# Molecular dynamics study of helium bubble pressure in titanium*

Zhang Bao-Ling(张宝玲), Wang Jun(汪 俊), and Hou Qing(侯 氢)†

*Key Laboratory for Radiation Physics and Technology (Sichuan University), Minister Education; and Institute of Nuclear Science and Technology, Sichuan University, Chengdu* 610064, *China*

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In this paper, the pressure state of the helium bubble in titanium is simulated by a molecular dynamics (MD) method. First, the possible helium/vacancy ratio is determined according to therelation between the bubble pressure and helium/vacancy ratio; then the dependences of the helium bubble pressure on the bubble radius at different temperatures are studied. It is shown that the product of the bubble pressure and the radius is approximately a constant, a result justifying the pressure-radius relation predicted by thermodynamics-based theory for gas bubble. Furthermore, a state equation of the helium bubble is established based on the MD calculations. Comparison between the results obtained by the state equation and corresponding experimental data shows that the state equation can describe reasonably the state of helium bubble and thus could be used for Monte Carlo simulations of the evolution of helium bubble in metals.

**Keywords:** helium bubble pressure, molecular dynamics simulation, state equation, titanium

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## 1. Introduction

In the field of nuclear material, the behaviour of helium in metals has attracted considerable attention. Helium atoms are usually introduced into metals through ion implantation, tritium decay or $(n, \alpha)$-reactions during neutron irradiation. It is well known that helium has extremely low solubility in metals and tends to be trapped by defects. With the accumulation of helium atoms, high-pressurized helium bubbles are formed gradually. The growth of high-pressurized helium bubbles causes swelling, cave, embrittlement and so on, which reduce the mechanical properties of the materials seriously, especially metals at high temperatures.[1−8] It is crucial to understand the detailed behaviours of helium in materials for the development of nuclear technology.

Since it is difficult to directly measure and observe the behaviour of helium bubbles in materials, Monte Carlo (MC) simulation and molecular dynamics (MD) are the most widely used tools to study the behaviour of helium in metals. The MD is usually applied to deal with the process on a time scale of nanoseconds. For a long time scale process, from seconds to thousands of second for instance, kinetic MC simulation is usually employed. However, the MD simulations provide insightful information and dynamics parameters for the physics model adopted for the MC simulations.

Recently, MC simulations for the evolution of helium bubbles in materials were performed by a number of authors, to explain the explosive growth of bubbles observed in experiments.[9,10] In these MC simulations, the helium bubbles were assumed to be always in equilibrium states described by the state-equation of ideal gas, and the dependence of the pressure of a bubble on its radius $R$ was assumed to be $p = 2\gamma/R$ with $\gamma$ being the surface energy of the bubble which is a given constant. The same physics model was also adopted by Suzudo *et al.* in their MC simulations for the bubble growth in metals.[11] Although these MC simulations were able to explain experimental observations, the results are quite qualitative and the two basic assumptions mentioned above need to be justified. In fact, the pressure of helium bubble in metals is very high, and it is inappropriate to describe the state of helium bubble by the state equation of ideal gas.

In this paper, using MD, we study the pressure of the helium bubble in titanium, an important nuclear material widely used in the structural component of nuclear devices.[12−15] First, the dependences of bubble pressure on helium/vacancy ratio, bubble radius and temperatures are obtained. Then, an equation of state for the helium bubble in titanium is established.

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†Corresponding author. E-mail: qhou@scu.edu.cn

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Comparisons between this state-equation and that of ideal gas as well as corresponding experimental data are made, although the available experimental data for the state equation of high-dense helium is quite few. It is indicated that the state equation obtained by MD is more suitable than the state equation of ideal gas to describe the pressure state of helium bubble in titanium.

## 2. Computation method

The simulation is performed in an NVT system, the temperature is in the range of 300 to 800 K. An electron–phonon coupling model is applied to maintain the temperature of the system each time.[16] The computational box size is $38a_0 \times 38b_0 \times 24c_0$, where $a_0$, $b_0$, and $c_0$ are the lattice constants of titanium, and the periodic boundary conditions are imposed in the three dimensions. The simulation time is 20–50 ps and the time step of integral is 1fs.

