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Molecular Dynamics Simulation of MgO Melting at High Pressure

Shou-yi Li*, Zheng-lai Liu, Ya-gong Nan, Zhi-rong Zhang

Department of Physics, Hexi University, Zhangye 734000, China

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Molecular dynamics simulation was used to study the melting of MgO at high pressures. The melting temperature of MgO was accurately obtained at elevated temperature and high pressure after corrections based on the modern theory of melting. The calculated melting curve was compared with the available experimental data and other theoretical results at the pressure range of 0-135 GPa. The corrected melting temperature of MgO is in good agreement with the results from Lindemann melting equation and the two-phase simulated results below 15 GPa.

Key words: Melting temperature, Molecular dynamics simulation, High pressure

I. INTRODUCTION

The phenomenon of melting has attracted much attention for a long time [1,2]. The knowledge of the melting temperatures of minerals of the Mg-Fe-Si-O system is very useful in chemical differentiation and rheology, and is also fundamental for understanding of the geodynamics of the Earth's lower mantle. Therefore, determination of the melting curves of these materials in a broad pressures range has remained a major challenge [3,4]. The difficulties in experimental measurement have greatly limited the availability of the melting data, resulting in a poor understanding of the melting mechanism of solids at high pressure conditions. Molecular dynamics (MD) simulation is quite suitable for calculation of thermoelastic properties of a solid or a melt. However, as a complex phenomenon, melting is believed to be initiated around defects, including various point defects and extended defects at the surface. In order to deal with the complexities, various techniques have been applied to evaluate the melting phenomenon, such as the two-phase, bulk transition, radial distribution functions (RDF), snap shot techniques, and so on. MD simulation not only allows one to track the physical property averages of the atoms globally, but also locally. This capability is indispensable for corrections between the theories and the atomic-level mechanisms at the onset of melting.

MgO has been extensively studied at high pressure because of its simplicity in structure and its geophysical importance. It is an important component of the Earth's lower mantle in the form of magnesiowüstite-(Mg, Fe)O, whose stability at high pressures [5] makes the pressure calibration standard for high pressure and temperature experiments. Estimation of the melting temperature and other thermodynamic parameters of MgO at elevated temperatures and high pressures is important for understanding the mantle structure. Several theoretical methods have been applied to MgO; and several of these studies used semiempirical or simplified nonempirical models (e.g., potential-induced breathing model) [6-8]. Lattice dynamics of MgO has been studied with first principles only at zero pressure, although its elasticity has been determined at high pressure [9,10]. MgO has also been extensively employed in the development of experiment methods for shear strength determination at low pressure (to 40 GPa). A major problem with current data, however, is that the equation of state from shock, ultrasonic, and static experiments are not consistent with each other. Furthermore, theoretical models for MgO have been complicated by questions concerning the degree of ionicity and characterization of the charge distribution of oxygen [5]. In this work, we apply the two-body empirical potential MD method to study the melting of MgO at high pressures. Meanwhile, the radial distribution function of MgO is also calculated.

II. THEORETICAL METHODS

MD simulation is a well-established technique for ionic solid studies [11], especially for studying the effects of high pressure and elevated temperature on the properties of the solids. This method solves the numerically equations of atomic motions, by assuming initial coordinates and velocities of atoms and a model of interaction potential between them. The system is made pseudo-infinite by the application of periodic boundary conditions. A simulation proceeds in a series of time steps. At each step the forces resulting from the interactions are evaluated.

Simulations in the *NTP* ensemble were performed. The system consisted of 216 particles (108 Mg and 108 O). For the rocksalt structure, this is equivalent to 3×3×3 unit cells. The results of MD simulations in the *NTP* ensemble with the chosen model of the in-

*Author to whom correspondence should be addressed. E-mail: lisy@hxu.edu.cn

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teratomic interaction depend on, apart from the initial arrangement of particles, the size of time step τ, the number of time steps n, and the number of particles N. Therefore, the influence of these parameters was carefully studied by carrying out runs at various T and P. It was found that equilibration was normally reached with n=2000 and τ=1 fs.

We used the following interaction potentials:

$$U_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \cdot \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{{r_{ij}}^6} \quad (1)$$

where the right-hand side terms represent Coulombic part, repulsion energy and van der Waals force, respectively. Here Z_i or Z_j is the effective charge, e is the electronic unit charge, A_{ij} and B_{ij} are parameters for the repulsive interaction, C_{ij} is the van der Waals constant.

