Diffusion Time For a Vacancy to Diffuse From One Stable State to The Next Within a Sublattice

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ABSTRACT

We considered two different mechanisms by which a vacancy diffuses from one stable state to the next within a sublattice for a two dimensional binary alloys. For both mechanisms, we have found that the diffusion time is a function of jumping probabilities which in turn depend on energy barriers and lattice spacing. We compared the diffusion times for the two mechanisms and identified conditions under which one is favored over the other.

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CHAPTER 1

Introduction

Any deviation in a crystal from a perfect periodic lattice or structure is an imperfection. The common point imperfections are vcacant lattice sites, chemical impurities and extra atoms not in regular lattice position. Real crystals are always imperfect in some respect. Many important properties are controlled as much by imperfection as by the nature of the host crystal which may act as a vehicle for the imperfection. For example diffusion of atoms and the mechanical properties are usually controlled by imperfections.

The simplest imperfection is a lattice vacancy which is a missing atom or an ion, also known as Frenkel defect in which an atom is transferred from lattice site to an interstitial position, a position not normally occupied by an atom. There is also a Schottky defect in which an atom is transferred from lattice site in the interior to lattice site on the surface of the crystal[1].

When there is a concentration of vacancies or impurities in a solid, there will be a diffusion through the solid. In equilibrium the vacancies or impurities are distributed uniformly. In order to diffuse an atom must surmount the potential energy barrier presented by its neighbors. The atom of vacancies or impurities will have sufficient thermal energy to pass over the barrier only a fraction $e^{\frac{-U}{k_B T}}$ of the time, where U is the energy barrier height due to the neighbors, k_B is Boltzman‘s constant and T is the absolute temperature of the solid[1].

potential profiles for the two mechanisms of a vacancy jump are also depicted in Fig 1.2

In general the potential barrier height between successive states depends on the species involved in the exchange process. Hence, potential barrier height value for one type of exchange process is not the same as that for another type of exchange process. To make the analysis moderately simple, however, we assume symmetric potential profile.

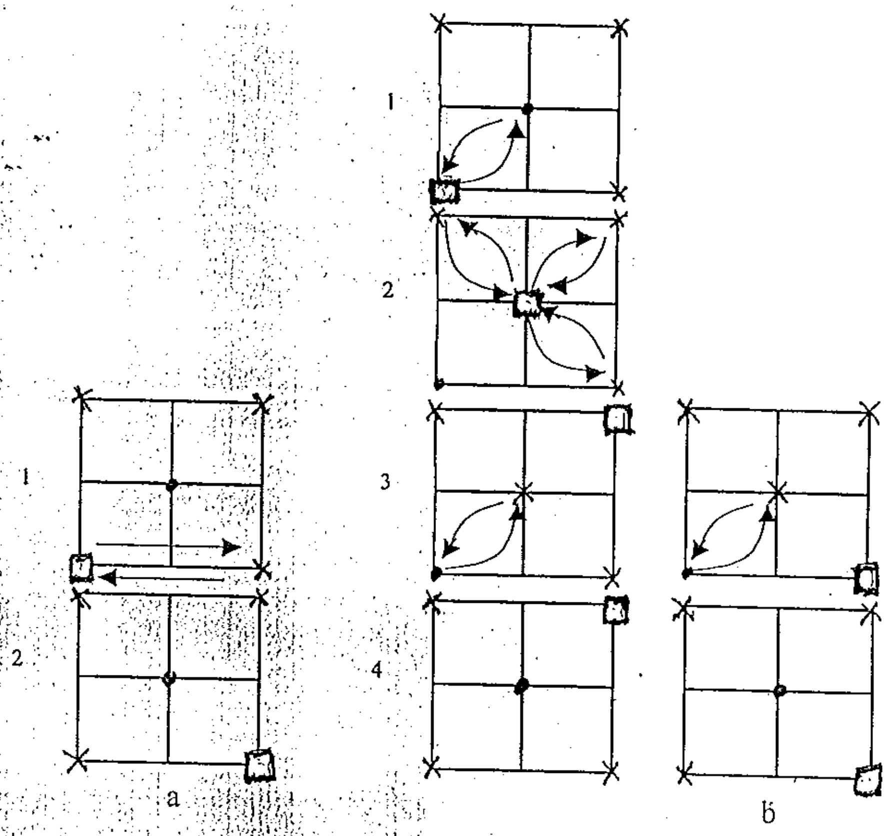

Figure 1.1: The two dimensional motion of a vacancy (a) one jump cycle and (b) three jump cycle.

In elementary pure metals there is self-diffusion often mediated by random nearest-neighbor jumps of monovacancies. In ordered compounds the situation is more complicated. Because the various constituent atoms are preferentially located on various sublattices, so that the nearest-neighbor sites are often occupied by another constituent atom. Therefore in ordered binary alloys or compounds, random vacancy motion is not possible as it would disturb the equilibrium ordered arrangement of atoms on lattice sites. In view of this limitations, few atomistic models have been proposed for the diffusion of vacancies in binary alloys, which allows prescribed atom-vacancy exchange to take place without long range disordering.

Basically there are two simple ways or mechanisms by which a vacancy jumps to its nearest or next-neighbor on the same sublattice in binary alloys[5]. One way is what we call a one jump cycle or a direct jump. This jump occurs through direct exchange in position of the vacancy with a nearest-neighbor atom on the same sublattice. The other way is a coupled three jump cycle which is made up of two successive exchange in position of the vacancy with its nearest-neighbor atom followed by one exchange in position of an atom with its nearest-neighbor atom and ultimately arriving at the ordered arrangement of atoms on the lattice site. This three jump cycle has two intermediate states that are metastable due to the local disordering created by the exchange. Both jump cycles are shown in Fig. 1.1 for a two dimensional lattice structure of a binary alloy which is made up of a single two interpenetrating square sublattices. The corresponding schematic

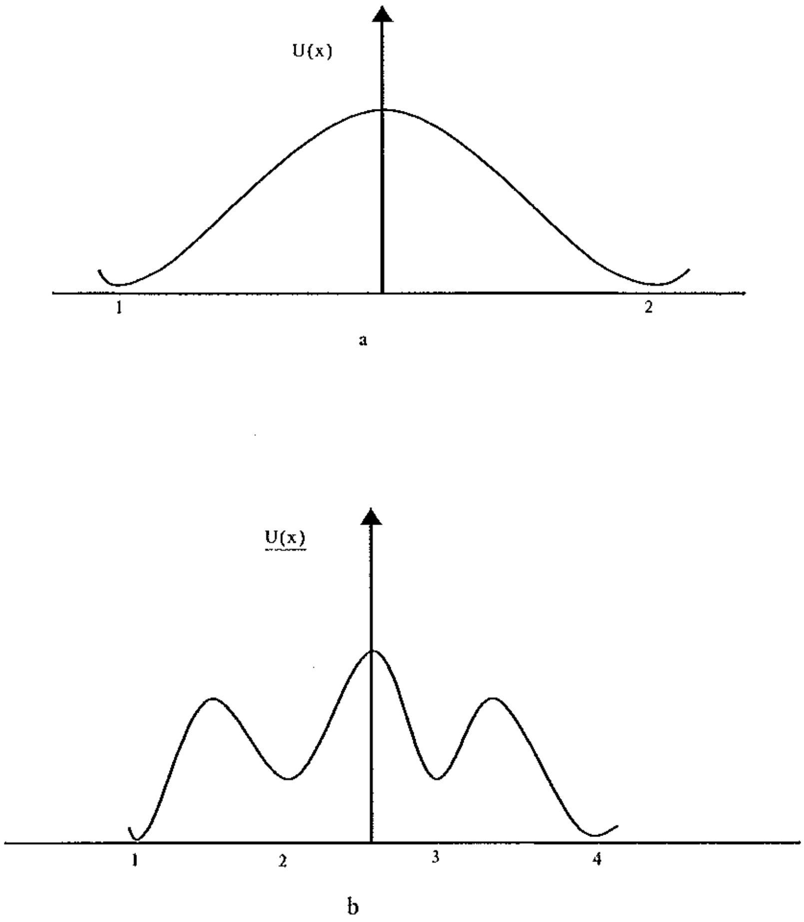

Figure 1.2: The corresponding potential profiles of the two cycles.

