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Melting and Grüneisen parameters of NaCl at high pressure*

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The Buckingham potential has been employed to simulate the melting and thermodynamic parameters of sodium chloride (NaCl) using the molecular dynamics (MD) method. The constant-volume heat capacity and Grüneisen parameters have been obtained in a wide range of temperatures. The calculated thermodynamic parameters are found to be in good agreement with the available experimental data. The NaCl melting simulations appear to validate the interpretation of superheating of the solid in the one-phase MD simulations. The melting curve of NaCl is compared with the experiments and other calculations at pressure 0–30GPa range.

Keywords: NaCl, melting, Grüneisen parameter, constant-volume heat capacity, molecular dynamics method

PACC: 6250, 7115Q, 6540

1. Introduction

The melting mechanism of solids has attracted the attention of researchers both theoretically and experimentally.[1−4] Recent advances, particularly the development of high-temperature diamond anvil cell (DAC) techniques [5,6] have led to an order of magnitude increase in the pressure range accessible for study, but due to the experimental difficulties, only limited results have been generated as available data. As for theoretical investigations, molecular dynamics (MD) has been used as a powerful tool to simulate the melting of solids.

As a first-order phase transition, melting exhibits discontinuities in the first derivatives of the free energy, volume and entropy. The changes of these physical properties are often used for identification of melting at high pressures. In the MD simulations, Jin *et al*[7] examined the validity of the Born criterion. They found that the idealized crystal could be superheated by about 20% (in terms of absolute temperatures); melting occurred when the elastic shear modulus of the crystal lattice came very close to zero. Mechanical melting was identified by a sudden change in the atomic volume.

The Grüneisen parameter (γ) is an important quantity in geophysics as it often occurs in equations which describe the thermoelastic behaviour of materials at high pressures and temperatures. The value for γ is used to place constraints on geophysical important parameters such as the pressure and temperature dependence of the thermal properties of the mantle and core, the adiabatic temperature gradient and the geophysical interpretation of Hugoniot data. Meanwhile, γ is closely related to classical melting equations: Lindemann, Simon and Kraut–Kennedy equations. But the experimental determination of γ is extremely difficult.[8] Complementary to experiment, MD simulations have been employed to calculate the Grüneisen parameter and melting curve of NaCl at high pressures and temperatures.

2. Method of simulation

2.1. Technique of simulation

Molecular dynamics simulation is a well-

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established technique in ionic solids, especially for studying the effects of high pressure and high temperature on the properties of solids. The simulations used 1000 ions. Systems of 1000 ions were simulated within periodic boundaries with Coulombic interactions handled by means of the Ewald method.[9] The system is then allowed to evolve in time by solving the classical equations of motion using a specified time step τ. We took a time step τ=1fs. Volumes were determined by carrying out simulation at constant pressure and temperature. These measurements are very accurate. Usually we re-equilibrated at the required temperature and pressure for 10ps and then measured the temperature, pressure and volume over a further 10ps. Typically the actual temperature differs from the required temperature by less than 1K, the actual pressure differs from the required pressure by less than 1MPa, and the standard discrepancy in the volume was less than $0.002\text{cm}^3/\text{mol}$.

The calculations have also been carried out under constant volume. Heat capacity at constant volume C_V and Grüneisen coefficient γ are calculated by the following definitions:

$$C_\text{V} = \left(\frac{\partial E}{\partial T}\right)_\text{V}, \tag{1}$$

and

$$\gamma = V\left(\frac{\partial P}{\partial E}\right)_\text{V}. \tag{2}$$

2.2. Interatomic potentials

The potential energy function $U(r_1,\ r_2, \ldots, r_N)$ expresses the energy of an assembly of N atoms or ions as a function of nuclear coordinates $r_1,\ r_2, \ldots, r_N$. It is commonly expanded as follows:

$$U = \sum_i^N \sum_j^N {}' u_{ij}(r_i, r_j) + \sum_i^N \sum_j^N \sum_k^N {}' u_{ijk}(r_i, r_j, r_k) + \cdots, \tag{3}$$

where the u_{ij} are two-body functions which depend only on the positions of pairs of atoms i and j; u_{ijk} are the three-body terms depending explicitly on the positions of atoms i, j, and k. The expanded form can be extended to four-body terms u_{ijkl} and higher order terms. And it has been common to approximate U by including only the two-body component u_{ij}, which may be usefully decomposed into the Coulombic and non-Coulombic terms:

