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To link to this article: DOI: 10.1016/j.actamat.2015.10.018
URL: http://dx.doi.org/10.1016/j.actamat.2015.10.018


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Influence of trap connectivity on H diffusion: Vacancy trapping

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A B S T R A C T

A model is given for the effective diffusion of interstitial solutes in the presence of traps. It goes beyond Oriani’s by taking into account, in a simple way, the connectivity between interstitial trap sites. It shows, in particular, that the typical dimension of a network of trap sites, connected by low barriers, appears squared in the diffusion coefficient. Therefore, a large precipitate can be inefficient if it offers a fast diffusion path, even if each individual trap site is deep. The model is illustrated in the case of hydrogen trapping at vacancies in Ni, using ab initio calculations for migration barriers and Kinetic Monte Carlo for validation. Trapping/detrapping kinetic parameters for “Thermal Desorption Spectra” analysis are also given.

Keywords:
Diffusion
Hydrogen embrittlement
ab initio calculation

1. Introduction

Hydrogen trapping plays a key role in the environmental damage of structural metallic alloys. It can be seen from two points of view. Trapping can lead to high H concentrations along potential fracture paths, whether at grain boundaries [1–4] or along intense slip bands [5,6], which lead to H embrittlement. Alternatively, alloy design could be used to enhance trapping away from potential fracture paths [7–10], for example, at matrix precipitates instead of dislocations or grain boundaries, opening the possibility to optimize the resistance against H damage. Of particular importance is the role of vacancies. In plasma facing materials for fusion reactors, where H isotopes uptake occurs at the same time as irradiation, vacancy-hydrogen clusters might be at the origin of the formation of bubbles which participate to the deterioration of the surface and also contribute to tritium retention in the material [11,12]. It has also been proposed that such clusters play a direct role in room temperature embrittlement when the vacancies are produced by intense localized plasticity [13,14].

Continuum diffusion equations incorporate trapping [15–17] through an effective diffusion coefficient $D_{\text{eff}}$ which reflects the local equilibrium between trap sites and regular interstitial sites in their immediate neighborhood. As shown by Oriani [18], the ratio $D_{\text{eff}}/D_i$ ($D_i$ is the diffusion coefficient in the perfect lattice) depends only on the segregation energy $\Delta E_s$ and the density of trap sites. Sometimes, the parameters in $D_{\text{eff}}$ are misunderstood [19,20] and, indeed, its formulation is not intuitive. First, even if the equilibrium hypothesis is coherent with the absence of any kinetic parameter in $D_{\text{eff}}/D_i$, the absence of any detail concerning the spatial distribution of traps, for example in the case of a trap composed of multiple interstitial sites connected by low energy barriers, is puzzling. Second, it is believed that crystalline defects affect the jump barriers not only in their core but also within a certain radius, creating correlations among H jumps that increase the trap efficiency.

In this paper, we want to discuss these different aspects in the case of the vacancy. The goals are: to derive a physically based model, which contains all the details of the multiple trap [21], show in which conditions Oriani’s model is valid and give a methodology applicable to more complex traps, like small precipitates. Furthermore, we choose Ni–H as a model metal-hydrogen system because it is the subject of many experimental and theoretical studies: vacancy-hydrogen clusters are known to be stable [22,23] and have been proposed to play a role in embrittlement [14] (together with other aspects [24,3]), and maybe in oxidation at intermediate temperature [25–27,23]. Therefore, an additional purpose is to give materials specific energy barriers. Such information is also important to model vacancy diffusion in the presence of H [28].

To achieve this, a combination of atomic scale simulations is used: DFT calculations provide material specific jump barriers and “accelerated” Kinetic Monte Carlo (KMC) integrates this information to provide effective diffusion coefficients, taking into account all correlations among jumps. Finally, a semi-analytical model,
based on random walk theory and First Passage Time Analysis [29], is derived. It quantitatively reproduces the KMC results and gives a simple picture of trap efficiency which is both a useful guideline for the design of complex traps and an efficient alternative to KMC.

The paper is organized as follows. First, the methods are detailed. Then, the study of diffusion starts with the calculation of the jump barriers for H, inside the vacancy (among the multiple trap sites), and for escaping the vacancy. Then, these data are used to calculate effective diffusion coefficients, as a function of the concentration of vacancies and temperature. The model is used to analyse the results in the discussion section. Its detailed derivation is given in given in the Appendix, together with a discussion of the approximations.

