DETERMINATION OF MEAN FIRST PASSAGE TIME FOR A VACANCY DIFFUSING IN ORDERED BINARY ALLOY

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Zerihun Getahun

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Zerihun Getahun

Department of Physics

Faculty of Science

APPROVED BY THE EXAMINATION COMMITEE

Name	**Signature**
Dr. Mulugeta Bekele, Advisor	_______________
Dr. Mesfin Asfaw, Examiner	_______________
Prof. A. K. Chaubey, Examiner	_______________

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"Thanks be unto God for his unspeakable gift"

Zerihun Getahun
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Addis Ababa.

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Abstract

The Mean First Passage Time (MFPT) of a vacancy diffusing in a highly viscous and homogenous medium of two dimensional ordered binary alloy is studied by using the random walk on network technique. We consider two types of models, i.e. single path and all possible paths models. We compare the MFPT for $One - Jump$ and $Six - Jump$ cycles for both models. We study how the MFPT behaves as a function of temperature fixing other parameters. At high temperature $One - Jump$ cycle is dominant over $Six - Jump$ cycle except for the case when $\frac{E_0}{2E_1} \leq 1$ that the MFPT of a vacancy via $One - Jump$ cycle is always less than the MFPT via $Six - Jump$ cycle in a single path model. However, at low temperature regime, the reverse is true. It is also investigated how the MFPT behaves as a function of potential barrier height. When the potential barrier height of the $One - Jump$ cycle is less than that of the $Six - Jump$ cycle, the $One - Jump$ cycle is dominant. On the contrary, the MFPT for the $Six - Jump$ cycle is longer than that of the $One - Jump$ cycle if the potential barrier height for the $Six - Jump$ cycle is less than the potential barrier height for $One - Jumpcycle$.

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Chapter 1

Introduction

Crystalline solids inherently posses considerable amount of defects and imperfections that affect their physical, chemical, mechanical and electrical properties. The presence of these defects within the host crystal also plays an influential role in various technological processes and phenomena such as annealing, precipitation, diffusion, sintering, oxidation and others. It should be taken into consideration that defects do not necessarily have adverse effects on the properties of the material. For instance, the electrical behavior of semiconductors is largely controlled by crystal imperfections. All crystalline defects and imperfections may be classified in to four basic categories: point defects, line defects, plane defects and volume defects. The common point defects are: vacancies (atom sites normally occupied in the perfect crystal, from which atoms are missed), interstitial atoms (atoms in a wrong site) and extrinsic point defects (point defects involving foreign atoms).

A vacancy is an example of point defects inherited to the crystal in equilibrium state. It is also called either Schottky or Frenkel defect. The former type of point defect is formed when an atom leaves its site (thereby creating a vacancy) and then moves to the surface of the crystal. In the latter case, the atom vacates its position in the lattice and transfers to an interstitial position in the crystal. The formation of Frenkel defect therefore creates two defects within the lattice - a vacancy and the interstitial defect, while the formation of a Schottky defect leaves only one defect within the lattice, a vacancy.

Atomic diffusion in crystals is usually mediated by point defects. The two basic mechanisms of atomic diffusion are vacancy mechanism and interstitial mechanism. However atoms located at the crystal lattice sites usually diffuse by a vacancy mechanism, while interstitial atoms diffuse by jumping from one interstitial site to the other interstitial site without displacing any of the matrix. In both cases the atom must pass through a state of high energy and this creates an energy barrier. Our work mainly deals with the vacancy mediated atomic diffusion. For a vacancy to jump from one lattice site to another lattice site, energy is needed to break bonds with the neighboring atoms and to cause the necessary lattice distortions.

Self diffusion in ideally pure crystals is mediated by the random jumps of mono-vacancies to the nearest neighbor lattice sites. In our case, the vacancy diffusion in two dimensional ordered binary compound, the situation is more complicated. This material consists of two interpenetrating simple cubic sublattices which are predominantly occupied by two different atoms, say A and B. The random walk of a vacancy on that material through the nearest-neighbor jumps would generate a string of anti-structure atoms and the material would become disordered. In view of this limitation, various atomistic models have been proposed for diffusion in ordered binary alloys, which allow prescribed atom-vacancy exchanges to take place with out concomitant long-range disordering. Huntington [1] first suggested the possibility of $Six - Jump$ vacancy cycle which allows diffusion to take place exclusively by means of nearest-neighbor vacancy jump. Elcock and McCombie [2] examined the detailsof such a highly correlated series of vacancy jumps for the ordered simple cubic binary alloy. On the other hand, Wynblatt [3] discussed the relative importance of three different mechanisms in the B_2 lattice: cyclic vacancy motion by a correlated set of six nearest neighbor jumps, next nearest neighbor jumps ($One - Jump$ cycle) and divacancy migration; the energetically favourable mechanism has been concluded to be the $Six - Jump$ vacancy cycle [4].