The initial configuration of the system is constructed by placing one helium bubble in the centre of the titanium substrate. The bubble is spherical and its radius ranges from 0.2951 to 1.4755 nm. Wang *et al.*[17] had carried out a set of simulations on the growth of helium cluster in Ti. In their work, the helium atoms were introduced to the trapping site one by one, a process emulating more closely to the real physical process. However, this simulation approach is very computational expensive, especially when the helium cluster is large (over 100 helium atoms for instance); in the present paper, the helium bubble concerned may contain more than one thousand helium atoms, thus the simulation approach used by Wang *et al.* is too computational expensive to be feasible here. It was shown also by Wang *et al.* that the defect formed around a helium bubble, due to emission of metal atoms, would collectively drift away at certain point in the bubble growing and the substrate around the helium cluster would restore its original crystal structure. Based on the study of Wang *et al.*, in this paper, we can firstly make a cave with a given radius in the substrate by removing some metal atoms, and then place the helium atoms in the cave with a certain helium/vacancy ratio. An example of the initial configuration of the titanium–helium system including 198 helium atoms is shown in Fig. 1.

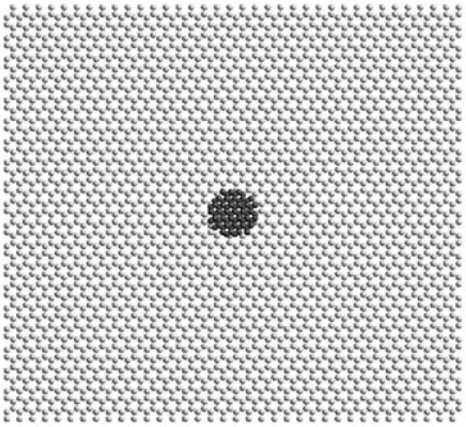


**Fig. 1.** The initial configuration of Ti–He system including 198 helium atoms.

For the choice of the interatomic potentials, an empirical tight-binding potential is used to describe the Ti–Ti interaction.[18] The Lennard–Jones potential is applied to describe the interaction between helium atoms.[19] The choice of interaction potential of He–Ti is crucial for the simulation success, in this paper, the He–Ti interaction potential is constructed by fitting the Lennard–Jones function to *ab initio data*, which is written as follows,[20]

$$V(r) = \varepsilon \left[ \left( \frac{r_0}{r} \right)^{4.35} - 3.21 \left( \frac{r_0}{r} \right)^{1.4} \right], \qquad (1)$$

where $\varepsilon = 0.02617$ eV, $r_0 = 0.47288$ nm, $r$ denotes the distance between He and Ti atoms. It should be mentioned that direct experimental verifications for the accuracy of the interaction potentials used in MD simulations are usually unavailable. However, the accuracy of the potentials can be indirectly verified by comparing the MD results with corresponding experimentally measurable quantities. The interatomic potentials used in this paper has also been used for simulating the growth of helium cluster in titanium.[17] It was found that clustering of helium atoms induces the ejection of metal atoms and the formation of vacancies with the helium/vacancy ratio around 2, a result that is in agreement with experimental observations[19,21,22] and also validates the use of the potentials. Moreover, as it will be shown in this paper, the use of the potentials also results in reasonable surface energy and state equation of helium bubbles in comparison with corresponding experimental data.

Helium bubble pressure is very high, the state equation of ideal gas and van der Waals gas model are all inappropriate. The pressure of helium bubble

is thus written as[23]

$$p = \left\langle \frac{1}{V} \right\rangle N k_{\rm B} T + \frac{1}{3V} \left\langle \sum_{i=1}^{N} r_i \bullet f_i \right\rangle, \qquad (2)$$

where $N$ is the number of helium atoms, $V$ is the volume of the spherical region containing the $N$ helium atoms; $k_{\rm B}$ is the Boltzmann's constant, $T$ is the absolute temperature, $r_i$ is the position of the $i$th atom, and $f_i$ is the force on the atom.

## 3. Results and discussion

For the initial helium bubbles radius of 0.2951, 0.5902, and 0.8853nm, the MD simulations are performed at temperature 300 K for various initial helium/vacancy ratios. The bubble pressure as a function of helium/vacancy ratio is shown in Fig. 2. As the overall trend, the pressure first increases to a maximum value and then decreases rapidly with increasing helium/vacancy ratio. For the small helium bubble ($R = 0.2951$ nm and $R = 0.5902$ nm), the maximum pressure occurs at the helium/vacancy ratio=3; when the radius of the helium bubble is 0.8853 nm, the maximum moves to the helium/vacancy ratio=2.