$$u_{ij}(r_i, r_j) = \frac{1}{4\pi\varepsilon_0}\frac{Z_i Z_j e^2}{r_{ij}} + u_{ij}^\text{NC}(r_{ij}), \tag{4}$$

where r_{ij} is the interatomic distance between ions i, j and Z_i is an effective charge of the ith ion. The non-Coulombic part of the interaction u_{ij} is usually approximated by analytical functions which generally include both attractive and repulsion components. For many ionic materials, the predominant short-range potential is the Buckingham (with a possible inverse eight power term) potential. The two-body potential consists of a repulsive exponential term and an attractive dispersion term between pairs of species:

$$u_{ij}^\text{NC}(r_{ij}) = A_{ij}\exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8}, \tag{5}$$

where C_{ij} and D_{ij} are van der Waals constant, A_{ij} and B_{ij} are parameters for the repulsive interaction. Values of the parameters [10] of NaCl used in simulations are listed in Table 1.

Table 1. Parameters of the potential of NaCl used in simulations.

Source	A/eV	B/nm	$C/10^{-6}\text{eV}\cdot\text{nm}^6$	$D/10^{-8}\text{eV}\cdot\text{nm}^8$
Na–Na	487	0.4208	1.05	0.499
Na–Cl	14514	0.4208	6.99	8.675
Cl–Cl	405774	0.4208	72.40	145.425

The performance of these potential is rather good for describing NaCl at pressures up to 100GPa.[10]

3. Results and discussion

3.1. NaCl melting curve

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. At the microscopic level, melting occurs when there is a marked and continuous increase in the mean squared displacements of the individual species as their increased energy allows them to dissociate from the solid

structure.[11] The melting curve of NaCl was calculated by the method of constant pressure MD simulations. MD calculated volumes at 1×10^5Pa and at temperatures from 1000 up to 1600K are shown in Fig.1. Note that the sudden change of the MD calculated volume of NaCl occurs at a temperature of

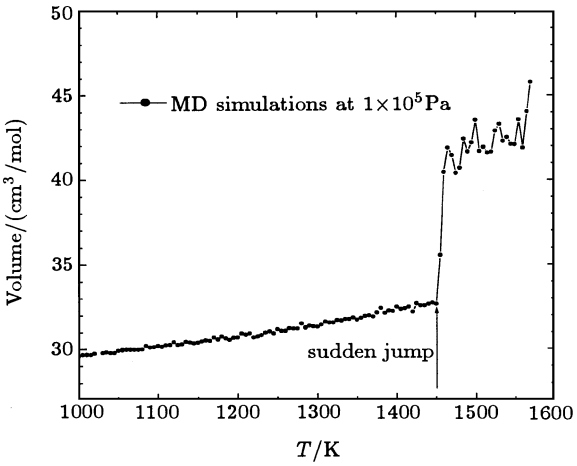


Fig.1. The calculated volume of NaCl at a pressure of 1×10^5Pa as a function of temperature.

about 1445K, which is about 25% higher than normal equilibrium melting point. This is the result of the existence of a substantial metastable overheating. Instable 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. But, according to modern theory, melting is a dynamic process and the melting temperature of a crystal can be modified by a certain melting mechanism,[12] and the corresponding overheating melting of NaCl at ambient pressure can be described as

$$(T_{\rm m} - T_{\rm mo})/T_{\rm m} = 0.25, \qquad (6)$$

where $T_{\rm mo}$ is the conventional melting temperature for the bulk. This melting process resulting from the temperature increasing rate is not much dependent on the pressure, and will be applied to correct the melting temperatures for overheating of crystal. Figure 2 compares the calculated pressure dependence of the melting transition of NaCl with experimental results and other calculations. Note that the present melting curves of NaCl are in good agreement with the theoretical data of two-phase MD simulations by Belonoshko and Dubrovinsky.[13] In the lower pressure range (<7GPa), the estimates using the Lindemann melting equation, MD simulations and Wang's empirical model [14] for the melting of NaCl are in excellent agreement with the experimental results obtained by Boehler *et al* using a laser-heating DAC technique,[5] and by Akella *et al* using a piston cylinder apparatus and differential thermal analysis.[15] In the pressure above 7GPa, MD calculation curves for the melting of NaCl are systemically higher than Boehler *et al*'s experiments. This is the reason 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.[5] 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 eye-sighted surface texture is in fact a result of surface melting. In experiments, large variation might occur, as discussed by Chaplot *et al*,[16] due to the sample not being under thermodynamic equilibrium at a uniform temperature and hydrostatic pressure, and due to sample history etc. Thus, the alternative is that there is some systematic error in the experiments. The estimations from the Lindemann melting equation are quite different at pressure above 7GPa. With increasing pressure, the difference tends to be remarkable. 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 (<7GPa).[14]