2. Methods

2.1. DFT calculations

The energy barriers for the Ni–H–vacancy system are obtained by first-principles calculations based on the density functional theory (DFT) [30,31], using the Vienna ab initio simulation package (VASP) [32–34]. The generalized gradient approximation (GGA) of the Perdew-Wang (PW 91) form [35,36] for electron-exchange and correlation is used. A plane-wave basis set is employed within the framework of the Blochl projector-augmented wave (PAW) method [37] to describe the electron–ion interactions. On the basis of a previous work [38], an energy cut-off as large as 400 eV (29.4 Ryd) and a 24 × 24 × 24 Monkhorst-Pack [39] sampling of the primitive Brillouin zone (BZ) are chosen to obtain accurate energy differences. The equilibrium lattice structure is determined by minimizing the Hellmann-Feynman forces on the atoms and the stress on the unit cell. The magnetic moments are taken into account in all calculations. The force convergence criterion is set to 0.01 eV/Å. Two sizes of supercells are tested: 32 and 108 atoms. The differences, with cell size, in segregation energies are less than 0.03 eV. Therefore, the more computationally demanding calculation of the energy barriers for H migration are done on a supercell containing 32 atoms. The Nudged Elastic Band (NEB) method [40] is used to locate the minimum energy pathways (MEP) for hydrogen migration. A spring force-constant of 5 eV/Å is used between images. The NED method is a second random number between 0 and 1. The interstitial sites inside the vacancy can trap H [46,21]. We will show below that energy barriers within the vacancy are very low with respect to escape barriers. This low-barrier problem precludes KMC simulations from reaching long times. An acceleration method, known as the mean rate method (MRM) [47,29], is used in this situation. More details are given in the KMC section. H on bulk sites is treated with a normal KMC procedure, and H in the basin (vacancy) with the MRM. With the H trajectories obtained by KMC, the diffusion coefficient is measured by the Einstein expression:

\[ D = \frac{\langle (\vec{r}(t) - \vec{r}(0))^2 \rangle}{6t} \] (4)

where \( \vec{r} \) is the position of the H atom at t. To get a better statistics, we follow the approach proposed by Kirchheim [48,49], and divide a long trajectory into a number of segments of time length \( \Delta t \), calculate \( D_i = \langle (\vec{r}(t) - \vec{r}(t-\Delta t))^2 \rangle / 6\Delta t \) and average \( D_i \) over the entire simulation duration t to get \( D = \sum D_i \Delta t / t \). The simulation is long enough so that D does not depend on the chosen \( \Delta t \).

2.3. Oriani’s model

Within the framework of the random walk theory [50,51], the bulk diffusivity D on a cubic lattice is

\[ D = \frac{1}{6} n \Gamma^2 \] (5)

In this expression, \( n \) is the number of equivalent jumps (\( n \) equals 12 for direct jumps from an octahedral site to another), \( \Gamma \) is the average jump length (\( \Gamma = \sqrt{2/3} a_0 \)), \( a_0 \) being the lattice parameter, \( \Gamma \) is the jump rate given by Eq. (1). With the harmonic transition state approximation, D is expressed as

\[ D = \frac{k_B T}{h^2} e^{-\Delta_G m / k_B T} \] (6)

with \( \Delta_G m \), the free energy of activation for a O → O jump. When the tetrahedral interstitial site is sufficiently deep, the diffusion atom temporarily equilibrates in the tetrahedral site [41] and the
diffusion coefficient is:

\[
D_l = D \frac{1}{2} \left( 1 + 2e^{-\Delta_{\text{Gert-oct}}/k_B T} \right)^{-1}
\]

where \(\Delta_{\text{Gert-oct}}\) is the difference in the free energies for H at the tetrahedral and octahedral sites, and D is given by Eq. (6) with \(\Delta G_m\) the barrier for a \(O \rightarrow T\) jump.

