

ARTICLE

Simulated Equations of State of MgSiO₃ PerovskiteZi-jiang Liu^{a,b}, Xin-lu Cheng^a, Fang-pei Zhang^a, Xiang-dong Yang^{a*}, Yuan Guo^c

a. Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China; b. Department of Physics, Lanzhou Teachers College, Lanzhou 730070, China; c. Institute of Electronic Information Science and Technology, Lanzhou Teachers College, Lanzhou 730070, China

(Dated: Received on December 31, 2004; Accepted on April 27, 2005)

The equation of state of MgSiO₃ perovskite under high pressure and high temperature is simulated using the molecular dynamics method. It was found that the molecular dynamics simulation is very successful in accurately reproducing the measured molar volumes of MgSiO₃ perovskite over a wide range of temperatures and pressures. The simulated equation of state of MgSiO₃ perovskite matched experimental data at up to 140 GPa at 300 K, as well as the fitting data of others and results from the first-principles simulation based on the local density approximation. The simulated equations of state of MgSiO₃ perovskite at higher temperatures and higher pressures also correspond to the other calculations. In addition, the volume compression data of MgSiO₃ perovskite is simulated up to 120 GPa at 300, 900, 2000 and 3000 K, respectively.

Key words: Equation of state, Molecular dynamics, High pressure, MgSiO₃

I. INTRODUCTION

MgSiO₃ in its various polymorphic forms constitutes a major component of the Earth's mantle. MgSiO₃ perovskite is believed to be the most abundant mineral on Earth, comprising about 70%, by volume, of the lower mantle. The equation of state of MgSiO₃ perovskite, at the simultaneously high pressures and temperatures of the lower mantle, is crucial for interpreting seismological data and constructing reliable chemical, mineralogical, and thermal models of the lower mantle. Furthermore, accurate modeling of the physical properties of MgSiO₃ perovskite is of the utmost importance as experimental studies at the high pressures and temperatures characteristic of the Earth's interior are often not feasible. For instance, little is known about the thermal expansion coefficient of MgSiO₃ perovskite, even at the ambient pressure [1]. Whereas, the highest hydrostatic pressure achieved in experiments at lower mantle temperatures, to date, is 94 GPa [2]. This is still well below the core-mantle boundary pressure of 136 GPa. The difficulties in obtaining accurate thermoelastic parameters for MgSiO₃ perovskite by experiment were discussed in detail by Shim and Duffy [3]. Since the lower mantle comprises over 50% of the Earth's volume, spanning depths of 670 to 2891 km, it is characterized by very high pressures (24–136 GPa) and temperatures, roughly between 2000 and 3000 K, possibly rising to about 4000 K [4]. At such high temperatures atomic motion is essentially classical and possibly significantly anharmonic, making it appropriate to use the molecular dynamics approach to simulate. We have therefore taken advantage of recent advances in computer technology, and have performed molecular dynamics simulations of the physical properties of MgSiO₃ perovskite at the relevant thermodynamic conditions.

Previously [5, 6], we accurately simulated the structural and thermodynamic properties of other materials over wide temperature and pressure ranges using interatomic potential by molecular dynamics. In this work, we apply the same interatomic potential to simulate the volume thermal expansiveness at a wide temperature range of 300 to 2000 K, the room-temperature volume compressions data up to 120 GPa and equation of state for MgSiO₃ perovskite up to 140 GPa, and compare our results with available experimental results and theoretical data.

II. METHOD

Molecular dynamics simulation is a well-established technique in mineralogy, especially for studying the effects of high pressure and high temperature on the properties of a solid and its melting point. A detailed description of the molecular dynamics method has been provided elsewhere [7, 8]. In short, the molecular dynamics method consists of solving numerical equations for atomic motion, assuming initial coordinates and velocities of atoms and a model of interaction between them. Normally, as is also the case in molecular dynamics calculations, periodic boundary conditions are applied. Periodic boundary conditions imply that if a particle leaves a computational cell on one, that the identical particle enters the cell from the opposite side.

