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Molecular dynamics of $MgSiO_3$ perovskite melting*

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The melting curve of $MgSiO_3$ perovskite is simulated using molecular dynamics simulations method at high pressure. It is shown that the simulated equation of state of $MgSiO_3$ perovskite is very successful in reproducing accurately the experimental data. The pressure dependence of the simulated melting temperature of $MgSiO_3$ perovskite reproduces the stability of the orthorhombic perovskite phase up to high pressure of 130GPa at ambient temperature, consistent with the theoretical data of the other calculations. It is shown that its transformation to the cubic phase and melting at high pressure and high temperature are in agreement with recent experiments.

Keywords: melting temperature, molecular dynamics, high pressure
PACC: 9160H, 7115Q, 6250, 9160F

1. Introduction

When containing some Fe, $MgSiO_3$ perovskite is the most abundant mineral in the Earth, comprising 60–100 vol.% of the lower mantle, and dominating many of its properties.[1] Therefore, the properties of $MgSiO_3$ perovskite at high temperature and high pressure are of great interest to geophysicist.[2−5] At present, however, such information is difficult to obtain directly through laboratory experiments. The lower mantle comprises over 50% of the Earth's volume, extending between the depths of 670 km and 2,891 km, it is characterized by very high pressure (24–136 GPa) and high temperature, ranging roughly between 2,000 K and 3,000 K, possibly extending to about 4,000 K.[6] At such high temperature atomic motion is essentially classical and possibly significantly anharmonic, making it appropriate to use the molecular dynamics approach to simulate. We have therefore performed molecular dynamics simulations of the physical properties of $MgSiO_3$ perovskite under the relevant thermodynamic conditions.

The melting temperature of $MgSiO_3$ perovskite plays a fundamental role in the chemical differentiation, rheology and geodynamics of the Earth's lower mantle. The prediction of melting temperature by molecular dynamics simulations has been found to be rather successful recently,[7] and, furthermore, it allows tracking the physical properties of the atoms not only as global averages but also locally. This capability is indispensable for correlating the theories and the atomic-level mechanisms at the onset of melting. In this paper, we simulate the melting curve of $MgSiO_3$ perovskite by the method of molecular dynamics simulation at constant pressure, and compare our results with that of previous works.[8,9]

2. Method

2.1. Interatomic potential

Following our previous studies,[10−13] the crystal lattice energy is taken to be the sum of interactions between atoms of the form

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

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where Z_i or Z_j is the effective charge of the ith atom, e is the electronic unit charge, A_{ij} and B_{ij} are parameters for the repulsive interactions, and C_{ij} are the van der Waals constants. The first term represents the Coulomb interaction, the second one is due to overlap repulsion. Here r_{ij} is the interatomic distance between atoms i and j. Because the interparticle interaction is the most important factor in molecular dynamics simulations, a proper choice of interaction potential is necessary for good results. Values of the parameters[14] of $MgSiO_3$ perovskite used in the simulations are listed in Table 1.

Table 1. Parameters of the potential of $MgSiO_3$ perovskite used in simulations.

source	A/eV	B/nm^{-1}	$C/10^{-6}$eV·nm^6
Mg–O	1041.4350	34.8918	
Si–O	1137.0280	35.3732	
O–O	2023.8000	37.3972	13.8300

2.2. Technique of simulation

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 solid and their melts. Detailed description of the molecular dynamics method has been given elsewhere.[15,16] In short, the molecular dynamics method consists in solving numerically equations of 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 condition is applied. Periodic boundary condition means that if a particle leaves a computational cell on one side of the cell, an identical particle enters the cell from the opposite side. The electrostatic interactions are evaluated in both real and reciprocal spaces according to the Ewals method.[17]

Simulations in NTP (constant N is the number of particles, T is the temperature, and P is pressure) ensemble[18] are performed. Simulations are started from an orthorhombic perovskite lattice adjusted for density. Simulation runs are carried out with 360 particles (72 Mg, 72 Si, 216 O atoms). The results of molecular dynamics simulations in the NTP ensemble with the chosen model of the interatomic interaction depend on, apart from the initial arrangement of particles, the size of time step τ, the number of time steps n, number of particles N, and temperature of windows $T_{\rm win}$. Therefore, the influence of these parameters was carefully studied by carrying out runs at various T and P. It was found that correct results could normally be obtained with equilibration and measurement of the number of time-step n=5000, a time-step τ=1fs, temperature of windows $T_{\rm win}$=23K. These measurements are very accurate. Usually we re-equilibrated at the required temperature and pressure for 5ps and then measured the temperature, pressure and volume over a further 5ps. Typically, the actual temperature differed from the required temperature by less than 1 K, the actual pressure differed from the required pressure by less than 1 MPa, and the discrepancy in the volume was less than 0.002cm^3/mol.