As briefly mentioned in the introduction, an analytical expression to describe the effect of trapping sites on bulk diffusion of H atom was proposed by Oriani [18]. It was generalized by Kirchheim [48] for multiple-traps in the framework of random walks, in the case of an idealized energy landscape where all saddles have the same energy (but the trap sites have different energies). In this case the jumps are uncorrelated and it can be shown that

\[
D_{\text{eff}} = D_l \left( 1 + \sum_i \frac{n_i}{n_l} K_i \right)^{-1}
\]

where \(n_i\) the number of trap sites of type \(i\), \(n_l\) is the number of bulk sites, \(K_i\) the equilibrium constant, is equal to \(\exp(-\Delta E_i/k_B T)\) with \(\Delta E_i\) being the segregation energy of H at trap sites of type \(i\). It is defined as the energy difference of a configuration where H is on site \(i\) and the one where H is on a bulk site. \(o_i\) is the occupancy of trapping sites of type \(i\). The simulation results will be compared to this model. We will call Eq. (8) “Oriani’s model” and it will constitute a reference for KMC simulations and for the new model.

3. H interstitial diffusion and trapping

3.1. H migration barriers: DFT results

H occupies interstitial sites in the fcc lattice of Ni. Our previous calculations [46] show that, in the perfect crystal, the energy is lowered by 0.222 eV when H occupies an octahedral site (O) in comparison to a tetrahedral site (T). The zpe correction enlarges this difference by 0.084 eV, in favor of the O site. In agreement with Wimmer’s calculations [41]. The segregation energies on the specific sites of the vacancy (Fig. 1) were also investigated [46]. Segregation is strong on \(O_1\) (\(\Delta E_i = -0.273\) eV, including zpe corrections), closely followed by \(T_1\) (\(\Delta E_i = -0.222\) eV with zpe) and moderate on \(O_2\) (\(\Delta E_i = -0.046\) eV with zpe). Segregation on more remote sites is negligible. In particular, we recall [46] that the \(\Delta E_i\) profile is oscillating, with a small repulsion on \(O_1\) which is not in favor of the dragging of H atoms towards the vacancy. The study of the “radius of capture” effect will therefore be limited to the study of the influence of \(O_1\), \(T_1\), \(T_2\) and \(O_2\) on the H diffusion coefficient.

Direct jumps between adjacent bulk octahedral sites are not possible, since the energy landscape exhibits a local maximum along this path and not a saddle point [41]. Hence, we consider only migrations through T sites (O-T-O paths). Two pathways are possible for H at \(O_1\) to jump out of the vacancy: \(O_1 \rightarrow T_2\) (\(T_2\) is already a bulk site \(T_b\), from the segregation energy point of view, however the barrier to come back to the vacancy is much lower than the one to move away, as shown on Fig. 2) and \(O_1 \rightarrow T_1 \rightarrow O_2 \rightarrow T_b\). The relevant values of barriers, evaluated by the NEB, are given in Table 1. The inner barrier \(O_1 \rightarrow T_1 \rightarrow O_1\) is very small. Finally, the barrier for the \(O \rightarrow T\) jump in the bulk is 0.444 eV, with ZPE correction, which is close to the experimental value (0.43 eV) given by thermal desorption measurements [52].

3.2. KMC-MRM results

With these values of energy barriers, transformed into frequencies by Eq. (1), we perform KMC simulations, first with a simple model containing only \(O_1\) and \(T_b\) (one O site and 2 T sites per metal atom in the fcc lattice, with the connectivity shown on Fig. 1 of [41]). The diffusion coefficient \(D_l\) is in very good agreement with Eq. (7). A fit to the Arrhenius expression \(\ln(D) = \ln(D_0) - (Q/k_B) 1/T\) to the simulation results give

\[
\ln(D) = \ln(D_0) - \left( \frac{Q}{k_B} \right) \frac{1}{T}
\]

where \(Q = 1.488\) eV for \(O_1\) and \(T_b\) and \(Q = 1.544\) eV for \(O_2\) and \(T_2\). On the other hand, \(D_{\text{eff}}\) is halved between these two models, in agreement with the ratio of 1:2 for the number of vacant sites.

