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 of the major Earth-forming mineral, orthorhombic MgSiO$_3$ perovskite: molecular dynamics, lattice dynamics, and Debye model. 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 Debye model based on elastic properties of the crystal, and compare its results with results of more rigorous lattice dynamics and molecular dynamics simulations with the same potential model. We show that the Debye model reproduces quite accurately harmonic constant-volume heat capacity above 500 K, but gives thermal expansion and Grüneisen parameter ($\gamma$) 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 $\gamma$’s, often used in geophysical studies, are a very crude approximation to the true $\gamma$. To obtain good accuracy, one needs to know the $\gamma(V)$ function more accurately than the Debye model 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 $q=d\ln \gamma/d\ln V$ 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 lattice dynamics and molecular dynamics indicates importance of intrinsic anharmonic contributions in the thermal expansion and $\gamma$. Therefore, molecular dynamics 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.

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**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 2000-3000 K) is crucial for interpreting seismological data and constructing reliable chemical, mineralogical, and thermal models of the lower mantle. Yet, accurate experimental EOS’s of MgSiO$_3$ perovskite are available only at the 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 equations of state. 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 O.L. Anderson (1998) advocated that ‘MgSiO$_3$-perovskite is one of a small, select group of Debye-like minerals, for which thermoelastic properties and the equation of state (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 (Wentzcovich 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 $P_{th}$, which is a relatively small correction to the well-known static (or ambient temperature) EOS: 

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

(1)

where $P_{stat}(V)$ is the athermal equation of state, $E_{vib}$ is the vibrational energy, $V$ is the volume, and $\gamma$ the thermodynamic Grüneisen parameter. Using eq.(1), the thermal expansion can be written as:

$$\alpha = \gamma C_V \beta_V V,$$  

(2)

where $C_V$ is the constant-volume heat capacity, and $\beta_V$ isothermal compressibility. [Eq. (2) yields $\gamma = \alpha V/C_V \beta_V$, 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 $\gamma$ as a function of temperature and volume. Vočadlo et al. (2000) have examined a number of approximate theories, correlating $\gamma$ with $K''=dK/dP$ (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 $\gamma$ using lattice-dynamical models, of which the Debye model (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 O.L.
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 \( \alpha \) and \( \gamma \). 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 in 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)

DM 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 (\( k \to 0 \)): elastic constants determine the slopes of the acoustic dispersion curves \( \omega(k) \) at \( k \to 0 \). Monatomic solids have only 3 vibrational modes, all of which are acoustic. For these solids, the model has only two approximations: 1) assumption that phonon dispersion curves \( \omega(k) \) are straight lines (with slopes given by elastic constants); 2) quasiharmonic 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 1 compressional, and one for 2 shear modes:

\[
\theta_D = \frac{\hbar}{k} \left( \frac{6\pi \nu}{V_{aat}} \right)^{1/3},
\]  

(3)

where \( \nu \) is the sound velocity, \( V_{aat} \) is the volume per atom, and \( \hbar \), \( k \), and \( \pi \) are fundamental constants. Average compressional (\( \nu_c \)) and shear (\( \nu_s \)) wave velocities, which yield the corresponding Debye temperatures, are

\[
\nu_c = \sqrt{\frac{3K + 4G}{3\rho}} \quad \text{and} \quad \nu_s = \sqrt{\frac{G}{\rho}},
\]

(4)

where \( \rho \) is the density.

A further approximation is introduced, giving one Debye temperature by using the average sound wave velocity \( \langle \nu \rangle \) in (3):

\[
\langle \nu \rangle = \left( \frac{1}{3\nu_c^3} + \frac{2}{3\nu_s^3} \right)^{1/3}.
\]

(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:

\[
g(\omega) = \begin{cases} \frac{n}{k\theta_D} \omega^2 \text{, if } \omega < k\theta_D / \hbar \\ 0 \text{, if } \omega > k\theta_D / \hbar \end{cases}
\]

(6a)

(6b)

