

## A comparative study of helium atom diffusion via an interstitial mechanism in nickel and palladium

Jixing Xia<sup>1</sup>, Wangyu Hu<sup>\*1</sup>, Jianyu Yang<sup>1</sup>, Bingyun Ao<sup>2</sup>, and Xiaolin Wang<sup>2</sup>

<sup>1</sup> Department of Applied Physics, Hunan University, Changsha 410082, P.R. China

<sup>2</sup> China Academy of Engineering Physics, P.O. Box 919-71, Mianyang 621900, Sichuan, P.R. China

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At low temperatures, helium atoms diffuse primarily by an interstitial mechanism due to the lower activation energy. Using a modified analytic embedded-atom model (MAEAM) and the molecular dynamics method, a study of the interstitial diffusion for helium atoms in perfect nickel and palladium was performed. Consequently, the diffusion coefficient was calculated from the jump-frequency method. The temperature dependency of the diffusion coefficient was found to agree well with the Arrhenius relation. The activation energies of the interstitial mechanism in these two metals were obtained by fitting to the Arrhenius relation, and the results agree with the available experimental and other theoretical data. In addition, by comparing the diffusion activation energies of helium atoms in nickel and palladium, it is found that the helium atom is less mobile in palladium than in nickel.

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### 1 Introduction

Helium atoms are produced in metals by nuclear reaction of energetic particles such as reactor neutrons or light ions or tritium decay. Due to the low solubility of helium, helium atoms tend to cluster and precipitate into bubbles that tend to grow at extended defects (dislocations, grain boundaries) and result in decreased macroproperties in nuclear materials. However, experimental studies can not show the micro-mechanism, but computer simulation is an effective method to study the microbehavior of helium in metals.

The growth of bubbles strongly depends on the mobility of helium atoms [1]. Helium atoms diffuse primarily by three mechanisms: interstitial mechanism, vacancy mechanism and dissociative mechanism, and the latter two appear only when the temperature is sufficiently high and there exist lattice defects. Since the helium atom is highly mobile as long as it occupies an interstitial position [2], it can diffuse easily by an interstitial mechanism in perfect fcc metals without any defects. Adams and Wolfer [3] calculated the activation energy of the interstitial diffusion in perfect nickel with a static method. They obtained the activation energy by determining the “saddle-point” energy of the minimum-energy path of a diffusing helium atom using an embedded-atom method (EAM) with 250 atoms.

Similar to helium, palladium has a closed-shell electronic configuration; the diffusion behavior of a helium atom in palladium may be different from in other fcc metals. Palladium could be used to store tritium or as the first-wall material in a fusion reactor environment, although the diffusion micromechanism of a helium atom in palladium is still unknown. As the computing technology develops rapidly, longer time and larger system simulations with molecular dynamics are more and more feasible. Com-

\* Corresponding author: e-mail: wangyuhu2001cn@yahoo.com.cn

pared to the static method, molecular dynamics could trace the detailed trajectories of particles and provide more precise results. In the present paper, we simulated the diffusion process of one helium atom in perfect nickel and palladium with molecular dynamics, and the method and results will be shown in the following sections.

## 2 Simulation method

In the previous simulation studies for many-particles systems, the suitability of the embedded-atom method (EAM) [4] has been confirmed. In this work, a modified analytic EAM model (MAEAM) [5] was adopted to describe the interactions between metal atoms. The interaction between a helium atom and a metal atom is described by a Morse potential that was determined by fitting to the first-principle result [2]. The potential function is given by

$$\phi = \phi_0 \left[ \exp \left( -2\alpha \left( \frac{r}{r_0} - 1 \right) \right) - 2 \exp \left( -\alpha \left( \frac{r}{r_0} - 1 \right) \right) \right] \quad (1)$$

The referred parameters are shown in Table 1.

A system in a  $6a \times 6a \times 6a$  box that contained 864 metal atoms was constructed, where  $a$  was the lattice constant of Pd or Ni. Periodic boundary conditions were employed. The system was first relaxed in an NPT ensemble to an equilibrium state to obtain the box dimensions at the temperature of interest and then continued in an NVE ensemble to generate the trajectories. In the NPT ensemble, the constant temperature of interest and a pressure of 0 Pa were maintained by the velocity-scaling [6] and Parinello–Rahman [7] methods, respectively. The time step was fixed at 2 fs. The atomic trajectories were generated by integrating Newton's equations of motion using a predictor-corrector method [8]. The simulation time should be long enough to reduce the statistical errors, thus, the system was fluctuated for half a million steps, which was about 1 ns.