![Fig. 1. Schematic representation of the interstitial sites around a vacancy (gray ball) in fcc Ni. O₁ (olive green ball) and O₂ (green ball) are octahedral (O) sites in first and second nearest neighbor (NN) position of the vacancy. T₁ (blue ball) and T₂ (violet ball) are 1NN and 2NN tetrahedral (T) sites. T₂ is already considered as a bulk site, from the segregation point of view (see text).](image)

![Fig. 2. Energy profile seen by a hydrogen atom in the vicinity of a vacancy. There are two paths to exit the vacancy: one goes through T₂ sites and the other goes through T₁ sites.](image)

| Table 1 Jump barriers \(\Delta G_m\) (eV) (row (initial state) → column (final state)) for H in the vacancy and in the bulk calculated by the NEB method. ZPE corrections are included. |
|---------------------------------|--------|--------|--------|--------|--------|--------|
| \(\Delta G_m\)              | \(O_1\) | \(T_1\) | \(T_2\) | \(T_2/T_b\) | \(O_2\) |
| \(O_1\)                      | –      | 0.069  | –      | 0.640  | –      |
| \(T_1\)                      | 0.020  | –      | 0.554  | –      | –      |
| \(O_2\)                      | –      | 0.385  | –      | 0.490  | –      |
| \(T_2\)                      | 0.061  | –      | 0.138  | –      | 0.138  |
| \(T_b\)                      | –      | –      | –      | –      | 0.444  |
The impact of the vacancy is studied. An atom is “removed” from the lattice, i.e. 6 O1 sites, 8 O2 sites, 8 T1 sites and 24 T2 sites, with the connectivity of the vacancy (Fig. 1) and the jump frequencies corresponding to the barriers of Table 1 are included in the network of O2 and T3 sites used above. The vacancy concentration is adjusted by changing the box size. Only one H atom is considered in the simulation. Therefore, the trapping effect on the diffusion is maximum (we give an upper bound) [55].

From Table 1, the barriers in between O1 and T1 are very low (0.069 eV and 0.02 eV) in comparison to the barriers to exit the vacancy (0.64 eV and 0.554 eV). Therefore, a simple KMC is very inefficient since most of the CPU time is spent to simulate inner vacancy jumps. We have noticed that the statistics is so low that we could not recover the equilibrium occupancy of the vacancy, not even after long runs. The Mean Rate Method [29,47] is used to overcome this limitation. The states formed by an isolated H atom occupying one of the 6 O1 sites or 8 T1 sites are considered to form a basin of states connected by low barriers (“transient states” in the formalism of absorbing Markov chains [29,47]). There are two different paths for a H to exit the vacancy: the jump from O1 to T2 (0.64 eV) or the one from T1 to O2 (0.554 eV). The states where H occupies T2 or O2 sites are the “absorbing states”. Having defined the transient and absorbing states, we follow the procedure given in Ref. [29] to select one transition out of the basin and simulate the corresponding waiting time. In such KMC, only one step is necessary to exit the vacancy. We checked that the equilibrium occupancy of the vacancy is recovered after a sufficiently long time is simulated (ergodicity). Note that the correlations related to O2 and T2 are preserved. The effect of CV (the atomic vacancy concentration) and T on H diffusion are studied. The simulated effective diffusion coefficient Deff are presented in Fig. 3. The results are in good agreement with Oriani’s model (Eq. (8)), taking into account the vacancy sites O1O2 and T1 (there is almost no difference if O2 is ignored), but only at low vacancy concentrations. The trapping effect becomes independent of the vacancy concentration at high CV.

4. Discussion

We want to analyze the origin of the good agreement between Oriani’s phenomenological model and the KMC simulations. For this, a model of Deff is derived from random walk theory (Appendix):

\[
D_{\text{eff}} = D_{\text{bulk}}P_{\text{bulk}} \left(1 + \frac{\Gamma_{\text{exit}}}{\Gamma_{\text{bulk}} \Gamma_{\text{vac}}} \sum_{i} \frac{p_{i} \Delta E_{i}^{2}}{\Delta r_{i}^{2}} \right) \quad (9)
\]

\[
P_{\text{bulk}} = \frac{1}{1 + 2e^{-\Delta E_{b}^{\text{eff}}/kT} + C_{V} \left(6e^{-\Delta E_{b}^{\text{eff}}/kT} + 8e^{-\Delta E_{c}^{\text{eff}}/kT} \right)} \quad (10)
\]

