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Dissociation of migrating particle from trap with long-range interaction field

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Abstract

Some lattice defects, such as dislocations, interact with migrating species, *e.g.* vacancies, interstitial atoms and their clusters, via long-range strain fields. In this paper, an equation for the mean dissociation time of a migrating particle from a trap is derived in terms of the potential well function for the interaction energy. The distribution of dissociation times is studied by the Monte Carlo method, and the problem of particle exchange between spatially separated traps is considered.

Key words: lattice defects, reaction-diffusion theory, defect complexes, dissociation.

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1. Introduction

Solving various problems of diffusion-reaction kinetics requires knowledge of the time a migrating particle spends trapped by lattice defects before dissociation. This information allows considering longer time and length scales using a rate theory [1] or a kinetic Monte Carlo approach, which treats complexes as single entities. These dissociation times have been or can readily be obtained only in simple cases, *e.g.* for vacancy-solute pairs with short-range bonding. In more complicated cases, the solution is generally unknown. A particular example of such a case is that of a vacancy executing three-dimensional (3-D) random walk,

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2 which is trapped inside a Cu precipitate in an iron matrix (see [2-5] for molecular dynamics
3 results). Another example is that of a one-dimensionally migrating cluster of self-interstitial
4 atoms trapped in a long-range field of an edge dislocation (see, *e.g.* [6] for observations in Ni
5 and Mo). Yet another example is that of an interstitial cluster trapped between Cu
6 precipitates in Fe; it can penetrate inside one of them and this requires overcoming an energy
7 barrier (see [4,5] for molecular dynamics results). The importance of the processes
8 mentioned above in microstructure evolution and changes of mechanical properties,
9 especially under irradiation conditions, is discussed in [1-5] for Cu precipitation and, in [6,7],
10 for dislocation decoration with interstitial clusters.
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15 In this paper, we first derive an equation for the mean dissociation time for a well of
16 arbitrary shape in section 2. We start with a simpler case of one-dimensionally diffusing
17 particles in section 2.1, and then generalise to higher-D diffusion in section 2.2. Some
18 particular potential energy wells and limiting cases are considered in section 3. Monte Carlo
19 calculations of the probability distribution of dissociation times are presented in section 4 for
20 two particular 1-D wells. In section 5, we generalise the problem to the case of particle
21 exchange between spatially separated wells for two particular cases: vacancy evaporation
22 from void and interaction of interstitial clusters with dislocation. The conclusions are drawn
23 in section 6.
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32 **2. Mean dissociation time from well**

33 **2.1. One-dimensional diffusion**

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35 Consider a particle that hops on a lattice containing a potential well $U(x_i)$ (interaction energy
36 in equilibrium positions i , see Figure 1a) in the diffusion direction and ‘free’ states. The
37 ‘free’ states are those, where $U(x_i)=0$ and all the migration barriers are the same as in
38 perfect crystal. The mean time-delay between jumps in these states is denoted by τ . A
39 dissociation event occurs when particle jumps from the well to a ‘free’ state and an
40 association event is a reverse jump. The dissociation time τ_{diss} is the mean time from
41 association to dissociation. (This definition is discussed further in sections 4.3 and 5)
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50 [Insert Figure 1 about here]
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4 Consider a well and one adjacent 'free' state in periodic boundary conditions. In this
5 system, a dissociation event is followed by an association event, hence for each time that
6 particle spends time τ_{diss} on average in the well region, it spends time τ in the 'free' state.
7 Hence, the probability to find particle in the 'free' state is equal to
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9

$$10 \quad p_{\text{free}} = \frac{\tau}{\tau + \tau_{\text{diss}}}. \quad (1)$$

11
12 The same probability can be written through the partition function of the canonical ensemble
13 $Z = 1 + \sum_{\text{well}} e^{-\beta U(x_i)}$, where $\beta = 1/k_B T$, k_B is the Boltzmann constant, T is the temperature and
14 unity corresponds to the 'free' state, where $U = 0$, (see, e.g. [8]) as:
15
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$$17 \quad p_{\text{free}} = \left(1 + \sum_{i=1}^N e^{-\beta U(x_i)} \right)^{-1}. \quad (2)$$

18
19 In this equation and further in the text, the summation is taken over all N equilibrium states
20 of the well. From equations (1) and (2) one obtains
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$$23 \quad \tau_{\text{diss}} = \tau \sum_{i=1}^N e^{-\beta U(x_i)} = \tau N \left\langle e^{-\beta U(x_i)} \right\rangle_{\text{well}}, \quad (3)$$

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25 where the brackets denote averaging over sites representing equilibrium states of the well.
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28 **2.2. Higher-dimensional diffusion**

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30 The analysis can readily be extended to two and three dimensionally diffusing particles.
31 Consider a well $U(\mathbf{r}_i)$ of N states surrounded by a shell of adjacent 'free' states, m in total,
32 each separated from the well by one jump distance. Assume that a particle in a 'free' state
33 jumps successfully only to the well. This assumption does not influence the results but makes
34 the derivation easier. It affects, however, the times spent by a particle in 'free' states. If the
35 mean value of these times, τ_{free} , is known, the probability of finding the particle in a 'free'
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state can be written in two ways: as the ratio of times (left-hand side of the following equation) and via the partition function (right-hand side):

$$\frac{\tau_{\text{free}}}{\tau_{\text{free}} + \tau_{\text{diss}}} = \frac{m}{m + \sum_{i=1}^N e^{-\beta U(r_i)}}. \quad (4)$$