We carry out molecular dynamics simulations at high pressures and temperatures using the empirical potential on a system of 360 atoms. Our interatomic potential is pairwise, and has the following form:

$$V(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where the right terms represent Coulomb, repulsive interactions, and van der waals, respectively. Also, Z_i or Z_j is an effective charge of the i th atom, e the electronic unit charge, A_{ij} the magnitude of repulsion force, B_{ij} the softness parameter, C_{ij} van der waals coefficient of

* Author to whom correspondence should be addressed. Tel: +86-28-85405526. E-mail: xdyang@seu.edu.cn

TABLE I Parameters of the potential of MgSiO₃ perovskite used in simulations

Source	A/eV	B/nm^{-1}	$C/\text{nm}^6\mu\text{eV}$
Mg–O	1041.4350	34.8918	
Si–O	1137.0280	35.3732	
O–O	2023.8000	37.3972	13.8300

ion. Here r_{ij} is the interionic distance between atoms i and j . Values of the parameters [9] of MgSiO₃ perovskite used in simulations are listed in Table I.

All of the simulations were performed using the interaction potential in equation (1). To ensure the reliability of our results, some of the simulations are duplicated using our molecular dynamics code, and no relevant difference was found. Simulations in NTP (constant N is the number of particles, T is the temperature, and P is pressure) ensemble [10] are performed. Simulations were started from an orthorhombic perovskite lattice adjusted for density. Simulation runs were carried out with 360 particles (72 Mg, 72 Si and 216 O atoms). The cut-off radius was chosen to be $L/2$, where L is the shortest of edges of the computational box. Time steps were varied from 2 fs at low temperatures to 1 fs at high temperatures. Run durations were varied from 6000 steps to 4000 steps, depending on the time step. The Coulombic interaction was calculated using Ewald method [11].

III. RESULTS AND DISCUSSION

The simulated molar volume V_0 (24.698 cm³/mol) matches the study by Belonoshko *et al.* [12] to within 0.7% under 300 K at zero pressure. The volume thermal expansiveness is obtained by fitting the computed $T-V$ results to the equation $\alpha = \alpha_0 + \alpha_1 T + \alpha_2 T^{-1} + \alpha_3 T^{-2}$, where α_0 , α_1 , α_2 and α_3 are the coefficients of thermal expansion. The molecular dynamics α values at 300 K are estimated to be 2.09/K, which are comparable to the previously measured value [13] of 2.2/K. Figure 1 illustrates the simulated temperature dependences over the wide temperature range of 300 to 2000 K at 36 GPa of MgSiO₃ perovskite. It was found that the simulated T dependence of V/V_{300} (where V_{300} is molar volume of molecular dynamics simulation and experiment at 300K and $P = 36$ GPa) values at 36 GPa is in line with the experimental values [14]. Therefore, the result provides strong support for further potential of the equations of state MgSiO₃ perovskite at high pressures and high temperatures.

Mao *et al.* [15] performed diamond-anvil cell static compression experiments on MgSiO₃, (Mg_{0.9}Fe_{0.1})SiO₃ and (Mg_{0.8}Fe_{0.2})SiO₃ perovskite at up to 28.4 GPa at 300 K, using neon as a pressure-transmitting medium. They have shown that the 300 K volume-compression data of these three perovskites are indistinguishable, within the range of experimental error, when normalized volumes are used for comparison. Shanker *et al.* [16] calculated the volumetric expansion due to temperature along isobars for MgSiO₃ perovskite, up to a

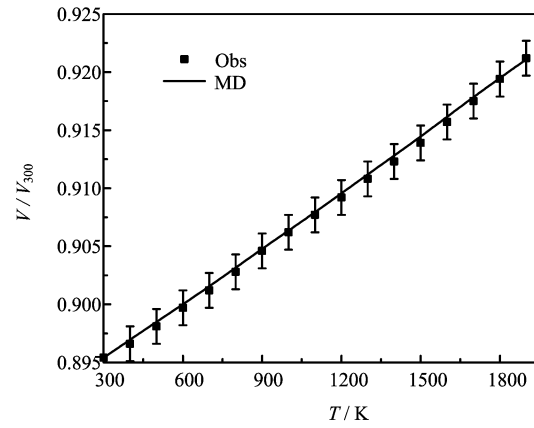


FIG. 1 Simulated and observed [14] thermal expansion as a function of temperature for MgSiO₃ perovskite at 36 GPa

