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Influence of New Interaction Potential on MD Simulation of MgSiO₃ Perovskite Thermodynamic Properties

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The interaction potential plays an important role in molecular dynamics (MD) simulations. Pair potential has been used to simulate the melting temperature of MgSiO₃ perovskite in previous studies, but considerable discrepancy of melting temperature exists between these simulations. Comparisons of potential energy curves are performed to explain the discrepancy. To further investigate the influence of the interaction potential parameters on the MD simulation result, a new set of potential parameters is developed based on two fitting potential parameters of previous studies, and is applied in the present study. The simulated molar volume MgSiO₃ perovskite agrees well with the study by Belonoshko and Dubrovinsky at ambient condition. The equations of state, constant-pressure heating capacity and the constant-pressure thermal expansivity of MgSiO₃ perovskite are close to the experimental data. Calculated melting temperatures are also comparable with those derived from previous studies.

Key words: Interaction potential, Molecular dynamics, Melting temperature

I. INTRODUCTION

The most common mineral in the Earth's lower mantle is MgSiO₃ with the perovskite structure. An understanding of its thermodynamic properties is important to describe the Earth's evolution. Therefore the physical properties of MgSiO₃ perovskite under extreme pressure and temperature conditions have attracted the attention of geophysicists [1-3].

The subject of MgSiO₃ perovskite melting has not yet been well understood. The experimental data on material properties at high pressures is still limited, especially under the conditions of both high temperature and high pressure. Computer modeling is particularly useful and powerful for problems that may be inaccessible to direct experiment study, such as extremes in temperature and pressure prevailing deep in the Earth. The prediction of melting by molecular dynamics simulations has been found to be rather extensively applicable, and, furthermore it allows tracking of the physical properties of the atoms not only by global averages but also locally. However, a long-standing disagreement exists concerning the melting of MgSiO₃ perovskite. The melting temperatures simulated on a perfect lattice system [4] appear to be rather high compared to the melting temperature observed in experiments (ZB [5], HJ [6], KJ [7], and SH [8]). The experimental melting temperatures are significantly lower than the values calculated by Chaplot using a system with 1% vacancies [4], and lower than the values reported [9,10]. Alfe *et*

al. have enumerated possible reasons for the discrepancy [11]. For example, the sample may have been subjected to nonhydrostatic or thermal stress (leading to crystal failure for $T < T_m$ [12]). The method of locating the melting point in diamond anvil cell (DAC) experiment at ~ 4000 K may be questioned, because the eye-evident surface texture change is usually used as the melting criterion to the melting of sample heated by laser. Aguado considers that the premelting effect in the melting process is a possible explanation for the difference between experiment and simulation [13]. The above discussions indicate that melting may be a complicated phenomenon.

The previous studies have chosen the same pair-potential model, but with different potential parameters [9,10]. The melting curve of Ref.[10] is in better agreement with the experimental data. It is important to know the influence of the interaction potential parameters on simulation results, but there is no such study to the best of our knowledge. In this contribution, the authors investigate the influence of the potential parameters on the simulation results of MgSiO₃ perovskite. First of all, comparisons of potential energy curves are made to explain the difference of melting temperature that exists in previous studies [9,10]. The rigid-ion two-body potential [14], which is another form of potential used in simulating melting of MgSiO₃ perovskite, is also compared with the pair potential energy curve. To further study the influence of the interatomic potential parameters on the molecular dynamics (MD) simulation result, a new set of potential parameters is developed, based on combining two fitting potential parameters of Ref.[9,10]. Finally, the new set of parameters is employed to calculate the equations of state, the constant-pressure heating capacity and the constant-pressure thermal expansivity which have not

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been calculated in studies [9,10]. The calculated results are in good agreement with experimental data. The ability of the new set of potential parameters to predict these thermodynamics properties provides strong support when applying the new set of potential parameters to further study of the melting curve of MgSiO₃ perovskite at high pressure and high temperature.

II. METHOD

A. Simulation technique

MD simulation is a well-established technique to determine the properties of materials. This method has been applied extensively in previous works [15-18]. Normally, as is often the case in MD calculation, periodic boundary conditions (PBC) are applied. The electrostatic interactions are evaluated both in real and reciprocal space according to the Ewald's method [19].

The present calculations are performed with the shell-dynamo code [20]. Simulations in *NTP* (constant N is the number of particles, T is the temperature, and P is the pressure) ensemble [21] are applied. 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 chosen model of the interatomic interaction depend on, apart from the initial arrangement of particles, the size of the time step (Δt), the number of particles (N), and the temperature of windows (T_{win}). The influence of these parameters was studied by carrying out test runs at various temperatures and pressures. The correct results could be obtained with $\Delta t=0.001$ ps, $T_{\text{win}}=23$ K. Usually, the system was re-equilibrated at the required temperature and pressure for 3 ps and then temperature, pressure and volume were measured over a further 6 ps. 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 0.002 cm³/mol.