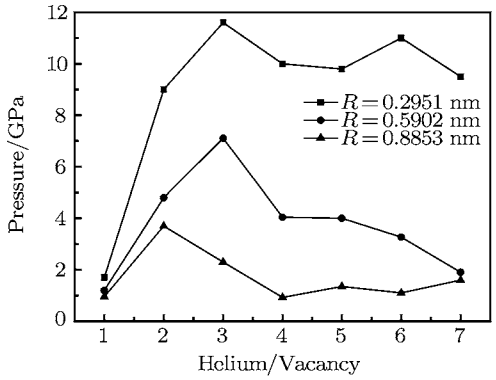



**Fig. 2.** The bubble pressure as a function of He/V.

The feature observed in the relationship between the pressure of the helium bubble and the helium/vacancy ratio can be understood as follows. With increasing helium/vacancy ratio, the increased density of helium atoms in the bubble results in a higher bubble pressure. However, the helium bubble pressure and the surface tension of the metal atoms surrounding the bubble are in quasi-balance. When the bubble pressure reaches a certain value, a large number of metal atoms are pushed out, and more vacancies are produced in the helium bubble with the release of pressure of the helium bubble.

Figure 3 demonstrates the re-configuring of defects before and after the release of bubble pressure when the radius of bubble is 0.8853 nm. There are few displaced metal atoms around the helium bubble before the pressure is relieved, but a lot of displaced metal atoms appear around the helium bubble after the pressure is relieved. Further increase of helium/vacancy ratio induces the bubble pressure increasing again until the next release point is achieved. This pressure-accumulation-and-release process gives an explanation of the zigzag feature in the pressure-helium/vacancy curve.

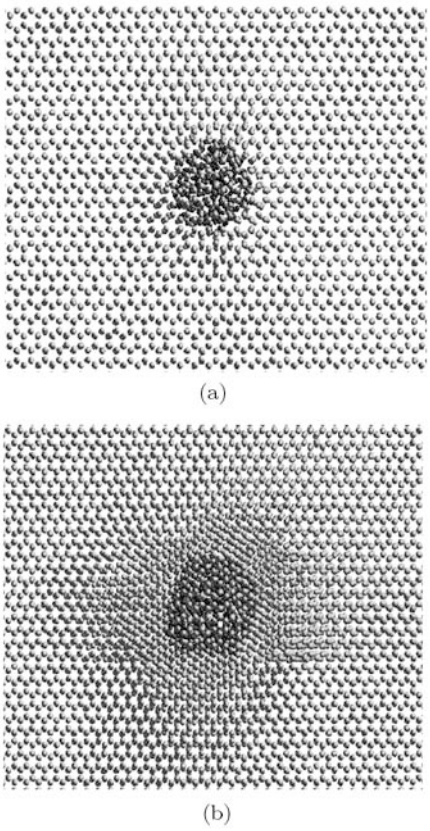



**Fig. 3.** The re-configuring of defects before and after the release of bubble pressure. (a) Before the release of bubble pressure, (b) After the release of bubble pressure.

According to the above analysis, it is reasonable to study the state equation of helium bubble under the condition that the initial helium/vacancy ratio is less than 3. Once the helium/vacancy ratio is larger than 3, more vacancies might be produced by emitting metal atoms and the helium/vacancy ratio is changed. In the study of small helium cluster in titanium,[17] it was shown that the collective drift of defects surrounding the bubble occurs as the helium/vacancy ratio reaches about 2. Thus, in the following calculations, we calculate the bubble pressure at various radii

and temperatures with the initial helium/vacancy ratio equal to 2.

Figure 4 demonstrates the dependence of helium bubble pressure on the bubble radius at different temperatures. The helium bubble radius ranges from 0.44265 to 1.4755 nm. It is observed that the bubble pressure decreases with increasing bubble radius. However, the value of $p \cdot r$ keeps to be around 1.615 N·m$^{-1}$ with an uncertainty of ±0.175 N·m$^{-1}$, in the temperature range from 300 to 500 K. This result is in agreement, at least in form, with that predicted by thermodynamics-based theory for gas bubble, in which the pressure of a gas bubble is required to balance the surface tension: $p = 2\gamma/R$, where $\gamma$ is surface energy of the bubble. Moreover, the surface energy of the liquid titanium is 1.588 N·m$^{-1}$,[24] and the surface energy at room temperature is about 8% higher than that of the liquid metal for most metals.[21] Accordingly, the surface energy of titanium at room temperature is about 1.715 N·m$^{-1}$, a value that is very close to the surface energy obtained in our simulations. In order to compare the bubble pressure with that of ideal gas, the pressures corresponding to different helium bubble radii are also calculated according to $pV = Nk_{\rm B}T$ at 300 K. It is clear as shown in Fig. 4 that the state of helium bubble in titanium is far from that of ideal gas; its pressure is much larger than that of ideal gas, especially at small bubble radius.