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

\[
E_{\text{vib}} = \frac{9}{8} k n\theta_D + 3k n D \left( \frac{\theta_D}{T} \right)
\]

(7)

\[
C_v(T) = \left( \frac{dE_{\text{vib}}}{dT} \right)_v = 3k n [4D (\frac{\theta_D}{T})^2 - 3 (\frac{\theta_D}{T}) e^{-\frac{\theta_D}{T}} - 1]
\]

(8)

\[
S(T) = \int_0^T C_v(T) dT = 3k n [4D (\frac{\theta_D}{T})^2 - 3 \ln (1 - e^{-\frac{\theta_D}{T}})]
\]

(9)

where \( D(x) = \frac{3}{x^3} \int_0^x e^y - 1 \), \( x = \frac{\theta_D}{T} \) (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:

\[
\gamma = \frac{d\ln \theta_D}{d\ln V},
\]

(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’s and elastic properties, intimately related to the EOS’s 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 3 of which are acoustic. Due to structural relation to a hypothetical cubic phase ($n=5$) 9 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.

O.L. 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 $C_\theta(T)$ with experiment, and near equality of the elastic $\theta_0$ and $\theta_0$ 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, $k\theta_0/\hbar$, c) DOS, given by eq.(6) at least in the limit of small $\omega$. 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 (Winkler and Dove 1992; Choudhury et al. 1988), meets conditions a-c. He demonstrated that $C_\theta(T)$ at atmospheric pressure, given by the experimental data above 400 K, agrees well with the experimental data from 0 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 (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 $\gamma$, 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, equation of state, 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 $k\rightarrow 0$, 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:

$$U_{ij}(R_{ij}) = \frac{Z_i Z_j}{R_{ij}} + b_{ij} \exp\left(\frac{R_{ij}}{\rho_{ij}}\right) - \frac{c_{ij}}{R_{ij}^6}$$  \hspace{1cm} (11)

where $R_{ij}$ is an interatomic distance. Atomic charges $Z_i$, and short-range potential parameters $b_{ij}$, $\rho_{ij}$, 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; Wall 1986, Matsui et al. 1987; Matsui 1988; Wall 1988; Leinenweber and Navrotski 1988; Choudhury et al. 1988; Kubicki and Lasaga 1991; Ghose at 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 work, 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 (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 to 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\(_j\) at the values, calculated from the first ionisation potentials I\(_i\) of the atoms using the formula (Urusov 1975):

\[
ρ_j = \frac{1.85}{\sqrt{I_i} + \sqrt{I_j}}.
\]  

(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\(_j\) 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, ρ\(_{O,O}\) = 0.2674 Å and c\(_{O,O}\) = 13.83 eV*Å\(^6\)) was taken from Gavezzotti’s works (e.g., 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\(_j\) to the one given by (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 molecular dynamics 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 4 independent parameters had to be fitted: atomic charges Z\(_Mg\) and Z\(_Si\) (Z\(_D\) = 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 lattice dynamics treatment with analytical free energy derivatives. We used a 2*2*2 Monkhorst-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, ρ\(_{Mg,O}\) = 0.2866Å; b\(_{Si,O}\) = 1137.028 eV, ρ\(_{Si,O}\) = 0.2827Å; b\(_{O,O}\) = 2023.8 eV, ρ\(_{O,O}\) = 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 manyparticle 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 (Knitlife and Jeanloz 1987) and theory (our LD calculations), respectively. These observations give us 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, which were derived from stress-strain relations (Barron and Klein 1965; Wallace 1972) using the GULP code (Gale 1997).

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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.
Table 1. Crystal structure and elastic properties of MgSiO₃ perovskite.
(elastic properties in GPa, α in 10⁻⁵ K⁻¹, Cᵥ and Sᵥ are in J/(mol*K)).