The helium atom in an octahedron interstitial is more stable than in a tetrahedron interstitial, thus the helium atom moves between the two closest octahedron interstitials during the diffusion process. To make the procedure simple, this migration was treated as the helium atom “jumps”. Without any influence of the other defects, the successive jumps have no correlations and thus the new jump is in a random direction. Therefore, the Einstein relation for the helium atom diffusion can be simplified as follows [9]:

$$D = f \frac{\alpha^2}{2d}, \quad (2)$$

where  $D$  is the diffusion coefficient,  $f$  is the jump frequency,  $\alpha$  is the jump distance,  $d$  is the diffusion dimension, which is three in our simulations. During the simulations, the jump number of the helium atom was recorded, and then the diffusion coefficient was calculated from the jump-frequency method. After being relaxed in an NPT ensemble to an equilibrium state, the NVE ensemble was continued, the jump numbers began to be accumulated after 10 000 step relaxations in this NVE ensemble. The jump frequencies were recorded each 50 000 steps after 200 000 steps, and then the average jump frequency at each temperature could be determined eventually. The jump distance could be regarded as the distance between the first-neighbor octahedron interstitials. The temperature ranged from 500 K to 1200 K for nickel and from 700 K to 1500 K for palladium.

**Table 1** The input parameters of potentials.

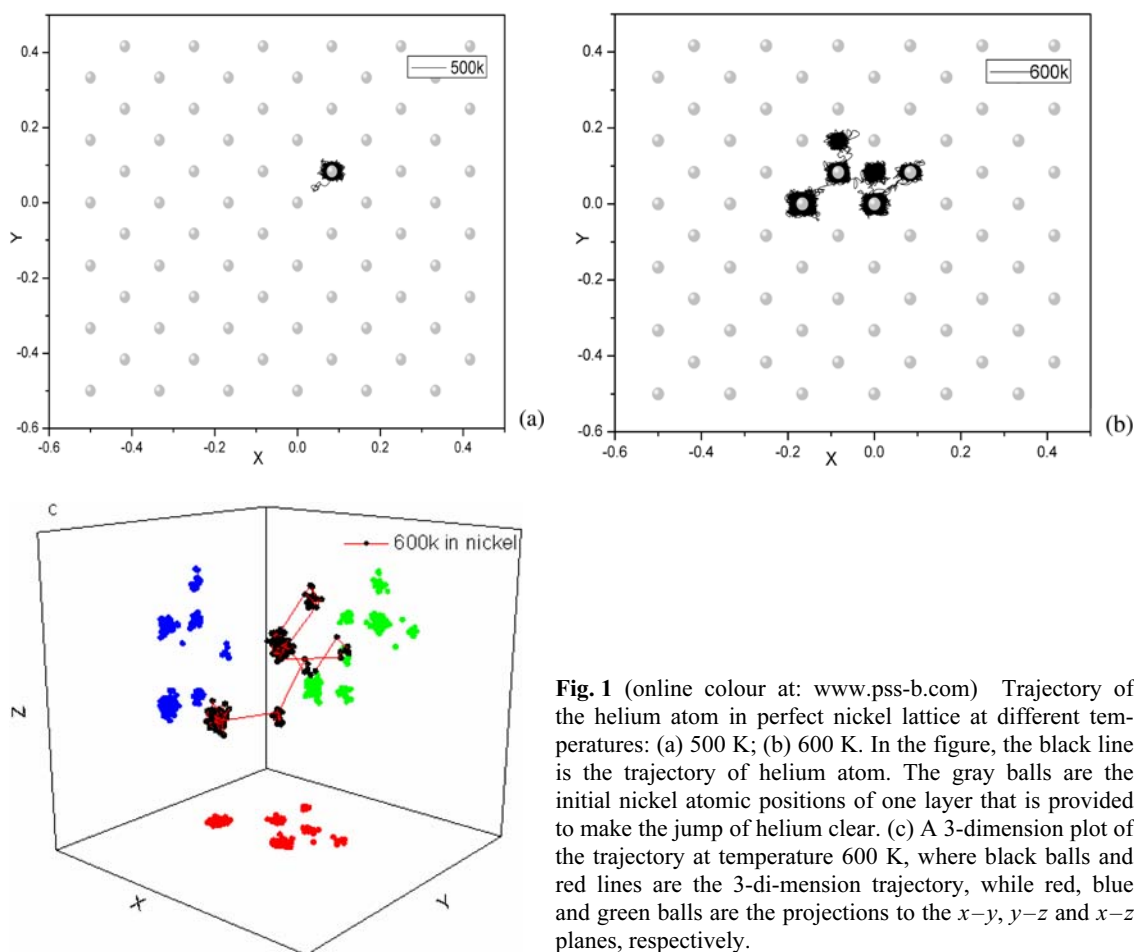
	$\phi_0$ (eV)	$r_0$ (Å)	$\alpha$
He–palladium	0.00099	3.51404	7.08259
He–nickel	0.00019	4.91572	6.46724

