# Accuracy Evaluation of Thermodynamic Model of Hydrogen Trapping by Monovacancies in Tungsten

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## 1. Introduction

Tungsten has a high melting point, high thermal conductivity, and low hydrogen solubility, making it a promising material for plasma facing components (PFCs) in fusion reactors. However, previous studies showed that hydrogen (H) isotopes retention is significantly increased in irradiated tungsten (W) [1], which should be investigated for the safety of nuclear fusion devices, including radiation safety for tritium beta decay and materials integrity with respect to tritium embrittlement.

Vacancy has been identified as one of the radiation defects that strongly capture hydrogen atoms in irradiated tungsten [2]. Density functional theory (DFT) calculations showed that several H atoms can be trapped by a monovacancy in bcc-W, and several thermodynamic models have been proposed [3-6]. However, the validity of the thermodynamic models has not been confirmed sufficiently.

In this study, we constructed and verified a thermodynamic model to predict the number of H atoms trapped by monovacancies in bcc-W at given three conditions (temperature, the concentration of monovacancies, and the concentration of solute hydrogen in lattice interstitial sites). For the model validation, data on vacancy-hydrogen complex distributions at various conditions were accumulated using molecular dynamics (MD) simulations and were compared with the prediction of the thermodynamic model. The established thermodynamic model can be used to estimate the tritium inventory of fusion reactors in future studies.

## 2. Methods

First, we specify the meaning of vacancy. In this study, vacancy only means monovacancy. The symbol V is also used to represent monovacancy.

### 2.1. MD simulations

A defective W crystal containing 0.1 at.% vacancies was modeled using a 30×30×30 supercells consisting of 53946 tungsten atoms and 54 vacancies. The initial lattice constant of the system was 3.14 Å. The total hydrogen concentration was set to 0.06%, 0.2%, or 0.6%. The stable interstitial site of hydrogen in lattice is the tetrahedral site and that of hydrogen trapped by vacancy is near the octahedral site [7]. Thus, the initial position of each hydrogen atom was randomly set to be a tetrahedral site for non-trapped hydrogen or an octahedral site for trapped hydrogen. The vacancies were also randomly created before introducing hydrogen atoms.

All MD simulations were performed using Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [8]. The embedded atom method (EAM) potential parameterized by Li-Fang Wang et al [9] was used because it has satisfactory performance in binding energy between vacancy and hydrogen. To obtain vacancy-hydrogen fractions at equilibrium, each defective system was equilibrated with an NPT ensemble of $1 \times 10^5$ Pa and 1200K for 1 ns. Subsequently, the distribution of vacancy-hydrogen complexes was obtained in a production run of 1 ns at the same temperature and pressure conditions. We validated the accuracy of the thermodynamic model by comparing the model prediction with these MD simulation results.

### 2.2. Thermodynamic model

A thermodynamic model was formulated to predict the number of H atoms trapped by vacancies at equilibrium. For simplicity, we assumed that the vibrational entropy is relatively negligible compared to the configurational entropy, vacancy can trap up to 6 hydrogen atoms, and that the system is in an equilibrium state. The unique point of the thermodynamic model in this study is to consider meta-stable vacancy-hydrogen complexes: $VH_2$, $VH_3$, and $VH_4$ complexes have meta-stable structures (Fig. 1). Details of the stable structures of vacancy-hydrogen complexes can be found in [10].
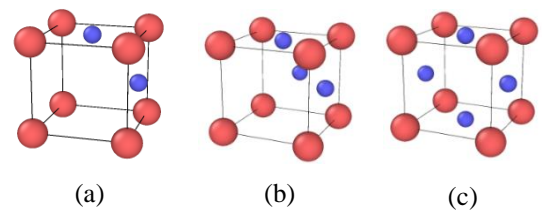


Fig. 1. Structures of meta-stable vacancy-hydrogen complexes: (a) $VH_2 - meta$, (b) $VH_3 - meta$, and (c) $VH_4 - meta$. The red balls are W atoms and the blue ones are H atoms.