The constant-pressure heat capacity C_P and thermal expansivity α_P are calculated from the following definitions.

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (1)$$

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

here, H , E , and V are enthalpy, pressure, and volume, respectively.

B. Interaction potential

In this study, the interaction potential is pair potential, and has the following form:

$$U(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (3)$$

here Z_i or Z_j is an effective charge, e is the electronic unit charge, r_{ij} is the interatomic distance between atoms i and j , A_{ij} and ρ_{ij} are the parameters for the repulsive interaction, and C_{ij} is the van der Waals constant. In Eq.(3) the first part is the long-range Coulomb term and the rest are the short-range terms in the form of a Buckingham [22] potential. The Buckingham potential is a rather traditional model that has been performed sufficiently well [23-26] and, therefore is widely used for modeling of various oxides. The advantages and shortcomings of this kind of model are known [27].

III. RESULTS AND DISCUSSION

A. Comparison of potential energy curves

Figure 1 shows a comparison of potential energy curves. The pair potential energy curve of Ref.[9] is below that of Ref.[10], and the interatomic interaction of Ref.[9] is stronger than that of Ref.[10], therefore the simulated melting temperatures of Ref.[9] are higher than that of Ref.[10]. This indicates that the potential parameters have an important influence on the MD simulations; In Ref.[14], the rigid two-body potential was adopted to study the melting of MgSiO₃ perovskite. However, the melting temperature of Ref.[10] was closer to the experiment data [5] than that of Ref.[14] at 30 GPa. This discrepancy may be explained by comparing energy curve of the pair potential with that of rigid two-body potential. As shown in Fig.1, compared with the study of Ref.[10], the study of Ref.[14] has a lower potential energy curve, and the interatomic interaction of Ref.[14] is stronger than that in Ref.[10]. Because of this, MgSiO₃ perovskite is relatively easier to melt by using the potential model in Ref.[10] than that of Ref.[14]. For the melting of MgSiO₃ perovskite, the rigid ion two-body potential model is not preferable

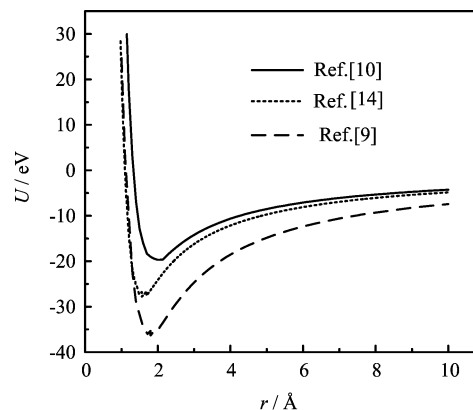


FIG. 1 The potential energy as a function of ion-ion separation for the MgSiO₃ perovskite.

to the pair potential model which is used in the present work.

B. Derivation of the new set of potential parameters

In the crystal structure of MgSiO₃ perovskite, there are two distinct oxygen sites at octahedral corners. Silicons lie in the octahedral centers. Each Si atom is octahedrally coordinated by O atoms. Magnesiums are isolated, compared to silicons and oxygens. The octahedral structure is rather stable. Consequently, the Si–O and O–O interaction may be more important for the properties of MgSiO₃ perovskite than the Mg–O interaction. To further investigate the influence of potential parameters on the MD simulation, the authors design a new set of potential parameters. In the new set of potential parameters, the Si–O and O–O interaction potential, shell charges and spring constants kept the values in Ref.[10], the Mg–O interaction potential is taken from the study of Ref.[9]. The method that transforming the potential parameters of one system into another similar system is available in other literatures. For example, in Ref.[28], the potential parameters of Al–O in Al₂O₃ were used in the MD simulation of MgAl₂O₄. As shown in Ref.[29], the technique generated a set of potential parameters for ZnAl₂O₄ and ZnGa₂O₄: The O–O potential parameters were taken from the work of Bush *et al.* [30]; Zn–O potential parameters were fitted to the hexagonal polymorph of ZnO (wurtzite) respectively. Consequently, the potential parameters used in the present study are derived using this technique, the parameters are: $A_{\text{Mg-O}}=1041.435$ eV; $\rho_{\text{Mg-O}}=0.2673$ Å; $A_{\text{Si-O}}=7363.45$ eV; $\rho_{\text{Si-O}}=0.1900$ Å; $A_{\text{O-O}}=1621.68$ eV; $\rho_{\text{O-O}}=0.3000$ Å; $Z_{\text{O}}=-1.298$; $C_{\text{O-O}}=1621.68$ eVÅ⁶; $Z_{\text{Si}}=+2.329$; $Z_{\text{Mg}}=+1.565$.