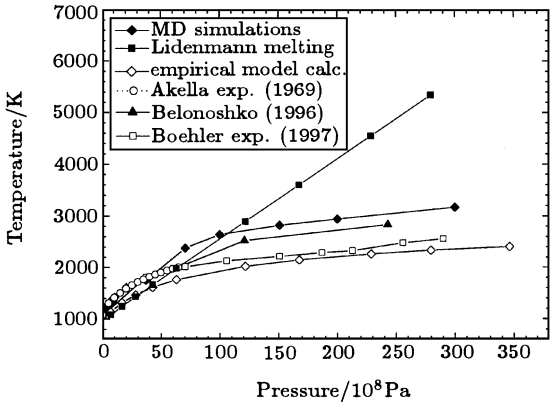


Fig.2. The melting temperature of NaCl as a function of pressure.

3.2. NaCl RDFs near the melting temperature

The radial distribution function (RDF) reflects the microscopic structure of the system. Melting and crystallizing can also be identified from the long-range order manifested in RDFs. Figures 3(a)–(c) show respectively RDFs calculated for Na–Cl, Na–Na, and Cl–Cl at three temperatures (1058, 1116, 1171K) and at a pressure of 1×10^5Pa. Note the change of NaCl from a solid to a solid-like, and to liquid structure when heated. Thus we found that at 1058K,

i.e $T < T_{mo}$=1078K (melting temperature),[5] the RDFs of Na–Cl , Cl–Cl, and Na–Na ion pairs have rather characteristic solid structure; at T=1116K, i.e $T > T_{mo}$, the NaCl remains in a solid-like structure; and at 1171K, the NaCl solid loses its long-range order and melts. So, T_{mo} lies between 1058 and 1171K.