Hence, the dissociation time is given by

$$\tau_{\text{diss}} = \frac{\tau_{\text{free}}}{m} N \left\langle e^{-\beta U(r_i)} \right\rangle_{\text{well}}. \quad (5)$$

Now let us find τ_{free} . Under the assumption that a particle in a ‘free’ state jumps successfully only towards the well, the time spent on average by the particle in a ‘free’ state i before jumping back to the well is higher than τ by the ratio of the total number of jump directions z to the number of directions towards the well, n_i : $\tau_{\text{free}}^i = \tau z / n_i$. The mean time is the sum of these times weighted with relative frequency of visiting these states, p_{free}^i , which is equal to the ratio of the number of directions from the well to this particular site, n_i , to the total number of directions from the well to ‘free’ sites, $\sum_{i=1}^m n_i$. Hence $p_{\text{free}}^i = n_i / \sum_{i=1}^m n_i$ and

$$\tau_{\text{free}} = \sum_{i=1}^m \tau_{\text{free}}^i p_{\text{free}}^i = \tau z / \langle n \rangle_{\text{free}}, \quad (6)$$

where the brackets denote averaging over adjacent ‘free’ states. Finally, by substituting equation (6) into equation (5), one obtains

$$\tau_{\text{diss}} = \frac{zN}{m \langle n \rangle_{\text{free}}} \tau \left\langle e^{-\beta U(r_i)} \right\rangle_{\text{well}}. \quad (7)$$

This is a general solution valid for any dimensionality of diffusion. In the case of 1-D diffusion, when the total number of jump directions is $z = 2$, the number of directions from a

‘free’ state to the well is $n = 1$ and the number of ‘free’ states adjacent to the well is $m = 2$, equation (7) reduces to equation (3).

We emphasise that equation (7) depends on the energy of equilibrium states (the exponent is averaged over these states) but is *independent of the saddle point energy profile within the well*. Note that τ depends on the energy barrier in the perfect part of the crystal only. (Obviously, the probability distribution of dissociation times does depend on the saddle point energy and this is considered below in section 4.)

Equation (7) is exact within the assumptions used, i.e. it gives the mean time a diffusing particle spends within a well region between association and dissociation events, which are defined as particle crossings of a dividing surface between the potential well and the rest of the system. It should be emphasised that equation (7) has the meaning of the time when the number of particle-potential well complexes reduces by e times only for exponential distribution of dissociation times. This is thus a necessary condition for the use of equation (7) together with the rate equations without memory effects. This in turn requires separation of the time scale of dissociation from other fast scales, e.g. time for crossing the barrier and equilibration time of a particle within the well (see e.g. [9], p.257). In particular, to ensure separation of the time scales, the potential well must be deep enough compared with the thermal energy, β^{-1} .

3. Mean dissociation times for particular wells

3.1. 1-D square well

For a square well and coordinate x (in units of jump length a)

$$U(x) = \begin{cases} -E, & x_{\min} \leq x \leq x_{\max}, \\ 0, & x < x_{\min}, x > x_{\max}. \end{cases} \quad (8)$$

Equation (3) yields

$$\tau_{\text{diss}} = N\tau e^{\beta E}, \quad (9)$$

where $N = x_{\max} - x_{\min}$ is the total number of equilibrium positions inside the well. Hence the frequency of dissociation events is given by

$$\nu_{\text{diss}} = \tau_{\text{diss}}^{-1} = \left(\frac{2}{N} \right) \frac{e^{-\beta E}}{2\tau}. \quad (10)$$

The physical significance of equation (10) can be understood as follows. The bracketed term stands for the probability to find a particle at one of the two well edges, τ^{-1} is the total jump frequency in perfect crystal in both directions, $\frac{1}{2}$ describes the probability to jump towards the barrier and the exponential factor accounts for the decrease of the probability of successful jump due to the barrier.

3.2. 1-D triangular well

A particular case of a triangular shape well:

$$U(x) = \begin{cases} -E(1 - x/x_{\min}), & x_{\min} \leq x < 0, \\ -E(1 - x/x_{\max}), & 0 \leq x \leq x_{\max} \end{cases} \quad (11)$$

is a more realistic approximation to real situations with no single energy. In this case:

$$\tau_{\text{tri}} = 2\tau e^{\beta E} \frac{[1 - e^{-\beta E(1+x_{\max}^{-1})}]}{1 - e^{-\beta E/x_{\max}}}. \quad (12)$$

It can readily be shown that, for deep enough triangular wells, such that $e^{\beta E} \gg 1$, the dissociation time is smaller than for a square well of the same depth and width by the ratio of the thermal energy to the well depth. This is due to a smaller effective binding energy.

3.3. Void

A void can be considered as a well for vacancies. Since vacancies are always at the void surface, $N = m$ in equation (7). Hence, for a large void of radius r_0 , such that $\langle n \rangle_{\text{free}} = z/2$,

and the vacancy binding energy $-U = E$, one obtains $\tau_{\text{diss}} \approx 2\tau e^{\beta E}$. The factor of two in this equation accounts for an increase of the time spent by a vacancy in the void, because successful jumps are only in the direction away from the void. The evaporation frequency is, hence, $\nu_{\text{diss}} = e^{-\beta E} / 2\tau$. In equilibrium conditions this frequency equals to that of the void-vacancy association events: $C_{\text{v}}^e / 2\tau$, hence the equilibrium vacancy concentration near the void is $C_{\text{v}}^e = e^{-\beta E}$ (see section 5 for derivation). This equilibrium concentration and equation (7) can be used to calculate the evaporation rate using the diffusion-reaction theory (see section 5 below).