C. Equation of state of MgSiO₃ perovskite

The simulated molar volume V_0 (25.071 cm³/mol) agrees well with the study by Belonoshko and Dubrovinsky at the room temperature and pressure of 0.1 MPa, the relative error is within 0.035% [31]. Figure 2 shows that the present pressure-volume relation at 300 K is in excellent agreement with the experimental data of Mao *et al.* [32], and close to the fitting data of Shanker *et al.* [33]. The present calculated values are below that of the studies of Ref.[9,10]. This indicates that MgSiO₃ perovskite using the new set of potential parameters is more easily compressed.

D. Heat capacity and thermal expansivity of MgSiO₃ perovskite

Figure 3 shows that the specific heat capacity at ambient pressure calculated from the present study agrees

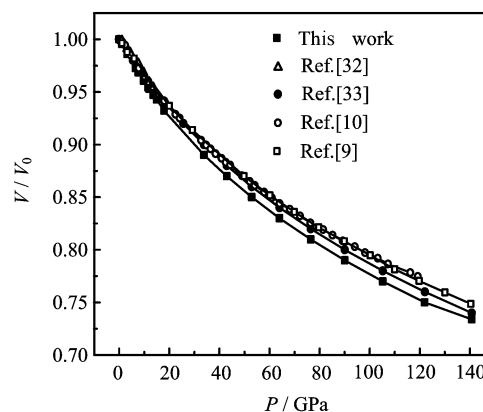


FIG. 2 The equations of state of MgSiO₃ perovskite at 300 K.

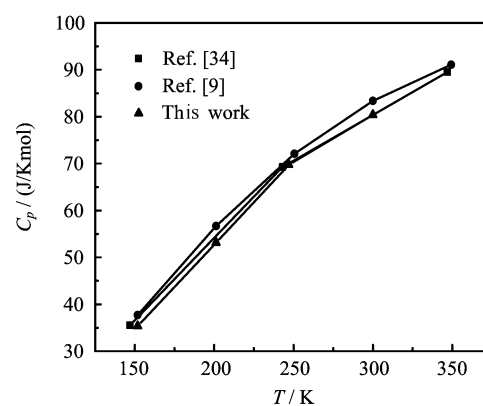


FIG. 3 Heat capacity of MgSiO₃ perovskite.

with the experimental data [34] and better than that of Ref.[10]. The importance of thermal expansivity to the Earth's mantle is well recognized, but it has not been calculated in previous studies [9,10]. The present calculated volume thermal expansivity at ambient pressure is shown in Fig.4. It is closer to the experimental data provided by Mao *et al.* [35] than the theoretical estimation of Anderson and Masuda [36] which was based on thermodynamic arguments from an examination of available data. Thereby, the above results provide a strong support for the new set of potential parameters with which the authors further study the melting curve of MgSiO₃ perovskite at high pressure and high temperature.

E. Melting curve of MgSiO₃ perovskite

Melting is a fundamental first-order change from an ordered solid to a disordered liquid. At the macroscopic level, distinct discontinuities occur in free energy, molar volume, entropy and enthalpy. The changes of these physical properties are often used for identification of melting. In the MD simulations, melting can be iden-

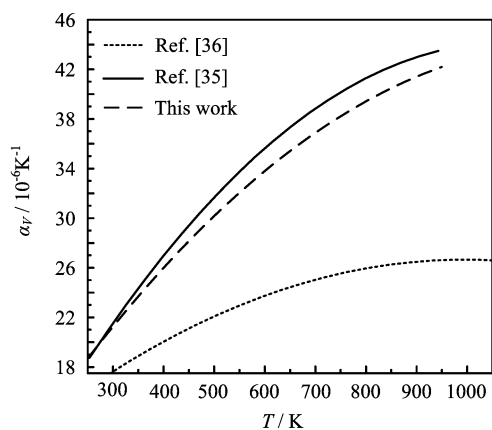


FIG. 4 The constant-pressure thermal expansivity of MgSiO_3 perovskite at 0.1 MPa.