<table>
<thead>
<tr>
<th>Property</th>
<th>This work (GULP)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₀, Å</td>
<td>4.7822</td>
<td>4.7747</td>
</tr>
<tr>
<td>b₀, Å</td>
<td>4.8960</td>
<td>4.9319</td>
</tr>
<tr>
<td>c₀, Å</td>
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<td>6.8987</td>
</tr>
<tr>
<td>V₀, Å³</td>
<td>162.31</td>
<td>162.45</td>
</tr>
<tr>
<td>Mg (x; y; z)</td>
<td>(0.5056; 0.5267; ¼)</td>
<td>(0.5143; 0.5556; ¼)</td>
</tr>
<tr>
<td>Si (x; y; z)</td>
<td>(0; ½; 0)</td>
<td>(0; ½; 0)</td>
</tr>
<tr>
<td>O₁ (x; y; z)</td>
<td>(0.1026; 0.4620; ¼)</td>
<td>(0.1037; 0.4655; ¼)</td>
</tr>
<tr>
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<td>(0.1974; 0.2011; 0.5538)</td>
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<tr>
<td>C₁₁</td>
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<tr>
<td>C₂₂</td>
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<td>264.0ᵇ</td>
</tr>
<tr>
<td>Gᵣᵣᵣᵣ</td>
<td>146.3</td>
<td>177.4ᵇ</td>
</tr>
<tr>
<td>θ₀ᵣ, K</td>
<td>984</td>
<td>1078ᵇ</td>
</tr>
</tbody>
</table>

α (1 atm, 300 K) 2.09ᶜ 1.57ᵇ; 2.2ᵇ

Cᵥ (1 atm, 300 K) 80.88ᶜ 80.6ᶜ
Sᵥ (1 atm, 300 K) 61.81ᶜ 57.2ᶜ

ᵃ – Voigt-Reuss-Hill averages.
ᶜ – Lattice-dynamical calculations (see section ‘Computational methods’).
ᵈ – Fiquet et al. (1998).
ᵉ – Ross et al. (1989). Experimental data on the volume thermal expansion coefficient of MgSiO₃ perovskite are still highly uncertain. The most plausible range is 1.5-1.9*10⁻⁵ K⁻¹ at 300 K and 1 atm.
ᶠ – Cᵥ and S from Akaogi and Ito (1993).

Our state-of-the-art lattice dynamics (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 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 density of states and its projections and heat capacity (Cᵥ) we used even denser grids – 12*12*12 and 20*20*20, respectively.

For molecular dynamics (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*3*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 2,000K and 4,000K), 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 MgSiO₃ perovskite and predictions of the Debye model

Here we discuss the following properties: vibrational DOS, heat capacity \( C_V \), Grüneisen parameter, \( \gamma \), and thermal expansion, \( \alpha \). 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 (\( \gamma \) and \( \alpha \)) 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 with 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 Anderson’s (1998) arguments.

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

\[
U_j = \sqrt{\int g_j(\omega)d\omega} \frac{3kT}{m\omega^2}, \tag{13}
\]

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 (6) and the full lattice-dynamical treatment, based on the harmonic formula:

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

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 \( (E_{zp}=3n<\frac{\hbar \omega_k}{2}>/2) \), are close. The same follows from the \( C_V(T) \) plot (Fig.2), because \( E_{zp} \).
\[ \lim_{T \to \infty} [3RT - \int_0^\infty C_V dT], \] 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.

![Figure 2. Heat capacity \( C_V \) of MgSiO_3 perovskite from the full harmonic calculation (filled squares) and Debye model (line).](image)

### 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:

\[
\gamma = \frac{\sum_{i,k} C_{ik} \gamma_k}{\sum_{i,k} C_{ik}} = \frac{\sum_{i,k} C_{ik} \gamma_k}{C_V}
\]  

reduces to a constant high-temperature limit, which is just an arithmetic mean over all the \( i \)-th mode Grüneisen parameters \( \gamma_k \)'s throughout the Brillouion zone:

\[
\gamma = \langle \gamma_k \rangle
\]  

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 \( \alpha, \beta_T \), 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 \( \gamma \) 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 \( \gamma \). A sudden rise and anomalously high values of \( \gamma \), 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 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 \( \gamma \) in comparison with predictions of the DM. Results of LD-calculations differ significantly from MD-results, especially at large volumes (low pressures), in line with the earlier work 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 K, 1500 K, 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.

