

Comparison between the lattice dynamics and molecular dynamics methods: calculation results for MgSiO₃ perovskite

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Abstract. The lattice dynamics (LD) and molecular dynamics (MD) methods have been used to calculate the structure, bulk modulus, and volume thermal expansivity of MgSiO₃ perovskite, in order to investigate the reliability of the two simulation techniques over a wide range of temperature and pressure conditions. At an intermediate temperature of 500 K and zero pressure, the LD and MD values are in excellent agreement for both the structure and bulk modulus of MgSiO₃ perovskite. At high temperatures and zero pressure, however, the LD method, which is based on the quasi-harmonic approximation, increasingly overestimates the molar volume of MgSiO₃ perovskite because of the neglect of higher-order anharmonic terms. At the high temperatures and high pressures prevailing in the lower mantle, the errors in the LD values for both the molar volume and bulk modulus, relative to the MD values, are generally small or negligible. However, since anharmonicity decreases substantially with pressure but increases rapidly with temperature, the error in the LD simulated volume thermal expansivity is serious, especially in the lower pressure region.

Introduction

The detailed description of the chemical and physical properties of the Earth's interior requires an accurate knowledge of the elastic and thermal properties of the constitutive minerals at high temperatures and high pressures. However, it is still extremely difficult to carry out experiments to measure accurately such properties at the combined temperature and pressure conditions to be found in the Earth's deep interior. As an alternative to direct experimental study, therefore, atomistic computer simulations have recently been extensively applied to predict the properties of various minerals thought to exist in the interior of the Earth [e.g. Wolf and Bukowinski, 1985; Cohen, 1987; Price et al., 1987; Matsui, 1988; Matsui and Price, 1992].

Given a set of interatomic potentials, there are two major types of simulation techniques that can be used to calculate static and dynamic properties of crystals at a specified temperature T and pressure P , namely the lattice dynamics (LD) and molecular dynamics (MD) methods.

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In the LD method the crystal potential is usually estimated in the harmonic or quasi-harmonic approximation. LD calculations are very useful and powerful for predicting vibrational frequencies and thermodynamic properties of crystals over a wide temperature range, but break down at very high temperatures [Price et al., 1987; Parker and Price, 1989]. For such high temperatures, where anharmonicity is important and quantum effects are small, it is generally more practicable to use the MD method. In this method the average structural parameters are simulated by using Newton's classical equations of motion for atoms in crystals, as a function of time. The MD method can be applied to predict not only equilibrium properties [e.g. Matsui, 1988; Matsui and Price, 1992] but also time-dependent phenomena, such as first-order phase transitions [Tsuneyuki et al., 1989] and transport properties [Wall and Price, 1989].

MgSiO₃ perovskite is thought to be the major component of the lower mantle. The LD and MD methods have therefore been extensively applied to simulating the structural and physical properties of this phase. Examples of the application of the LD method to the simulations of MgSiO₃ perovskite include the calculation of the equation of state [Hemley et al., 1987], and the establishment of constraint on mineral composition models of the lower mantle from simulated structural and elastic properties of MgSiO₃ perovskite [Cohen, 1987; Bukowinski and Wolf, 1988]. The MD technique has been used to predict the possible existence of a high temperature and/or high pressure phase transition in MgSiO₃ perovskite [Matsui and Price, 1991; Kapusta and Guillopé, 1993].

The aim of the present investigation is to compare the values computed using the LD and MD techniques for the structure, molar volume, V , volume thermal expansivity, α , and isothermal bulk modulus, K_T , of MgSiO₃ perovskite, and to assess the reliability and applicability of the two methods over a wide temperature and pressure range, with special reference to the simulation of lower mantle conditions.