Dbulk is the diffusion coefficient in the absence of any trap, Pbulk (resp. Pvac) is the probability for a H to be on a bulk (resp. vacancy) interstitial site (Eq. (10)). \(P_{\text{bulk}}\) is the jump rate from \(D_{\text{bulk}}\) to \(O_{\text{bulk}}\). \(\Gamma_{\text{exit}}\) is the average jump rate out of the vacancy. In general, it depends on the entry point and on the internal jump rates, i.e. the jump rates in between the interstitial sites of the vacancy: T1, O1 and others, as shown below. \(A \Gamma_{\text{bulk}}\) is the squared jump distance relative to \(\Gamma_{\text{bulk}}\), i.e. 1/2\(a_{0}^{2}\). In the case of vacancy jumps, an average is taken over all possible path through the vacancy: \(\sum_{i} p_{i} \Delta r_{i}^{2} \), where \(p_{i}\) is the probability of path \(i\) and \(\Delta r_{i}\) is the vector connecting the entry and exit sites (i.e. first site in the vacancy and first octahedral site out of the vacancy). The geometrical factor \(\sum_{i} p_{i} \Delta r_{i}^{2}/A \Gamma_{\text{bulk}}\) is called g. \(\Gamma_{\text{exit}}\) is calculated, exactly, by solving the master equations for the occupations of the interstitial sites inside the vacancy (Appendix). As the inner barriers are low and the network of connected sites has a small dimension, the occupations reach their equilibrium values before hardly any exit from the vacancy occurs. Therefore \(\Gamma_{\text{exit}}\) can be approximated by \(\Gamma_{\text{exit}}^{\text{eff}}\) (Eq. (A.7)). In this case, g, which depends on temperature and relative trap depth, can be easily calculated \((g \approx 1.8, \text{see Appendix})\). It is not much greater than unity for a point defect, but it can be large for other defects like precipitates or dislocation lines, if they offer easy diffusion paths.

The last term to be analyzed is the product \(\Gamma_{\text{exit}}/\Gamma_{\text{bulk}} \times P_{\text{vac}}/P_{\text{bulk}}\). There is no compensation among the thermally activated terms, contrary to the usual assumption that the activation energy to jump out of the vacancy is \(\Delta E_{V} = \Delta E_{b} - \Delta E_{c}\) [12]. Finally, the product scales like 6\(C_{V}\)\(a_{0}^{2}\). At low vacancy concentration, this term is negligible and Eq. (9) reduces to Oriani’s model \((D_{\text{eff}} = P_{\text{bulk}}D_{\text{bulk}})\). The result is counter intuitive: the inner sites of the vacancy have the same trapping effect on H whether they are far apart, or connected by low barriers. Indeed, equation (9) shows that, at first order, it is the probability of being on a bulk site which matters for diffusion. It is an equilibrium quantity which does not depend on the details of the escape from the traps. This is valid only if: (i) the density of interstitial trapping sites is low and (ii) these traps are not connected or form networks of small dimensions. In the specific case of the vacancy, CV has to be pushed high to observe an effect of the connection. The maximum value used for KMC is 3 \(10^{-2}\) (Fig. 3).

At this concentration, the vacancies are put on a square lattice of dimension 2 \(a_{0}\). They are sufficiently far apart not to interact. Indeed, the effect of the vacancy is negligible beyond the T3 site [46] and beyond this distance only bulk sites are considered in KMC. The effect comes from the connectivity in between the 6 O1, 8 T1, 8 O2 and 24 T2 interstitial sites of the same vacancy.

A quantitative agreement between the model and KMC (Fig. 3) requires O2 and T2 sites be taken into account. They have almost no influence on Deff at low CV (Fig. 3), where all the effect is due to segregation, because the segregation energy on these sites is close to zero \((\Delta E_{2}^{\text{eff}} = 0, \Delta E_{1}^{\text{eff}} = -0.05 \text{ eV})\). Nevertheless, O2 and T2 play a
large role on $\Gamma_{\text{exit}}$ and therefore show up at large $C_H$ as shown by the difference between the curves "RW" and "RW" on Fig. 3 (model with and without $O_2$ and $T_2$ respectively, i.e. Eqs. 9 and A.9 versus Eqs. 9 and A.7). The reason is that diffusion jumps starting from $O_2$ and $T_2$ are biased: the reduced energy barriers in the direction of the vacancy (Fig. 2) imply jump rates 20 to 70 times higher, at 300 K, in this direction. It brings back H to the vacancy and increase trapping.

Finally, for comparison with thermal desorption spectra [56], $\Gamma_{\text{exit}}^{\text{eq}}$ (Eq. (A.9)) is fitted on the Arrhenius pre-exponential factor $k\text{g}_\text{TH}$: the activation energy is 0.69 eV and the pre-exponential factor is $9 \times 10^{13}$ Hz, slightly different from the values obtained for a single jump [12], from $E^{\text{act,eq}} = E^{\text{act,eq}} - \Delta E_c$: 0.74 eV and $10^{13}$ Hz. Note that the pre-exponential factors used are only valid at low temperature [41] and that lower activation energies for H detrapping are expected for VHs due to repulsive H–H interactions.