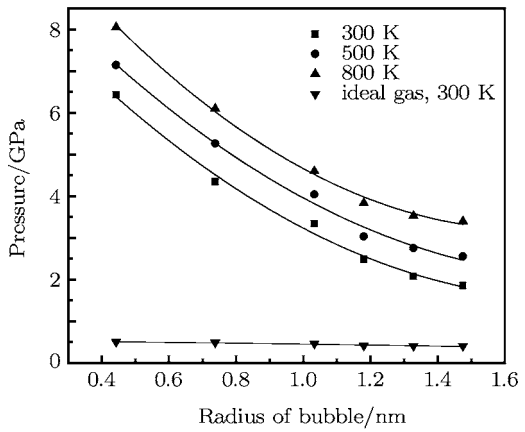



**Fig. 4.** The bubble pressure as a function of the bubble radius.

Figure 5 shows the pressure of a bubble as a function of temperature for various bubble radii. It is well known that titanium has two allotropes: $\alpha$-Ti exists at temperatures below 1155K, while $\beta$-Ti at temperatures higher than 1155 K.[13,25] To avoid the influence of phase transition on the pressure, we only analyse the pressure of helium bubble at temperatures less than 800 K. It is observed from Fig. 5 that the pressures increase approximately linearly with increasing temperature.

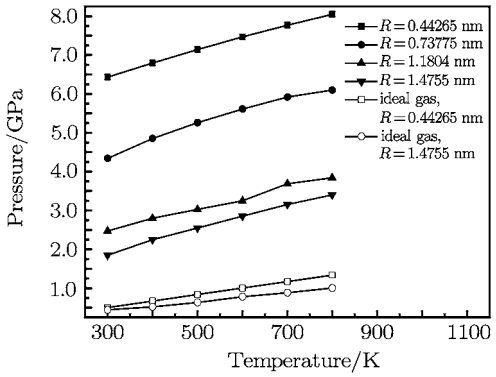



**Fig. 5.** The bubble pressure as a function of temperature.

Since it is quite difficult to measure the state of highly-pressurized helium gas, very few experimental data are available for the state equation of the helium bubble. In the review of Donnelly,[21] one of the suggested state equations for highly pressurized helium is written as

$$\frac{pV}{Nk_{\rm B}T} = 1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \frac{B_4}{V^3} + \ldots, \qquad (3)$$

where $B_2$, $B_3$, $B_4$ are the virial coefficients associated with temperature, $p$ is the pressure in $10^8$ Pa, $V$ is the molar volume of the helium bubble in cm$^3$ and $T$ is the absolute temperature. Here in this paper, we also adopt Eq. (3) for the state equation of helium bubble. To establish the state equation of helium bubble, MD calculations have been performed also for cases with initial helium/vacancy from 1 to 2 to cover a wider range of molar volume. We first rewrite Eq. (3) in the form

$$y = 1 + m_0x^0 + m_1x^1 + m_2x^2 + m_3x^3 + \ldots, \quad (4)$$

where $y = pV/Nk_{\rm B}T$, $x = 1/V$. The coefficient $m_i$ is temperature dependent and is obtained by fitting Eq. (4) to the pressure data given by MD simulation at given temperature and various initial helium/vacancy ratios and bubble radii. Table 1 shows the coefficient $m_i$ at different temperatures.

**Table 1.** The fitting coefficient $m_i$ for Eq. (4).

| temperature | $m_0$ | $m_1$ | $m_2$ | $m_3$ |
|---|---|---|---|---|
| 300 K | –1.1668 | 5.1024 | –41.1492 | 113.2856 |
| 400 K | –1.1729 | 4.8831 | –37.5846 | 99.3486 |
| 500 K | –1.1254 | 3.5649 | –26.7625 | 70.325 |
| 800 K | –1.1213 | 3.2809 | –24.1484 | 61.0676 |

We further obtain the virial coefficients by letting $m_i$ as a function of temperature, and finally the state equation of helium bubble with the pressure in GPa is written as

$$\begin{aligned}\frac{pV}{Nk_{\rm B}T} &= 0.1 + [(-0.0024\times10^{-5}T^2 \\ &\quad + 0.0371\times10^{-3}T - 0.12646)V^0 \\ &\quad + (0.1027\times10^{-5}T^2 \\ &\quad - 1.5335\times10^{-3}T + 0.89489)V^{-1} \\ &\quad + (-1.0346\times10^{-5}T^2 \\ &\quad + 15.0647\times10^{-3}T - 7.82484)V^{-2} \\ &\quad + (3.1519\times10^{-5}T^2 \\ &\quad - 45.7654\times10^{-3}T + 22.50049)V^{-3}]. \quad (5)\end{aligned}$$

Figure 6 shows the pressure–volume isotherms at different temperatures obtained by using Eq. (5).