3. Results and discussions

3.1. Equation of state of $MgSiO_3$ perovskite

The simulated molar volume V_0 (=24.698 cm^3 / mol) value agrees well with the study by Belonoshko and Dubrovinsky[19] within 0.7% under 300 K at zero pressure. The volume thermal expansivity is obtained by fitting the computed $T-V$ results to the equation $\alpha=\alpha_0+\alpha_1T+\alpha_2T^{-1}+\alpha_3T^{-2}$, where α_0, α_1, α_2 and α_3 are the coefficients of thermal expansion. The molecular dynamics α value at 300 K are estimated to be 2.09 K^{-1}, which compare very well with the measured value[20] of 2.2 K^{-1}. As shown in Fig.1, we illustrate the simulated temperature dependence of volume over the wide temperature range between 300 K and 2000K at 25GPa of $MgSiO_3$ perovskite. It is found that the simulated T dependence of V/V_0 (V_0 being the molar volume at 300 K and P=25GPa) values at 25GPa is in excellent agreement with the experimental values.[21] The equation of state of $MgSiO_3$ perovskite at T=300K obtained by our simulation is shown in Fig.2, and it is in good agreement with the experiment data,[22] the fitting data of Shanker and Kushwah[23] and the first-principles simulation result of Wentzcovitch *et al* based on the LDA.[24] Thereby, the above results provide a strong support for the po-

tential with which we further study the melting curve of $MgSiO_3$ perovskite at high pressure and high temperature.

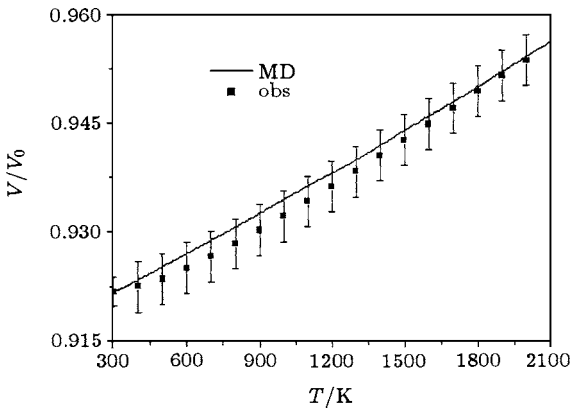


Fig.1. Volume as a function of temperature for $MgSiO_3$ perovskite at 25GPa.

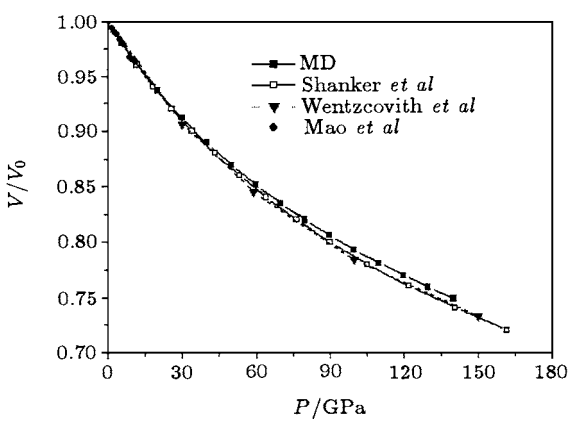


Fig.2. The equations of state of $MgSiO_3$ perovskite at 300K. The closed squares are for the present study. The opened squares are the fitting data of Shanker and Kushwah.[23] The closed triangles and the closed circles are the first-principles simulation at T=0K based on the LDA by Wentzcovith *et al*[24] and experimental data of Mao *et al*,[22] respectively.