Calculation methods

All the LD and MD calculations were made using the pair potential MAM0K [Matsui, 1988], which has been shown to reproduce the observed structural and physical properties of MgSiO₃ perovskite quite accurately [Matsui and Price, 1992]. The LD calculations were carried out using the PARAPOCS computer code, which obtains the

equilibrium structure by minimizing the free energy of the crystal with respect to the structural parameters, within the framework of the quasiharmonic approximation, as described in Parker and Price [1989]. The MD simulations were performed in the isothermal–isobaric ensemble, i.e., with fixed T , P , and number of ions. The equilibrium structural parameters were derived by taking averages over a sufficiently long time–interval, and quantum corrections to the classical MD values were made using the Wigner–Kirkwood expansion of the free energy in terms of Planck constant, by the technique proposed by Matsui [1989]. In the present MD work, we took a basic cell composed of 27 ($3a \times 3b \times 3c$) unit cells, containing 540 atoms. In an attempt to estimate the sensitivity of the system to ensemble size, we also performed MD calculations with a larger basic cell containing 960 atoms. Simulations with such an ensemble carried out at 500, 1000 and 1500 K under zero pressure were compared with the calculated values of V and α obtained for the system composed of 540 atoms. Within the limit of statistical uncertainties, we found no significant system size effect.

MgSiO₃ perovskite is orthorhombic with space group $Pbnm$ [Horiuchi et al., 1987]. We note, in each of our LD and MD calculations, no symmetry constraint was imposed either on the cell parameters or on the atomic coordinates in the unit cell. The K_T 's, were obtained by fitting the simulated P – V relations to a third–order Birch–Murnaghan equation, while the α 's were derived by fitting the computed T – V results to the equation $\alpha = (1/V)(\partial V/\partial T) = \alpha_0 + \alpha_1 T + \alpha_2 T^2$, where α_0 , α_1 and α_2 are the coefficients of thermal expansion.

Results and discussion

Since the MD method is exact in the high temperature limit, then when combined with quantum corrections through the Wigner–Kirkwood expansion, it is the best approach to determining properties at high temperatures. On the other hand the LD technique, with the quasiharmonic approximation, is accurate at lower temperatures, where anharmonic effects are negligible.

Table 1. LD and MD simulated structures of MgSiO₃ perovskite at 500 K and zero pressure.

	LD	MD		LD	MD
<i>Cell parameters</i>		<i>Mg–O distances/Å</i>			
$a/\text{Å}$	4.77	4.78	Mg–O1	2.00	2.00
b	4.93	4.93	–O2 [2]	2.05	2.05
c	6.97	6.95	–O1	2.13	2.13
			–O2 [2]	2.29	2.30
<i>Si–O distances/Å</i>			–O2 [2]	2.48	2.47
Si–O2 [2] [†]	1.78	1.79	–O1	2.85	2.85
–O2 [2]	1.79	1.79	–O1	2.93	2.92
–O1 [2]	1.82	1.81	–O2 [2]	3.09	3.08
<Si–O>	1.80	1.80	<Mg–O>	2.48	2.48

[†] Multiplicity of bond

The Debye temperature of MgSiO₃ perovskite is reported to be about 1000 K at 0 GPa [Akaogi and Ito, 1993]. We first made a comparison between the LD and MD results, therefore, at intermediate conditions, 500 K and 0 GPa, under which both methods are expected to be valid. Table 1 gives the LD and MD calculated cell parameters and interatomic distances for MgSiO₃ perovskite at these conditions. We find that at 500 K and 0 GPa the simulated structural data for the two methods are in excellent agreement. The maximum error in the cell parameters is only 0.2 %, and the errors in the interatomic distances are within only 0.01 Å. The isothermal bulk modulus at 500 K and 0 GPa, calculated by LD, is 237 GPa, which is again in excellent agreement with the value obtained from MD of 236 GPa (see Table 2). These agreements, in both the structure and bulk modulus, are quite satisfactory, considering the greatly different nature of the two calculation methods.

Fig. 1 shows the temperature dependence of the simulated molar volumes of MgSiO₃ perovskite at zero pressure. As expected, the LD–simulated molar volume increases more rapidly with temperature than the MD

Table 2. LD and MD calculated values for the molar volume, V , volume thermal expansivity, α , and isothermal bulk modulus, K_T , of MgSiO₃ perovskite at selected temperatures T and pressures P .