Another jump cycle known as the six-jump cycle has also been suggested by ref [4, 5] as one of the mechanism for diffusion of vacancies in binary alloys. In this work we will not deal with this mechanism of vacancy diffusion.

The two simple mechanisms for vacancy diffusion are expected to hold for low concentration of vacancies in the material and close to stoichiometry (low concentration of structural defects). Jumps between successive states represent stochastic processes. In other words, one can see the vacancy diffusion as a random walk of a Brownian particle on a lattice. The Brownian particle is not the vacancy per se but an idealized particle (quasi-particle) of the vacancy-medium system. The vacancy-medium system changes from one state to another in a configuration space either as the vacancy moves from one site to the next or as the disorder changes to order. Therefore this can be taken as a random walk of a Brownian particle on a lattice.

The central aim of this work is to find out which one of the two mechanisms for vacancy diffusion is favored over the other and under what condition. This is done by comparing for the two mechanisms, the mean time taken by the vacancy to move to its nearest-neighbor or next nearest-neighbor on the same sublattice.

For the direct jump case, the mean time is determined by the potential profile and the distance between the initial and final states, i.e the distance between nearest-neighbor on the same sublattice. For the three jump cycle case, the situation is slightly complicated in two ways. First of all, there are two or more paths for the vacancy to choose in order for it to move to its next stable site.

Secondly, motion along one of the paths by itself is composed of jumps to two intermediate metastable states before the final state is reached. Therefore, we have to first address how to handle a random walk problem on a lattice with two or more paths.

The structure of this thesis is as follows, In chapter two, we introduce the random walks on networks and then develop the basic functions that sum up all possible walks from some initial point to a final point We calculate the diffusion time for the two models in terms of jump probabilities. In chapter three,we find local jump probabilities for model potential profiles. This is done by converting vacancy diffusion problem to motion of a Brownian particle in bistable or multistable potential. We will compare the diffusion times of the two mechanisms in terms of their energy barriers in chapter four. Finally we conclude and summarize our result in chapter five.

CHAPTER 2

Vacancy Diffusion As Random Walks On a Lattice

In chapter one, we have pointed out that diffusion of a vacancy in a crystalline material can be taken as motion of a Brownian particle on a lattice. For binary alloys, in particular, we have identified two mechanisms by which a vacancy diffuses. In the present chapter, we want to calculate the main property of vacancy diffusion for the two mechanisms. To do so, we first introduce a method of calculating properties of random walks on networks[2, 3].

2.1 Random walks on Networks

Consider a random walk on a finite collection of points that form a network. In particular, take a random walker moving on lattice sites which form a line segment. We denote these lattice sites by 0,1, 2,..., N as shown in Fig. (2.1).

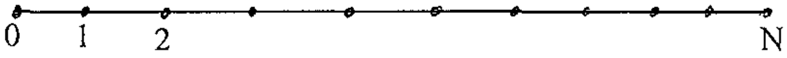

Figure 2.1: A striaght segment

Let p_i stand for the probability that the walker (per time step) to move from site i to site i+1 and q_i stand for the probability that the walker move from site i to site i-1. It is clear that $p_i+q_i \leq 1$. Note that $p_N = q_0 = 0$, since the random walker is confined to move within the segment. The probability to stay at site i for n-consecutive time steps is $(1-p_i-q_i)^n$. We define the generating function $X_i(\phi)$,corresponding to staying at site i as

$$X_i(\phi) = \sum_{n=0}^{\infty} (1 - p_i - q_i)^n e^{i\phi n} \tag{2.1.1}$$

which takes a simple expression

$$X_i(\phi) = \frac{1}{1 - (1 - p_i - q_i) e^{i\phi}}. \tag{2.1.2}$$

We also define two more basic types of walks and their corresponding generating functions.

a. Let $\tilde{Q}_{ij}(n)$ be the probability to leave site i at the first step and return to i in n-steps without having reached site j in the process. The corresponding generating function, $Q_{ij}(\phi)$, will be given by

$$Q_{ij}(\phi) = \sum_{n=0}^{\infty} \tilde{Q}_{ij}(n) e^{i\phi n}. \tag{2.1.3}$$

b. Let $\tilde{T}_{ij}(n)$ be the probability of the walker starting at site i, move out at the first step and reach site j for the first time in n-steps without having returned to i in the process. We then take the corresponding generating function as $T_{ij}(\phi)$ defined in a similar way.

Generating functions add and multiply like regular probabilities, except that one doesn't have to keep track of the number of steps. Due to these properties they are customarily called ϕ probabilities. The generating functions $Q_{ij}(\phi)$ and $T_{ij}(\phi)$ are usually related to the basic jump probabilities in a complicated way.

We are interested in finding the time, τ_{ij}, required by the random walker to reach site j for the first time after starting from site i. This time is related to the probability, $\widetilde{G}_{ij}(n)$, of the walker starting from site i to reach site j in n-steps for the first time and its corresponding generating function $G_{ij}(\phi)$. τ_{ij} is defined as

$$\tau_{ij} = \sum_{n=0}^{\infty} \frac{n\,\widetilde{G}_{ij}(n)}{\widetilde{G}_{ij}(n)}. \tag{2.1.4}$$

It is straight forward to show that τ_{ij} can be calculated from the generating function

$$\tau_{ij} = \frac{1}{G_{ij}(\phi)} \frac{dG_{ij}(\phi)}{d(i\phi)} |_{\phi=0} \tag{2.1.5}$$

From now on we call such time,τ, as the *diffusion time.*

2.2 Diffusion Time Expression For Three Jump Cycle On a Segment-An Illustration

As a simple illustration of calculating diffusion time, let us take a random walk on a one-dimensional line segment with four lattice sites. These four lattice sites correspond to the stable and metastable states of the three jump cycle. The local jump probabilities can be extracted from the way the Brownian particle moves in the potential profile. Due to symmetry of the potential profile, there are only three distinct jump probabilities: p_1, p_2 and p_3 as shown in Fig. (2.2).

