Isothermal bulk modulus and its first pressure derivative of NaCl at high pressure and high temperature*

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The isothermal bulk modulus and its first pressure derivative of NaCl are investigated using the classical molecular dynamics method and the quasi-harmonic Debye model. To ensure faithful molecular dynamics simulations, two types of potentials, the shell-model (SM) potential and the two-body rigid-ion Born–Mayer–Huggins–Fumi-Tosi (BMHFT) potential, are fully tested. Compared with the SM potential based simulation, the molecular dynamics simulation with the BMHFT potential is very successful in reproducing accurately the measured bulk modulus of NaCl. Particular attention is paid to the prediction of the isothermal bulk modulus and its first pressure derivative using the reliable potential and to the comparison of the SM and the BMHFT potentials based molecular dynamics simulations with the quasi-harmonic Debye model. The properties of NaCl in the pressure range of 0–30 GPa at temperatures up to the melting temperature of 1050 K are investigated.

Keywords: isothermal bulk modulus, NaCl, high pressure, high temperature

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1. Introduction

The pressure–volume–temperature relationship and the bulk modulus data are required for investigating the equation of state (EOS) and characterizing the anharmonic dynamic properties under the effects of pressure and temperature. The isothermal bulk modulus, especially its pressure and temperature dependences, has been studied by many researchers because of its basic role in the EOS and the description of the behavior of solids in the high-pressure and high-temperature science.[1−3] Experiments prove that the bulk modulus K_T depends on volume V and pressure P at a constant temperature T. It is usually defined as

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T. \tag{1}$$

NaCl is an important material and a typical ionic solid used as a pressure gauge in laboratory measurements of compression data.[4] This is one of the most widely used internal pressure standards in high-pressure diffraction experiments due to the availability of the large body of experimental data. NaCl has a stable structure under the pressure up to about 30 GPa,[5] and its melting temperature is nearly 1074 K.[6] Thus we have wide ranges of pressures and temperatures for studying the isothermal bulk modulus of NaCl. The variation of isothermal bulk modulus K_T, which plays a central role in the formulation of approximate EOS at high pressure and high temperature, is still limited. On the other hand, the development of computer simulations changes substantially the relationship between theory and experiment. The simulation results of NaCl can sometimes be compared directly with the experimental results. Therefore, the computer simulations based on the interionic interactions have been applied extensively to investigate the microscopic structures of a wide variety of chemical and physical properties at high pressure and high temperature.

In the present work, we use molecular dynamics (MD) simulations with two different potential models respectively to predict the isothermal bulk modulus K_T for NaCl crystal under high pressure and high temperature. The first one is the shell-model (SM) potential,[7] which is due to the short-range in-

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teraction between pairs of ions when they are moved together. This interaction is similar to that due to the motion of the positive and the negative ions in the polarization of a crystal. And the second one is the two-body rigid-ion Born–Mayer–Huggins–Fumi-Tosi (BMHFT) potential[8] with a full treatment of the long-range Coulomb forces. The first pressure derivative of isothermal bulk modulus K_T for NaCl is investigated by means of first-principles density functional theory calculations combined with the quasi-harmonic Debye model,[9] in which the phononic effects are considered. In the following section, we briefly describe the calculated methods used in this work. In Section 3, we present and discuss our results obtained from the effective pair-wise interactions and the quasi-harmonic Debye model, and predict the isothermal bulk modulus K_T and its first pressure derivative K'_T for NaCl under extreme P and T conditions (up to 30 GPa and 1050 K) where the reliable experimental data are scarce. The paper ends with the main conclusion of our investigation in Section 4.

2. Computational details

The MD calculation for NaCl was performed in a system of 512 ions (Na^+: 256, Cl^-: 256) initially arranged in the rock-salt type crystal structure. In the present study, all of the calculations were performed using a program developed by ourselves. The standard constant pressure–temperature calculation on the thermodynamic equilibrium was performed. The lattice containing a fixed number of atoms was assumed to be repeated periodically throughout the material, and there was no edge or surface effect.