3.4. Vacancy in solute precipitate

For a vacancy and a large solute precipitate of radius r_0 with a constant interaction energy between the vacancy and any site within the precipitate $U = -E$: $\langle n \rangle_{\text{free}} = z/2$, $N = 4\pi r_0^3 / 3\Omega$, where Ω is the atomic volume, $m = 4\pi r_0^2 a / 2\Omega$, where the surface layer is assumed to be of thickness $a/2$, and, hence, $\nu_{\text{diss}} \approx e^{-\beta E} a / r_0 \tau$. The ratio a / r_0 accounts for the probability to find a vacancy near the surface. Hence, the frequency of dissociation events is equal to the vacancy concentration near the surface times the frequency of jumps away from the precipitate, which seems to be an obvious description in such a simple case. To take into account the interaction energy profile $U(x_i)$ within the precipitate, one should use $\langle e^{-\beta U(r_i)} \rangle_{\text{well}}^{-1}$ for the probability of successful jump in this case. This is useful in calculations of an enhanced vacancy concentration inside precipitate.

For example, in conditions typical for thermal ageing, when the concentration in the matrix outside a precipitate is kept constant and equal to the equilibrium vacancy concentration, C_{v}^e , at given temperature, the enhanced mean vacancy concentration in the precipitate $\langle C^{\text{in}} \rangle$ can be obtained using the detailed-balance condition at the precipitate surface. The frequency with which vacancies enter the precipitate is $C_{\text{v}}^e m \langle n_{\text{free}} \rangle / z\tau$, while the frequency with which vacancies leave the precipitate is $\langle C^{\text{in}} \rangle N / \tau_{\text{diss}}$. The equality of these frequencies implies that

$$\langle C^{\text{in}} \rangle = C_{\text{V}}^{\text{e}} \left\langle e^{-\beta U(\tau, \cdot)} \right\rangle_{\text{well}}. \quad (13)$$

4. Distribution function of dissociation times

4.1. Definitions and Monte Carlo scheme

A more detailed description of the stochastic process of dissociation than by the statistical average value of dissociation time, equations (3) and (7), is given by the probability density function of dissociation times, $dP(t)/dt$. Here, $P(t)$ is the probability that a dissociation event occurs before time t . For a random process without memory, such as the radioactive decay:

$$1 - P(t) = \exp(-t / \tau_{\text{diss}}) \quad (14)$$

and the probability density function is given by

$$dP(t) / dt = \exp(-t / \tau_{\text{diss}}) / \tau_{\text{diss}}. \quad (15)$$

It will be shown below that this is valid in the cases characterised by a unique binding energy such as a single-site trap, but not for spatially distributed wells.

To study the influence of the well shape on the distribution of dissociation times, we performed Monte Carlo calculations of particle diffusion in the same system as used for derivation of the mean dissociation times in section 2, *i.e.* it consisted of a well and one ‘free’ state with periodic boundary conditions. Two particular cases are considered below, namely 1-D square and triangular wells (see sections 3.1 and 3.2). In the case of a square well, the jump frequencies of the diffusing particle in forward and backward directions, ν^+ and ν^- , were equal to those in perfect crystal: $\nu^+(x) = \nu^-(x) = (2\tau)^{-1}$ for all but two frequencies for two border sites, where $\nu_{\text{right border}}^+ = \nu_{\text{left border}}^- = e^{-\beta E} / \tau$. In the case of triangular wells, the frequencies were calculated as $\nu^{\pm}(x) = e^{\mp\beta\Delta U^{\pm}} / \tau$, where $\Delta U^{\pm} = \pm[U(x \pm 1) - U(x)]/2$ are the changes of the migration barriers due to the interaction energy (see Figure 2). The

probabilities that particle jumps forward or backward are defined by ratios $\nu^+ / \nu_{\text{total}}$ and $\nu^- / \nu_{\text{total}}$, where $\nu_{\text{total}} = \nu^+ + \nu^-$ is the total jump frequency. The value $\langle t \rangle = \nu_{\text{total}}^{-1}$ is the mean waiting time before a jump, which is generally site dependent. The value τ normally obeys the Arrhenius relationship for the temperature dependence with activation energy equal to the saddle point energy in perfect crystal (E_0 in Figure 2). In most of our calculations, τ was a constant chosen to be the unit of time. Some calculations revealing influence of the saddle-point energy profile on the distribution function, thus with τ dependent on the position inside the well, are presented in section 4.4. The calculations were performed until a specified number of dissociation events occurred. The distribution of dissociation times was obtained as the number of dissociations within a specific time window (a bin of the distribution) divided by the total number of events and the bin width. In our calculations, the bin width was taken as $0.1\tau_{\text{diss}}$ and calculated using equations (9) and (12) for the square and triangular wells, respectively. The main purpose of calculations was to compare the probabilities calculated with those described by equation (15). We use a dimensionless variable t / τ_{diss} and function $\tau_{\text{diss}} dP(t) / dt$ to represent the results, since they are independent of the mean dissociation time.