3.2. Heat capacity and entropy of $MgSiO_3$ perovskite

In Fig.3, it is shown that the specific heat capacity at ambient pressure calculated from the present model is in an excellent agreement with the experimental data.[25] Because the present theory is able to reproduce the above thermodynamical experimental data satisfactorily, we use it for prediction of properties at high temperatures and pressures where experimental data are not yet available. The calculated entropy of $MgSiO_3$ perovskite is shown in Fig.4.

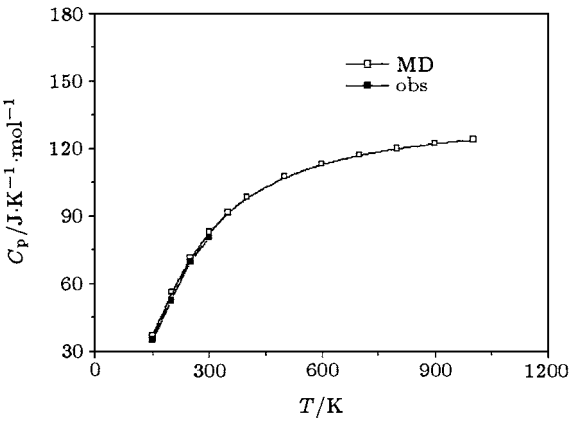


Fig.3. Heat capacity as a function of temperature of $MgSiO_3$ perovskite. The opened squares are from the present study. The closed squares are experimental data of Akaogi *et al*.[25].

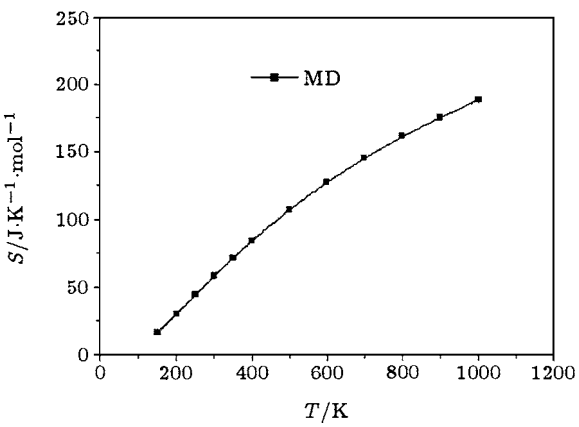


Fig.4. Molecular dynamics simulated temperature dependence of entropy of $MgSiO_3$ perovskite.

3.3. Melting curve of $MgSiO_3$ perovskite

Melting is the first-order phase transition from an ordered solid to disordered liquid. The melting curve of $MgSiO_3$ is calculated by method of constant pressure molecular dynamics simulations. The calculated volume changes at 10^5Pa and at temperatures from 300 up to 4200 K are shown in Fig.5. It is shown that the sudden change of the calculated volume of $MgSiO_3$ occurs at a temperature of about 3396 K. This value is higher than the normal melting temperature. The reason is that molecular dynamics simulations in free space are known to exhibit high hysteresis,[26] which prevents us from judging how well the experimental value of melting temperature at 10^5Pa pressure is reproduced. Cohen and Gong[26] noted the high hysteresis at 10^5Pa. This hysteresis decreases with increasing pressure, and it is also the result of the existence of a substantial metastable overheating. Overheating of a crystalline solid occurs when the long-range order of

the crystalline structure is maintained up to certain temperature above the equilibrium melting temperature. Unstable overheating due to the melting kinetics during the rapid heating is insignificant because of the transient nature of melting at such a high degree of overheating. Melting is a dynamic process and melting temperatures of a crystal can be modified by certain melting mechanism. According to catastrophic melting[27,28] and homogeneous nucleation[29,30] theories, the equilibrium melting temperature T_m due to overheating melting of $MgSiO_3$ perovskite at ambient pressure can be described as

$$\frac{(T_m - T_{mo})}{T_{mo}} = 0.212, \qquad (2)$$

where T_{mo} is the conventional melting temperature for the bulk. A substantial overheating melting process results from heating rate, it is not much dependent on pressure, and will be applied to correct the melting temperatures for overheating of crystal (T_m in Eq.(2)) to T_{mo} as the first approximation.