5. Conclusion

This paper delivers two messages. First, we studied in detail the trapping capacity of vacancies, specifically in Ni, calculating jump frequencies ab initio, for all the relevant paths in and around the vacancy. This information is included in KMC simulations to obtain the H diffusion coefficient. The influence of temperature and vacancy concentration on $D_{\text{eff}}$ is well reproduced by Oriani’s model, including $T_1$ and $O_2$ sites, with multiplicity 8 and 6. This model shows that very high concentrations of vacancies are necessary to have a significant effect on diffusion: beyond 1 ppm at 300 K and beyond 100 ppm at 600 K. These values are orders of magnitude higher than equilibrium VH$_c$ concentrations (i.e. including Fukui’s superabundant vacancy effect) which are at maximum of $10^{-15}$ at 300 K and $10^{-6}$ at 600 K [23] at very high H concentrations, beyond 1% atomic. Nevertheless, such high vacancy concentrations were reported under very intense localized plasticity conditions [14,57,58].

Second, we model the impact of trap connectivity on H diffusion by deriving Oriani’s formula in the framework of random walks and introducing the mean escape frequency from the vacancy. The First Passage Time Analysis from Puchala [29], applied to the basin composed of the states where H occupies the interstitial sites of the vacancy (Appendix), enables a rigorous calculation of the escape frequency with the real connectivity in between the various sites involved. The limitations of Oriani’s formula are determined. They have two physical origins. First there is not an exact compensation between the various activation energies involved, namely: the bulk diffusion activation energy, the exit activation energy and the segregation energy. In the case of Ni, this enhances diffusion with respect to Oriani’s formula (i.e. the trapping efficiency is lower than predicted by Oriani) below room temperature and at high trap concentration. Second, the trap connectivity is at the origin of a geometric factor which scales like the square of the characteristic length of the network of traps connected by low barriers. It has a weak influence for a point defect but can be important for larger defects, like intragranular precipitates, if they provide long, fast, diffusion paths. The method exposed in the Appendix gives the tools for establishing traps efficiency quantitatively, which can be useful for designing microstructures optimized for resisting to H damage.

Acknowledgments

This work was granted access to the HPC resources of CALMIP (CIT Toulouse, France) under the allocations 2014-p0912 and 2014-p0749. The authors acknowledge the support of the French Agence Nationale de la Recherche (ANR), under grant EChyDNA (Blanc 10-19424). It’s a pleasure to thank Danny Perez for discussions about FPTA during visits at LANL, funded by CNRS (PICS program).

Appendix A

$D_{\text{eff}}$ is derived from Einstein’s formula Eq. (4) [59]. The jumps on regular lattice sites are separated from those which involve the multiple-traps (traps composed of several interstitial sites), for which a mean exit frequency $\Gamma_{\text{exit}}$ is used. In Eq. (4), the position can be written as a sum along a sequence of discrete jumps, that we consider, for the moment, uncorrelated: $\vec{r} = \sum_{n=0}^{N} \Delta \vec{r}_n$. The diffusion coefficient becomes:

$$D = \frac{1}{2d} \lim_{N \to \infty} \sum_{i=0}^{N} \Delta \vec{r}_i^2$$

(A.1)

The sum can be rearranged by grouping the terms that correspond to each specific type of jump, labeled i:

$$D = \frac{1}{2d} \lim_{N \to \infty} \sum_{i=1}^{N} \frac{N_i}{\Gamma_i} \Delta \vec{r}_i^2$$

(A.2)

where $N_i$ is the number of type i jumps among the N jumps and $\Delta \vec{r}_i$ the corresponding jump vector.

Following the general TST, the system evolves by a sequence of transitions in between microstates. A microstate is an energy local minimum in the configuration space of the position of the particles, in particular, H occupying interstitial sites, in the bulk, or in the multiple traps. Following Novotny [60], the microstates which are connected by low energy barriers, i.e. which are frequently revisited by the system, are grouped in a “basin” of states. In the specific case of a single H, trapped in a vacancy composed of several interstitial sites (6 $O_1$, 8 $T_1$ etc), the basin is composed of all the microstates obtained by placing the H on the various sites inside the vacancy, i.e. 14 states.