[Insert Figure 2 about here]

4.2. Results for 1-D square wells

The MC calculations were performed for wells of different width (50, 100 and 200 one jump distances) and depth ($\beta E = 3.87$ and 7.74 , which correspond to $E = 0.1$ and 0.2 eV, respectively, at $T = 300\text{K}$) and $\sim 500,000$ dissociation events were accumulated in each case. The range of well widths was chosen with a particular interest in the migration of a self-interstitial atom cluster in the long-range stress-field of an edge dislocation [6,7]. The calculations reproduced equation (9) with high accuracy, which was one of the tests for the code. The main aim of the following calculations was to study the deviation of $dP(t) / dt$ from equation (15). The results are presented in Figure 3. Typical error bars are shown for one calculation (the upper parts of errors bars are omitted in order to keep presentation clear). As can be seen, for wells deep and/or narrow enough (e.g. for $\beta E = 7.74$ or $N = 50$), the probability density approaches equation (15), which is characteristic of a random process

without memory. For shallow and/or wide wells, the distribution deviates from exponential dependence, especially at small times. More specifically, the deviation occurs for such wells, where the mean dissociation time is not significantly longer than $\tau_{\text{diff}} = N^2\tau/2$, which is the time corresponding to the diffusion length equal to the half of the well width $l = Na/2$, where a is the jump distance. The diffusion length, *i.e.* the mean-free path, is defined from equation $l^2 = 2D\tau_{\text{diff}}$, where $D = a^2/2\tau$ is the diffusion coefficient in 1-D. The last column of the legend in Figure 3 contains necessary ratios $\tau_{\text{diss}}/\tau_{\text{diff}}$. We note that wells for which $\tau_{\text{diss}} \approx \tau_{\text{diff}}$ can hardly be treated as traps at all. Thus, we conclude that for square wells strong enough to be considered as traps, *i.e.* with $\tau_{\text{diss}} \gg \tau_{\text{diff}}$, the distribution under interest is described reasonably well by the exponential dependence. Note that the condition $\tau_{\text{diss}} \gg \tau_{\text{diff}}$ is one of the basic ones required for separation of the time scales (see section 2).

[Insert Figure 3 about here]

4.3. Results for 1-D triangular wells

Calculations similar to those described above for a square well were performed for triangular symmetrical wells, *i.e.* when $|x_{\text{min}}| = x_{\text{max}}$ in equation (11). The statistics were accumulated for about 1,000,000 events. Equation (12) for the mean dissociation time was reproduced within reasonable accuracy, usually about 1%. The distribution function of dissociation times is presented in Figure 4. As can be seen, the distribution deviates from the exponential dependence much more significantly than for square wells. Similar to square wells, the deviation is stronger for shorter times and smaller ratio $\tau_{\text{diss}}/\tau_{\text{diff}}$. This is because of a high fraction of dissociation events occurring before particle visited the deep region of the well. It is evident that the higher the ratio $\tau_{\text{diss}}/\tau_{\text{diff}}$, the lesser the contribution of shallow regions to the mean time. Unlike that for the square well, the probability of short time dissociation in a triangular well is always high, even for deep and narrow wells, and the distribution at short times has quite different slope in logarithmic scale. This feature is due to geometry of the well, where shorter times correspond to smaller energy. At long times the distribution becomes exponential but with different slope, as shown in the comparison with exponential function plotted in Figure 4.

[Insert Figure 4 about here]

Figure 5 shows the distribution of $1 - P(t)$, *i.e.* the probability that a dissociation event does not occur before time t , for triangular wells of different width and depth. The error bars were very small for calculations of this type, not visible on the graph. One calculation for a square well (labelled 'Square') is also shown and it demonstrates a dependence which is close to exponential decay. In contrast, the distributions for triangular wells deviate from simple exponential dependence. The time dependence exhibits different behaviour at short and long times. The function at short times is steep and decreases quickly, while an exponential dependence evolves at long times. The curve for $\beta E = 3.87$ and $N = 100$, which is labelled ' $x=0$ ', is the distribution of escape times from the bottom of the triangular well. That is, the trajectories of all the diffusing particles in this calculation started from $x = 0$ corresponding to the deepest position in the well. In this calculation the mean dissociation time was about 15200τ and more than an order of magnitude longer than that given by equation (12) and corresponding calculations, which is 1210τ . We also note that this time was about twice higher than the corresponding value of 7230τ for the square well of the same depth and width when all trajectories started from ' $x=0$ ', *i.e.* the middle of the well. This does not seem trivial, since the simple average depth of the former well is smaller. As seen from Figure 5, this calculation also shows the exponential decay. This indicates that the deviations from an exponential relationship are due to trajectories, which do not reach the bottom of the well. For such trajectories the dissociation times are short, so that the time scales are not well separated (see end of section 2). In addition, we make an important observation. When the time is equal to the mean dissociation time, the probability for the triangular wells is not equal to e^{-1} as expected for a random process, such as radioactive decay, described by equation (14). This means that the dissociation events are not randomly distributed, *i.e.* their time distribution does not obey equation (14), and hence actual distribution function is required to characterise the process.

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It seems important to mention that, strictly speaking, such a process cannot be treated by chemical reaction equations, where the dissociation rate is the reciprocal of the mean dissociation time. These equations predict exponential decay for the trap concentration, thus describe random process. In reference [10] we show that by redefining the dividing surface (boundary of the well) the fast time scales can be eliminated and the exponential distribution of the dissociation times thus restored.