In order to get τ_{AB}, we need the expression for $G_{AB}(\phi)$ in terms of the ϕ probabilities for the basic types of walks: X_A, Q_{AB} and T_{AB}. Let us define one

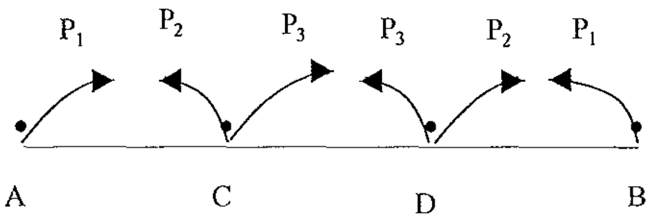

Figure 2.2: A line segment with four lattice sites.

more ϕ probability, R_{AB}, which is the ϕ probability of the walker starting at point A, leave A and return to A without touching B. $R_{AB}(\phi)$ is easily expressible in terms of X_A and Q_{AB} as

$$R_{AB}(\phi) = X_A + X_A Q_{AB} X_A + X_A Q_{AB} X_A Q_{AB} X_A + \dots \tag{2.2.1}$$

That is,

$$R_{AB}(\phi) = \frac{X_A}{1 - X_A Q_{AB}}. \tag{2.2.2}$$

For the sake of brevity, we write R_{AB} instead of $R_{AB}(\phi)$, etc and use also this notation from now on. Then,

$$G_{AB} = R_{AB} T_{AB}. \tag{2.2.3}$$

This says that the random walker starting from point A makes attempt to reach B but could fail and return to A until at last it leaves A for good and reach B for the first time. The ϕ probability to stay at point A, X_A is given by

$$X_A = \frac{1}{1-(1-p_1)\,e^{i\phi}} \tag{2.2.4}$$

while X_C and X_D have the same value and are given by

$$X_C = X_D = \frac{1}{1-(1-p_2-p_3)\,e^{i\phi}}. \tag{2.2.5}$$

On the other hand, the expression for Q_{AB} is a bit complicated. It is composed of two parts: (a)Those types of walks, Q_{AD}, that do not touch point D and (b) Those types of walks that touch point D, call it Q_{AB}^{D}. Q_{AB} is the sum of these two. That is,

$$Q_{AB} = Q_{AD} + Q_{AB}^{D} \tag{2.2.6}$$

Note that $Q_{AD} = T_{AC}X_CT_{CA}$ where $T_{AC} = p_1e^{i\phi}$ and $T_{CA} = p_2e^{i\phi}$. On the other hand, Q_{AB}^{D}=$T_{AD}R_DT_{DA}$ where $T_{AD} = T_{AC}X_CT_{CD}$, $T_{DA} = T_{DC}X_CT_{CA}$ with $T_{CD} = T_{DC} = p_3e^{i\phi}$ and $R_D = \frac{X_D}{1-X_DQ_{DA}}$. Lastly, the expression for T_{AB} is

$$T_{AB} = T_{AD}R_DT_{DB} \tag{2.2.7}$$

Hence, we have G_{AB} expressed in terms of the local jump probabilities and is given by

$$G_{AB} = R_{AB}T_{AB} = \frac{X_AT_{AB}}{1-X_AQ_{AB}} \tag{2.2.8}$$

Then the diffusion time,τ_{AB}, of the random walker to start from A and reach B for the first time is given by

$$\tau_{AB} = \frac{1}{G_{AB}} \frac{\partial G_{AB}}{\partial i\phi} |_{\phi=0} \,. \tag{2.2.9}$$

Expressing all the basic types of walks in terms of the local jump probabilities, the value of τ_{AB} finally turns out to be

$$\tau_{AB} = \frac{(p_1 + p_2)\,(p_2 + 2p_3)}{p_1 p_2 p_3} \tag{2.2.10}$$

For unbiased random walk on a one-dimensional lattice as shown in Fig. (2.1), it was found that $\tau_{ON} = 2N^2 + 2N$ where $p_i = q_i = \frac{1}{4}$ [2]. This result is identical with the one we have, Eq.(2.2.10). Since in our case N=3 and taking $p_1 = p_2 = p_3 = \frac{1}{4}$, we get $\tau_{AB} = \tau_{03} = 24$

2.3 Diffusion Time Expressions For The Two Mechanisms Of Vacancy Diffusion

The two-dimensional diffusion of a vacancy through the mechanism of one jump cycle can represented as a random walk on lattice sites of two perpendicularly crossed segments as shown in Fig. (2.3).

The local jump probability is the same in all directions. When we see the motion of the vacancy in bulk in two dimension it has four possible ways to move from the starting point. Because of this X_A^0 will have the form

$$X_A^0 = \frac{1}{1 - (1 - 4p_0)e^{i\phi}} \tag{2.3.1}$$

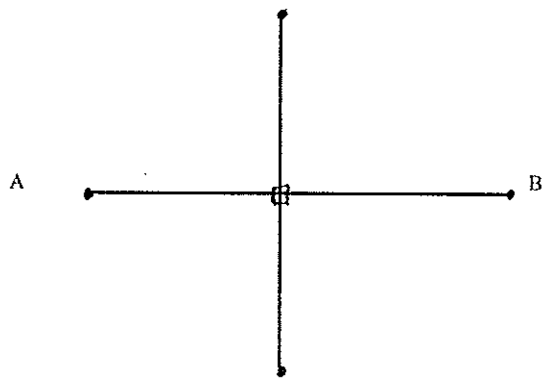

Figure 2.3: A perpendicular striaght segments.

And G^0_{AB} is

$$G^0_{AB} = \frac{p_0 e^{i\phi}}{1-(1-4p_0)e^{i\phi}} \tag{2.3.2}$$

Then the diffusion time of the vacancy to diffuse from one stable position to the next using this one jump cycle is

$$\tau_0 = \frac{1}{16p_0}. \tag{2.3.3}$$

On the other hand, the two-dimensional diffusion of a vacancy through the mechanism of a coupled three jump cycle can be represented by a random walk on loops and dangling bonds as shown in Fig. (2.4). Let us find the basic functions for a straight segment with two dangling bonds, which is one of the two identical parts of the loop see Fig. (2.5).

The local jump probabilities are the same as those shown in Fig. (2.2). In this case X_{C1} is given by

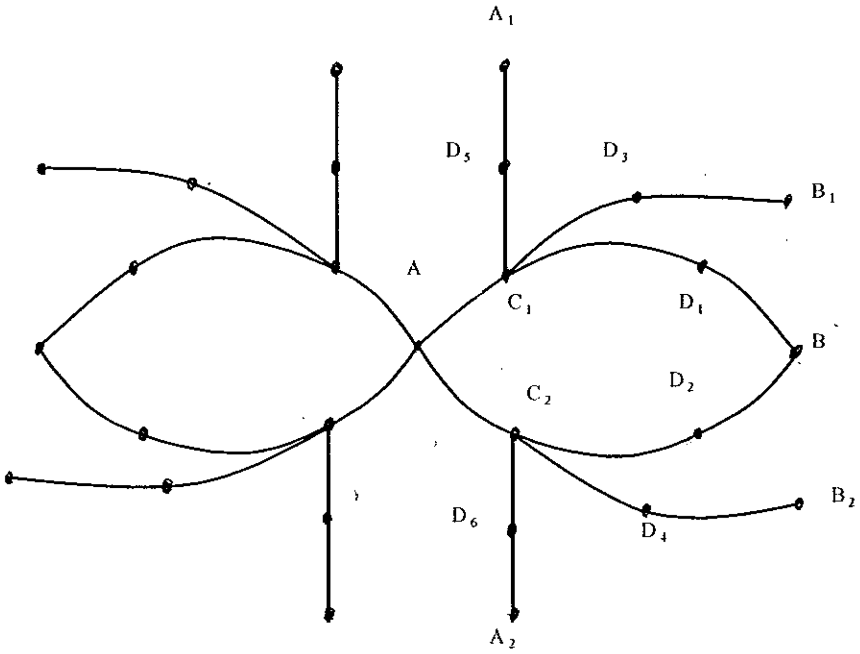

Figure 2.4: Four coupled striaght segment with two dangling bonds.