The prerequisite condition for the success of the MD simulation is the availability of reliable interatomic potentials describing the interaction between ions in the crystalline lattice. In the present MD simulations, the effective ionic two-body potential model reported in the previous papers[10−12] was employed for the interatomic potential function between sodium and chlorine

$$U_{ij}(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij}\exp\Big(-\frac{r_{ij}}{\rho_{ij}}\Big) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8}, \quad (2)$$

where e is the charge of one electron, q_i and q_j are the point charges associated with the ion species, r_{ij} is the distance between them, A_{ij} and ρ_{ij} are the parameters for the repulsive interaction, and C_{ij} and D_{ij} are the van der Waals constants. In order to obtain reasonable values for the static and the high frequency dielectric constants of NaCl, it was necessary to use the SM for the chlorine ions. The values of the parameters of NaCl used in the simulations were given in Ref. [13]. The equations of motion were integrated using Verlet's algorithm[14] with an integration time step of 1.0×10^{-15} s. At the beginning of the calculation, the initial velocity of each atom was assumed to take a random value, which was about 0.01 Å fs^{-1}. The simulation technique and the conditions were the same as those in our previous study.[15]

Various potential parameters for the NaCl system have been proposed,[12,13,16] and a cross-checking is necessary. A series of isotherms of MD simulations were performed in the temperature range from 298 K to 1000 K and the pressure range from 0 GPa to 30 GPa[6] by using the SM potential[13] and the other potentials. The calculated values using the SM potential were very close to the experimental data in the above temperature–pressure domain, while those obtained using the *ab initio* interionic potential given by Zhang and Chen[16] had a little difference from the experimental data in the high pressures. The reason for this is that the Na–Na interaction in the *ab initio* interionic potential only includes the Coulomb potential.[16] The above discussion shows that the present SM interionic potential supports the accuracy and realism of the calculations. The performance of this potential is good for describing the properties of sodium chloride. Meanwhile, the two-body rigid-ion Born–Mayer–Huggins–Fumi–Tosi (BMHFT) potential[8] with a full treatment of the long-range Coulomb forces was used and the performance of the potential is also rather good for describing NaCl at temperatures up to 1400 K.[12] Particular attention is paid to the comparison of the two simulations.

In the present study, efforts have also been taken to shed more light on the physical properties. The pressure derivative of isothermal bulk modulus was calculated by using the plane wave pseudo-potential density functional theory method and the quasi-harmonic Debye model,[9] which allowed us to obtain all thermodynamics quantities from the calculated energy–volume data. In the electronic structure calculations, the ultrasoft pseudo potentials introduced by Vanderbilt[17] have been employed for all the ionelectron interaction. The exchange correlation potential of Ceperley and Alder[18] parameterized by Perdew and Zunger[19] in the local density approximation (LDA) for the electron–electron interactions was used. It is needed to mention that the used ultrasoft pseudo potentials with $2s^2 2p^6 3s^1$ and $3s^2 3p^5$ valence-electron configurations for Na and Cl atoms respectively should be compatible with the special

type of LDA. To confirm the convergence of the calculations for the Brillouin-zone sampling, we tested the dependence of the total energy on the plane wave cut-off energy and the k-point mesh according to the Monkhorst–Pack grid scheme.[20] It was found that for the cut-off energy of 500 eV and the k-point set of $15 \times 15 \times 15$, the change in total energy was minimum for NaCl. The calculated energy–volume (per formula unit) data were converted into static and finite-temperature pressure–volume isotherms based on the quasi-harmonic Debye model using the numerical procedures coded in the GIBBS program.[9] A description of the quasi-harmonic Debye model can be found elsewhere.[21−23]

3. Results and discussion

The isothermal bulk modulus K_T of NaCl with the rock-salt structure is calculated at 300 K and shown in Fig. 1.

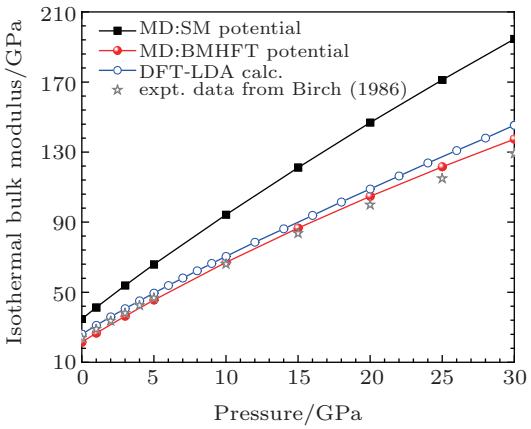


Fig. 1. (colour online) MD-calculated isothermal bulk modulus K_T of NaCl as a function of pressure at 300 K. The experimental data reported by Birch[24] and our *ab initio* values are presented for comparision.