Deleted: The work is currently in progress investigating possibility of overcoming these problems

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4 [Insert Figure 5 about here]
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7 **4.4. Influence of saddle-point energy profile on time distribution**

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10 As has already been mentioned in section 2.2, the mean dissociation time is independent of
11 the saddle point energy profile within the well, and this follows from the general equation (7).
12 We verified this statement by calculations for a triangular potential well where all saddle-
13 point energies were taken to be the same and equal to those in perfect crystal. An example of
14 such a well is shown in Figure 1b. In the calculations performed, the time delay was defined
15 according to the actual saddle-point energy by including an additional Arrhenius factor. The
16 results are presented in Figure 4 in the curve labelled 'SP' for $\beta E = 3.87$ and $N = 100$. The
17 mean dissociation time was the same as in corresponding calculation above for triangular
18 well (see section 4.3) and given by equation (12) within accuracy of less than 2%. The
19 probability distribution was different, however, with the probabilities of shorter-time
20 dissociations increased. This is because there is no longer preference for a diffusing particle
21 to jump towards deeper well regions. In other words, in this calculation, the well represents a
22 region where only jump frequencies, but not the probabilities of different jumps, are affected.
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29 | Similar effect was studied in [11] for diffusion of vacancy and Cu atoms in a dilute
30 Fe-Cu alloy. The analysis showed that the diffusion mechanism of Cu atoms, namely the
31 crossover from 'exchange' (when a vacancy executes only exchange jumps with Cu atom) to
32 'drag' (when the vacancy co-migrates with Cu atom) mechanisms depends critically on the
33 saddle-point energy profile of the vacancy around Cu atom (see [11], especially section 3.2).
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39 **5. Exchange frequency between wells**

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42 In the preceding sections we used the term 'dissociation', which can be inappropriate in some
43 cases where the term 'escape' would be a better word. An important example is a dilute
44 solution of traps. In this case, a migrating defect escaping from a trap has a high probability
45 of returning to the same trap after a short-time migration in pure crystal. In diffusion-reaction
46 kinetics, however, we are concerned mainly with events that result in complete dissociation in
47 the sense that *the memory is lost* and the next reaction will occur with high probability at
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another trap. In other words, the quantity of interest is the frequency with which diffusing objects are exchanged between wells. This is the origin for the Eyring transmission factor in the reaction rate theory [9]. A clear distinction between escape and dissociation events can be seen in the example of vacancy evaporation from voids. The evaporation takes place at the void surface; hence, the total escape frequency is proportional to the surface area, *i.e.* the void radius squared. The well-known result of the diffusion-reaction theory gives proportionality to the void radius. Obviously and as demonstrated below, this difference is due to correlated absorption of vacancies by the same void they are emitted from. This indicates that accounting for correlated events can change even qualitative description of the process. Note also that the events contributed to the short-time non-exponential part in the distribution function of dissociation times, see section 4.3, can also be viewed as correlated events and thus part of the same problem. Below we consider this problem for two specific cases: vacancy evaporation from a void and de-trapping of interstitial cluster from dislocation.

5.1. Vacancy evaporation from void

Consider a void of radius r_0 , which emits τ_{diss}^{-1} vacancies per second per surface site, in a spherical coordinate system. Vacancies migrate three-dimensionally with the diffusion coefficient $D = a^2 / 6\tau$. The diffusion equation for vacancy concentration C is

$$\nabla^2 C = 0. \quad (16)$$

To calculate the number of vacancies emitted from the void that reach some distance R from the void surface we use absorbing boundary conditions at this distance

$$C(R) = 0. \quad (17)$$

One more boundary condition must specify the vacancy-void interaction process. Assuming that vacancies are absorbed by the void, which is a realistic scenario, the vacancy concentration at one jump distance a from the surface can be written as

$$C(r_0 + a) / \tau = \nu_{\text{diss}} + C(r_0 + 2a) / 2\tau. \quad (18)$$

The left-hand side of the equation describes the frequency with which vacancies leave the site. The first term on the right-hand side stands for the production of vacancies due to evaporation from the void. The last term on the right-hand side accounts for vacancies coming to this site from the sites further way from the void surface. After representing the latter term using Taylor series, in the limit of $r_0 \gg a$, the boundary condition, equation (18), assumes the following form

$$C(r_0) = 2\tau v_{\text{diss}} + \nabla C(r_0)a. \quad (19)$$

Using this condition, one finds the concentration to be equal to

$$C = 2\tau v_{\text{diss}} \frac{r^{-1} - R^{-1}}{r_0^{-1} - R^{-1}}. \quad (20)$$

It can readily be estimated using the last two equations that the gradient of concentration in equation (19) is smaller than the other terms by a factor of a/r_0 and does not contribute to equation (20). This means that most vacancies emitted from the void return back to it. As a result, the equilibrium condition for the concentration near the void surface is defined by the equality of frequencies of evaporation and jumps back to the surface and is not affected by the flux of vacancies away from the surface. The vacancy equilibrium concentration at the void surface is readily obtained from equation (20) as $C_v^e = C(r_0) = 2\tau v_{\text{diss}}$.

The total number of vacancies passing through a spherical surface of radius R and area $S = 4\pi R^2$ per unit time is equal to

$$R_v^a = -\frac{SD}{\Omega} \nabla C(R) = \frac{DC_v^e}{\Omega} \frac{4\pi r_0}{1 - r_0/R}, \quad (21)$$

where superscript 'a' denotes absorbing boundary. There are three points to be made. First, equation (21) becomes independent of the distance R from the surface, when $R \gg r_0$. Thus, vacancies reaching this distance lose their memory and can be counted as dissociated from the void. Second, despite the fact that the total vacancy emission frequency is proportional to the void surface area, the total vacancy flux far away from surface is proportional to the void

radius. This is a well-known result of the reaction-diffusion theory (see, *e.g.* [12]). Third, as can be seen from equation (21), significant deviation from the proportionality to the void radius occurs at distances of the order of void radius.