$$X_{C1} = \frac{1}{1-(1-p_2-3p_3)e^{i\phi}} \tag{2.3.4}$$

And X values for points D_1,D_3 and D_5 are given by

$$X_{D1} = X_{D3} = X_{D5} = \frac{1}{1-(1-p_2-p_3)e^{i\phi}}. \tag{2.3.5}$$

Q_{CD}, which is the ϕ probability of leaving point C on the first step to either CD_1or CD_3 or CD_5 and finally returning to the point C_1 for the first time without touching either A or A_1, B or B_1, it is the sum of $Q_{CD1}, Q_{CD3}$and Q_{CD5} where $Q_{CD1} = Q_{CD3} = Q_{CD5} = p_3^2e^{2i\phi}X_{D1}$. Hence, $Q_{CD} = 3p_3^2e^{2i\phi}X_{D1}$. On the other hand the ϕ probability which lead from C to C, R_C, is given by

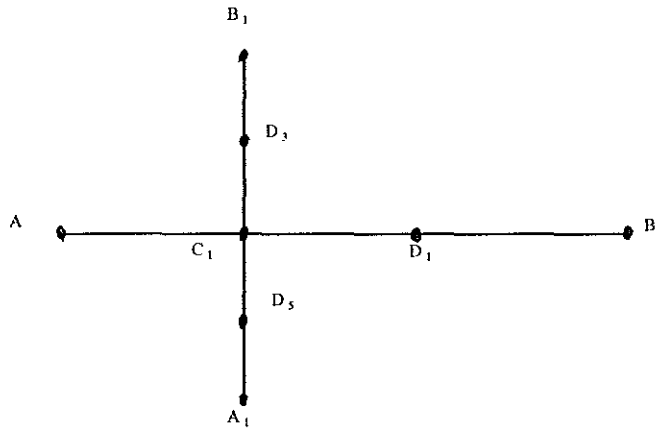

Figure 2.5: A striaght segment with two dangling bonds.

$$R_C = \frac{X_C}{1 - X_C Q_{CD}} \tag{2.3.6}$$

We have already defined T_{AC} and T_{CA} in the previous section. But $T_{CB} = p_2 p_3 e^{2i\phi} X_{D1}$. Therefore,

$$T_{AB} = T_{AC} R_C T_{CB} \tag{2.3.7}$$

And because of this R_C motion our Q_{AB} will be

$$Q_{AB} = T_{AC} R_C T_{CA} \tag{2.3.8}$$

For the case of loop shown in Fig. (2.4), the probability to stay at point A is different from that of a straight segment with two dangling bonds. That is,

$$X_A = \frac{1}{1 - (1 - 4p_1) e^{i\phi}} \tag{2.3.9}$$

And we have also four Q_{AB} motion for the four different paths. Then our R_A motion will be

$$R_A = \frac{X_A}{1 - 4X_A Q_{AB}} \tag{2.3.10}$$

And Finally G_{AB} becomes

$$G_{AB} = 8R_A T_{AB} \tag{2.3.11}$$

Therefore, the diffusion time of the vacancy will be

$$\tau_{AB} = \frac{(4p_1 + p_2)(p_2 + 4p_3)}{12p_1p_2p_3} \tag{2.3.12}$$

Note that the above diffusion time corresponds to the situation when the vacancy begin inside the material and diffuse in one direction.

In summary, we have found the expressions for the diffusion times for the two mechanisms of vacancy diffusion in terms of the local jump probabilities. Our task ahead is to find these local jump probabilities in terms of the potential profile under which the random walker moves from one stable or metastable state to the next.

CHAPTER 3

Calculation of Local Jump Probabilities

In chapter one we have identified two mechanisms of vacancy diffusion in binary alloys. In both cases, it is assumed that a vacancy moves from onesite to the next through the exchange of its position with a nearby atom. For low concentration of vacancies in the alloy, we pointed out that vacancy motion can then be taken as motion of a Brownian particle in multistable potential.

Considering such a motion as a random walk on a network, chapter two addressed the problem of finding diffusion time for the two mechanisms. The diffusion times calculated were expressed as function of the local jump probabilities of the Brownian particle as it moves from one stable or metastable state to the next in the multistable potential.

In the present chapter, we calculate the local jump probabilities for a given simple multistable potential profiles. We will first introduce a method of finding local jump probabilities in a general multistable potential. This will be followed by calculation of local jump probabilities for the two mechanisms of vacancy diffusion.

3.1 Mean First Passage Times For Homogeneous Process

Consider the one dimensional motion of a Brownian particle in a bistable or multistable potential. We confine our problem to the high friction limit where the Fokker-Planck equation governing the particle's dynamics takes the familiar Smoluchowski equation [6]. It is given by

$$\frac{\partial p(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[\beta U'(x)\, p(x,t)\right] + D\frac{\partial^2 p(x,t)}{\partial x^2} \tag{3.1.1}$$

where p(x,t) is the time dependent probability density of the particle associated with the particle's position, $U'(x) = \frac{dU}{dx}$ with U(x) being the potential function, D is the diffusion constant and $\beta = \frac{1}{k_B T}$. We are interested in finding the jump probabilities from one stable or metastable state to the other for our jump cycles. This jump probability is equal to the inverse of the mean time taken to go from the particular stable or metastable state to the other.

Let us briefly describe the method of finding the mean time taken by the Brownian particle to jump from one stable or metastable state to the next. In particular, let us find the mean time T(1→ 2) taken by the Brownian particle to jump from state 1 to state 2 for the bistable potential shown in Fig. (3.1). We use the backward Fokker-Planck equation to find T(1 → 2) or T(2 → 1). (Since the backward Fokker-Planck equation is not commonly encountered, its derivation is given in the Appendix). We more or less follow Gardiner's approach to the problem of *mean first passage time* [6].

First, we define the probability $F(x_1,t)$ that at time t the particle is still in the interval (-∞, x_2) and has not reached point x_2, given that it was initially at point x_1. That is,

$$F(x_1,t) = \int_{-\infty}^{x_2} p(x,t \mid x_1,0)\, dx, \tag{3.1.2}$$

where $p(x,t \mid x_1,0)$ is the probability density of finding the particle at position

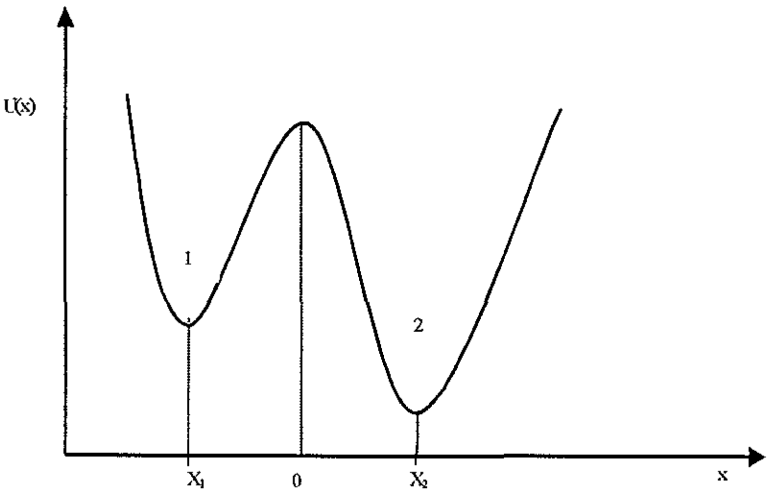

Figure 3.1: A bistable potential.