We compare the calculated results with the experimental data reported by Birch[24] and our *ab initio* values. Note that the calculated isothermal bulk modulus using the SM potential is smaller than that obtained with the BMHFT potential and the effect of pressure on K_T of NaCl is very large. Compared to that with the SM potential, the MD simulation with the BMHFT potential is very successful in reproducing accurately the measured bulk modulus[24] and the *ab initio* values of NaCl. Obviously, the BMHFT potential is the more reliable one for the simulation of high-pressure properties like the isothermal bulk modulus of NaCl, although Chen *et al.* have successfully obtained the melting curve of NaCl using the SM-MD simulations.[10] Despite its achievement in rendering the effects in a computationally tractable form, the SM is known to have limitations. These are associated with the parametrization of the model rather than the incompleteness of the underlying physics of the interactions for all but the strongly covalent materials. The problems manifest themselves in a lack of transferability of SM parameters between chemically related materials and even between different phases of the same material and also in the emergence of unphysical values for parameters from empirical fits. We contend that these difficulties arise from an overly restrictive representation of the many-body effects within the SM.

Using the more reliable BMHFT potential, we have predicted the pressure dependence of the isothermal bulk modulus K_T of the NaCl crystal at different temperatures, as shown in Fig. 2. It is easily seen that the isothermal bulk modulus of NaCl with the rock-salt structure increases with the increase of pressure, and decreases with the increase of temperature.

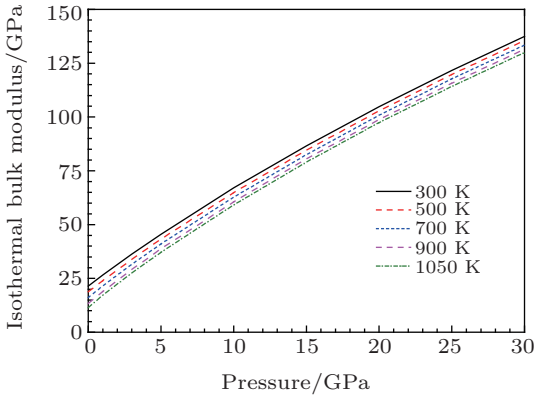


Fig. 2. (colour online) Predicted isothermal bulk modulus K_T of NaCl obtained with the BMHFT potential versus pressure at different temperatures.

Figure 3 shows the comparison of the MD-calculated isothermal bulk modulus with the results obtained from our *ab initio* density functional theory calculations combined with the quasi-harmonic Debye model,[9] Birch's fitting,[24] and Boehler's experiment[25] at zero pressure. Note that the isothermal bulk modulus of the MD simulation with the BMHFT potential is in good agreement with Boehler's experiment and Birch's fitting results above the temperature of 500 K, but at the temperature below 500 K, the isothermal bulk modulus of the MD simulations is lower than theirs. The little discrepancy indicates a limited validity of the BMHFT potential used. In considering some materials. such as NaCl, the pair-wise potentials are not all satisfactory after all. The results from the MD simulations based on the SM potential are somewhat scattered. As we know

that the polarization forces, though not negligible for the quantitative description of particles, do not appear to be crucial for the two-body rigid-ion BMHFT model. They are neglected in order to concentrate on the BMHFT model, whose greater simplicity allows a much more extensive computational exploration of the thermodynamic properties.

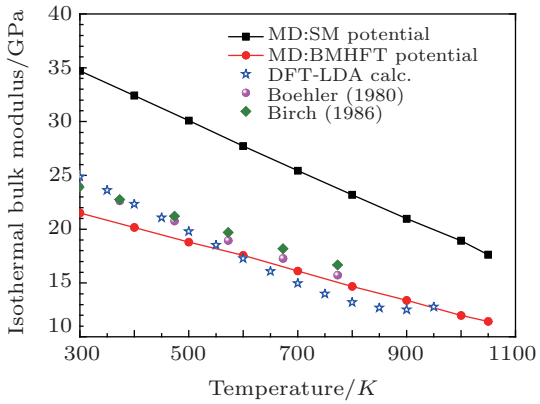


Fig. 3. (colour online) MD-calculated isothermal bulk modulus K_T of NaCl as a function of temperature at zero pressure. Our *ab initio* values, Birch's fitting,[24] and Boehler's experiment results[25] are presented for comparision.

Figure 4 shows the predicted values of the isothermal bulk modulus K_T versus temperature using the BMHFT potential in the pressure range of 0–30 GPa. We can see that as the temperature increases, K_T decreases, reflecting the fact that the solid is more compressible as it is heated up. As expected, the converse is true for the increased pressure. Note that there is a constant value for $\partial K_T/\partial T$ at each isobar and that it decreases as the pressure increases.