A comparison between our pressure-volume isotherm and the available experimental data is illustrated in Fig. 7. In the experiment of Mills *et al.*,[26] the dependence of pressure on the volume and temperature of melting helium was measured for pressure ranging from 0.2 to 2 GPa, and an equation of state was obtained by fitting their experimental data. As is shown in Fig. 7(a), the MLB data is very close to our results at 300 K. It is also observed that the experimental data of Vidal and Lallemand (VL)[27] at 298 K also well agrees with our results. At 338 K, our theoretical curve is compared with the data of MLB and the experimental data of Bridgman[28] in Fig. 7(b). Due to the uncertainty of experiments, the data of Bridgman's result for a molar volume are 30% larger than that of MLB. Our theoretical curve lies between the data of Bridgman and of MLB, but closer to the data of MLB. This observation indicates that Eq. (5) can be used, at least qualitatively, to describe the pressure–volume–temperature state of helium bubbles in metals, in considering the large uncertainty of experimental data.

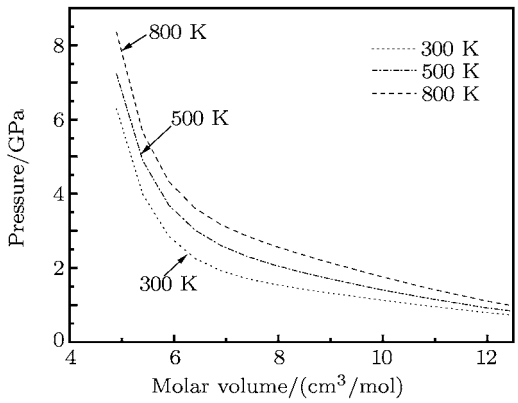



**Fig. 6.** Pressure–Volume isotherms for helium bubble.

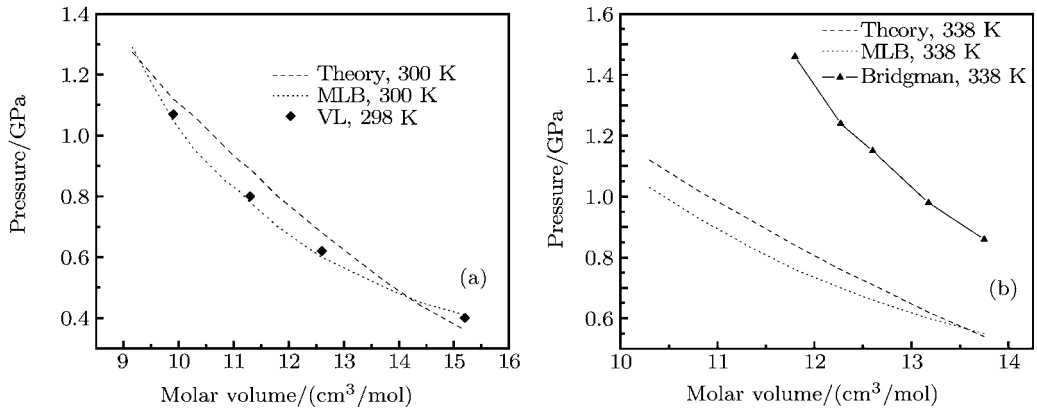



**Fig. 7.** Experimental and theoretical $p$–$V$ curves for helium at different temperatures. (a) The theoretical curve, the experimental curve of MLB at 300 K and the experimental data of VL at 298 K; (b) The theoretical curve, the experimental curve of MLB and the experimental data of Bridgman at 338 K.

## 4. Conclusions

We have studied the pressure state of the helium bubble in titanium by using the molecular dynamics method. The results show that the pressures in the bubble first increase and then decrease with increasing helium/vacancy ratio; the possible ratio of helium/vacancy should be less than 3 in titanium. At a given temperature, helium bubble pressure decreases with the increasing radius of the bubble, but the product of the bubble pressure and the radius is approximately a constant. This result justifies the pressure-radius relation of helium bubbles predicted by thermodynamics-based theory for gas bubble. Furthermore, based on the MD calculations of the helium bubble pressure at different helium/vacancy ratio and bubble radius and temperature, a state equation of helium bubble is established. A comparison is made between the results obtained from the state equation and the corresponding experimental data. Although the comparison is very limited due to the rareness and uncertainty of experimental data, it is shown that the state equation of helium bubble can give reasonable description for the state of helium bubble. These results are instructive to long term simulation, such as Monte Carlo simulations, for the behaviour of helium bubble in metal. How the state equation of helium bubble influence the evolution of helium bubbles in metals will be studied in our future works.

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