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Molecular dynamics study on the effect of interaction potentials on the pressures of high density helium

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ABSTRACT

The thermodynamic properties of pure high density helium and helium bubbles in metals are investigated using molecular dynamics method. The Lennard-Jones potential and the exponential-six potential are used to describe the interaction between helium atoms respectively. The results show that the short-range repulsive part of He–He potential has a great effect upon the pressure of pure high density helium. Because the exponential-six potential is softer than the Lennard-Jones potential in short-range part, the pressures of pure high density helium obtained by the exponential-six potential are lower and have a better agreement with available experimental data. For helium bubbles in metals, the He-Metal interactions can influence the uniformity of helium atoms within helium bubbles so that the pressures inside helium bubbles are higher than that of pure helium with the same average density. However, the differences between them decrease with increasing temperature.

1. Introduction

Helium atoms are usually introduced into nuclear materials either by (n,α) reactions in fusion reactor environment or by radioactive decay of tritium in metal tritides. The introduced helium atoms strongly tend to agglomerate into bubbles due to their extremely low solubility in materials. The pressures inside bubbles often range from several hundred megapascals to gigapascals (GPa), which can lead to the drastic modification of the materials' microstructures and the mechanical properties [1–6]. As a result, it is necessary to study the behavior of helium bubbles in materials. However, it is difficult to directly study the thermodynamic property of helium bubbles in materials. For example, the accurate measurement of the volumes of helium bubbles is almost impossible. An indirect way to predict the thermodynamic property of helium bubbles in metals is high pressure experiment. In high pressure experiment, helium gas can be compressed to a high density that reaches the atom density within helium bubbles in materials [7,8]. The equation of state of high density helium can be established by measuring the dependence of pressure on volume and temperature. In the past few decades, numerous high pressure experiments have been performed. However, whether helium bubbles in materials have completely the same thermodynamic property with high density helium in high pressure experiments (for convenience, we name it pure high density helium in this paper) almost has never been concerned.

Molecular dynamics (MD) simulation is a powerful tool for the investigation of the thermodynamic properties of materials [9,10]. The quality of the simulation results strongly depends on the accuracy of the potential function used. In the study of pure high density helium, exponential-six potential has been widely recognized as a good description of the interaction in helium [11–13]. However, Lennard-Jones potential which can be well fitted to the properties of noble gases has been popularly used to study the helium effects in materials [14–16]. Although many theoretical simulations of high density helium have been performed using the two He–He potential functions, there is still a lack of understanding about the differences between the simulation results obtained by them.

In this work, we study the thermodynamic properties of high density helium by Molecular Dynamics (MD) approach. Firstly, we calculate the pressure of pure high density helium using Lennard-Jones (L-J) potential and exponential-six (exp-6) potential respectively to analyze the effect of He–He potential on the pressure of pure high density helium. Then we study the equation of state (EOS) of helium bubbles in metals, and make a comparison with that of pure high density helium to find the differences between them.

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2. Computational method

Loubeyre et al. have found the solid helium with the stable hcp structure in the experiment of single-crystal x-ray diffraction of solid helium [8]. Based on the experimental observation, in our simulations of pure high density helium, we firstly assume solid helium with hcp structure. Then change the helium density by changing the initial lattice constant and subsequently calculate the pressures of helium at different densities. The constructed box contains 8640 helium atoms and the periodic boundary conditions are imposed in three dimensions. The He–He interaction is described either by the exp-6 potential [11],

$$\varphi(r)=\varepsilon\left\{\frac{6}{\alpha-6}\exp\left[\alpha\left(1-\frac{r}{r^*}\right)\right]-\frac{\alpha}{\alpha-6}\left(\frac{r^*}{r}\right)^6\right\} \tag{1}$$

with the parameters $\alpha=13.1$, $r^*=0.29673$ nm and $\varepsilon/k=10.8$ K, or by the L-J potential [17]

$$\phi(r)=4\phi_0\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^6\right], \tag{2}$$

where ϕ_0 is the depth of the potential well, σ is the finite distance at which the inter-atom potential is zero, r is the distance between the atoms.

For the simulations of helium bubbles in metals, perfect titanium and copper are used as substrates. The Cu substrates contain 54,208 atoms and the Ti substrates contain 69,536 atoms. The three-dimensional periodic boundary conditions are also used. In previous experiment, helium bubbles in metals tended to become spherical [5]. Therefore, in this work a spherical cavity with required size is firstly created in the center of a substrate, and helium atoms are then placed in the cavity with a certain helium density, i.e., producing a helium bubble in the center of the metal. An example of the initial configuration of the substrate containing a helium bubble is shown in Fig. 1.