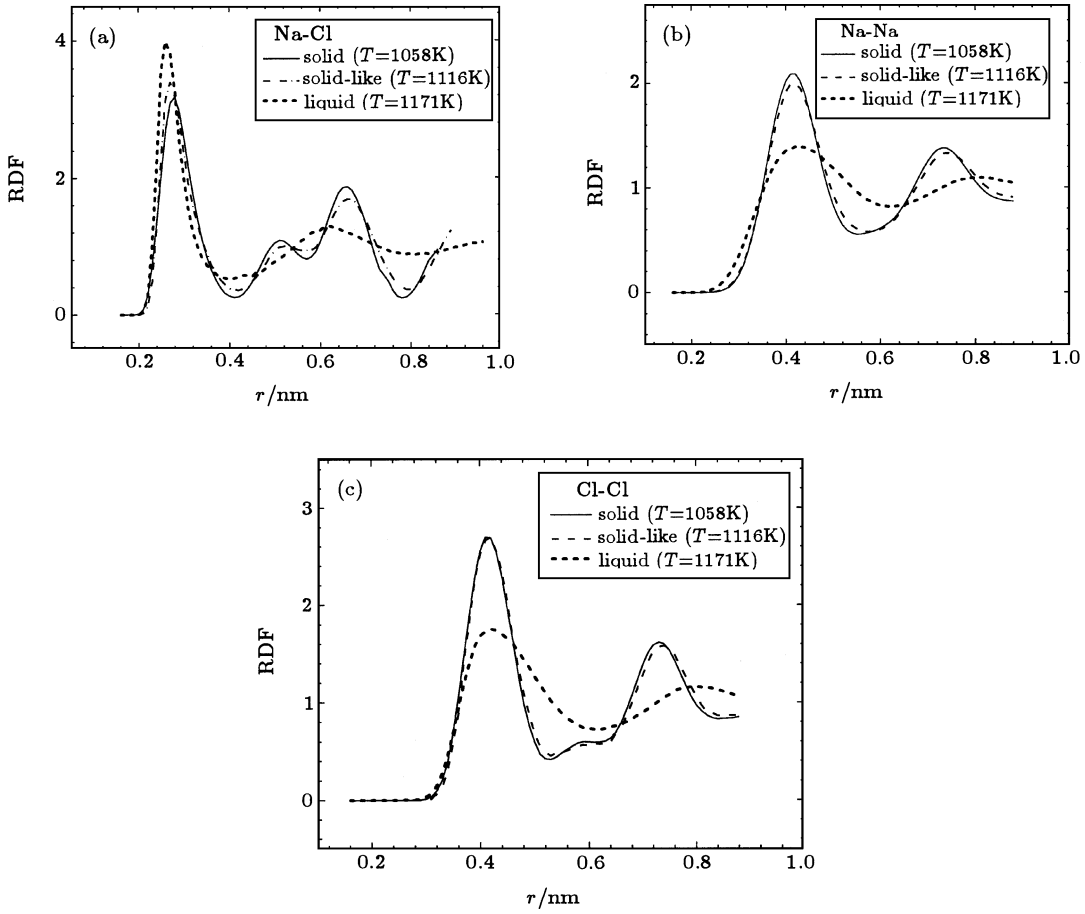


Fig.3. RDFs calculated for Na–Cl, Na–Na, and Cl–Cl at three temperatures (1058, 1116, 1171K) and at a pressure of 10^5Pa.

3.3. Grüneisen parameter and constant-volume heat capacity of NaCl

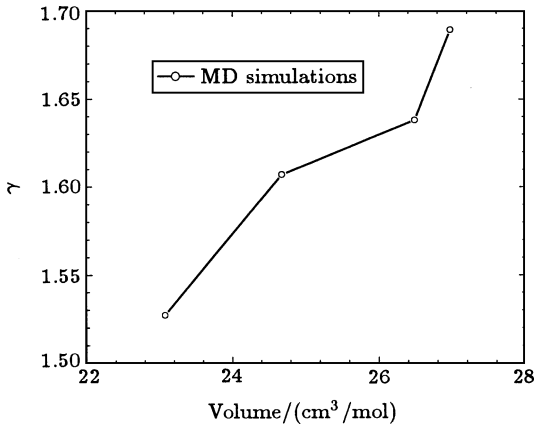


Fig.4. Volume dependence of Grüneisen parameter (γ).

Some useful thermodynamic parameters for NaCl solid was calculated by the method of constant-volume molecular dynamics simulations according to the definitions of Grüneisen parameter (γ) and constant-volume heat capacity (C_V), as shown in Figs.4 and 5. Note that Grüneisen parameter (γ) depends strongly on volume. The experimental Grüneisen parameter γ at the normal state is 1.63.[17] We have calculated the Grüneisen parameter (γ=1.69) at the normal state: about 3.6% discrepancy. The constant-volume heat capacity C_V increases as the specific volume decreases (or the density increases) and increases as temperature grows (as shown in Fig.5), but increases slowly at high density as temperature grows. We can see that the influence of increasing temperature at high density on the constant-volume heat capacity is very

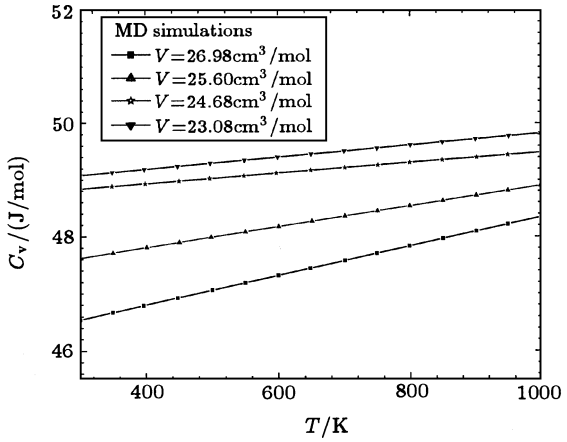


Fig.5. The constant-volume heat capacity at different volumes versus temperature.

small and even may be neglected at above 2.5g/cm^3. The experimental constant-volume heat capacity C_V of NaCl solid at the normal state is C_V=47.6J/mol.[18] We calculated the constant-volume heat capacity of NaCl solid at the normal state (V=26.98cm^3/mol, T=300K) and obtained C_V=46.54J/mol. Both results agree very well.

4. Summary

The Buckingham potential has been employed to simulate the thermodynamics of NaCl using the MD method. The constant-volume heat capacity, Grüneisen parameter, and melting curves of NaCl have been obtained. The simulated results are in general agreement with previous experimental and formal theoretical studies. The NaCl melting simulation appears to validate the interpretation of superheating of solid.[7] Grüneisen parameter γ is strongly dependent on volume. The influence of increasing temperature at high density on the constant-volume heat capacity is very small.

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