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Kinetic Monte Carlo simulation of hydrogen diffusion in tungsten

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HIGHLIGHTS

- Kinetics Monte Carlo (KMC) method is developed to model H diffusion in W.
- KMC determined diffusion coefficient for H in W is = $8.45 \times 10^{-7} \exp(-0.440/k_BT)$ [m^2/s].
- KMC result matches experiment value very well.
- KMC result is much more accurate than other simulation methods.

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ABSTRACT

This research developed a Kinetic Monte Carlo (KMC) method for simulating hydrogen diffusion in tungsten bulk. The KMC inputs such as diffusion paths and energy barriers are based on the first principle calculations in the literatures. In this simulation model, stable hydrogen interstitial sites in tungsten are the tetrahedral sites on each surface of the bcc lattice, and each site has four tetrahedral neighboring sites. A numerical program has been developed to perform the diffusion simulation for any hydrogen concentration and tungsten temperature combination. The KMC calculated diffusion coefficients fitted to the Arrhenius equation is $D\ [m^2/s] = 8.45 \times 10^{-7} \exp(-0.440/k_BT)$, which match the experiment data very well. The pre-exponential factor D_0 is found to be proportional to the hydrogen concentration, and a more general diffusion coefficient equation is derived for other concentrations. At last, the neighbor condition as a function of the concentration is analyzed.

1. Introduction

Nuclear fusion is considered as the most promising sustainable energy source. During the reaction, the fusion ash is continuously removed from the magnetic gap, the divertor region, and the divertor facing component is subjected to intense plasma bombardment. It is proposed to use tungsten as the divertor facing material, due to its low physical sputtering yield and superior thermomechanical properties. However, the high mobility of hydrogen in tungsten and the high bombardment flux bring the hydrogen isotopes deep into the tungsten bulk. It is important to have a detailed understanding of the hydrogen diffusion in tungsten bulk.

Diffusivity is a fundamental property affecting hydrogen isotope migration and retention in tungsten. Diffusion coefficients of hydrogen in tungsten have been studied by a number of experiments. The widely accepted diffusivity was reported by Frauenfelder: $D = 4.1 \times 10^{-7} \exp(-0.39\,eV/k_BT)$ m^2/s based on hydrogen degassing and permeation experiments [1]. This earlier investigation is considered as the most reliable result, because it was obtained at elevated temperature (1200–2400 K), and was less likely influenced by surface and trapping effect [2–4]. Several recent experiments based on tritium tracer technique also confirmed Frauenfelder's results without appreciable influence of trapping and surface effects even at lower temperature, e.g. Otsuka et al. ($D = 3 \pm 2 \times 10^{-7} \exp(-0.39 \pm 0.03\,eV/k_BT)$ m^2/s, 473–673 K) [5]. Ikeda et al. [6] proposed a diffusion coefficient formula: $D = 3.8 \pm 0.4 \times 10^{-7} \exp(-0.412 \pm 0.016\,eV/k_BT)\,m^2/s$, 300–2500 K, which is considered as the most reliable hydrogen diffusivity valid for a wide temperature range [2], [7], [8]. A few other researchers reported hydrogen diffusivities in tungsten deviating from Frauenfelder and Ikeda's conclusions: Benamati et al. ($\sim 1.5 \times 10^{-10}\,m^2/s$, 850–885 K) [9], Hoshihira et al. ($D = 4.3 \times 10^{-9} \exp(-0.39\,eV/k_BT)$ m^2/s, 293–323 K) [10], Garcia-Rosales et al. ($D = 3.5 \times 10^{-11} \exp(-0.39\,eV/k_BT)$ m^2/s, 300–1400 K) [11], Franzen el al. ($D = 3 \times 10^{-10} \exp(-0.25\,eV/k_BT)$ m^2/s, 300–900 K) [12], Matsuyama et al. ($2.4 \times 10^{-19}\,m^2/s$, 300 K) [13], Esteban et al. ($D = 5.68 \times 10^{-10} \exp(-0.096\,eV/k_BT)$ m^2/s, 673–1073 K) [14]. Those experimental data are often considered

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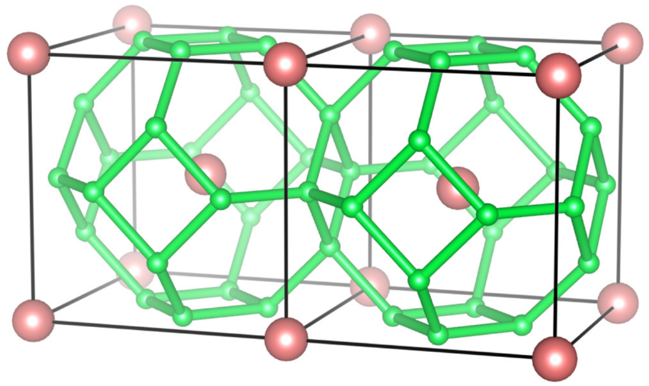

Fig. 1. Tetrahedral sites in bcc tungsten lattice. Large pink spheres: tungsten atoms; small green spheres: tetrahedral interstitial sites; green sticks: hydrogen diffusion paths. (Figure is created by VESTA v3.15 [23]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

unreliable because the experiments were performed within a small range of temperature and/or the surface/trapping and recombination effects were not taken into consideration [3]. The extrapolation of Frauenfelder's data to lower temperatures is always used as reliable diffusion coefficients for defect free tungsten sample [2].