Consider a vacancy, initially at one of the lattice sites of type A atom. It can perform two types of jumps to the neighboring sites, i.e, either to the nearest sites of different species (type B) or to the next nearest sites within the same sublattice of type A ($One - Jump$ cycle). At sufficiently low temperature the former type of jump is the most likely to occur and the latter one is insignificantly involved. $Three$ and $Six - Jump$ cycle models are examples of the former type of jumps.

For the six-jump cycle a vacancy has to make six successive jumps through sublattice to bring the system to its original state. The first three jumps of the vacancy progressively disorder the lattice and the next three jumps of the vacancy re-order the lattice back to its most stable state. In the case of $One - Jump$ cycle the system comes to its next similar stable state after a single jump [5].

$Three - Jump$ cycle is made up of two successive exchange in position of the vacancy with its nearest atom followed by one exchange in position of an atom with its nearest atom and ultimately arriving at the ordered arrangement of atoms on the lattice site [6].

It is assumed that the jumps between the various states of the Six and $One - Jump$ cycles represent stochastic process and that consequently the system completely thermalizes in each stable or meta stable state before performing the next jump. A pre-condition for the existence of a $Six - Jump$ cycle is the existence of stable or meta-stable in all states of the complete cycle [7].

In this work the diffusion of a vacancy via $Six - Jump$ and $One - Jump$ cycles is discussed for materials with low concentration of thermal defects and close to stoichiometry (low concentration of structural defects). We further assume that for both atomic species the potential barrier height to be the same while they are involved in vacancy- atom exchange process. In other words, the potential barrier height value for A type atom-vacancy exchange is the same as that for B type atom-vacancy exchange [7].

Figure 1.5 shows a schematic representation of the energy change taking place during vacancy motion through the $Six - Jump$ cycle. The individual jump probabilities per unit time of a vacancy are denoted by p and q, p is the probability for the vacancy to cross the barrier E_1 while q is the probability for the vacancy to cross the barrier E_2.

Each positions of a vacancy when it jumps from one state to the other is shown in detail in the Figs. 1.3 and 1.4 for Six and $One - Jump$ cycles, respectively. The corresponding potential profiles of the whole system are clearly plotted in the Figs. 1.5 and 1.6. As clearly shown in Fig. 1.7, a vacancy initially at point A can start its motion in one of eight alternative paths (path 1, 2, 3, 4, 5, 6, 7, 8) with equal probabilities and finally reach to the point B.

A vacancy is not a real particle but it is an idealized particle (quasi-particle) considered as a Brownian particle. Its motion (jump restricted to the lattice sites) is taken to be the Random Walk of a Brownian particle on the lattice sites.

The main purpose of this work is to determine the mean first passage time (MFPT) taken by the vacancy to reach lattice site B (of the same state as A) and M starting from site A through a $Six - Jump$ and $One - Jump$ cycles respectively in a two dimensional ordered binary alloy and to compare which cycle dominates over the other. One should note that the vacancy has to pass through a series of intermediate states to reach state B as shown in the Fig. 1.3.

The structure of this thesis is organized as follows. Chapter two introduces the method used in calculating mean first passage time of a particle moving from a stable state to another stable state. The dynamics of a vacancy and its MFPT are investigated when the vacancy accomplishes one cycle through $Six-Jump$ and $One-Jump$

cycles is discussed in Chapter three. Chapter four deals with the result and discussion. In Chapter five we present summary and conclusion of the result obtained.