In Eq. (A.2), we separate the jumps that bring the system out the basin, ignore the intra basin jumps, isolate the bulk jumps, and introduce the total time spent in the basin $t_{\text{bas}}$ and on bulk sites $t_{\text{bulk}}$:

$$D = \frac{1}{2d} \lim_{N \to \infty} \sum_{i=1}^{N} \frac{N_i}{\Gamma_i} \left( t_{\text{bas}} \Delta \vec{r}_i^2 + N_{\text{bas}} t_{\text{bulk}} \Delta \vec{r}_i^2 + N_{\text{bas}} t_{\text{bulk}} \Delta \vec{r}_i^2 \right)$$

(A.3)

$\Delta \vec{r}_i$ is now a vector joining a specific entry site in the vacancy and an exit site (a jump out of the basin, after entrance at a specific site, independent of how precisely the atom visits the inner sites). Now, we introduce $N_{\text{bas}}$, the total number of jumps out the basin:

$$D = \frac{1}{2d} \lim_{N \to \infty} \sum_{i=1}^{N} \frac{N_i}{\Gamma_i} \left( t_{\text{bas}} \Delta \vec{r}_i^2 + t_{\text{bulk}} \Delta \vec{r}_i^2 \right)$$

(A.4)

$N_{\text{bas}}/t_{\text{bas}}$ is the mean exit frequency from the basin ($\Gamma_{\text{exit}}$), $t_{\text{bas}}/t_{\text{bulk}}$ is the equilibrium probability of being in the vacancy ($P_{\text{vac}}$) and $N_{\text{bas}}/N_{\text{bas}}$ is the probability of a specific exit jump that we call $p_\text{exit}$, of length $\Delta \vec{r}_i$. The bulk part is simply the probability of a bulk jump times the bulk diffusion coefficient that we factorize to isolate a term equivalent to Oriani’s model. The final expression is equation (9).

$\Gamma_{\text{exit}}$ is calculated [29] by solving the master equation [61] for the occupancy of the basin states ($o_i(t)$), before first exit:

$$\frac{do_i}{dt} = \sum_{j} o_j(t) \Gamma_{ij} - o_i(t) \sum_{k} \Gamma_{ik} - o_i(t) \sum_{k} \Gamma_{ik}$$

(A.5)
\[
\frac{dO_{\text{out}}}{dt} = \sum_i \sum_k o_i(t) \Gamma_{\text{exit}}^{\text{exit}}_{ik}
\]  

(\text{Eq. (1)})

\(\Gamma_{\text{exit}}^{\text{exit}}\) is the rate of exit from state \(i\) towards \(j\) in the basin (Eq. (1) and Table 1). \(\Gamma_{\text{exit}}^{\text{exit}}\) is the rate towards state \(k\), out of the basin (exit state, or “absorbing state”). It is not necessary to know the filling of each absorbing state to calculate \(\Gamma_{\text{exit}}\), and therefore they are all grouped in one state, labeled “out” (Eq. (A.6)). There are 15 equations in the case of a vacancy where only sites \(O_1\) and \(T_1\) are considered for constructing the basin. From the \(o_i\), \(\Gamma_{\text{exit}}\) can be calculated by Eq. 12 in Ref. [29].

\(\Gamma_{\text{exit}}^{\text{exit}}\) is a very simple approximation of \(\Gamma_{\text{exit}}\) when the barriers in between the states of the basin are low in comparison to exit barriers. In this case, it can be considered that the occupations in the basin follow the equilibrium distribution. The validity of the approximation also depends on the dimension of the basin. In the case of the basin constructed from \(T_1\) and \(O_1\) sites, \(\Gamma_{\text{exit}}^{\text{exit}}\) is:

\[
\Gamma_{\text{exit}}^{\text{exit}} = \nu \left( 4 \times p_{O_1} e^{-\Delta G_{O_1-T_1}/kT} + 1 \times p_{T_1} e^{-\Delta G_{T_1-O_1}/kT} \right)
\]  

(\text{Eq. (A.7)})

with

\[
p_{O_1} = \frac{6 e^{-\Delta G_{O_1}/kT}}{6 e^{-\Delta G_{O_1}/kT} + 8 e^{-\Delta G_{T_1}/kT}}
\]  