150 GPa, are: \( V_0 = 171.5 \text{ Å}^3 \), \( K_0 = 191.4 \text{ GPa} \), and \( K' = 4.997 \).

Analysis of these EOS’s shows that at the lower mantle conditions the DM overestimates density of MgSiO₃ 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 high-temperature LD and MD EOS’s, 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-

4. Discussion
In this paper we have compared thermal expansion coefficients \( \alpha \), thermodynamic Grüneisen parameters \( \gamma \), and equations of state given by three independent theoretical methods – molecular dynamics, quasiharmonic lattice dynamics, and quasiharmonic Debye model. A particular attention was given to the analysis of the assumption that MgSiO₃ perovskite is a Debye-like solid, often used in geophysical literature.
Table 2. EOS of MgSiO₃ perovskite at high temperatures.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>T = 500 K</th>
<th>T = 1500 K</th>
<th>T = 2500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DM</td>
<td>LD</td>
<td>MD</td>
</tr>
<tr>
<td>$K_0$, GPa</td>
<td>254.99</td>
<td>258.67</td>
<td>261.01</td>
</tr>
<tr>
<td>$K'$</td>
<td>4.42</td>
<td>4.37</td>
<td>4.35</td>
</tr>
</tbody>
</table>

Our theoretical analysis was carried out using our new interatomic potential for MgSiO₃ in conjunction with state-of-the-art lattice dynamics and molecular dynamics simulations. We show that the new potential, although very simple, describes well interatomic interactions in MgSiO₃ perovskite, reproducing very well experimental heat capacity, entropy, thermal expansion, and equation of state (EOS) at 298 and 2000 K. A self-consistent quasiharmonic Debye model was constructed using static elastic properties and equation of state, calculated with the same interatomic potential.

We have considered the total phonon density of states (DOS) and its projections onto atomic species, heat capacity $C_v$, $\alpha$, $\gamma$, and high-temperature equation of state. 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 Debye model.

Grüneisen parameter and thermal expansion pose a more stringent test, and the Debye model predicts them poorly. Values of $\gamma$ and $\alpha$, predicted by the Debye theory, are ~30% too low. Therefore, MgSiO₃-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 $\gamma$. When deriving the temperature profile my matching PREM bulk modulus and density with the properties of plausible mineral assemblages, errors of ~30% (i.e., ~1000 K) in the temperature would arise from the use of acoustic $\gamma$.

The Debye model 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 to seismic observations) and represents 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 Debye model is used self-consistently (like in Hama et al. 2000), i.e. the Grüneisen $\gamma$ is related to the volume change of acoustic velocities, we expect significant errors. On the other hand, it should be safe to use the Debye model for inverting experimental data sets (e.g., Stixrude et al. 1992; Jackson and Rigden 1996; Yagi and Funamori 1996; Fiquet et al. 2000; Shim and Duffy 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, $q=\text{dln}\gamma/\text{dln}V$ 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 (Debye model, lattice dynamics, and molecular dynamics) 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 molecular dynamics simulations to 2.6 from the Debye model calculations, despite the same interatomic potential was used throughout.

Although most experiments and semiclassical simulations have errors in $\gamma$ and $\alpha$ comparable to 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 $ab initio$ molecular dynamics 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.

5. Acknowledgements

A.R.O. would like to acknowledge the financial support from the Russian President Scholarship for Education Abroad, UCL Graduate School Research Scholarship, U.K. Overseas Research Scholarship, and the International Soros Science Foundation (grant a99-44). J.P.B.
gratefully acknowledges the receipt of a Royal Society University Research fellowship. We thank Dr. Julian Gale (Imperial College London) for permission to use the latest version of GULP code, Dr. Keith Refson (Oxford University) for the use of Moldy code, and Drs. Hugh Barron (Bristol University) and John Harding (University College London) for useful discussions.

References