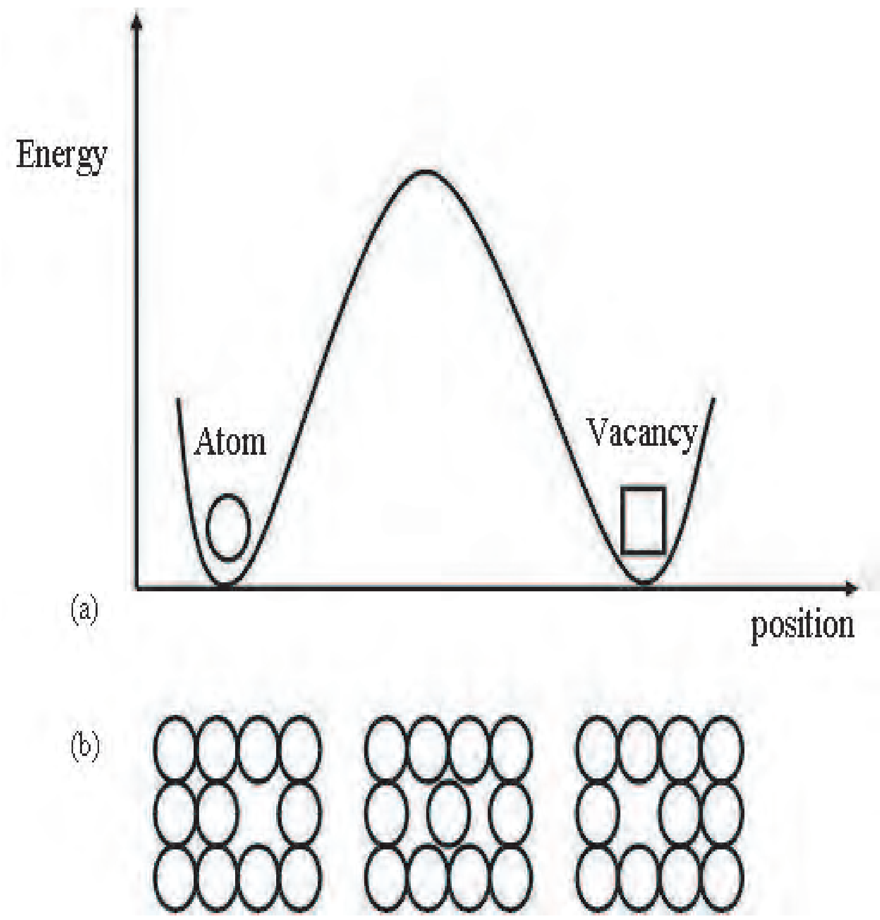

Figure 1.1: (a) Plot of energy barrier that a vacancy has to cross verses distance. (b) Hopping of vacancy to the next nearest state.

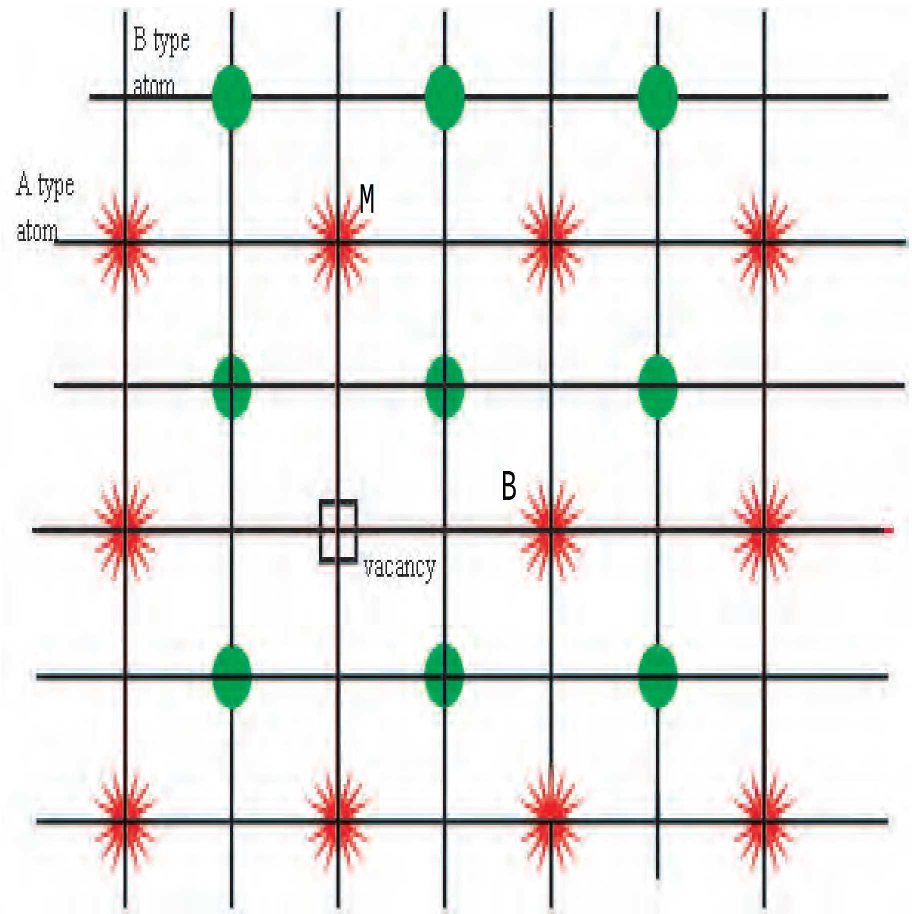

Figure 1.2: Two dimensional crystal structure of ordered binary alloy.