The Helmholtz free energy ($A$) of a system containing vacancies and hydrogen atoms is expressed as

$$A = U - TS = N_V \sum_{i=1}^{9} \left( e_i f_i \right) - kT \ln W_{config}, \qquad (1)$$

where $U$ and $S$ are the internal energy and entropy of the system, respectively. $N_V$ is the number of

vacancies in the system, $e_i$ is the total binding energy of $VH_i$ complex, $f_i$ is the fraction of $VH_i$ complex which is the ratio of the number of $VH_i$ complexes to the number of all vacancies, $k$ is the Boltzmann constant, and $W_{config}$ is the number of configurations of vacancy and hydrogen atoms in the system. $W_{config}$ can be divided into three terms: the number of configurations of interstitial H atoms over all tetrahedral sites ($W_{H,int}$), the number of configurations on the location of vacancy-hydrogen complexes in the lattice ($W_i$), and the number of configurations on the location of H atoms in each vacancy-hydrogen complex ($W'_i$). Using Stirling's approximation, $\ln W_{config}$ can be developed as follows:

$$\ln W_{config} = \ln W_{H,int} + \sum_{i=1}^{9} \ln W_i + \sum_{i=1}^{9} \ln W'_i$$

$$= \ln_{N_{site}} C_{N_{H_i}} + \sum_{i=1}^{9} \ln \left( \sum_{j=i-1}^{9} N_V f_i \, C_{\sum_{j=i}^{9} N_V f_i} \right) + \sum_{i=1}^{9} \ln \left( w_i \right)^{N_V f_i},$$

$$\sim N_{site} \ln N_{site}$$
$$- \alpha \ln \alpha - \beta \ln \beta + N_V \ln N_V$$
$$- \left( N_V \left( 1 - \sum_{m=1}^{9} f_m \right) \right) \ln \left( N_V \left( 1 - \sum_{m=1}^{9} f_m \right) \right) \quad (2)$$
$$- \sum_{m=1}^{9} \left( N_V f_m \right) \ln \left( N_V f_m \right) + \sum_{m=1}^{9} \left( N_V f_m \right) \ln w_m,$$

$$\alpha = \left( N_{site} - \left( N_H - N_V \sum_{m=1}^{9} n_{H,m} f_m \right) \right), \quad (3)$$

$$\beta = \left( N_H - N_V \sum_{m=1}^{9} \left( n_{H,m} f_m \right) \right), \quad (4)$$

$$\sum_{i=0}^{9} f_i = 1, \quad (5)$$

where $N_H$ is the number of H atoms in the system, $N_{site}$ is the number of tetrahedral sites in the system, $n_{H,m}$ is the number of H atoms in each $VH_m$ complex, and $w_m$ is the geometric multiplicity of $VH_m$ complex. $n_{H,m}$ and $w_m$ of each vacancy-hydrogen complex are presented in Table 1. Note that $f_0$ represents the fraction of vacancies that do not trap H atoms.

The fractions of vacancy-hydrogen complexes in an equilibrium state were obtained by minimizing $A$ with respect to $f_i$ ($i = 1 \ldots 9$) as

$$\frac{\partial A}{\partial f_1} = \cdots = \frac{\partial A}{\partial f_9} = 0 \quad (6)$$

This yields the simultaneous equations for determining $f_1$ through $f_9$.