pressure of 160 GPa and a temperature of 3000 K using the equation of thermal expansivity. Wentzcovitch *et al.* [17] developed a constant pressure *ab initio* molecular dynamics algorithm with variable cell shape, and applied it to predict the behavior under pressure of the major Earth-forming mineral phase MgSiO₃ perovskite. Fig.2 shows the equations of state MgSiO₃ perovskite at $T = 300$ K, as observed in the molecular dynamics simulation, which matches the experimental data [15], the fitting data of Shanker *et al.* [16] and results from the first-principles simulation at $T = 0$ K based on the LDA [17]. Such excellent concurrence lends much credibility to the predicted molecular dynamics results on the pressure-temperature-volume equations of state and volume compressions of MgSiO₃ perovskite at higher temperature and pressure. The simulated volume compressions of MgSiO₃ perovskite up to 120 GPa at 300, 900, 2000 and 3000 K are shown in Fig.3.

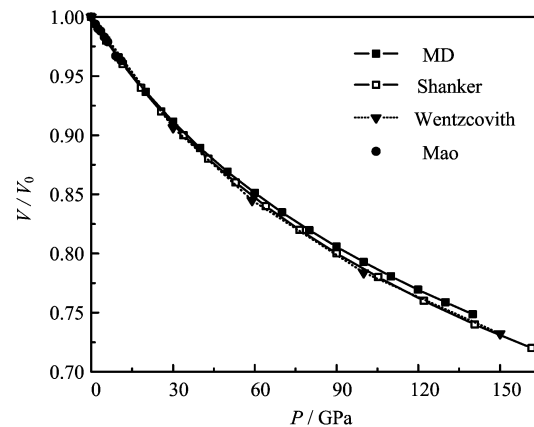


FIG. 2 The equations of state of MgSiO₃ perovskite at 300 K. The closed squares are for the present study. The open squares are the fitted data of Shanker *et al.* [16] The closed triangles and the closed circles are the first-principles simulation at $T = 0$ K based on the LDA by Wentzcovitch *et al.* [17] and experimental data of Mao *et al.* [15], respectively.

In high temperature and high pressure experiments, known pressure-temperature-volume equations of state

TABLE II The fitted and simulated data of V/V_0^a versus P and T for MgSiO₃ perovskite

P/GPa		T/K						
		300	500	1000	1500	2000	2500	3000
0.0	Fitting data ^b	1.000	1.0054	1.0195	1.0349	1.0518	1.0709	1.0934
	MD ⁺	1.000	1.0056	1.0248	1.0412	1.0559	1.0786	1.1029
5.5	Fitting data	0.980	0.9849	0.9975	1.0113	1.0261	1.0426	1.0613
	MD	0.980	0.9854	1.0024	1.0167	1.0283	1.0485	1.0664
11.6	Fitting data	0.960	0.9644	0.9758	0.9880	1.0012	1.0155	1.0314
	MD	0.960	0.9652	0.9806	0.9927	1.0024	1.0185	1.0345
18.3	Fitting data	0.940	0.9439	0.9542	0.9647	0.9768	0.9893	1.0029
	MD	0.941	0.9452	0.9592	0.9699	0.9775	0.9934	1.0049
25.7	Fitting data	0.920	0.9236	0.9328	0.9425	0.9529	0.9639	0.9758
	MD	0.921	0.9253	0.9380	0.9476	0.9536	0.9669	0.9778
33.9	Fitting data	0.900	0.9032	0.9115	0.9203	0.9294	0.9392	0.9495
	MD	0.902	0.9056	0.9170	0.9254	0.9309	0.9429	0.9525
43.0	Fitting data	0.880	0.8829	0.8904	0.8982	0.9064	0.9150	0.9240
	MD	0.882	0.8857	0.8965	0.9036	0.9080	0.9178	0.9264
53.0	Fitting data	0.860	0.8627	0.8694	0.8763	0.8837	0.8913	0.8993
	MD	0.863	0.8661	0.8761	0.8824	0.8859	0.8960	0.9031
64.1	Fitting data	0.840	0.8424	0.8484	0.8547	0.8612	0.8680	0.8750
	MD	0.844	0.8465	0.8557	0.8616	0.8644	0.8726	0.8789
76.5	Fitting data	0.820	0.8221	0.8275	0.8332	0.8390	0.8450	0.8512
	MD	0.824	0.8268	0.8353	0.8406	0.8427	0.8507	0.8566
90.1	Fitting data	0.800	0.8019	0.8068	0.8118	0.8170	0.8224	0.8278
	MD	0.805	0.8074	0.8154	0.8176	0.8216	0.8292	0.8343
105.3	Fitting data	0.780	0.7817	0.7861	0.7906	0.7952	0.7999	0.8049
	MD	0.786	0.7879	0.7954	0.7995	0.8006	0.8078	0.8120
122.1	Fitting data	0.760	0.7615	0.7655	0.7695	0.7736	0.7779	0.7822
	MD	0.767	0.7685	0.7755	0.7761	0.7800	0.7860	0.7904
140.8	Fitting data	0.740	0.7413	0.7449	0.7685	0.7522	0.7559	0.7598
	MD	0.747	0.7492	0.7558	0.7560	0.7594	0.7656	0.7691