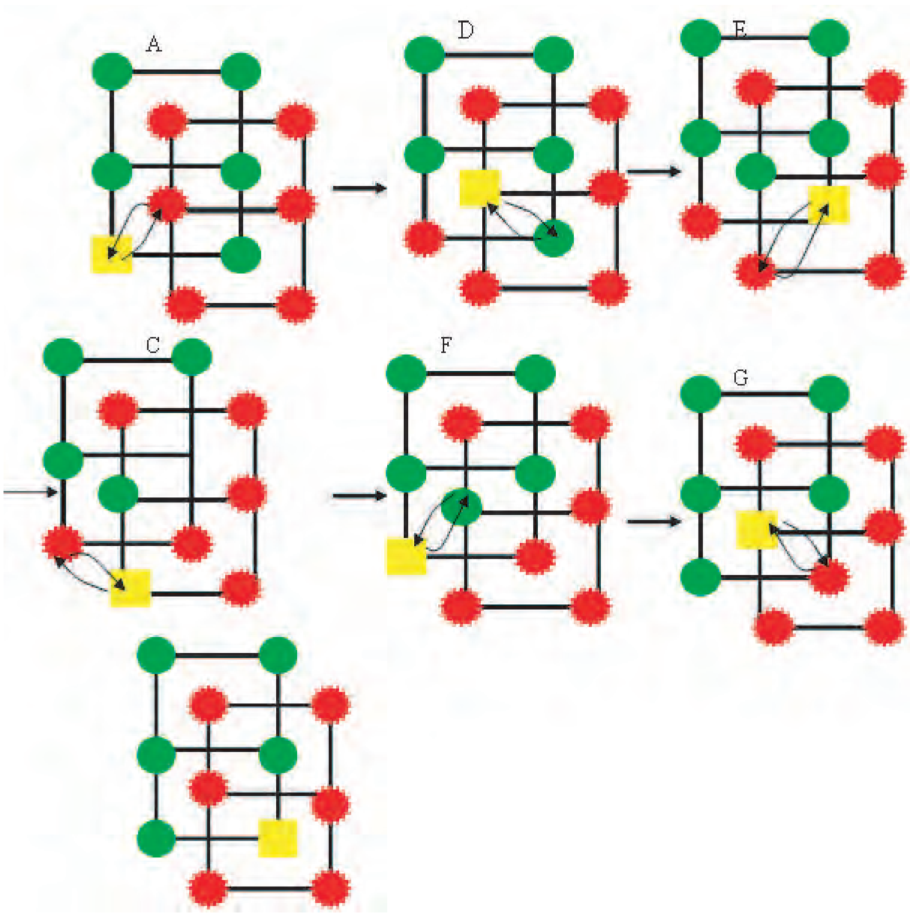

Figure 1.3: The possible states when the vacancy undergoes a $Six - Jump$ cycle.

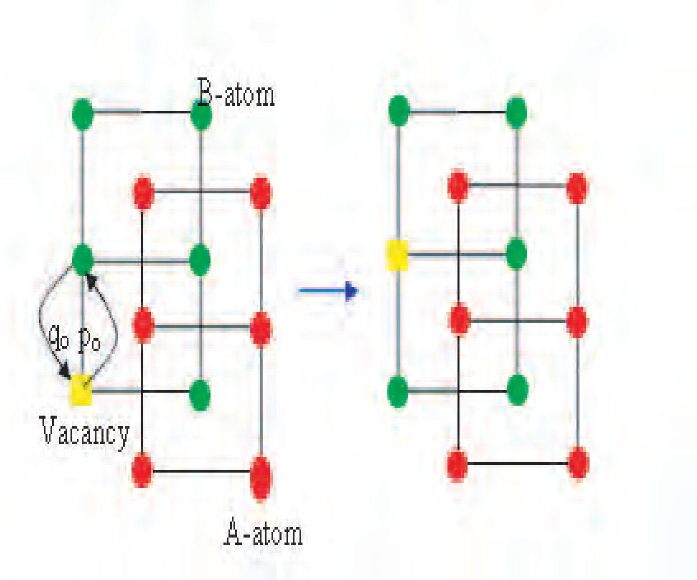

Figure 1.4: The possible states when the vacancy undergoes a $One - Jump$ cycle.