Table 1. The number of trapped H atoms ($n_{H,m}$) and the geometric multiplicity on the location of trapped H atoms ($w_m$) for each vacancy-hydrogen complex.

| | Type | $n_{H,m}$ | $w_m$ |
|---|---|---|---|
| $f_0$ | V | 0 | 0 |
| $f_1$ | $VH_1$ | 1 | 6 |
| $f_2$ | $VH_2$ | 2 | 3 |
| $f_3$ | $VH_2 - meta$ | 2 | 12 |
| $f_4$ | $VH_3$ | 3 | 12 |
| $f_5$ | $VH_3 - meta$ | 3 | 8 |
| $f_6$ | $VH_4$ | 4 | 12 |
| $f_7$ | $VH_4 - meta$ | 4 | 3 |
| $f_8$ | $VH_5$ | 5 | 6 |
| $f_9$ | $VH_6$ | 6 | 1 |

In Eqs. (1) and (6), the total binding energy of $VH_i$ complex ($e_i$) was obtained by LAMMPS code in a 30×30×30 supercell. The effect of lattice thermal expansion was considered. The total binding energy of vacancy-hydrogen complex in equilibrium volume at temperature $T$ K, which is denoted as $e_i(T)$, is defined as

$$e_i(T) = \{i \times E_{TIS,H}(T) + E_V(T)\} - \{E_{VH_i}(T) + i \times E_{pure,W}\}, \quad (7)$$

where $i$ is the number of H atoms trapped in a vacancy, $E_{TIS,H}(T)$ is the energy of the system containing one H atom in tetrahedral site, $E_V(T)$ is the energy of the system containing a $VH_i$ complex, and $E_{pure,W}$ is the energy of the perfect crystal system.

## 3. Results and Discussions

*3.1. Comparison regarding distribution of V-H complexes*

The distribution of vacancy-hydrogen complexes predicted by the thermodynamic model was compared to that from MD in Fig. 1 for (a) 0.06% H, (b) 0.2% H, and (c) 0.6% H.

(a)
0.1 % *V*-0.06 % H-1200K



(b)
0.1 % *V*-0.2 % H-1200K
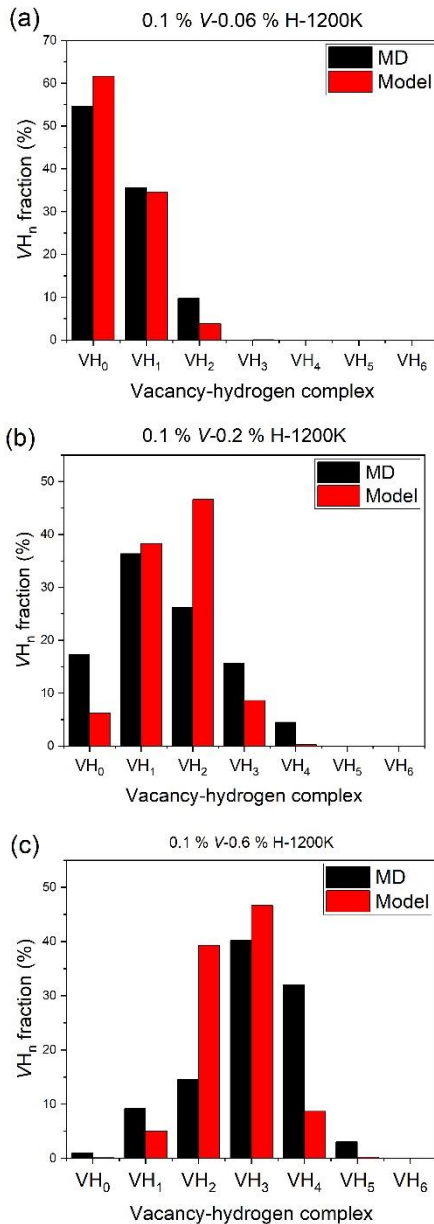


(c)
0.1 % *V*-0.6 % H-1200K



Fig. 2. Comparison between the thermodynamic model and MD results regarding the distribution of vacancy-hydrogen complexes at 1200 K with different H concentrations: (a) 0.06%, (b) 0.2%, and (c) 0.6%. $VH_0$ represents vacancies that do not trap any hydrogen atoms.