^a Present study $V_0=24.698 \text{ cm}^3/\text{mol}$, ^b The fitting data from Ref. [16].

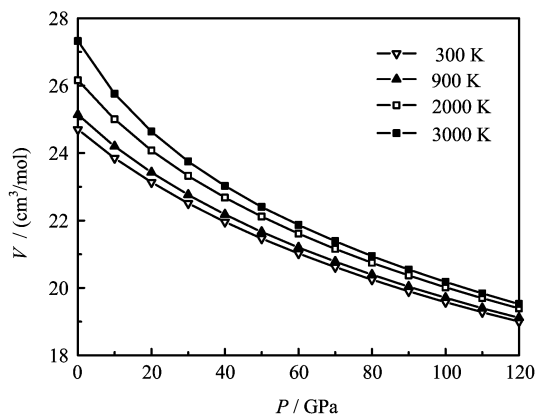


FIG. 3 The simulated volume compressions of MgSiO₃ perovskite at 300, 900, 2000 and 3000 K, respectively.

of standard materials, such as NaCl and Au, or the ruby-fluorescence pressure scale are usually used to measure the pressure of the system. However, there are problems inherent in these pressure calibration meth-

ods, as cited previously [18, 19]. Namely, NaCl transforms from the B1 to the B2 structure at about 27 GPa, 300 K, and 21 GPa, 1000 K [20]; Au melts at 1340 K [21] at zero pressure; and the ruby pressure scale is unsuitable at high temperatures due to the broadening of the ruby R lines, as well as the decreasing of their intensity [18]. In addition, the proposed high temperature and high pressure equation of state, for both NaCl and Au, can contain errors resulting from inaccuracy of temperature and pressure dependencies of key physical properties, including the heat capacity, the thermal expansivity, and the elasticity, from which the equation of state is derived. Indeed it has recently been reported that careful diamond-anvil-cell experiments [22], conducted at room temperature, indicated that the pressure values calibrated using the Au scale by Anderson *et al.* [23] are systematically lower than those using the NaCl scale by Decker [24] at high pressures. Hence, accurate pressure measurements require attentive cross-checking of these pressure calibration standards.

We have demonstrated that the molecular dynamics simulation is especially successful for MgSiO₃ per-

ovskite in reproducing accurately not only the measured molar volume up to 2000 K and 36 GPa, but also the observed volume compression data up to 120 GPa at 300 K. Most workers [2, 25, 26] have found that perovskite is more stable than oxides. Such concurrence lends much credibility to the predicted molecular dynamics simulations results on the pressure-temperature-volume equations of state of MgSiO_3 perovskite at high temperatures and high pressures. Thus, we propose to use MgSiO_3 perovskite as an additional, high temperature, pressure calibration mechanism. The molecular dynamics computed V/V_0 values and the fitted data, where V_0 ($24.698 \text{ cm}^3/\text{mol}$) is the molar volume at 300 K and 0 GPa, are listed in Table II up to 3000 K and 140 GPa. As noted in Table II, there are slight underestimations in the simulated V/V_0 values at high pressure and 300 K with the error of 0.94% at 140 GPa.