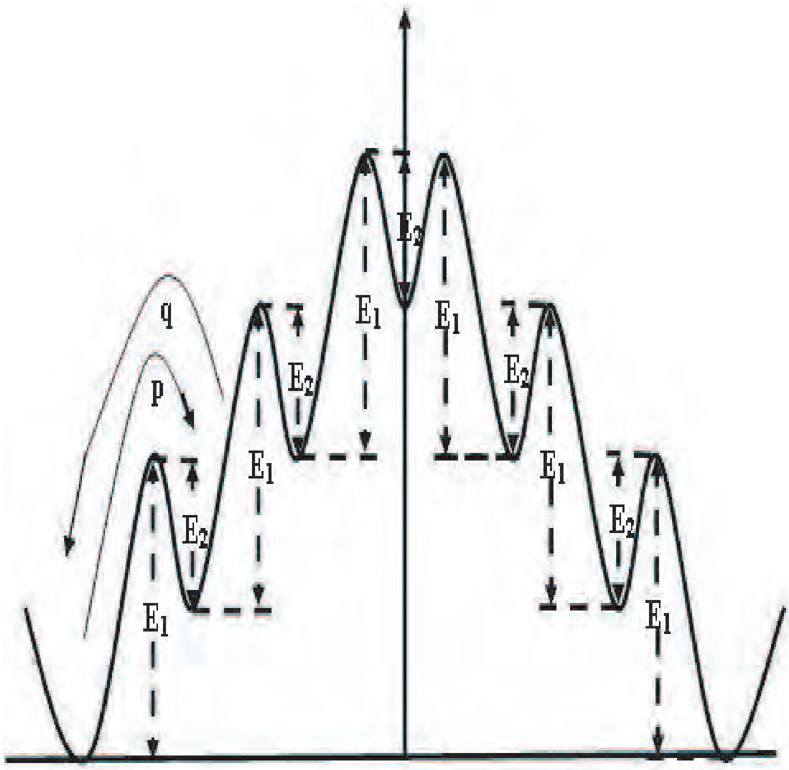

Figure 1.5: Schematic diagram which shows the energy barrier that the vacancy has to cross when it hopes from one state to other during a $Six - Jump$ vacancy cycle.

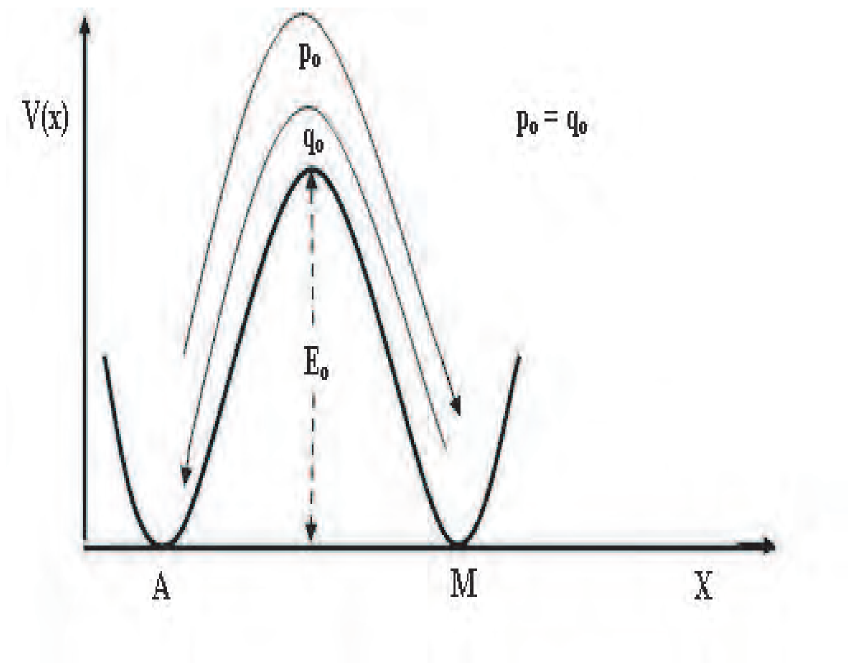

Figure 1.6: Schematic diagram which shows the energy barrier that the vacancy has to cross when it hopes from one state to other during a $One - Jump$ vacancy cycle.

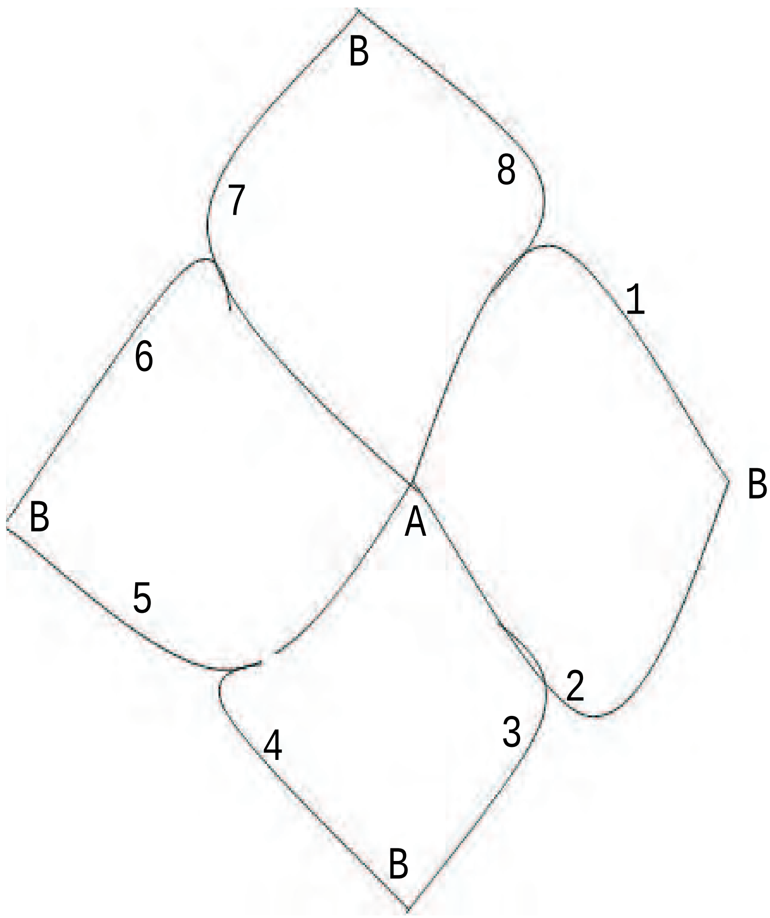

Figure 1.7: Eight alternative ways for a vacancy to reach point B starting from the stable state point A during $Six - Jump$ cycle.