### 3 Result and discussion

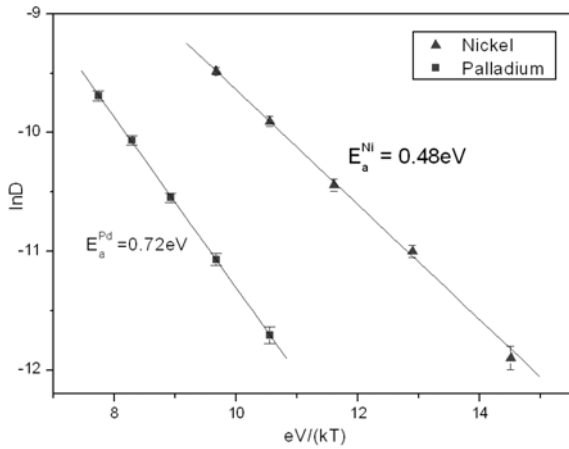
The mobility of a helium atom depends on the temperature. The helium atom was placed near the center of box initially. At low temperature, the helium atom vibrates around a stable octahedron interstitial in equilibrium, as is depicted in Fig. 1a for nickel. In Fig. 1, the black line is the trajectory of the helium atom, and gray balls are the initial lattice atoms of the same layer, which made it easy to understand the motion of this helium atom. When the temperature is below 500 K, the jump of a helium atom from one stable position to another can not be found. When the temperature is increased to 600 K, there are several stable positions for the helium atom, as is shown in Fig. 1b; it is obvious that the helium atom diffuses. To show the motion of the helium atom in a better way schematically, we also offer a three-dimension plot of the trajectories in Fig. 1c. When the temperature is above 800 K, the helium atom can diffuse to the boundary of the box easily.

The diffusion coefficient  $D$  can be calculated from the jump-frequency method. The Arrhenius relation can be transformed as follows:

$$\ln D = \ln D_0 - \frac{E_a}{k_B T}, \quad (3)$$



**Fig. 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Trajectory of the helium atom in perfect nickel lattice at different temperatures: (a) 500 K; (b) 600 K. In the figure, the black line is the trajectory of helium atom. The gray balls are the initial nickel atomic positions of one layer that is provided to make the jump of helium clear. (c) A 3-dimension plot of the trajectory at temperature 600 K, where black balls and red lines are the 3-di-mension trajectory, while red, blue and green balls are the projections to the  $x$ - $y$ ,  $y$ - $z$  and  $x$ - $z$  planes, respectively.



**Fig. 2** Arrhenius plots of the diffusion coefficients of one helium atom in nickel and palladium, respectively. Squares and triangles correspond to the results in palladium and nickel, respectively.