IV. CONCLUSION

In summary, the simulated molar volume and pressure-temperature-volume equations of state for MgSiO_3 perovskite match the available experimental data, as well as that of Shanker *et al.* [16], over wide temperature and pressure ranges, respectively. Hence, it is possible that the molecular dynamics simulated pressure-temperature-volume equations of state of MgSiO_3 perovskite could be employed as a useful internal pressure calibration standard at high temperatures and high pressures.

V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (NSFC No. 10274055), the Natural Science Foundation of Gansu Province of China (No. 3ZS051-A25-027) and the Natural Science Foundation of Education Department of Gansu Province of China (No. 0410-01).

[1] E. Knittle and R. Jeanloz, *Science* **235**, 668 (1987).

- [2] G. Fiquet, A. Dewaele, D. Andrault, M. Kunz and T. Le Bihan, *Geophys. Res. Lett.* **27**, 21 (2000).
- [3] S. H. Shim and T. S. Duffy, *Am. Mineral.* **84**, 354 (2000).
- [4] C. da Silva, R. M. Wentzcovitch, A. Patel and G. D. Price, *Phys. Earth. Planet. Inter.* **118**, 103 (2000).
- [5] Z. J. Liu, X. L. Cheng, H. Zhang and L. C. Cai, *Chin. Phys.* **13**, 384 (2004).
- [6] Z. J. Liu, X. L. Cheng, X. R. Cheng, H. Zhang and L. Y. Lu, *Chin. Phys.* **13**, 1096 (2004).
- [7] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford: Clarendon. (1987).
- [8] J. M. Hail, *Molecular Dynamics Simulation: Elementary Methods*, New York: Wiley. (1992).
- [9] A. R. Oganov, J. P. Brodholt and G. D. Price, *Phys. Earth Planet. Inter.* **122**, 277 (2000).
- [10] W. G. Hoover, *Phys. Rev. A.* **31**, 1695(1985).
- [11] P. P. Ewald, *Annal. Physik.* **64**, 253 (1921).
- [12] A. B. Belonoshko and L. S. Dubrovinsky, *Geochim. Cosmochim. Acta.* **60** 1645 (1996).
- [13] N. L. Ross and R. M. Hazen, *Phys. Chim. Miner.* **16**, 415 (1989).
- [14] N. Funamori and T. Yagi, *Geophys. Res. Lett.* **20**, 387 (1993).
- [15] H. K. Mao, R. J. Hemley, Y. Fei, J. F. Shu, L. C. Chen and A. P. Jephcoat, Y. Wu, *J. Geophys. Res.* **96** 8069 (1991).
- [16] J. Shanker and S. S. Kushwah, *Phys. B.* **254**, 45(1998).
- [17] R. M. Wentzcovitch, J. L. Martins and G. D. Price, *Phys. Rev. Lett.* **70**, 3947 (1993).
- [18] S. L. Wunder and P. E. Schoen, *J. Appl. Phys.* **52**, 3772 (1981).
- [19] D. L. Heinz and R. Jeanloz, *J. Appl. Phys.* **55**, 885 (1984).
- [20] X. Li and R. Jeanloz, *Phys. Rev. B.* **36**, 474 (1987).
- [21] J. Akella and G. C. Kennedy, *J. Geophys. Res.* **76**, 4969 (1971).
- [22] T. Uchida, T. Yagi, K. Oguri and N. Funamori, *First International Pressure Calibration Workshop*, Misasa: Japan. 18 (1997).
- [23] O. L. Anderson, D. G. Isaak and S. Yamamoto, *J. Appl. Phys.* **65**, 1534 (1989).
- [24] D. L. Decker, *J. Appl. Phys.* **42**, 3239 (1971).
- [25] G. Serghiou, A. Zerr and R. Boehler, *Science* **280**, 2093 (1998).
- [26] S. H. Shim, T. S. Duffy and G. Y. Shen, *Science* **293**, 2437 (2001).