expansion (b) of $MgSiO_3$ perovskite as a function of T at $P = 50$ GPa. DM, solid curves; LD, dashed lines with filled squares; MD, long-dashed lines with empty circles.

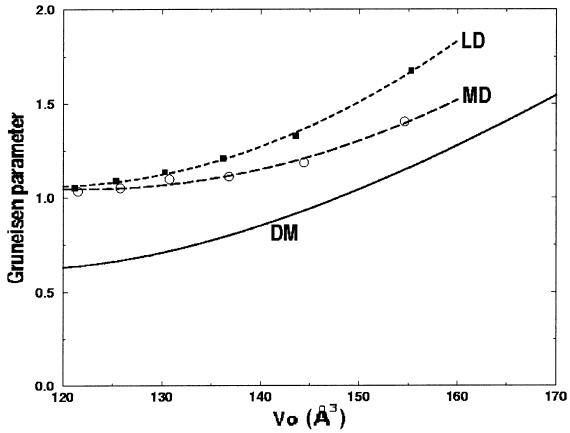

Fig. 4. Grüneisen parameter of $MgSiO_3$ perovskite in the temperature interval 1500–2500 K as a function of volume. DM, solid curves; LD, dashed line with filled squares; MD, long-dashed lines with empty circles. Average values of $q = \mathrm{d}\ln\gamma/\mathrm{d}\ln V$ are 2.6, 1.8 and 1.2 for the DM, LD, and MD curve, respectively. Contrary to the common assumption, q is found to vary considerably with V.

a more justified technique. DM shows no signs of breakdown at high temperatures, but also does not converge to the true high-temperature limit. A similar picture is observed for the thermal expansion coefficient (Fig. 3b).

Fig. 4 shows the results of full-phonon calculations of the high-temperature γ in comparison to predictions of the DM. Results of LD calculations differ significantly from MD results, especially at large volumes (low pressures), in line with the earlier study by Matsui et al. (1994). This is because of the neglect of intrinsic anharmonic effects in the quasiharmonic approximation. Errors of the DM are typically about −30% at all volumes, and reach ≈50% at the bottom of the lower mantle. This implies an error of typically 30% in the thermal expansion coefficient, Eq. (2). This is a serious drawback of the DM in application to $MgSiO_3$ perovskite, which affects calculations of the thermal EOS.

3.4. Thermal EOS

We have determined the EOS parameters, fitting the Vinet EOS (Vinet et al., 1989) to the $P(V)$ data obtained from LD, MD and DM calculations in the pressure range 0–150 GPa at temperatures 500, 1500, 2500 K, which span all pressures and, probably, most of the temperature conditions of the lower mantle. Resulting parameters are given in Table 2.

At zero pressure, LD calculations give dynamical instabilities at and above 1500 K, so LD values of the zero-pressure V_0, K_0 and K' at these temperature in Table 2 are merely extrapolated figures. No such phonon catastrophes were observed in the MD and DM calculations.

Analysis of these EOS shows that at the lower mantle conditions the DM overestimates density of $MgSiO_3$ perovskite by ∼1%. This seemingly small error would lead to the error of 3 mol% in Fe content or ∼1000 K in temperature for the perovskite lower mantle. Fig. 5 shows a visible difference between

Table 2
EOS of $MgSiO_3$ perovskite at high temperatures

Parameter	$T = 500$ K			$T = 1500$ K			$T = 2500$ K		
	DM	LD	MD	DM	LD	MD	DM	LD	MD
V_0 (Å^3)	162.89	163.10	162.44	167.64	168.18	167.99	174.82	176.17	174.85
K_0 (GPa)	254.99	258.67	261.01	211.17	220.97	216.72	158.01	167.65	174.12
K'	4.42	4.37	4.35	4.85	4.63	4.73	5.45	5.15	5.10

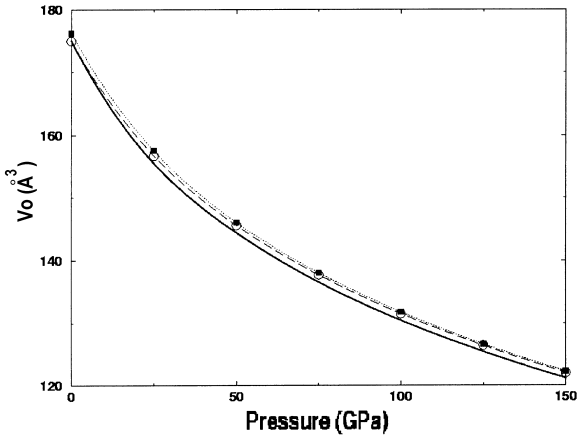

Fig. 5. EOS of $MgSiO_3$ perovskite at 2500 K from the DM (solid curve), LD (dotted curve with filled squares) and MD calculations (dashed curve with open circles).

high-temperature LD and MD EOS, especially at low pressures. This once again suggests that intrinsic anharmonic effects are significant.