Chapter 2

MOTION OF A VACANCY AS A RANDOM WALK ON A LATTICE

As previously mentioned in Chapter one, diffusion of a vacancy in a two dimensional crystalline structure of ordered binary alloy can be modeled as the motion of a Brownian particle over ragged potential. In this Chapter, we are going to look the details how the vacancy moves through such a crystal structure in a $Six - Jump$ and $One - Jump$ cycles. To carry out this, we have to present a particular method of determining MFPT, Random Walk on Network, suggested by I. Goldhirch and Y.Gefen [1, 2].

2.1 Random Walk on Networks

The significance of the random walk problem in many areas of science and technology and as a mathematical problem in its own right is well known [1]. Numerous dynamical processes in nature can be successfully modeled as a random walks. The best known physical example is the Brownian motion of a small particle immersed in a medium. In this case the "walk" is ideally unbiased and continuous both in space and time. Another example which is believed to model some configurational properties of linear polymers, is the self-avoiding random walk. Many transport phenomena in solids (e. g. hopping conductivity) are modeled by random walks. In the latter case the random walk is restricted to a lattice. The mathematical theory of relevant random walks on regular systems (e.g. regular lattices) is fairly complete (except the self-avoiding case). Another subject of importance is the motion of particles or quasi-particles in a system containing randomly distributed impurities [2]. In this section we are going to demonstrate the technique that we used for calculating the mean first passage time for a straight and bent segments.

Consider a straight line segment with N number of points as shown in the Fig. 2.1.

Figure 2.1: Straight line segment.

Let p_i be the probability that the walker jumps from i to i+1 and q_i be the probability that the walker jumps from i to i-1. Obviously, $p_i + q_i \leq 1$, as the walker has the probability to stay at i. As far as the walker is confined to move within the segment, $p_N = q_0 = 0$. The probability to stay at a given initial point i in a single time step is $1-p-q$. After n consecutive steps the probability to stay at the same initial point i is $(1-p-q)^n$. Let us define the corresponding generating function $\chi(\phi)$, for this probability to be,

$$\chi(\phi) = \sum_{n=0}^{\infty}(1-p-q)^n \exp(in\phi) \tag{2.1}$$

which can be expressed as:

$$\chi(\phi) = \frac{1}{1-(1-p-q)\exp(i\phi)}. \tag{2.2}$$

In general, if $P(n)$ denotes the probability to perform a given walk in n steps, then the corresponding generating function $\tilde{P}$ is defined as:

$$\tilde{P}(\phi) = \sum_{n=0}^{\infty} \exp(in\phi)P(n). \tag{2.3}$$

Before we go to the detail of the chapter first lets define two more basic functions.

1. Let $T(n)$ be the probability of the walker to start at the point $i=0$, leave it on the first step and reach $i=N$ for the first time without having returned to $i=0$ in the process. The corresponding generating function $\tilde{T(\phi)}$ can be expressed as

$$\tilde{T(\phi)} = \sum_{n=0}^{\infty} \exp(in\phi)T(n). \tag{2.4}$$

2. Let $Q(n)$ be the probability of the walker to leave $i=0$ in its first step and return to $i=0$ in n steps with out having reached to $i=N$ with the associated generating function $\tilde{Q(\phi)}$,

$$\tilde{Q(\phi)} = \sum_{n=0}^{\infty} \exp(in\phi)Q(n). \tag{2.5}$$

Generating functions defined above can be added and multiplied like regular probabilities, except that one doesn't have to keep track of the number of steps.

Our aim is to determine the average time required by the random walker (a vacancy) to reach $i = N$ for the first time starting from $i = 0$. This time is usually called mean first passage time, highly related to the probability $P_w(n)$ that the walker reaches $i = N$ for the first time starting from $i = 0$. The generating function $G(\phi)$ corresponding to $P_w(n)$ is,

$$G(\phi) = \sum_{n=0}^{\infty} \exp(in\phi) P_w(n). \tag{2.6}$$

The MFPT can then be defined as,

$$MFPT = \frac{\sum_{n=0}^{\infty} nP_w(n)}{\sum_{n=0}^{\infty} P_w(n)}. \tag{2.7}$$