tified by a sudden change in the atomic volume. The corresponding temperature is the melting temperature under given pressure. In the present simulation, at 0.1 MPa, the sudden change of the calculated volume occurs at the temperature of about 2407 K. Note that simulated melting temperature is higher than the experiment melting temperature. This is the result of the existence of substantial metastable overheating. Overheating of a crystal in MD simulation of melting is a well-known phenomenon [37]. It occurs when the long-range order of the crystalline structure is maintained up to certain temperature above the equilibrium melting temperature. According to the modern theory of melting, melting is a dynamic process and melting temperatures of a crystal can be modified by certain melting mechanisms [38], the overheating melting of some crystalline solids at ambient pressure can be concluded as $\theta = T/T_m - 1$, where T_m is the conventional melting temperature for the bulk. This melting process results from temperature increase rate, is not much dependent on pressure, and will be applied to modify the melting temperatures for overheating of crystal. Luo *et al.* [39] have investigated the systematics of nucleation energy barrier (β) for elements and compounds, and the corresponding overheating (θ) as a function of heating rate (Q). They pointed out that significant overheating was achievable via ultrafast heating, and demonstrated that the degree of overheating achieved in shock-wave loading and intense laser irradiation, as well as in molecular dynamics simulations ($Q \sim 10^{12}$ K/s), agree with the established θ - β - Q systematics based on undercooling experiments and homogeneous nucleation theory. Crystalline solids can be superheated by $0.05T_m$ - $0.35T_m$ and $0.08T_m$ - $0.43T_m$ at 1 and 10^{12} K/s, respectively [40]. According to catastrophic melting [41,42] and homogeneous nucleation [38,43] theories, the overheating temperature is about 21.2% higher than normal equilibrium melting point at room pressure. Therefore, in this work the overheating temperature of MgSiO_3 perovskite is assumed to be $0.212 T_m$ in the whole pressure-

temperature range. According to this value, the authors can conclude the melting curve of MgSiO_3 perovskite.

In Fig.5, the present melting curve of MgSiO_3 perovskite agrees with experimental data [5] and better than the study of Ref.[9]. Meanwhile, the present melting curve has a slight difference from that in the study of Ref.[10]. Part of the reason may be that the Si-O and O-O potential parameters used in present work are the same with those used in the study of Ref.[10]. This indicates that the Mg-O potential parameters have smaller influence on the melting of MgSiO_3 perovskite, compared to the Si-O and O-O potential parameters.

IV. CONCLUSION

In this work, comparison of potential energy curves was performed. The data not only provided a possible explanation for the discrepancy of melting temperature between previous studies, but also gave a support for using the pair potential of the present simulation. A new set of potential parameters based on adopting fitting empirical potential parameters was used to simulate the thermodynamic properties of MgSiO_3 perovskite. The

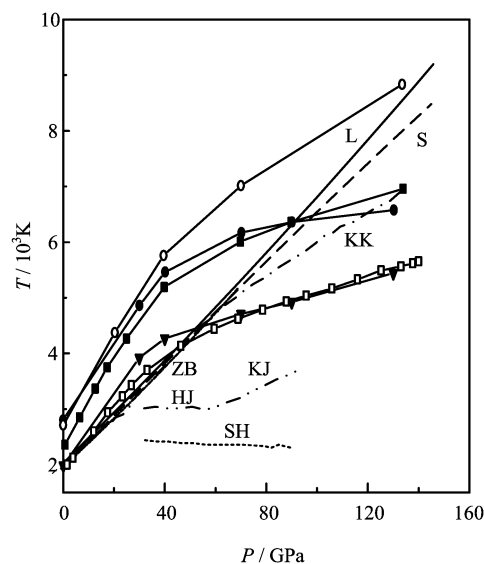


FIG. 5 The melting curve of MgSiO_3 perovskite. The melting temperatures are significantly lower for the present study (closed triangles) than that for the perfect lattice system [4] (open circles), the system with 1% vacancies [4] (closed squares) and the simulation [9] (closed circles). The melting temperatures are close to simulation [10] (open squares). Comparison is made with the experimental data [5] up to 62.5 GPa and its extrapolations Lindemann, Simon, Kraut-Kennedy (L, S, KK) to higher pressures using different melting relations as reported in ZB and also with earlier laser heating experiment (HJ [6], KJ [7], SH [8], (SH indicates a lower bound only)). The present MD simulation is closer to the experimental data by ZB [7]. The data below 25 GPa are from Ref.[44,45].

resulting molar volumes, equation of state, constant-pressure heating capacity and constant-pressure thermal expansivity are close to the experimental data. It was found that the Si–O and O–O interaction is more important than Mg–O interaction for the melting of MgSiO₃ perovskite.

V. ACKNOWLEDGMENT

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