x at time t given that it was initially at position x_1. $p(x,t \mid x_1,0)$ is governed by the Smoluchowski equation, Eq. (3.1.1), and its corresponding backward Fokker-Planck equation can be written as

$$\frac{\partial}{\partial t}p(x,t \mid x_1,0) = -D\beta U' \frac{\partial}{\partial x_1}p(x,t \mid x_1,0) + D\frac{\partial^2}{\partial x_1^2}p(x,t \mid x_1,0). \qquad (3.1.3)$$

Note that $p(x,t \mid x_1,0) = p(x,0 \mid x_1,-t)$ as the system is homogenous in time. Hence,

$$\frac{\partial F(x_1,t)}{\partial t} = -D\beta U'(x_1)\frac{\partial F(x_1,t)}{\partial x_1} + D\frac{\partial^2 F(x_1,t)}{\partial x_1^2} \qquad (3.1.4)$$

Next, we define the probability density $P_{x_1}(t)\,dt$, that the particle was in the interval $(-\infty, x_2)$ until time t and left the interval between times t and t+dt. Then, *the mean first passage time* $(MFPT)$, T(1 → 2), will be given by

$$T\left(1\rightarrow 2\right)=\int\limits_{0}^{\infty} tP_{x_1}\left(t\right)dt. \tag{3.1.5}$$

On the other hand,

$$P_{x_1}\left(t\right)dt=F\left(x_1,t\right)\int\limits_{x_2}^{\infty} dy\int\limits_{-\infty}^{x_2} p\left(y,t+dt\mid x,t\right)dx, \tag{3.1.6}$$

which implies,

$$P_{x_1}\left(t\right)dt=F\left(x_1,t\right)\left[1-\int\limits_{-\infty}^{x_2} dy\int\limits_{-\infty}^{x_2} p\left(y,t+dt\mid x,t\right)dx\right] \tag{3.1.7}$$

or

$$P_{x_1}\left(t\right)dt=F\left(x_1,t\right)-F\left(x_1,t+dt\right)=\frac{-\partial F\left(x_1,t\right)}{\partial t}dt. \tag{3.1.8}$$

Hence,

$$T\left(1\rightarrow 2\right)=-\int\limits_{0}^{\infty} t\frac{\partial F\left(x_1,t\right)}{\partial t}dt=\int\limits_{0}^{\infty} F\left(x_1,t\right)dt, \tag{3.1.9}$$

since $F\left(x_1,\infty\right)=0$. Noting that,

$$\int\limits_{0}^{\infty}\frac{\partial F\left(x_1,t\right)}{\partial t}dt=F\left(x_1,\infty\right)-F\left(x_1,0\right)=-1, \tag{3.1.10}$$

from Eqs. (3.1.7) and (3.1.4) we get

$$-D\beta U'\left(x_1\right)\frac{\partial T\left(1\rightarrow 2\right)}{\partial x_1}+D\frac{\partial^2 T\left(1\rightarrow 2\right)}{\partial x_1^2}=-1. \tag{3.1.11}$$

When we solve this equation using the two boundary conditions: $\frac{\partial F(x_1,t)}{\partial x_1}\mid_{x_1=\infty}=0$ (reflecting boundary) and $F(x_2,t)=0$ (absorbing boundary), we get

$$T(1\rightarrow 2)=\frac{1}{D}\int_{x_1}^{x_2}dx\exp\left[\beta U(x)\right]\int_{-\infty}^{x}\exp\left[-\beta U(y)\right]dy. \tag{3.1.12}$$

When the barrier separating the two states is high compared to the thermal energy, Eq. (3.1.12) approximately becomes

$$T(1\rightarrow 2)\simeq\frac{1}{D}\left[\int_{-\infty}^{0}\exp\left[-\beta U(y)\right]dy\right]\int_{x_1}^{x_2}dx\exp\left[\beta U(x)\right]. \tag{3.1.13}$$

For our problem we take the high barrier limit and, hence, use Eq. (3.1.13) to calculate $T(1\rightarrow 2)$. Following the same procedure $T(2\rightarrow 1)$, the mean first passage time for the Brownian particle to jump from state 2 to state 1, is given by

$$T(2\rightarrow 1)\simeq\frac{1}{D}\left[\int_{0}^{\infty}\exp\left[-\beta U(y)\right]dy\right]\int_{x_1}^{x_2}dx\exp\left[\beta U(x)\right] \tag{3.1.14}$$

For simple potential profiles, the integrals in Eq. (3.1.13) can be evaluated so that we get an explicit expression for $T(1\rightarrow 2)$, which is equivalent to the inverse of the probability of jump from state 1 to state 2. In the next section, we will take simple model potential profiles that capture both the one and three jump cycle potentials and get the explicit expressions for the local jump probabilities.

3.2 Local Jump Probabilities

We have seen in chapter one the two possible mechanisms of vacancy diffusion and their corresponding potential profiles. We now take simplified model potentials that are *symmetric, piecewise linear and having same magnitude in slope.*

For the three jump cycle case the model potential shown in Fig. (3.2b). The Brownian particle crosses three energy barriers E_1, E_2 and E_3 with the corresponding jumping probabilities; p_1, p_2 and p_3. Note that it covers a distance of 2b to start from one stable state to its next stable state on the same sublattice. Here b denotes the lattice distance between the two different constituent atoms of the binary alloy. On the other hand, for the one jump cycle case which is shown in Fig. (3.2a), it only crosses energy barrier E_0 with jumping probability p_0 and covers a distance of $\sqrt{2}b$ in the process.

To find the local jump probabilities of the three jump cycle, we break the potential profile into three parts: from 0 to 2b/3, from 2b/3 to 4b/3 and from 4b/3 to 2b. We approximate that each jump takes place *in isolation in a bistable potential.* For instance the first jump from 0 to 2b/3 is approximated to take place in a bistable potential with an absorbing barrier at 2b/3 and reflecting barrier at -∞ as shown in Fig. (3.3).

