

Influence of Potential Parameters on the Melting Temperature of MgSiO₃ Perovskite

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Abstract The melting temperatures MgSiO₃ perovskite have been calculated in previous studies by using MD simulation, but considerable discrepancy of melting temperature exists between these simulations. In this contribution, 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 combining two fitting potential parameters of previous studies, and is applied in the present study. The melting temperatures are calculated, and also compare with those derived from previous studies.

Keywords Potential parameters · Molecular dynamics · Melting temperature

1 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

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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 MgSiO_3 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 in the Refs. [9] and [10]. Alfè et al. [11] have enumerated possible reasons for the discrepancy. For example, the sample may have been subjected to non-hydrostatic 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 $\sim 4,000$ 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 [13] considers that the premelting effect in the melting process is a possible explanation for the difference between experiment and simulation. The above discussions indicate that melting may be a complicated phenomenon.

The previous studies [9, 10] have chosen the same pair-potential model, but with different potential parameters. 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 MgSiO_3 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 [11], which is another form of potential used in simulating melting of MgSiO_3 perovskite, is also compared with the pair potential energy curve. To further study the influence of the interatomic potential parameters on the MD simulation result, a new set of potential parameters is developed, based on combining two fitting potential parameters of Refs. [9, 10]. Finally, the new set of parameters is employed to simulate the melting curve of MgSiO_3 perovskite.

2 Method

2.1 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 particules (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, $T_{win} = 23$ 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 $0.002 \text{ cm}^3/\text{mol}$.

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.

2.2 Interaction Potential

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

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

where 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 from Ref. [27]. 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.

3 Results and Discussion

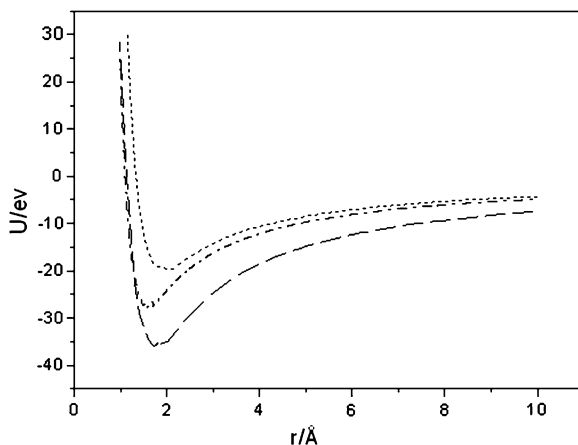
3.1 Comparison of Potential Energy Curve

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 the study of Ref. [14], the rigid two-body potential is adopted to study the melting of MgSiO_3 perovskite. However, the melting temperature of study 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, the study of Ref. [14] has a lower potential energy curve than the study of Ref. [10], and the interatomic interaction of Ref. [14] is stronger than that of Ref. [10]. Because of this, MgSiO_3 perovskite is relatively easier to melt by using the potential model in Ref. [10] than that of Ref. [14]. For the melting of MgSiO_3 perovskite, the rigid ion two-body potential model is not preferable to the pair potential model which is used in the present work.

3.2 Derivation of the New of Potential Parameters

In the crystal structure of MgSiO_3 perovskite, there are two distinct oxygen sites at octahedral corners. Silicones lie in the octahedral centers. Each Si atom is octahedrally coordinated by O atoms. Magnesiums are isolated, compare to silicones and oxygens. The octahedral structure is rather stable. Consequently, the

Fig. 1 The potential energy as a function of ion–ion separation for the MgSiO_3 perovskite. The dash dot line represents potential energy curve of Matsui et al. [14], the dots represent the potential energy curve of the study of Ref. [10] and the dashes represent the potential energy curve of the study of Ref. [9]



Si–O and O–O interaction may be more important for the properties of MgSiO_3 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 potential parameters, shell charges and spring constants are kept at the values used in the study of Ref. [10], the Mg–O potential parameters are taken from the study of Ref. [9]. The method that transforming the potential parameters of one system into another similar system is available in the other literatures for example, in the study of Ref. [28], the potential parameters representing short-range interactions between Al_{3+} and O_{2-} in Al_2O_3 were used in the MD stimulation of MgAl_2O_4 . As shown in Ref. [29], the technique generated a set of potential parameters for ZnAl_2O_4 and ZnGa_2O_4 : The Oxygen–Oxygen short range potential were taken from the work of Bush et al. [30]; Zn–O potential were fitted to the hexagonal polymorph of ZnO (wurtzite); and the Al–O and Ga–O potential parameters were determined by fitting to $\alpha\text{-Al}_2\text{O}_3/\text{ZnAl}_2\text{O}_4$ and $\text{Ga}_2\text{O}_3/\text{ZnGa}_2\text{O}_4$ respectively. Consequently, the potential parameters used in the present study are derived using this technique, the parameters are: $\text{AMg-O} = 1,041.435 \text{ eV}$; $\rho\text{Mg-O} = 0.2673 \text{ \AA}$; $\text{ASi-O} = 7,363.45 \text{ eV}$; $\rho\text{Si-O} = 0.1900 \text{ \AA}$; $\text{AO-O} = 1,621.68 \text{ eV}$; $\rho\text{O-O} = 0.3000 \text{ \AA}$; $\text{CO-O} = 1621.68 \text{ eV \AA}^6$; $\text{ZMg} = +1.565$; $\text{ZSi} = +2.329$; $\text{Zo} = -1.298$.

3.3 Melting Curve of MgSiO_3 Perovskite

Melting is probably the most familiar first-order transition; it covers the widest range of pressures and temperature. It exhibits discontinuities in the first derivatives of the volume, free energy and entropy. The changes of these physical properties are often used for identification of melting. In the MD simulations, melting can be identified 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 a temperature of about 2,407 K. Note that simulated melting temperature is higher than the experiment melting temperature. The reason is that MD simulations in free space are usually known to exhibit high hysteresis especially at low pressure [31]. This prevents us from judging how well the experimental value of melting temperature at 0.1 MPa pressure is reproduced. Cohen and Gong [31] noted the high hysteresis at 0.1 MPa; this hysteresis decreases with the increasing pressure. The high simulated temperature 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. 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 [32], the overheating melting of some crystalline solids at ambient pressure can be written as $\theta = T/T_m - 1$, where T_m is the conventional

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 same with those used in the study of Ref. [10]. This indicates that the Mg–O interaction parameters have smaller influence on the melting of MgSiO₃ perovskite than the Si–O and O–O interaction parameters.

4 Summary

In this paper, 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 suitable empirical potential parameters was used to simulate the thermodynamic properties of MgSiO₃ perovskite. The 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.

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