It is observed that the fractions of vacancy-hydrogen complexes trapping many H atoms, such as $VH_3$ and $VH_4$, increase as the total hydrogen concentration increase in the system. Except for Fig. 2 (a), a relatively large discrepancy is seen between MD and the thermodynamic model. There are two reasons of this discrepancy. The first one is the validity of binding energy. The potential model shows nice performance in the total binding energy of vacancy-hydrogen complex at 0 K compared to the results of DFT calculations [11]. This fact cannot guarantee that the total binding energy of vacancy-hydrogen complex is still valid at 1200 K

compared to the results of DFT calculations in the expanded system which has the same lattice constant at 1200 K. The second one is the vibrational entropy, which was ignored in the present model for simplicity. The vibrational entropy is determined from the frequencies of normal mode is the system, and the frequency is affected by the interactions between atoms. As more H atoms are trapped in one vacancy, the interactions between trapped H atoms would be enhanced. In addition, the entropy contribution in the free energy increases as the temperature increases. Therefore, the influence of vibrational entropy should increase at high temperature and for large vacancy-hydrogen complex. For these reasons, large differences between MD and the thermodynamic model are expected in large vacancy-hydrogen complex such as $VH_3$, $VH_4$, and $VH_5$, and at high temperature. The summation of the number of vacancy-hydrogen complexes is constant as in Eq. (5). If the fractions of some types of vacancy-hydrogen complexes are underestimated in the thermodynamic model, for example, the model should overestimate the fractions of other types of vacancy-hydrogen complexes. Hence, we consider that the error in $VH_2$ fraction is induced by the errors in the fractions of large vacancy-hydrogen complexes in the thermodynamic model.

### 3.2. Prediction of increased hydrogen inventory in defective tungsten from thermodynamic model

A critical purpose of the thermodynamic model is to predict the increase in tritium inventory by radiation damage. Although the thermodynamic model did not explain the MD results well for the distribution of vacancy-hydrogen complexes, if the thermodynamic model can predict the total hydrogen inventory with reasonable accuracy, it is still useful in the engineering application.

Fig. 3 shows the total hydrogen concentration in the system with respect to the concentration of solute hydrogen in the lattice. If the system were a perfect crystal, $C_{tot}$ should be the same with $C_{lat}$. Fig. 3 indicates that the thermodynamic model reasonably agrees with the MD results for the increase in hydrogen inventory. The discrepancy between the thermodynamic model and MD results is considered to come from the same reasons as the discrepancy in the distribution of vacancy-hydrogen complexes. The inclusion of vibrational entropy is expected to improve the accuracy of the thermodynamic model, and we plan to implement it in future studies. Note that the vibrational entropy is also important to consider the isotope effect between H and T.
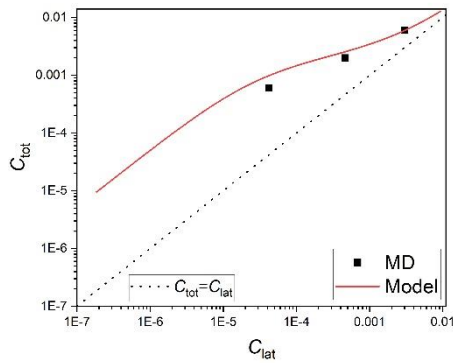
Fig. 3. Comparison between MD and the thermodynamic model for the impact of 0.1 % vacancies on hydrogen inventory in W. $C_{tot}$ is the total hydrogen concentration in the system and $C_{lat}$ is the concentration of solute hydrogen in lattice interstitial sites.

## 4. Conclusion

We constructed a thermodynamic model to predict the number of H atoms trapped by monovacancies in bcc-W based on the equilibrium theory. The thermodynamic model considers the effect of thermal expansion in trapping energy, and meta-stable structures of vacancy-hydrogen complexes. MD simulations were used to validate the thermodynamic model. The model shows relatively good performance at low hydrogen concentration in terms of distribution of vacancy-hydrogen complexes. Also, the model has generally good agreement with MD results regarding the prediction of total hydrogen inventory. We consider that the vibrational entropy is the cause of the discrepancy between the model and MD results, and plan to implement the vibrational entropy in the thermodynamic model in future studies.

## 5. Acknowledgment

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