To calculate the local jump probabilities we use the expression for *the mean first passage* [$MFPT$] derived in the previous section. Accordingly,

$$T\left(0 \to \frac{2b}{3}\right) = \frac{1}{D}\left[\int_{-\infty}^{a} \exp\left[-\beta U\left(y\right)\right] dy\right] \int_{0}^{2b/3} dx \exp\left[\beta U(x)\right] \qquad (3.2.1)$$

The potential profile from -∞ to 2b/3 satisfy the following equations:

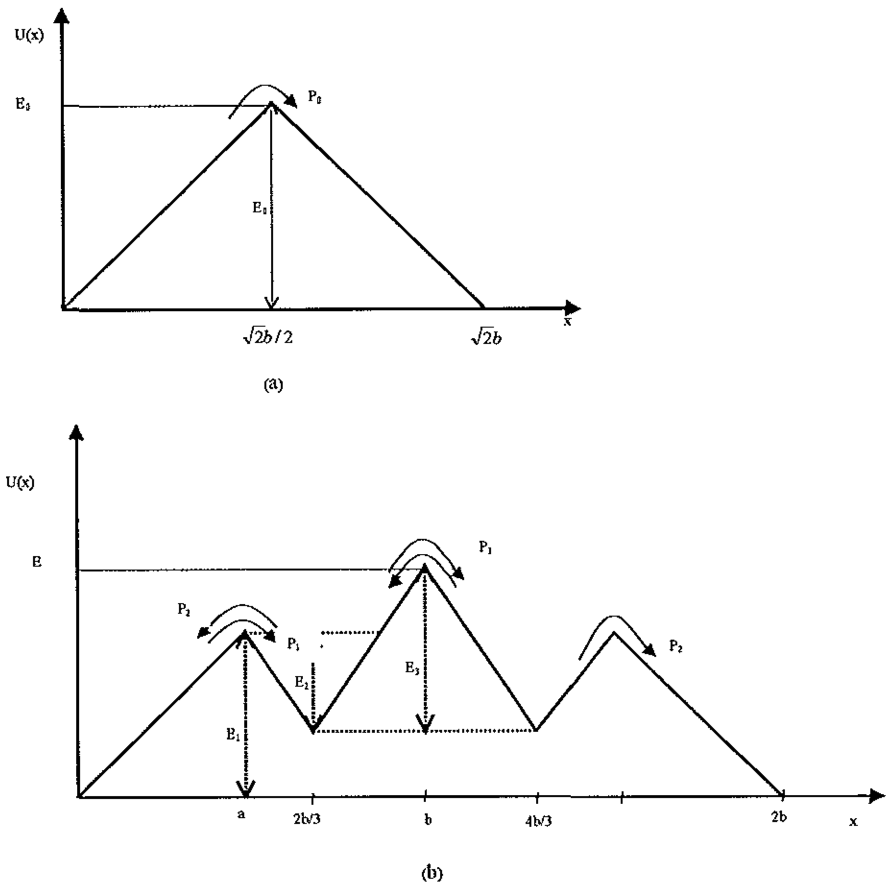

Figure 3.2: Schematic potential profile of (a) one jump cycle and (b) three jump cycle.

$$U(x) = \begin{cases} -\frac{E_1 y}{a} & when\ y < 0 \\ \frac{E_1 y}{a} & when\ 0 < y < a \\ 2E_1 - \frac{E_1 y}{a} & when\ a < y < 2b/3 \end{cases} \tag{3.2.2}$$

Taking the slope of the potential profile to have the same magnitude, we will also have the following relation,

$$\frac{E_1}{a} = \frac{3E_2}{2b - 3a} \tag{3.2.3}$$

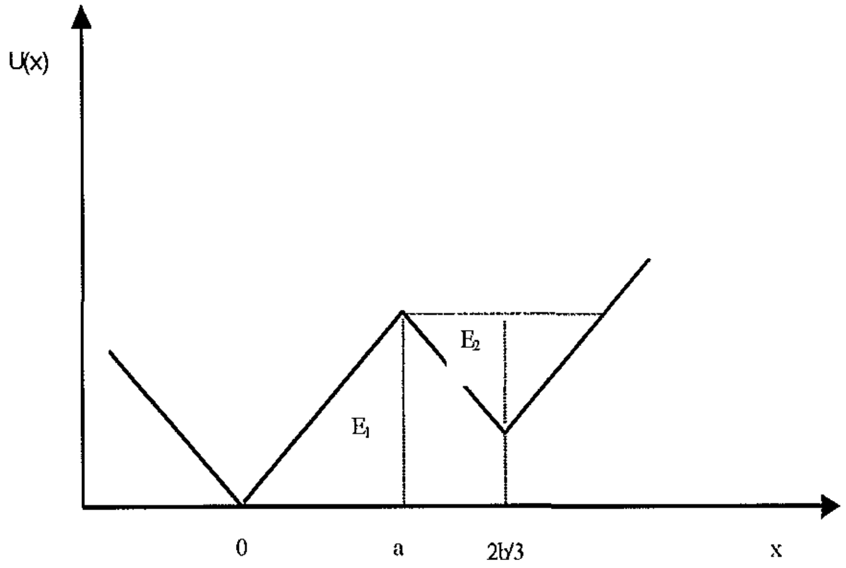

Figure 3.3: A bistable potential used to calculate MFPTs from 0 to 2b/3 and vice versa.

Taking $E_1 = \alpha_1 E$, $E_2 = \alpha_2 E$ and $E_3 = \alpha_3 E$, the α' satisfy the relation,

$$\alpha_1 - \alpha_2 + \alpha_3 = 1. \tag{3.2.4}$$

From Eq. (3.2.3) we solve for a and get,

$$a = \frac{2\alpha_1 b}{3\left(\alpha_1 + \alpha_2\right)}. \tag{3.2.5}$$

After evaluating the two integrals in Eq. (3.2.1)separately by using Eqs. (3.2.2) , (3.2.5) and considering $E_1 >> k_B T$, we get

$$T(0 \rightarrow \frac{2b}{3}) = \frac{4}{D}\left(\frac{2b}{3\beta E(\alpha_1 + \alpha_2)}\right)^2 \exp\left[\alpha_1 \beta E\right]. \tag{3.2.7}$$

This is the mean first passage time taken by the Brownian particle to jump from 0 to 2b/3. In the same fashion, the mean first passage times for the jumps from 4b/3 to 2b and from, 2b/3 to 4b/3 are, respectively,

$$T(\frac{4b}{3} \to 2b) = \frac{1}{D}\left(\frac{2b}{3\beta E\left(\alpha_1+\alpha_2\right)}\right)^2 \exp\left[\alpha_2\beta E\right], \tag{3.2.8}$$

and

$$T(\frac{2b}{3} \to \frac{4b}{3}) = \frac{2}{D}\left(\frac{b}{3\alpha_3\beta E}\right)^2 \exp\left[\alpha_3\beta E\right] \tag{3.2.9}$$

Similarly, using the potential profile of one jump cycle that is shown in Fig.$(3.2a)$,the MFPT taken by the Brownian particle to jump from 0 to $\sqrt{2}b$ is

$$T\left(0 \to \sqrt{2}b\right) = \frac{1}{D}\left(\frac{b}{\beta E_0}\right)^2 \exp\left[\beta E_0\right]. \tag{3.2.10}$$

Since the mean first passage time is the inverse of jump probability, the p_1, p_2, $p_3$and p_0 values are, respectively, given by

$$p_1 = \frac{1}{T(0 \to \frac{2b}{3})} = \frac{D}{4}\left(\frac{3\beta E(\alpha_1+\alpha_2)}{2b}\right)^2 \exp\left[-\alpha_1\beta E\right], \tag{3.2.11}$$

$$p_2 = D\left(\frac{3\beta E\left(\alpha_1+\alpha_2\right)}{2b}\right)^2 \exp\left[-\alpha_2\beta E\right], \tag{3.2.12}$$

$$p_3 = \frac{D}{2}\left(\frac{3\alpha_3\beta E}{b}\right)^2 \exp\left[-\alpha_3\beta E\right]. \tag{3.2.13}$$

and

$$p_0 = D\left(\frac{\beta E_0}{b}\right)^2 \exp\left[-\beta E_0\right]. \tag{3.2.14}$$

We now have the explicit expressions for the local jump probabilities. In the next chapter, we will use these local jump probabilities to calculate the time for the vacancy to diffuse from one site to the next site on the same sublattice for the two mechanisms. Comparison between the two diffusion times will enable us see the conditions under which one mechanism is favored over the other.