As discussed above most vacancies emitted return to the void. The fraction of vacancies which do not return is equal to the ratio of the frequency defined by equation (21) and $\sim 4\pi r_0^2 \nu_{\text{diss}} / a^2$, which is for the total frequency of vacancy emission. It is thus equal to a / r_0 . The same result can be demonstrated considering another, although unrealistic, scenario in which vacancies are reflected by the voids. In this case all vacancies produced contribute to the flux far away from the void. Indeed, in this case, we should multiply the left hand side of equation (18) by $\frac{1}{2}$ to account for the fraction of unsuccessful jumps towards the void surface. Then, only the gradient and source terms remain in the boundary condition, equation (19):

$$\nabla C(r_0)a = -2\tau\nu_{\text{diss}} \quad (22)$$

and the vacancy concentration becomes

$$C = \frac{2\tau\nu_{\text{diss}}r_0^2}{a} \left(\frac{1}{r} - \frac{1}{R} \right). \quad (23)$$

The quantity defined by equation (21) modified for the case of reflecting boundary conditions (superscript 'r') is now proportional to the surface area:

$$R_V^r = \frac{4\pi r_0^2}{\Omega} \frac{2D\tau\nu_{\text{diss}}}{a} = \left(\frac{r_0}{a} \right) R_V^a, \quad (24)$$

and is higher than that for absorbing conditions by a factor of r_0 / a .

We also note that the first non-vanishing correction to the proportionality of the vacancy flux to the void radius is positive and proportional to the void radius squared, see equation (21), where $r_0 \left(1 - r_0 / R \right)^{-1} \approx r_0 + r_0^2 / R$. This is the same result as obtained previously *e.g.* by Göselle [13] considering void capture efficiency. Thus, with increasing volume fraction more and more vacancies become absorbed at other voids and the

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proportionality to the void radius squared would be restored. The first correction term just shows the right tendency. Similar transition of the radius dependence of the reaction rate from R to R^2 can be found in [14] for precipitation kinetics for different absorption abilities of the solute precipitate-matrix interface.

5.2. Interstitial cluster exchange between dislocations

Consider a random spatial arrangement of dislocations and interstitial clusters migrating one-dimensionally with the diffusion coefficient $D = a^2 / 2\tau$. This problem is similar to that considered above in section 5.1. It is readily obtained that, with absorbing boundary conditions at the well boundary at $x = 0$, equation (18), and at distance L from the well, the cluster concentration is described by the following equation

$$C = 2\tau v_{\text{diss}} \left(1 - \frac{x}{L} \right). \quad (25)$$

The distance L here can be interpreted as the mean distance between dislocations in 1-D and will be discussed further below. In this case, other dislocations absorb clusters passing this distance and, hence, the memory is lost. This process can be considered as cluster exchange between wells represented by dislocations. The total flux of clusters emitted from the well at distance L is

$$J^a = -DVC(L) = \frac{D}{\Omega} \frac{2\tau v_{\text{diss}}}{L}. \quad (26)$$

We note that, in contrast to 3-D diffusion, the total flux for 1-D diffusion always depends on the distance; namely, it decreases with increasing distance (decreasing dislocation density).

Similar to the problem of vacancy evaporation from a void considered above, one can show that, for reflecting boundary conditions, equation (22), the vacancy concentration and the flux of clusters are both L/a times higher. Hence, the fraction of clusters, which do not return to the well after escaping from the potential well, and, hence, the frequency with which clusters are exchanged between dislocations, f is equal to a/L :

$$f = v_{\text{diss}} a / L. \quad (27)$$

Now let us make some estimates of the effect. The mean distance between randomly arranged dislocations in 1-D is described by the dislocation density ρ_D and capture radius d as $L = 2 / \pi \rho_D d$ (see, e.g. [15]). The jump distance in bcc lattice is the distance between atoms in $\langle 111 \rangle$ direction: $a = \sqrt{3} a_0 / 2$, where a_0 is the lattice parameter. Hence, the frequency of cluster exchange between dislocations is

$$f = \sqrt{3} \pi v_{\text{diss}} \rho_D d a_0 / 4. \quad (29)$$

For typical dislocation density $\rho_D = 10^{12} \text{ m}^{-2}$, the capture radius $d = 100 \text{ nm}$ estimated in [6] and $a_0 = 0.3 \text{ nm}$, the frequency is smaller than the rate of cluster emission from the well by about five orders of magnitude: $f \approx 4 \times 10^{-5} v_{\text{diss}}$.

Thus, the exchange frequency of the diffusing particles between spatially separated wells may be many orders of magnitude smaller than for frequency of dissociations from the well, and this is due to correlated recapture of the particles by the same well. And the effect depends strongly on the trap density.

5. Conclusions

1. An equation for the mean dissociation time of a migrating particle from a trap has been derived. It is independent of the saddle point energy profile within the well.
2. Generally, the distribution of dissociation times deviates from exponential function, especially in the region of small dissociation times. In such cases the probability function at the mean time may differ significantly from $1 - e^{-1}$, which is for a random process. The effect depends on the well shape (is stronger for shallower and/or wider wells) and on the saddle point energy profile within the well.
3. The exchange frequency of the diffusing particles between spatially separated wells is generally many orders of magnitude smaller than the frequency of dissociations from the well, and this is due to correlated recapture of diffusing particles by the same well.

Acknowledgments

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Figure captions

Figure. 1. Schematic diagram showing the potential energy profiles for a migrating particle in a crystal containing a) a potential well and b) a potential well, where all the saddle energies are equal. $U(x)$ is the interaction energy in equilibrium states.

Figure. 2. Schematic diagram illustrating calculation of energy barriers.