The long-range electrostatic interactions are evaluated both in real and in reciprocal space according to the Ewald's method [12]. The short-range non-Coulombic potential parameters (A_{ij}, B_{ij} and C_{ij} in Eq.(1)) are given in Ref.[13]. Mitchell *et al.* have studied the pressure-volume-temperature relations for MgO at high pressures and temperatures [14]. Our results were compared with those of other works, so agreement is available.

III. RESULTS AND DISCUSSION

Melting is the first-order phase change from an ordered solid to a disordered liquid. The melting curve of MgO was calculated at constant pressure MD simulations. The melting transition starts at 3758 K under the pressure of 0.1 MPa. As in Fig.1 the mean atomic volume undergoes a sudden upward jump, the temperature is higher than that for normal melting. It can be seen that the calculated temperature is about 22% higher than normal equilibrium melting point 3083 K. This is the result of the existence of a substantial metastable overheating. Overheating of a crystal in MD simulation of melting is a well-known phenomenon [15,16]. Overheating happens with several possibilities. Firstly, a nucleus of melt is unstable unless it reaches a certain size [17], and the size might be quite large compared with the size of the computation box (which usually does not exceed a few dozen angstroms). Therefore, the appearance of melt is suppressed by the size of a stable nucleus. Secondly, the creation of an interface between solid and melt requires excess energy, which can be available by increasing the system temperature. Thirdly, simulations at constant volume might lead to instability of both solid and liquid phases (the volume is too small for a liquid and too large for a solid) [18]. Therefore, we believe that bulk transition simulation

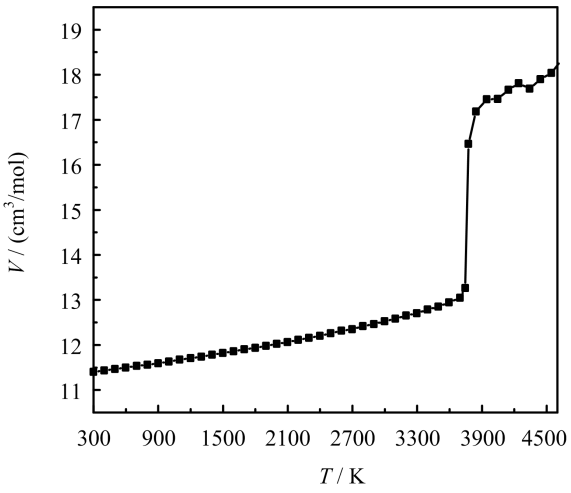

FIG. 1 The MD calculated volume of MgO at a pressure of 0.1 MPa. The volume exhibits a abrupt change at a temperature of about 3758 K.

at constant pressure indeed provides a useful tool for studying the melting transition. According to modern theory of melting, melting is a dynamic process and melting temperatures of a crystal can be modified by certainly melting mechanism [19], corresponding overheating melting of MgO at ambient pressure can be concluded from

$$\frac{T - T_m}{T_m} = 0.22 \quad (2)$$

where T_m is the conventional melting temperature for the bulk. This melting process resulting from the temperature increase is basically independent on the pressure, and can be applied to correct the melting temperatures for overheating of crystal.

Figure 2 compares the calculated pressure dependence of the melting transition of MgO with experimental data and other theoretical calculations. For a comparison, Lindemann law is used to extrapolate the high pressure melting temperatures. It is clear that the Lindemann melting equation, MD simulations, and two-phase simulated results of MgO are in excellent agreement in the lower pressure range [20]. At high pressure, Lindemann melting curve has a higher melting slope, significantly deviating from the exact melting of MgO. This is due to the fact that empirical melting equation is based on early experimental results with melting measurements covering a relatively lower pressure range [21]. MD calculation curves for the melting of MgO and other theoretical results are systemically with larger pressure range than that from experiments [22]. In experiments, the eye-evident surface texture change is usually used as the criterion of melting of the samples heated by laser in diamond anvil cell (DAC) experiments. 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

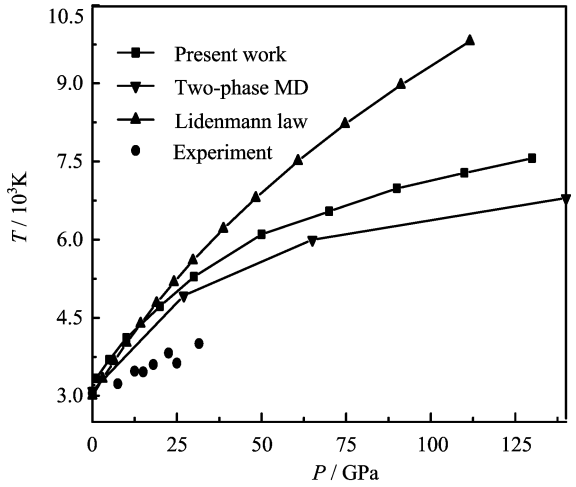

FIG. 2 Melting curve of MGO from MD simulation.