T/K	P/GPa	$V/(\text{cm}^3/\text{mol})$		error %	$\alpha/(10^{-5}\text{K}^{-1})$		K_T/GPa	
		LD	MD		LD	MD	LD	MD
500	0	24.68	24.70	0.1	3.75(7) [†]	3.31(19)	237(1)	236(1)
1000	0	25.25	25.19	0.2	5.32(9)	4.38(20)	200(2)	208(1)
500	30	22.35	22.37	0.1	2.02(4)	1.88(18)	378(1)	377(2)
1000	30	22.60	22.60	0.0	2.36(4)	2.24(10)	354(3)	356(1)
2000	30	23.21	23.16	0.2	3.05(5)	2.59(11)	304(6)	314(4)
3000	30	24.02	23.80	0.9	3.73(7)	2.89(13)	251(17)	279(5)
500	60	20.88	20.89	0.0	1.37(3)	1.26(12)	509(2)	509(3)
1000	60	21.04	21.05	0.0	1.68(2)	1.61(7)	496(6)	493(2)
2000	60	21.43	21.41	0.1	1.94(2)	1.79(8)	453(11)	455(7)
3000	60	21.87	21.81	0.3	2.16(2)	1.92(9)	402(30)	417(8)

[†] Parenthesized figures refer to the estimated standard deviation of least units cited.

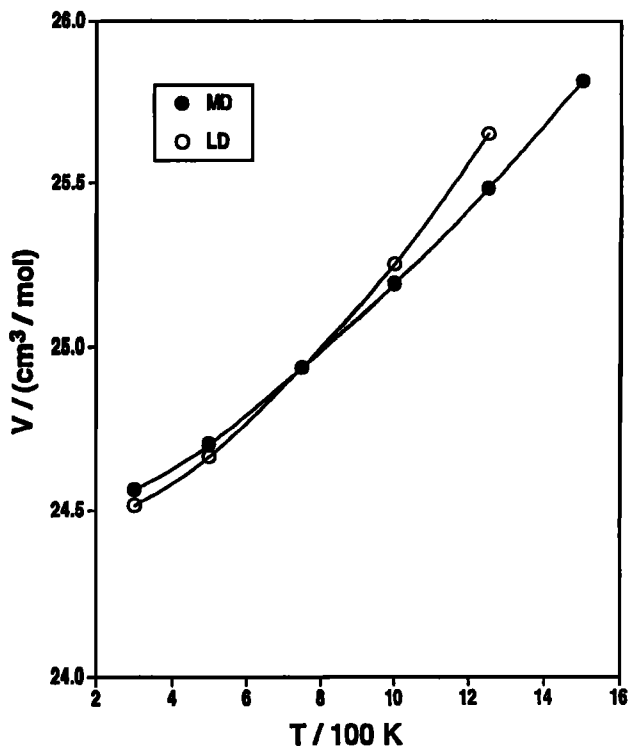


Figure 1. Temperature dependencies of the LD and MD computed molar volumes of MgSiO_3 perovskite at zero pressure.

volume, due to the neglect of higher-order anharmonic terms in the LD calculations at high temperature. The overestimation of the MD molar volumes relative to the LD results, at temperatures lower than approximately 700 K, might be explained by the neglect of higher-order quantum corrections in our MD simulations, as described previously [Matsui, 1989]. It is to be noted that although the difference in the LD and MD simulated molar volumes is generally very small, e.g. only 0.1 and 0.2 % at 500 and 1000 K respectively, the difference in the calculated volume thermal expansivities is significant, and reaches 22 % at 1000 K (see Table 2).

Above approximately 1500 K at zero pressure, the quasi-harmonic LD calculations indicate the orthorhombic MgSiO_3 perovskite structure to be dynamically unstable, with imaginary mode-frequencies, in accord with similar quasi-harmonic LD simulations of MgSiO_3 perovskite by Wolf and Bukowinski [1985], who used a modified electron gas potential. However, it is important to note that this dynamical instability is solely the result of the break down in quasi-harmonic approximation. Actually, in our MD simulations, the orthorhombic MgSiO_3 perovskite structure is found to remain stable at all temperatures up to the melting point (calculated to be about 2800 K at zero pressure), as described previously [Matsui and Price, 1991].