Figure. 3. Probability distribution of dissociation times of a migrating particle from wells of different depth E and width N . The typical error bars are shown for one set of calculations (the upper parts of errors bars are omitted in order to keep presentation clear).

Figure. 4. Same as in Figure 1 but for triangular wells. One curve, labelled 'SP' has been calculated for the energy profile where all saddle-point energies are equal.

Figure. 5. Probability that a dissociation event does not occur before time t for the wells of triangular shape of different width and depth. One curve labelled as 'Square' was calculated for square well. The curve labelled as ' $x=0$ ' shows the distribution of escape times from the bottom of the triangular well.

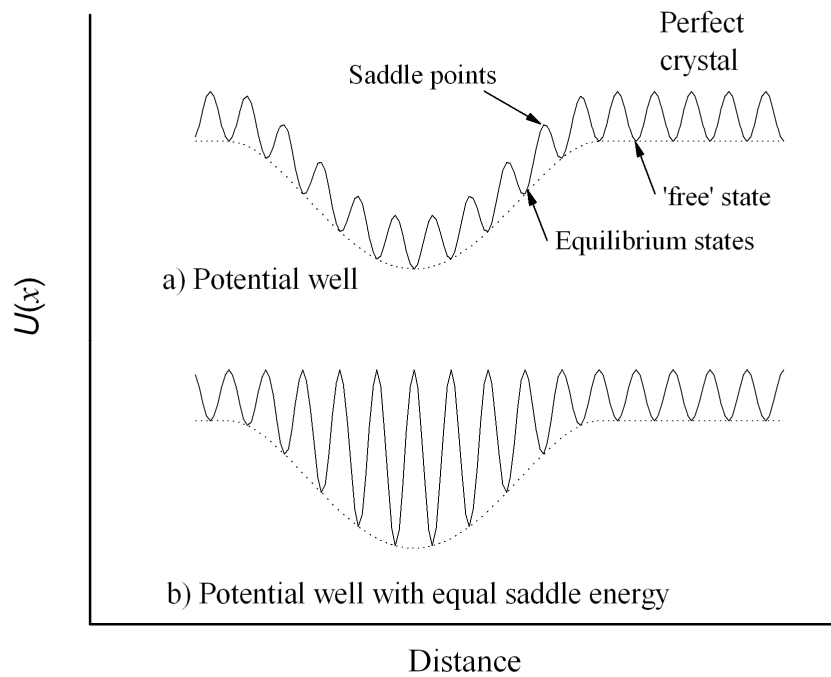


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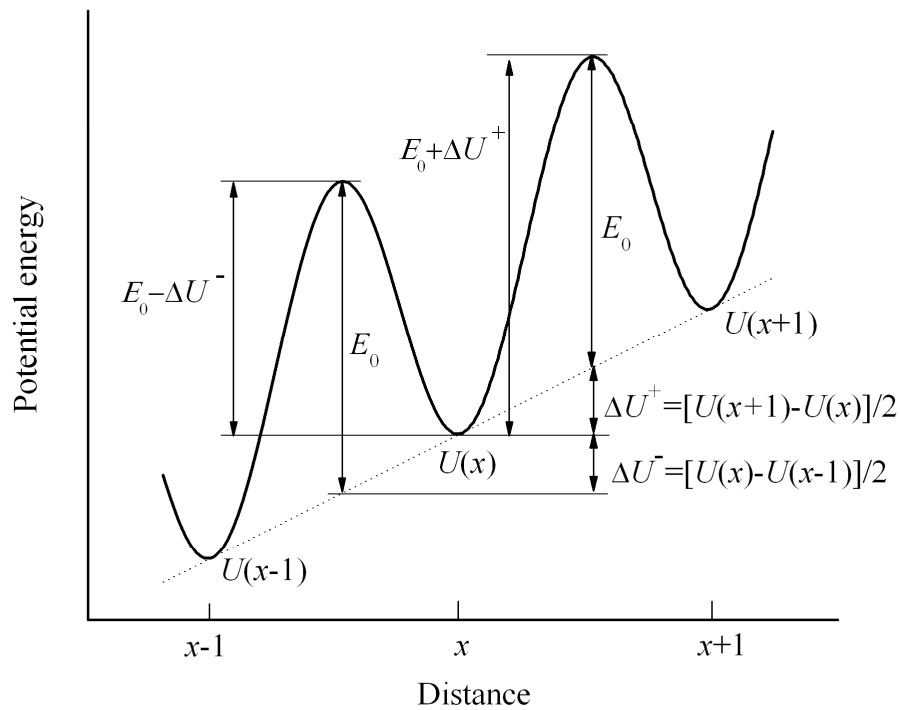
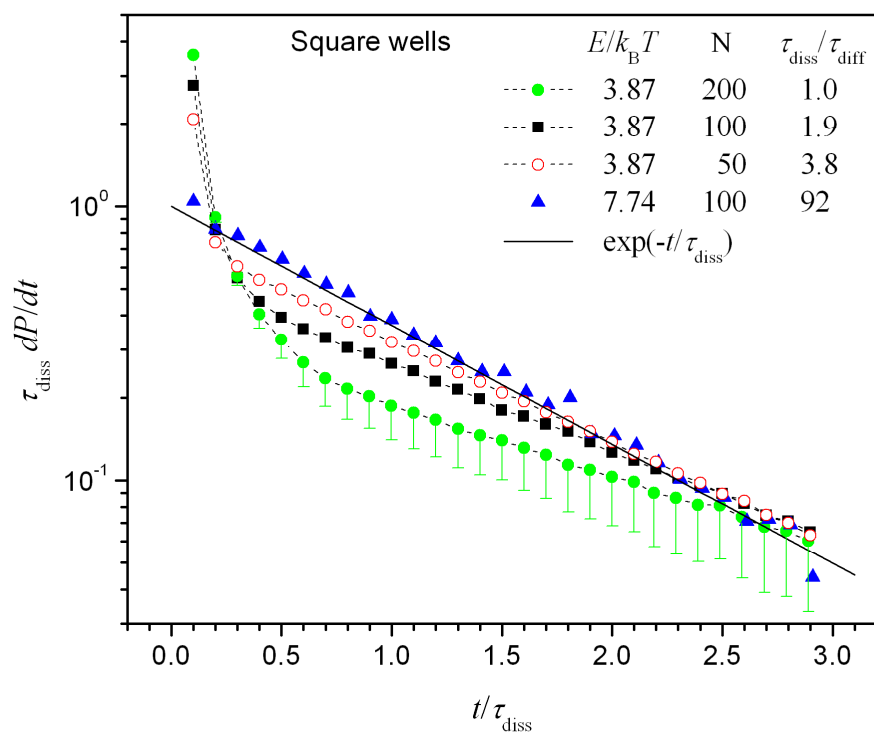