(\text{Eq. (A.8)})

and the equivalent for \(p_{T_1}\). The factors 4 and 1 in Eq. (A.7) are the number of exit path from \(O_1\) and \(T_1\) respectively. \(\nu\) is the frequency \(kT/\hbar\). Fig. A.4 shows \(\Gamma_{\text{exit}}^{\text{exit}}\) as a function of the \(O_1\) to \(T_1\) jump barrier height and temperature. The approximation is very good in the case of the vacancy, but its quality is dependent problem. A simple validity criterion can be derived by comparing the time for an exit out of the basin (\(t_{\text{exit}}\)) to the time to visit the states of the basin (\(t_{\text{eq}}\)). \(N_{\text{states}}\) is the number of states in the basin. An upper bound for \(t_{\text{eq}}\) is obtained by supposing that the basin is a linear chain of states, connected by a single barrier (\(E_{\text{exit}}^{\text{exit}}\) to \(T_1\) in the case where the basin states involve only the first shell of interstitial sites): \(t_{\text{eq}} = 2N_{\text{states}}/\nu_{\text{exit}}\) (one dimensional diffusion). Exit can occur from any state of the basin: \(t_{\text{exit}} = N_{\text{states}}/\nu_{\text{exit}}\). The criterion is simply \(\Gamma_{\text{exit}}^{\text{exit}}/\Gamma_{\text{exit}}^{\text{exit}} > 2N_{\text{states}}\). At 300 K, with \(N_{\text{states}} = 14\), it gives \(t_{\text{exit}}/t_{\text{eq}} \geq kT \ln(2 \times 14) \approx 0.077\ eV\) in good agreement with Fig. A.4 (\(t_{\text{eq}} = t_{O_1 \rightarrow T_1}\)).

(\text{Eq. (9)})

\[
T_2 \rightarrow O_1\) or through \(O_2\ (O_2 \rightarrow T_1)\) with probability 3/4 and 1/4 respectively (this is obtained by calculating the jump frequencies, assuming equilibrium occupancies of \(O_2\) and \(T_2\) and that the jumps barriers towards the vacancy are the same as bulk ones, to simplify). The probability of entering the vacancy at \(O_2\) (resp. \(T_2\)) is therefore 3/4 (resp. 1/4). The probability of being on a \(O_1\) site (resp. \(T_1\) site) before exit is \(p_{O_1}(T)\) (Eq. (A.8)) (resp. \(p_{T_1}(T)\)). Finally \(p_{i}\) is the product of these two probabilities. The term \(\sum \Gamma_{\text{exit}}/\Gamma_{\text{exit}}^{\text{exit}}\) can be calculated from a list of all possible paths connecting \(O_1\) and \(T_1\) sites. The variation with \(T\) is slow in the range 250–600 K, with an average value of 0.91 \(a_b^2\) \((a_b\) is the lattice parameter of Ni). For a bulk jump, \(\Delta T_{\text{bulk}} = 1/2 a_b^2\), which gives a ratio \(\approx 1.8\).

Equation (A.7) can be modified when the basin incorporate states corresponding to \(O_2\) and \(T_2\) sites:

\[
\Gamma_{\text{exit}}^{\text{exit}} = 8p_{O_2} x 5 e^{-\Delta G_{O_2-O_1}/kT} + 24p_{T_2} x 2 e^{-\Delta G_{T_2-O_1}/kT}\]

(\text{Eq. (A.9)})

where the factors 5 and 2 are the number of paths to leave the vacancy through sites \(O_2\) and \(T_2\) respectively. No migration barriers specific to the vacancy appears anymore, because exit jumps through \(O_2\) and \(T_2\) are bulk jumps. The trapping information is included in \(p_{O_2}\) and \(p_{T_2}\) (and also in the number of exit paths in Eq. (A.9)).

\[
p_{O_2} = e^{-\Delta G_{O_2}/kT} \left( \frac{6 e^{-\Delta G_{T_2}/kT}}{6 e^{-\Delta G_{O_2}/kT} + 8 e^{-\Delta G_{T_2}/kT}} + 24 e^{-\Delta G_{T_2}/kT} \right)
\]

(\text{Eq. (A.10)})

A similar expression can be written for \(p_{T_2}\).

References


D.N. Iljin, N. Santier, J.M. Olive, R. Abgrall, I. Aubert, Simulation of hydrogen