CHAPTER 4

Comparison Between The Two Diffusion Times

In chapter two, we haven seen two different mechanisms of vacancy diffusion. We have also calculated the diffusion time taken by the vacancy to diffuse from one stable state to the next within a sublattice in terms of local jump probabilities, i.e. τ in terms of p_1, p_2 and p_3 for the three jump cycle and τ_0 in terms of p_0 for the one jump cycle. In this chapter, we will express these diffusion times in terms of the corresponding energy barriers and the distance covered by the vacancy to complete the jump. Finally, we will compare the diffusion times of the two mechanisms.

4.1 Diffusion Times For The Two Mechanisms

In section two of chapter two, for one jump cycle we have already found out that the diffusion time, τ_0, for a vacancy to diffuse from one stable state to the next within a sublattice using one jump cycle is given by Eq. (2.3.3)

$$\tau_0 = \frac{1}{16 p_0}. \tag{4.1.1.}$$

On the other hand, local jump probability, p_0, was calculated in chapter three and given by Eq. (3.2.14)

$$\tau_0 = \frac{1}{16D}\left[\frac{b}{\beta E_0}\right]^2 \exp\left[\beta E_0\right]. \tag{4.1.2}$$

Note that τ_0 is expressed in terms of the energy barrier height to be crossed by the vacancy in the one jump cycle, E_0,and the distance to be covered by the vacancy in this process is, $\sqrt{2}b$.

For the three jump cycle, we have also found that the diffusion time,τ, taken by the vacancy to diffuse from one stable state to the next in terms of the local jump probabilities p_1, p_2 and p_3 to be given by Eq. (2.3.12),

$$\tau = \frac{1}{3p_1} + \frac{p_2}{12p_1p_3} + \frac{4}{3p_2} + \frac{1}{3p_3}. \tag{4.1.3}$$

Substituting the values of p_1, p_2 and p_3 from Eqs.(3.2.11), (3.2.12) and (3.2.13) in Eq. (4.1.3) we get

$$\tau = \frac{2}{27D}\left(\frac{b}{\beta E}\right)^2 \left\{\frac{1}{\alpha_3^2}\left(\exp\left[\alpha_3\beta E\right] + \exp\left[\beta E\right]\right) + \frac{8}{(\alpha_1+\alpha_2)^2}\left(\exp\left[\alpha_1\beta E\right] + \exp\left[\alpha_2\beta E\right]\right)\right\} \tag{4.1.4}$$

Note that τ is expressed in terms of the energy barriers E,lattice spacing b and in terms of α_1, α_2 and α_3.

To compare the two mechanisms of vacancy diffusion, let us take the ratio of the diffusion time for the three jump cycle to that of the one jump cycle using Eqs. (4.1.2) and (4.1.3), the expression for this ratio is given by

$$\frac{\tau}{\tau_0} = \frac{32}{27}\left(\frac{E_0}{\alpha_3 E}\right)^2 \exp\left[-\beta E_0\right] \left\{\begin{array}{c} \exp\left[\beta E\right] + \exp\left[\alpha_3\beta E\right] + \\ 8\left(\frac{\alpha_3}{\alpha_1+\alpha_2}\right)^2 \left(\exp\left[\beta\alpha_1\right] + \exp\left[\beta\alpha_2 E\right]\right) \end{array}\right\} \tag{4.1.5}$$

The energy barrier, E_0, of the one jump cycle is usually larger than the energy barrier , E, of the three jump cycle. For the sake of comparing the two mechanisms,let us express E as fraction of E_0, that is,

$$E = \gamma E_0 \tag{4.1.6}$$

Then Eq. (4.1.5), becomes

$$\frac{\tau}{\tau_0} = \frac{32}{27\alpha_3}\left(\frac{1}{\gamma\alpha_3}\right)^2 \exp\left[-\beta E_0\left(1-\gamma\right)\right] \left\{ \begin{array}{c} 1+\exp\left[-\beta E_0(1-\alpha_3)\right] + \\ 8\left(\frac{\alpha_3}{\alpha_1+\alpha_2}\right)^2 \left(\begin{array}{c} \exp\left[-\beta E_0(1-\alpha_1)\right] \\ +\exp\left[-\beta E_0(1-\alpha_2)\right] \end{array} \right) \end{array} \right\}. \tag{4.1.7}$$

For high barrier, $\beta E_0 >> 1$, the last three terms in the complex bracket are negligible compared to one (the first term). Hence,

$$\frac{\tau}{\tau_0} \sim \frac{32}{27}\frac{1}{\gamma^2\alpha_3^2}\exp\left[-\beta E_0(1-\gamma)\right]. \tag{4.1.8}$$

Let us see a criteria for determining which mechanism is favored over the other as follows:

1. If $\tau >> \tau_0$, then diffusion through the mechanism of the one jump cycle is fast and, as such, it is favored over the mechanism of the three jump cycle.

2. If, on the other hand, $\tau << \tau_0$, then diffusion through the mechanism of the three jump cycle is fast and as such, it is favored over the mechanism of one jump cycle.

3. The $\tau \sim \tau_0$ case is when the two mechanisms have the same time scale of diffusion. It is the transition point from one mechanism to the other mechanism.

To get a fell of this transition point, we set $\tau = \tau_0$ and evaluate γ for certain values of α_3 and βE_0.

βE_0	10	10	10	10
α_3	0.2	0.3	0.4	0.5
γ	0.53	0.66	0.74	0.8

βE_0	15	15	15	15
α_3	0.2	0.3	0.4	0.5
γ	0.8	0.86	0.9	0.93

Based on the numerical results above we can say the following regarding the two mechanisms of vacancy diffusion.

1. For barrier height $E_0 = 10k_BT$ and α_3=0.2, the barrier height E corresponding to the three jump cycle must be less than half of E_0 in order for the three jump cycle to be favored over the one jump cycle. On the other hand, when $\alpha_3 = 0.5$ (with $E_0 = 10k_BT$) E could be about as high as 80% of E_0 for the three jump cycle to be favored over the one jump cycle.

2. For barrier height $E_0 = 15k_BT$ and α_3=0.2, the barrier height E corresponding to the three jump cycle must be less than about three quarter of E_0 in order for the three jump cycle to be favored over the one jump cycle. On the other hand, when $\alpha_3 = 0.5$ (with $E_0 = 10k_BT$) E could be as high as 90% of E_0 for the three jump cycle to be favored over the one jump cycle.

3. In real crystal materials E_0 is of the order of 1ev so that at room temperature E $\sim$ 40k$_BT$. In this case, E could be very close but slightly less than E_0 for the three jump cycle.

CHAPTER 5

Summary And Conclusion

In this work, we have considered two mechanisms by which vacancies diffuse in a two dimensional binary alloy made up of two interpenetrating square sublattices. We confined ourselves to the low concentration of vacancies in the alloy so that the vacancy diffusion can be can be taken as motion of a single Brownian particle on a lattice. One main property of vacancy diffusion, diffusion time, was then calculated for the two diffusion mechanisms in terms of the local jump probabilities. To do so we used a method of calculating properties of random walks on networks.