Accurate data on V , α and K_T for MgSiO_3 perovskite at high temperatures and high pressures are necessary in order to estimate detailed chemical and physical properties of the lower mantle. Table 2 lists the LD and MD computed values for V , α , and K_T at T from 500 to 3000 K, and P of 30 and 60 GPa, which correspond approximately to depths of 800 and 1450 km in the lower

mantle [Dziewonski and Anderson, 1981]. Fig. 2 illustrates the calculated molar volumes of MgSiO_3 perovskite from the two simulations as a function of pressure up to 100 GPa, for the two temperatures 2000 and 3000 K, which can be thought to be typical for the lower mantle [Spiliopoulos and Stacey, 1984; Jeanloz and Morris, 1986]. The differences between the LD and MD values at high temperatures show the magnitude of the error in the LD calculations which results from the neglect of explicit anharmonic terms. In Fig. 2 and Table 2 we see the difference between the LD and MD results. At 30 GPa for example, the LD and MD values for α agree within uncertainties at 1000 K, however the values diverge by 18 % at 2000 K, and by 27 % at 3000 K. From Fig. 2 we also see that anharmonicity decreases substantially with increasing pressure; for both 2000 and 3000 K simulations, the LD values overestimate V at lower pressures, however the extent of these overestimations decrease with pressure, such that the LD values eventually agree with the MD results within statistical uncertainties at the highest pressures.

At typical T and P conditions in the lower mantle, the deviations of the LD results from those of MD for both V and K_T are generally small or negligible. However, since anharmonicity changes substantially with pressure and even more with temperature, the deviation in α is quite significant, especially in the lower pressure region in the lower mantle. In conclusion, therefore we believe that if accurate calculations of the physical properties (e.g. thermal expansion coefficient) of minerals under lower mantle conditions are required, full molecular dynamic simulations must be performed, or corrections to the quasi-harmonic approximation must be applied to lattice

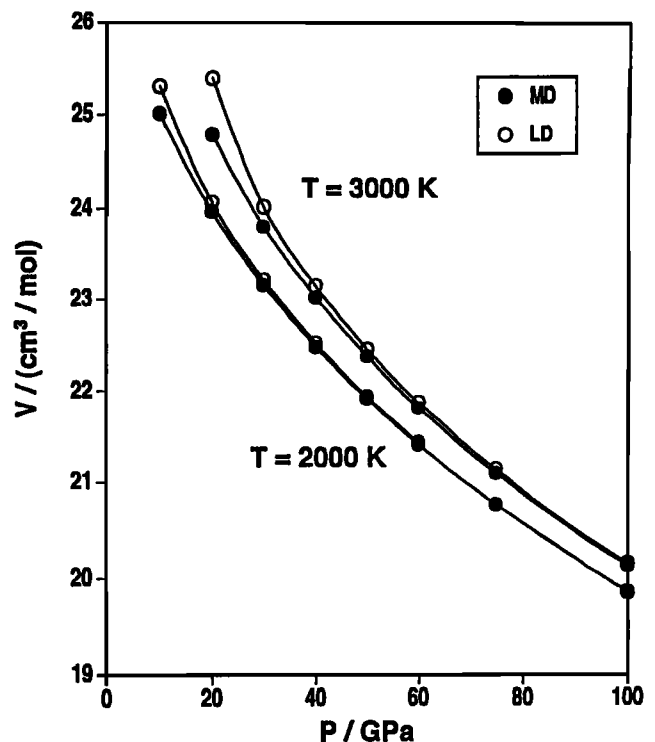


Figure 2. The LD and MD simulated molar volumes of MgSiO_3 perovskite at the temperatures 2000 and 3000 K as a function of pressure up to 100 GPa.

dynamical simulations to take full account of intrinsic anharmonic effects.

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