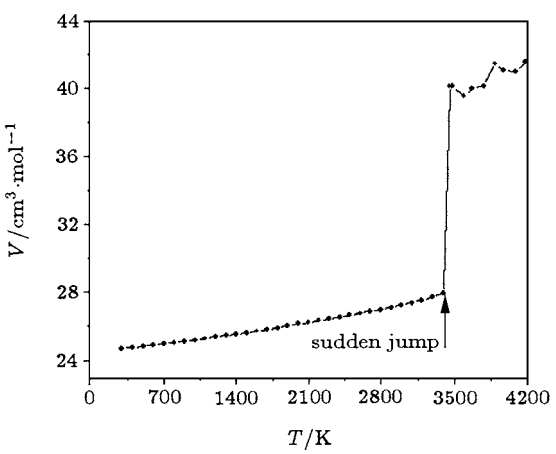


Fig.5. Molecular dynamics calculated volume of $MgSiO_3$ perovskite at the pressure of 10^5Pa as a function of temperature. The calculated points are connected by solid line for convenience. The volume is suddenly changed at a temperature of about 3396K.

As shown in Fig.6, the present melting curve of $MgSiO_3$ perovskite is in good agreement with the molecular dynamics simulations data of the system with 1% vacancies by Chaplot *et al.*[9] The various experimental data and the differences among them have been discussed by Brown.[31] Molecular dynamics simulated melting temperatures is significantly lower than that of the perfect lattice system which was reported by Chaplot *et al.*[9] The melting temperature in molecular dynamics simulation may be somewhat higher than those in experiments. This is the reason why the eye-evident surface texture change is usually used as the melting criterion to the melting of sample heated by laser in DAC experiments.[8] When a very thin melting layer exists at the sample/DAC interface and the heat balance between this thin layer and the crystal beyond this layer is built, the visually observed surface texture is in fact a result of surface melting. In experiment, large variations might occur, as discussed by Chaplot *et al*,[9] due to the sample not being under thermodynamic equilibrium at a uniform temperature and hydrostatic pressure, or due to sample history etc. Thus the alternative is that there is some systematic error in the experiments.

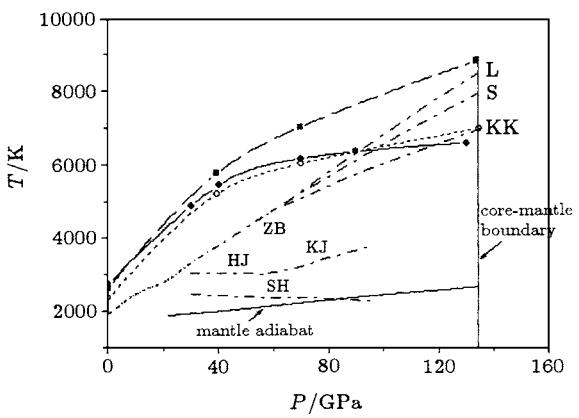


Fig.6. The melting curve of $MgSiO_3$ perovskite. The present simulated melting temperatures (closed circles) are significantly lower than for perfect lattice system (closed squares).[9] Comparison is made with the experimental data[8] up to 62.5GPa and its extrapolations(L, S, KK) to higher pressures using different melting relations as reported in ZB and also with earlier laser heating experiments(HJ,[32] KJ,[33] SH[34], (SH indicates a lower bound only)). The data below 25GPa are from Ito and Katsura[35] and Kato and Kumazawa.[36] The open circles are the molecular dynamics simulations data of the system with 1% vacancies by Chaplot *et al.*[9].

4. Conclusions

In summary, whereas our molecular dynamics simulations reproduce the stability of the orthorhombic perovskite phase up to high pressures of 130 GPa at ambient temperature and are consistent with the theoretical data of Chaplot *et al.*[9] At lower mantle pressures, the transitions are found to occur at temperatures substantially higher than the mantle temperatures. Therefore, it would appear that the 920 km seismic discontinuity[37] may not be related

to any phase transition of the perovskite structure. This strengthens the suggestion of possible chemical changes[37] at that depth, which would have far reaching consequences as it is at variance with the currently accepted mineralogical models assuming chemical homogeneity of the lower mantle.

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