Comparison of the experimental $P(V)$ isotherm at 2000 K and up to 90 GPa (Fiquet et al., 1998, 2000) with our MD data shows the pressure difference up to 5 GPa, which is however of the order of experimental uncertainties. Parameters of the Vinet EOS fitted to MD data at 2000 K and 0–150 GPa are: $V_0 = 171.46$ Å^3, $K_0 = 191.39$ GPa and $K' = 5.00$.

4. Discussion

In this paper we have compared thermal expansion coefficients α, thermodynamic Grüneisen parameters γ and EOS given by three independent theoretical methods — MD, quasiharmonic LD and quasiharmonic DM. A particular attention was given to the analysis of the assumption that $MgSiO_3$ perovskite is a Debye-like solid, often used in geophysical literature.

Our theoretical analysis was carried out using our new interatomic potential for $MgSiO_3$ in conjunction with state-of-the-art LD and MD simulations. We show that the new potential, although very simple, describes well interatomic interactions in $MgSiO_3$ perovskite, reproducing very well experimental heat capacity, entropy, thermal expansion, and EOS at 298 and 2000 K. A self-consistent quasiharmonic DM was constructed using static elastic properties and EOS, calculated with the same interatomic potential.

We have considered the total phonon DOS and its projections onto atomic species, heat capacity C_V, α, γ, and high-temperature EOS. The total DOS to a first approximation can be considered as Debye-like, but its atomic projections show structure incompatible with a Debye-like solid. Above 500 K, the heat capacity is well reproduced by the DM.

Grüneisen parameter and thermal expansion pose a more stringent test, and the DM predicts them poorly. Values of γ and α, predicted by the Debye theory, are $\approx$30% too low. Therefore, $MgSiO_3$-perovskite cannot be regarded as a good Debye-like solid, and its EOS cannot be accurately determined from acoustic data as suggested by Anderson (1998). Adiabatic thermal gradient of the lower mantle, $(\partial T/\partial P)_S = \gamma T/K_S$, also cannot be constructed without accurate knowledge of the Grüneisen parameter γ. When deriving the temperature profile my matching PREM bulk modulus and density with the properties of plausible mineral assemblages, errors of $\sim$30% (i.e. $\sim$1000 K) in the temperature would arise from the use of acoustic γ.

The DM owes its popularity to two factors. First, it relates thermal EOS to static properties (which are easy to determine) and to acoustic velocities (which can be compared with seismic observations) and repre-

sents the simplest model for the thermal pressure. Second, this model contains the minimum number of parameters, which makes it particularly convenient when the experimental bulk of (P, V, T) data is inverted into a set of parameters describing the EOS (e.g. Shim and Duffy, 2000). If the DM is used self-consistently (like in Hama et al., 2000), i.e. the Grüneisen γ is related to the volume change of acoustic velocities, we expect significant errors. On the other hand, it should be safe to use the DM for inverting experimental data sets (e.g. Stixrude et al., 1992; Jackson and Rigden, 1996; Yagi and Funamori, 1996; Shim and Duffy, 2000; Fiquet et al., 2000). However, in this case parameters of the model lose their original meaning and become unrelated to acoustic velocities.

We find that, in contrast with the common assumption, $q = \mathrm{d}\ln\gamma/\mathrm{d}\ln V$ is not a constant. Recently, Stacey and Isaak (2000) arrived at the same conclusion. The value of q is strongly dependent on the volume in all methods (DM, LD and MD) and may become negative at the bottom of the lower mantle. This can be important for discussing the anomalous properties of the core-mantle boundary layer D″. The q parameter also depends on the simulation method: its mean value varies from 1.2 in MD simulations to 2.6 from the DM calculations, despite the same interatomic potential was used throughout.

Although most experiments and semiclassical simulations have errors in γ and α comparable with or larger than 30%, much greater accuracy is needed for interpreting the thermal state of the Earth. Such accuracy may be achieved by using the novel ab initio MD simulations. We believe that such simulations, producing results of accuracy unprecedented in both theory and experiment, can make a breakthrough in our understanding of the composition, properties, and dynamics of the lower mantle.

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