It can be also expressed in terms of ϕ probabilities as,

$$MFPT = \frac{1}{G(\phi)} \frac{dG(\phi)}{di\phi}|_{\phi=0}. \tag{2.8}$$

The generating function, $G_{AB}(\phi)$ can be calculated in terms of $T\tilde{(\phi)}$, $Q\tilde{(\phi)}$ and $\chi(\phi)$. A walker at point A can stay there for a number of steps (with probability $\chi(\phi)$), move out of A and return to A without having touched N (with probability $Q\tilde{(\phi)}$), then stay at A and repeat the process a number of times. Eventually it will start out at A and reach N without returning to A again (with probability $T\tilde{(\phi)}$). Therefore, the normalized probability at vertex A, R_A, is given by

$$R_A = \chi_A + \chi_A \tilde{Q} \chi_A + ... \tag{2.9}$$

One can rearrange Eq. (2.9) and after some algebra, we get,

$$R_A = \frac{\chi_A}{1 - \chi_A \tilde{Q}}. \tag{2.10}$$

After wondering for some time, the walker leaves A forever and reaches N for the first time. Hence, the ϕ probability, $G(\phi)$, of the walker to reach N considering all the realizations is given by

$$G(\phi) = \frac{\chi_A(\phi)T(\phi)}{1-\chi_A(\phi)\tilde{Q}(\phi)}. \tag{2.11}$$

Let us consider again the random walk on the bent segment shown in the Fig. 2.2 in which a walker starts at the left end of A, goes to point C and finally bends to reach point B. The walker starting at A has to travel the segment AC of length N_1 and the segment CB of length N_2. The ϕ probability governing the motion of the walker on this segment is given as

$$G_{AB}(\phi) = \frac{\chi_A(\phi)T_{AB}(\phi)}{1-\chi_A(\phi)Q_A(\phi)} \tag{2.12}$$

where

$$T_{AB}(\phi) = T^{+}_{N_1}R_cT^{-}_{N_2} \tag{2.13}$$

$$Q_A(\phi) = Q_{N_1} + T^{+}_{N_1}R_cT^{-}_{N_1} \tag{2.14}$$

$$R_c = \frac{\chi_c}{1-\chi_c(Q_{N_1}+Q_{N_2}} \tag{2.15}$$

$$\chi_A = [1-(1-p)\exp(i\phi)]^{-1} \tag{2.16}$$

$$\chi_c = [1-(1-2q)\exp(i\phi)]^{-1}. \tag{2.17}$$

Equation (2.13) contains all the possible paths that the walkerto start at A, return an arbitrary number of times to A before reaching B and then start at A, leave A, and reach B without ever returning to A (T_{AB}). Here (T_{AB}) consists of the ϕ probability to leave A and reach C without ever returning to A, then stay at C or leave C and return to it (without reaching either A or B) unspecified number of times and then leave C towards B without returning to C. The first factor $\frac{\chi_A(\phi)}{1-\chi_A(\phi)Q_A(\phi)}$ refers to all possibilities to start at A and return to it without touching B. This includes the following processes: staying at A (χ_A), leaving A and returning to A without reaching C (Q_{N_1}); leaving A, reaching C at least once, and returning to A ($T^+_{N_1}R_cT^-_{N_1}$). Plus and minus sign on T is simply to indicate the direction of the walk.

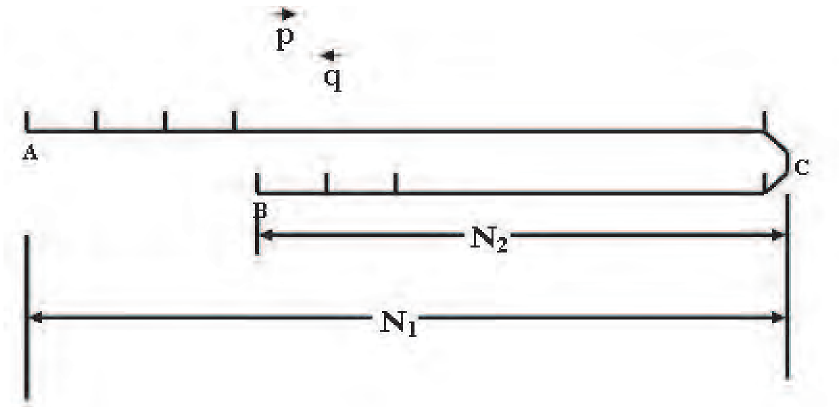

Figure 2.2: Random walk on a bent segment.

2.2 MFPT Of a Vacancy Diffusing Through a $Six-Jump$ Cycle

To calculate the mean first passage time of a vacancy diffusing through the $Six-Jump$ cycle analytically, it is better to propose some simplified models that can describe the targeted physical phenomena. The models we proposed here are a single path model and eight paths model.