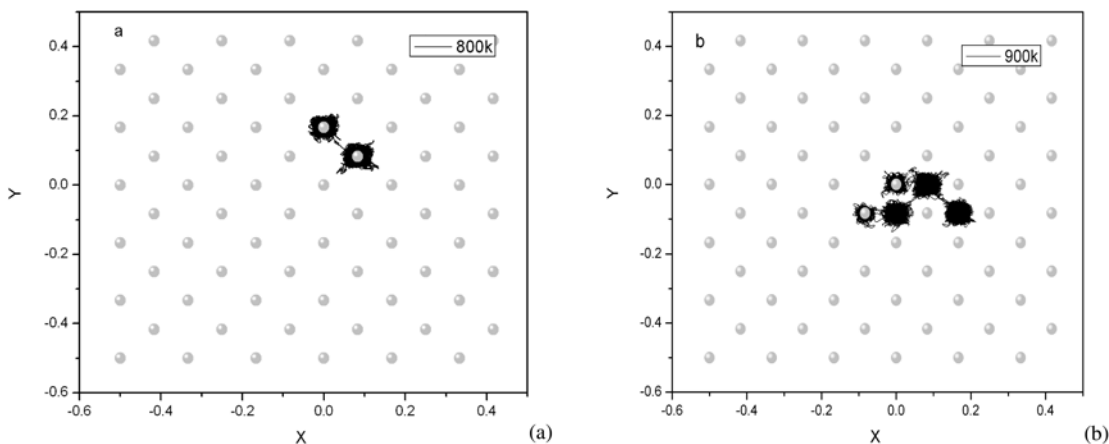
where  $E_a$  is the activation energy of the interstitial diffusion. With the plot of  $\ln(D)$  versus  $1/T$  as shown in Fig. 2, the values of  $\ln(D_0)$  and  $E_a$  were determined, and the temperature dependency of the diffusion coefficient of a helium atom in nickel with an error bar included can be derived as below:

$$D(T) = (0.0082 \pm 0.0012) \exp\left(-\frac{(0.48 \pm 0.01) \text{ eV}}{k_B T}\right) \text{ cm}^2/\text{s}. \quad (4)$$

The known experimental result of  $E_a$  is about 0.35 eV [10]. Baskes and Melius [2] obtained a value of 0.66 eV with pair potentials. Adams and Wolfer [3] found a value of 0.53 eV through their static calculations. Compared with these calculations, the MD result in this paper is more accurate.

The temperature at which the helium atom begins to jump in palladium is higher than in nickel, the helium atom in palladium does not jump until 800 K, which is 200 K higher than in nickel, as depicted in Fig. 3. This may result from the closed-shell electronic configuration of palladium. The relation of  $\ln(D)$  to  $1/T$  for the diffusion of a helium atom in palladium is also shown in Fig. 2. From the linear fitting result, the dependency of diffusion coefficient on temperature with an error bar included can be expressed as:

$$D(T) = (0.0161 \pm 0.0031) \exp\left(-\frac{(0.72 \pm 0.02) \text{ eV}}{k_B T}\right) \text{ cm}^2/\text{s}, \quad (5)$$



**Fig. 3** Trajectory of one helium atom in a perfect palladium lattice at different temperatures: (a) 800 K; (b) 900 K.

where the value of  $E_a$  is 0.72 eV, thus, the diffusion activation energy of a helium atom in palladium is evaluated by an interstitial mechanism. While using the pair potentials, Baskes and Melius [2] gained a value of 0.94 eV, concerning the result comparison in nickel, our result should be more reasonable.

The higher value of  $E_a$  in palladium reveals that the diffusion coefficient of a helium atom in palladium is lower than in nickel at the same temperature, which suggests that the helium atom in nickel is more mobile or more difficult to be retained in nickel. It was found in the previous experiment that palladium could retain more helium than other perfect metals with fcc structure [11], and the higher activation energy in palladium may be a reason for this.

#### 4 Conclusion

The mobility of a helium atom in nickel and palladium increases with increasing temperature. Using the MAEAM model and molecular dynamics, the Arrhenius relations for the interstitial diffusion of the helium atom in nickel and palladium were determined from the jump-frequency method, and the corresponding activation energies were found to be 0.48 eV and 0.72 eV. The activation energies obtained agree with the previous experimental and other theoretical calculation results. Comparing the activation energies in palladium and nickel, it is found that the helium atom in palladium is less mobile than in nickel, once a helium atom occupies a stable position, it is not easy for it to migrate. This is consistent with the experimental fact that palladium can retain more helium atoms than other fcc metals.

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