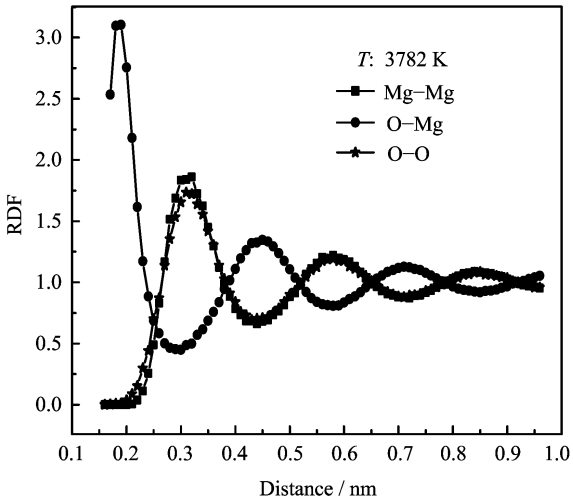

FIG. 4 RDFs for Mg−Mg, O−Mg, and O−O at 3782 K and at 0.1 MPa.

built, the eye-sighted surface texture is in fact a result of surface melting. In an experiment, large variations might occur, as discussed by Chaplot *et al.* [23], due to the sample not being under thermodynamic equilibrium at a uniform temperature and hydrostatic pressure, and due to sample history etc. Thus, there is generally some systematic error in the experiments.

RDF is one of the most important structural quantities used to characterize a system, particularly for liquids. Melting and crystallizing can also be identified from the long-range disorder and order manifested in RDF's. Figure 3 and 4 show the structure of MgO at pressure 0.1 MPa and two temperatures, i.e. 3000 and 3782 K. There are changes of MgO with the NaCl structure from a solid to liquid structure when heated. As one can see, the difference between two structures is quite evident. At 3000 K, the RDFs of Mg−Mg, O−Mg, and O−O ion pairs are rather clear with the solid structure. When the temperature is 3782 K, the RDFs of these ion pairs show an obvious first peak, a visible second peak and a featureless tail. The absence of strong peaks in the RDFs at distances larger than the position for the second peak is typical for non-crystalline structure, and this is the indication that the rocksalt structure has lost its long-range order and has begun melting. So, the simulated melting temperature is bracketed between 3000 and 3782 K.

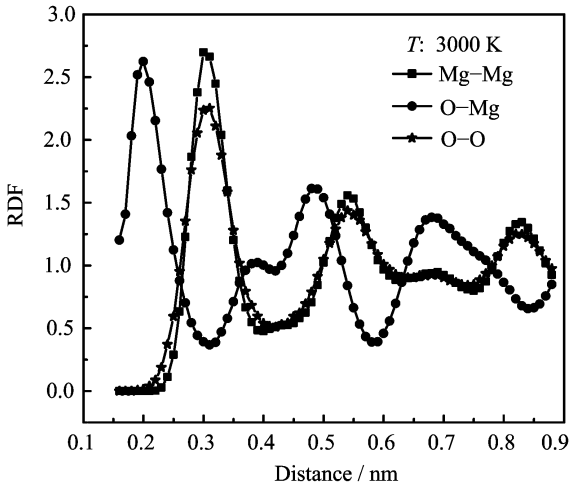

FIG. 3 RDFs for Mg−Mg, O−Mg, and O−O at 3000 K and at a pressure of 0.1 MPa.

IV. CONCLUSION

In this work, MD simulations of the MgO with two-body empirical potential were presented using the interaction potentials in order to investigate the behavior of melting behavior at high pressures. Our simulated melting temperature of MgO is consistent with results obtained from Lindemann melting equation and the two-phase simulated results with an ideal lattice in the lower pressure range. It can be see that MD simulated curves for the melting of MgO and other theoretical results are systemically higher than the experimental measurements. This is because that the eye-evident surface texture change is usually used as the melting criterion to the melting of samples heated by laser in DAC experiments. At the end, we have calculated the RDFs for each pair of Mg and O atoms at 0.1 MPa, and at the temperatures of 3000 and 3782 K, respectively. The melting properties of MgO are summarized in the temperature 300-4500 K ranges and the pressure up to 135 GPa.

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