In previous work, the authors developed a kinetic Monte Carlo (KMC) algorithm to simulate hydrogen diffusion process on tungsten reconstructed surface [15]. In this article, this KMC method is further extended to model the hydrogen diffusion in tungsten bulk [16]. The calculated diffusion coefficients are then compared with commonly accepted experiment measurements and other simulation results.

2. Methodologies

The KMC method is a stochastic computer simulation capable of predicting the time evolution of a certain system. Typically, at a given time, the system will evolve through a few possible paths with known probabilities. In each step, the KMC method analyzes the entire system and randomly determines the system evolving events based on the transition rates of all possible events and advance the physical time after performing the selected change. This process is repeated till the simulation of all the physical time is completed.

KMC diffusion simulation requires the locations of the hydrogen interstitial sites, diffusion paths and the corresponding diffusion energy barriers. The hydrogen interstitial sites in tungsten crystal have been thoroughly studied by density function theory (DFT). In general, all DFT research identify the tetrahedral site (T-site) as the most stable hydrogen interstitial sites in tungsten, and hydrogen diffuses from one T-site to its nearest T-site preferably [17–22]. Some DFT work also reported another hydrogen diffusion path from a T-site to the second nearest T-site via an octahedral site [17–19], [21], [22]. Due to the much higher energy barrier of the second path, it can be ignored in diffusion analysis. Using DFT calculation considering zero point energy (ZPE), the energy barrier between two adjacent T-sites has be determined by Johnson and Carter: 0.38 eV [17], Fernandez et al.: 0.17 eV [18], Heinola and Ahlgren: 0.21 eV [19], Degtyarenko and Pisarev: 0.35–0.38 eV [20], Xu and Zhao: 0.332 eV [21], Liu et al.: 0.20 eV [22]. The reason to this large discrepancies is not very clear [4], but the climbing image nudge elastic band (CI-NEB) method used by Johnson and Carter may provide an improved estimated [4], [17].

As shown in Fig. 1, all T-sites are located on the surfaces of the bcc lattice. There are four T-sites per surface and twelve T-sites per lattice cell. For example, the coordinates of the four T-sites on the bottom surface in Fig. 1 are (0.5, 0.25, 0)*a*, (0.75, 0.5, 0)*a*, (0.5, 0.75, 0)*a*, and (0.25, 0.5, 0)*a*, where *a* is the lattice parameter (3.165 Å for bcc tungsten). The hydrogen atoms diffuse by traveling from one T-site to one of its nearest four T-site neighbors. As illustrated in Fig. 1, each T-site is surrounded by four neighbors: two on the same surface, and one neighbor on each of the two adjacent surfaces perpendicular to the surface holding the center T-site. In this work, the diffusion barrier between two neighboring T-sites is 0.38 eV (with ZPE) [17].

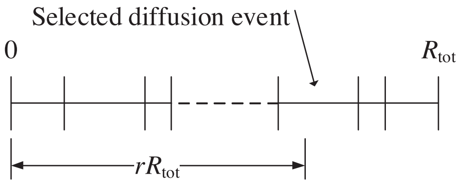

Fig. 2. Random selection of a diffusion event.

A list of possible events and the corresponding occurrence rates are the critical inputs to the KMC method. In diffusion simulation, those events are diffusion jumps, and the jump frequencies are defined by Eq. (1) [24].

$$k(E_a, T) = k_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{1}$$

where $k_0 = 2k_B T/h$ is the jump frequency (s^{-1}); k_B and h are the Boltzmann constant (8.6173×10^{-5} eV K^{-1}) and the Planck's constant (4.1357×10^{-15} eV s^{-1}), respectively; E_a is the energy barrier (eV); T is the system temperature (K).

Eq. (1) defines the jump rate (s^{-1}) for a hydrogen to jump from one T-site to one of its unoccupied neighbors. The hopping probability of entering a hydrogen occupied site is considered as zero or impossible, because hydrogen does not bond with other H atoms at the nearby solute sites. First principle calculation reveals that the hydrogen pair interaction is strongly repulsive with a binding energy much higher than the diffusion energy barrier [17], [19], [21]. Due to the huge energy difference, the hydrogen combination can be neglected.

The total occurrence rate of all possible diffusion events, R_{tot}, is computed as the summation of all individual hopping rates as

$$R_{tot} = \sum_i \sum_j k_{i,j} \tag{2}$$

Where $k_{i,j}$ represents the occurrence rate of the *j*-th diffusion event of the *i*-th hydrogen atom.

The simulation first randomly places the hydrogen atoms on the interstitial sites and pre-calculates the diffusion hoping rates for all hydrogen atoms. A uniform random number $r \in [0,1)$ is drawn and a diffusion event is selected based on Fig. 2, in which, each segment represents the hopping rate of each possible diffusion event. They form a staircase probability density function. The calculated rR_{tot} will uniquely determine the selected diffusion event for this step. Then, the hydrogen atom is moved to its new location, and the affected local occurrence rates are recalculated.

The physical time is advanced by the amount calculated by Eq. (3), where $r' \in [0,1)$ is another uniform random number.

$$\Delta t = -R_{\mathrm{tot}}^{-1} \ln r' \tag{3}$$

After the entire physical time is simulated, all hydrogen atoms will be shifted to their new locations. The diffusion coefficients will then be determined according to the Einstein relation:

$$D = \lim_{t \to \infty} \frac{\langle [r(t) - r(0)]^2 \rangle}{2dt} \tag{4}$$