Figure. 2. Schematic diagram illustrating calculation of energy barriers.

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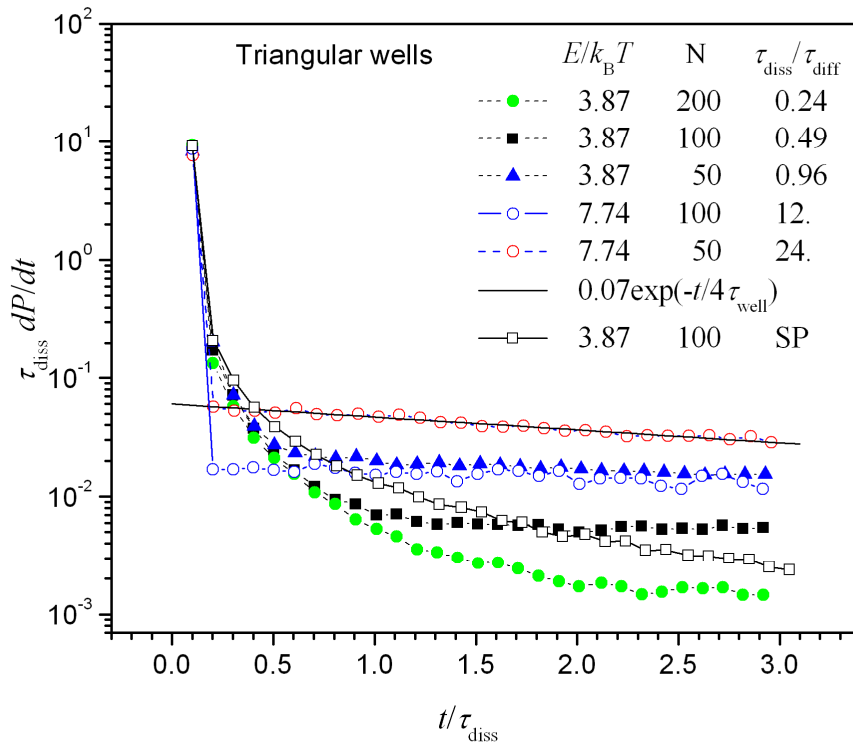
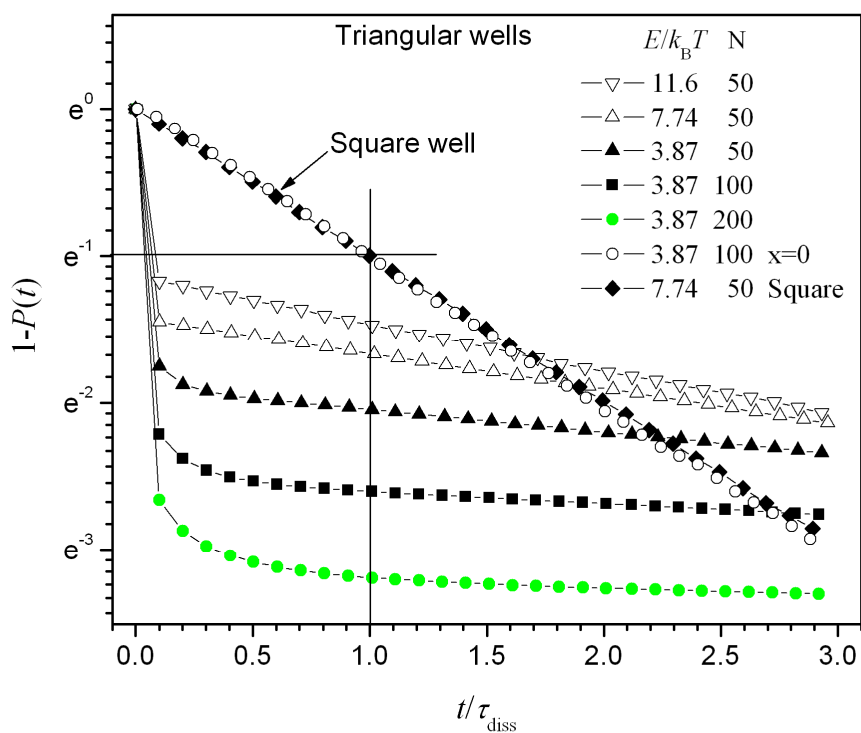


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