Subsequently, the system is relaxed to thermodynamic equilibrium. After the system reaches thermodynamic equilibrium, we begin to calculate the helium bubble pressure. Because the helium bubble pressure is very high, the state equation of ideal gas and van der Waals gas model are all inappropriate. As a result, we calculate the pressure inside helium bubble as follows [18]:

$$p=\left\langle\frac{1}{V}\right\rangle Nk_BT+\frac{1}{3V}\left\langle\sum_{i=1}^{N} r_i\cdot f_i\right\rangle, \tag{3}$$

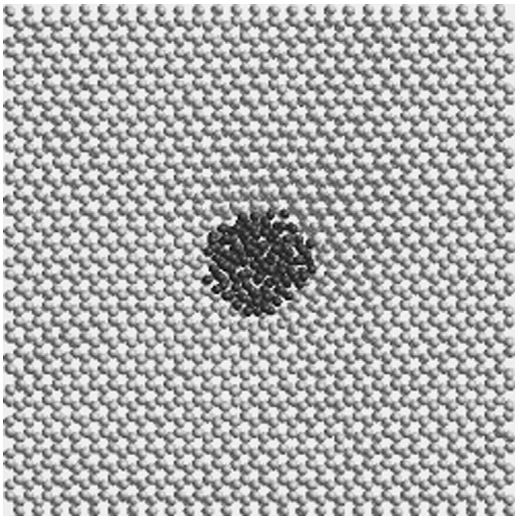

Fig. 1. The initial configuration of a substrate containing a helium bubble.

where N is the number of helium atoms, V is the volume of the spherical region containing the N helium atoms, k_B is the Boltzmann's constant, T is the absolute temperature, r_i is the position of the ith atom and f_i is the force on the atom. In the simulations, more interactions between atoms should be considered. The Ti–Ti and Cu–Cu potentials used were obtained by Fabrizio Cleri and Vitorio Rosato [19]. The Ti–He potential was constructed by fitting the pair potential to ab initio data [16]. The Cu–He potential was proposed by Chizimeshya and Zaremba [20].

All above simulations are performed in the NVT system. The temperatures range from 0 to 1000 K and an electron–phonon coupling model is applied to maintain the temperature of the system each time [21].

3. Results

3.1. Effect of He–He potential on the pressure of pure high density helium

Fig. 2 shows the Pressure–Volume isotherms of pure high density helium obtained by the L-J He–He potential and the exp-6 He–He potential, including comparisons with available experimental data [22–24]. When the molar volume of helium is larger than 5 cm^3/mol, the Pressure–Volume isotherms obtained by the two different He–He potentials are almost completely coincident with each other. However, when the molar volume of helium is less than 5 cm^3/mol, the pressures obtained by the L-J potential are higher than those obtained by the exp-6 potential, and the difference between them increases significantly with decreasing molar volume. The calculated pressures are compared with the experimental data. It is shown that the pressures calculated using the exp-6 potential is in good agreement with the experimental data when the molar volume is larger than 3.28 cm^3/mol. However, when the molar volume of helium is less than 3.28 cm^3/mol, the pressure calculated using the exp-6 potential is increasingly higher with density than the experimental data. The pressures calculated using the L-J potential is in good agreement with the experimental data when the molar volume is larger than 5 cm^3/mol.

In order to find the reason for the differences between the simulation results, we make a comparison between the L-J potential and the exp-6 potential, as shown in Fig. 3. It can be seen that there is a difference between them in the short-range repulsion region. When the interatomic distance is less than 0.227 nm, corresponding to the molar volume less than

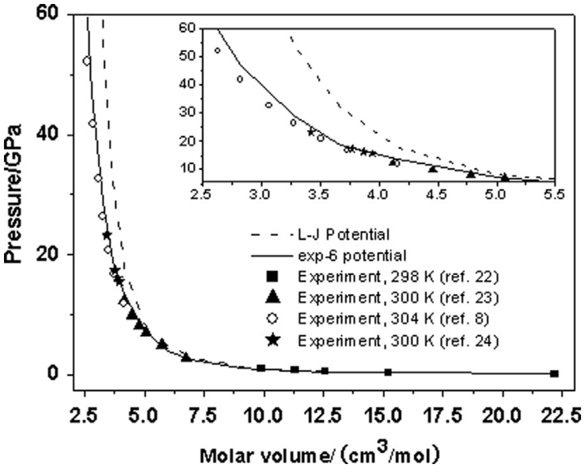

Fig. 2. The Pressure–Volume isotherms of pure high density helium at 300 K as well as comparisons with experimental data.