The local jump probabilities were themselves then calculated from the model potential profiles for the two diffusion mechanisms. These were then used to get the explicit expressions for the diffusion times in terms of barrier height (E) for the three jump cycle and (E_0) for the one jump cycle and lattice spacing b.

By comparing the diffusion times for the two mechanisms, a criteria was proposed to determine which mechanism is favored over the other. We have come up with a conclusion that for real materials where barrier heights are of order one electron volt, the three jump cycle is likely to be favored at room temperature as long as its barrier height (E) is slightly less than the barrier height (E_0) for the one jump cycle.

In conclusion, we would like to point out two things. The first point is that we should extend this work to deal with three dimensional binary alloy as most alloys in nature exist in three dimensions. The second and important point ahead is to check our prediction with experimental results. In particular, it is worth to get actual energetics profiles of defects for alloys as well as the experimental results of diffusion times.

Appendix A

In this appendix we will derive the backward Fokker-Planck equation. The (forward) Fokker-Planck equation which governs the dynamics of the random variable is given by

$$\frac{\partial p\left(x,t\mid y,t'\right)}{\partial t}=-\frac{\partial}{\partial x}\left[A\left(x,t\right)p\left(x,t\mid y,t'\right)\right]+\frac{1}{2}\frac{\partial^2}{\partial x^2}\left[B\left(x,t\right)p\left(x,t\mid y,t'\right)\right], \quad \text{(A.1)}$$

where $p\left(x,t\mid y,t'\right)$ is the probability that the random variable takes a value of x at time t given that it had earlier taken a value of y at time t', (t'$\leq t$). Note that that drift, A(x,t) and diffusion, B(x,t) quantities in the equation are given by

$$A\left(x,t\right)=\lim_{\Delta t\to 0}\frac{1}{\Delta t}\int\limits_{|x-y|<\epsilon}(x-y)p\left(x,t\mid y,t'\right)dx, \quad \text{(A.2)}$$

and

$$B\left(x,t\right)=\lim_{\Delta t\to 0}\frac{1}{\Delta t}\int\limits_{|x-y|<\epsilon}(x-y)^2p\left(x,t\mid y,t'\right)dx. \quad \text{(A.3)}$$

We are interested to derive the backward Fokker-Planck equation which is used to find the mean first passage time problems. The time development of $p\left(x,t\mid y,t'\right)$ with respect to t' is

$$\frac{\partial p\left(x,t\mid y,t'\right)}{\partial t'}=\lim_{\Delta t'\to 0}\frac{1}{\Delta t'}\left[p\left(x,t\mid y,t'+\Delta t'\right)-p\left(x,t\mid y,t'\right)\right] \quad \text{(A.4)}$$

Using Chapman-Kolmogrove equation,

$$\frac{\partial p\left(x,t\mid y,t'\right)}{\partial t'}$$

$$= \lim_{\Delta t' \to 0} \frac{1}{\Delta t'} \left[\begin{array}{c} p\left(x,t \mid y,t'+\Delta t'\right) \\ -\int p\left(x,t \mid z,t'+\Delta t'\right) p\left(z,t'+\Delta t' \mid y,t'\right) dz \end{array} \right] \tag{A.5}$$

Since $\int\limits_{-\infty}^{\infty} p\left(z,t'+\Delta t' \mid y,t'\right) dz = 1$

$$\begin{aligned} & \frac{\partial p\left(x,t \mid y,t'\right)}{\partial t'} \\ = & \lim_{\Delta t' \to 0} \frac{1}{\Delta t'} \int p\left(z,t'+\Delta t' \mid y,t'\right) dz \\ & \times \left[p\left(x,t \mid y,t'+\Delta t'\right) - p\left(x,t \mid z,t'+\Delta t'\right)\right] \end{aligned} \tag{A.6}$$

This can be written as

$$\frac{\partial p\left(x,t \mid y,t'\right)}{\partial t'} = \lim_{\Delta t' \to 0} \frac{1}{\Delta t'} \int p\left(z,t'+\Delta t' \mid y,t'\right) dz \left[p\left(x,t \mid y,t'\right) - p\left(x,t \mid z,t'\right)\right] \tag{A.7}$$

Take any function f(y) which is twicely differentiable and multiply Eq. (A.7) by f(y) and then integrate with respect to y. That is,

$$\begin{aligned} \frac{\partial}{\partial t'} \int f(y) p\left(x,t \mid y,t'\right) dy &= \lim_{\Delta t' \to 0} \frac{1}{\Delta t'} \int dy \int dz f(y) p\left(z,t'+\Delta t' \mid y,t'\right) \\ & \times \left[p\left(x,t \mid y,t'\right) - p\left(x,t \mid z,t'\right)\right] \end{aligned} \tag{A.8}$$

For a continuously varying stochastic variables y or z, z is infinitesimally close to y when $\Delta t' \to 0$. That is,

$$\lim_{\Delta t' \to 0} p\left(z,t'+\Delta t' \mid y,t'\right) = \delta\left(z-y\right) \tag{A.9}$$

Using Taylor expansion, we expand $p\left(x,t\mid z,t'\right)$ with respect to y which is given by

$$p\left(x,t\mid z,t'\right)=p\left(x,t\mid y,t'\right)+\left(z-y\right)\frac{\partial}{\partial y}p\left(x,t\mid y,t'\right)$$

$$+\frac{1}{2}\left(z-y\right)\frac{\partial^2}{\partial y^2}p\left(x,t\mid y,t'\right)+... \qquad \text{(A.10)}$$

Substituting Eq. (A.10) in to Eq. (A.8) we get

$$\begin{aligned}&\frac{\partial}{\partial t'}\int f\left(y\right)p\left(x,t\mid y,t'\right)dy\\ =\ &\lim_{\Delta t'\to 0}\frac{1}{\Delta t'}\int dy\int dz f\left(y\right)p\left(z,t'+\Delta t'\mid y,t'\right)\\ &\left[-\left(z-y\right)\frac{\partial}{\partial y}p\left(x,t\mid y,t'\right)-\frac{1}{2}\left(z-y\right)\frac{\partial^2}{\partial y^2}p\left(x,t\mid y,t'\right)+..\right] \qquad \text{(A.11)}\end{aligned}$$

Using Eq. (A.2) and Eq. (A.3) Eq. (A.11) will have the form.

$$\begin{aligned}&\frac{\partial}{\partial t'}\int f\left(y\right)p\left(x,t\mid y,t'\right)dy\\ =\ &\int dy f\left(y\right)\left[-A\left(y,t\right)\frac{\partial}{\partial y}p\left(x,t\mid y,t'\right)-\frac{1}{2}B(y,t)\frac{\partial^2}{\partial y^2}p\left(x,t\mid y,t'\right)\right]\text{(A.12)}\end{aligned}$$

Hence, we have

$$\frac{\partial}{\partial t'}p\left(x,t\mid y,t'\right)=-A\left(y,t\right)\frac{\partial}{\partial y}p\left(x,t\mid y,t'\right)-\frac{1}{2}B(y,t)\frac{\partial^2}{\partial y^2}p\left(x,t\mid y,t'\right) \qquad \text{(A.13)}$$

This is the backward Fokker-Planck equation.

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