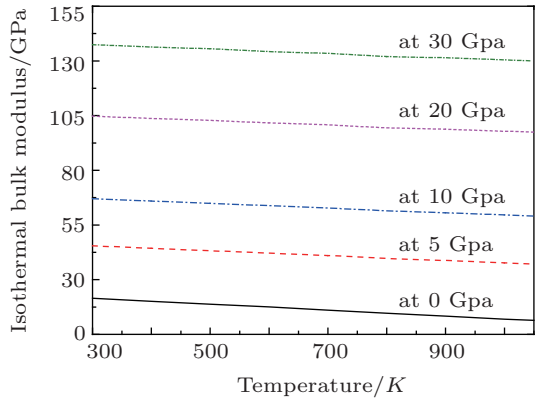


Fig. 4. (colour online) Predicted isothermal bulk modulus K_T of NaCl using the BMHFT potential versus temperature at different pressures.

The pressure derivatives of the isothermal bulk modulus at given temperatures and pressures are very important for high-pressure studies. From a geophysical point of view, the first pressure derivative of the isothermal bulk modulus $K'_{T,P}$ is a parameter that is necessary for the accurate inversion of the seismic data into composition, structure, and texture of the earth, as well as for determining the thermal profile of the deep earth[26] and the isothermal empirical equation of state of materials in the deep earth.[27] Since the variation of many macroproperties of solids with temperature and pressure is closely related to $K'_{T,P}$, then $K'_{T,P}$ is crucial for calculating the thermodynamic properties at high temperatures and high pressures.[28] Figure 5 shows the predicted first pressure derivative of the isothermal bulk modulus of NaCl versus pressure along the isotherms of 0 K, 300 K, 600 K, 900 K, and 1050 K using the quasi-harmonic Debye model. It is found that the values of $K'_{T,P}$ are practically identical with those obtained by the experiment at 300 K.[24] The predicted first pressure derivative of the isothermal bulk modulus of NaCl increases with the increase of temperature and decreases with the increase of pressure. It is rather steep under lower pressures, and rapidly flattens with the increasing pressure. The $K'_{T,P}$ of NaCl at high pressures is a weak function of temperature and pressure.

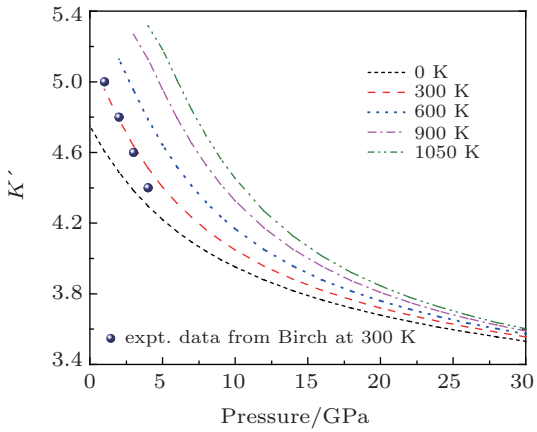


Fig. 5. (colour online) Predicted first pressure derivative of the isothermal bulk modulus of NaCl versus pressure at different temperatures.

4. Conclusion

In this paper, we have presented a comparative investigation of the isothermal bulk modulus and its first pressure derivative of NaCl with the rock-salt structure under high pressure and high temperature based on the shell-model molecular dynamics, the rigid-ion molecular dynamics, and the quasi-harmonic Debye model combines with the *ab initio* electronic structure calculations. Compared with the results obtained using the SM potential, the calculated isothermal bulk modulus and its first pressure derivative of NaCl using the BMHFT potential agree well with the exper-

imental and the other theoretical values. Despite its achievement, the SM is known to have limitations. Using the more reliable BMHFT potential, we have predicted the isothermal bulk modulus K_T of the NaCl crystal at high pressure and high temperature. It can be found that the isothermal bulk modulus decreases with the increasing temperature and increases with the increasing pressure. The first pressure derivative of the isothermal bulk modulus of NaCl $K'_{T,P}$ is predicted by means of first-principles density functional theory calculations combined with the quasi-harmonic Debye model. The research shows that $K'_{T,P}$ increases with the increase of temperature and decreases with the increase of pressure. It is rather steep under lower pressures, and rapidly flattens with the increasing pressure.

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