2.2.1 A Single Path Model

In this model, we take simply the motion of a vacancy through one of the paths indicated in the Fig. 1.5 which is the same as the random walk of a walker on a single bent segment. As a result, the ϕ probability governing the motion a vacancy can written as

$$G_{AB61}(\phi) = \frac{\chi_A(\phi)T_{AB}(\phi)}{1-\chi_A(\phi)Q_A(\phi)}, \tag{2.18}$$

where

$$T_{AB}(\phi) = T^{+}_{N_1}R_cT^{-}_{N_2}, \tag{2.19}$$

$$Q_A(\phi) = Q_{N_1} + T^{+}_{N_1}R_cT^{-}_{N_1}, \tag{2.20}$$

$$R_c = \frac{\chi_c}{1-\chi_c(Q_{N_1}+Q_{N_2}}, \tag{2.21}$$

$$\chi_A = [1-(1-p)\exp(i\phi)]^{-1}, \tag{2.22}$$

$$\chi_c = [1-(1-2q)\exp(i\phi)]^{-1} \tag{2.23}$$

and

$$\chi_D = \chi_E = \chi_F = \chi_G = [1 - (1-q-p)\exp(i\phi)]^{-1}. \tag{2.24}$$

For the $Six - Jump$ cycle, $N_1 = N_2 = 3$, $Q_{N_1} \equiv Q_{AC}$, $Q_{N_2} \equiv Q_{CB}$, $T^+_{N_1} \equiv T_{AC}$, $T^-_{N_1} \equiv T_{CA}$, $T^-_{N_2} \equiv T_{CB}$.

After some algebra, we get

$$Q_{AC} = Q_{CA} = \frac{T_{AD}\chi_D T_{DA}}{1 - T_{ED}T_{DE}\chi_D\chi_E} = \frac{pq\chi_D\exp(2i\phi)}{1 - pq\chi_D^2\exp(2i\phi)}. \tag{2.25}$$

$$T_{AC} = \frac{T_{AD}T_{DE}T_{EC}\chi_D\chi_E}{1 - T_{ED}T_{DE}\chi_D\chi_E} = \frac{p^3\chi_D^2\exp(3i\phi)}{1 - pq\chi_D^2\exp(2i\phi)}, \tag{2.26}$$

and

$$T_{CA} = T_{CB} = \frac{T_{AD}T_{DE}T_{EC}\chi_D\chi_E}{1 - T_{ED}T_{DE}\chi_D\chi_E}. = \frac{q^3\chi_D^2\exp(3i\phi)}{1 - pq\chi_D^2\exp(2i\phi)}. \tag{2.27}$$

The expression for $T_{AD}(\phi)$ in terms of the local jump probability, p, and ϕ is given by

$$T_{AD} = T_{DE} = T_{EC} = \sum_{n=0}^{\infty}\exp(in\phi)p(n)\delta_{n,1}. \tag{2.28}$$

with the simplified form.

$$T_{AD} = T_{DE} = T_{EC} = p\exp(i\phi). \tag{2.29}$$

Similarly,

$$T_{DA} = T_{ED} = T_{CE} = q\exp(i\phi). \tag{2.30}$$

Putting all the required terms in equation governing a single path model, we find expressions of G_{AB61} and $\frac{dG_{AB61}}{di\phi}$ at $\phi = 0$ as

$$G_{AB61}|_{\phi=0} = 1 \tag{2.31}$$

and

$$\frac{dG_{AB61}}{di\phi}|_{\phi=0} = \frac{(p^2+pq+q^2)(p^3+2p^2q+2pq^2+2q^3)}{p^3q^3}. \tag{2.32}$$

Therefore, the MFPT of a vacancy diffusing via $Six - Jump$ cycle through a single path is,

$$MFPT = T61 = \frac{(p^2+pq+q^2)(p^3+2p^2q+2pq^2+2q^3)}{p^3q^3}. \tag{2.33}$$

2.2.2 All Possible Paths Model

This model is a little bit complicated compared to a single path model. However, all the eight possible paths are the same or a vacancy is equally likely to complete its journey through one of eight paths. It is equivalent to repeat the situation of a single path eight times (i.e adding Q'_As and $T'_{AB}s$ eight times), i. e,

i.e,

$$G_{AB68}(\phi) = \frac{\chi_A(\phi)(T^1_{AB}(\phi)+T^2_{AB}(\phi)+T^3_{AB}(\phi)+T^3_{AB}(\phi)+T^5_{AB}(\phi)+T^6_{AB}(\phi)T^7_{AB}(\phi)T^8_{AB}(\phi))}{1-\chi_A(\phi)(Q^1_A(\phi)+Q^2_A(\phi)+Q^3_A(\phi)+Q^4_A(\phi)+Q^5_A(\phi)+Q^6_A(\phi)+Q^7_A(\phi)+Q^8_A(\phi))}. \tag{2.34}$$

One should note that

$T^1_{AB}(\phi) = T^2_{AB}(\phi)) = T^3_{AB}(\phi) = T^4_{AB}(\phi) = T^5_{AB}(\phi) = T^6_{AB}(\phi) = T^7_{AB}(\phi) = T^8_{AB}(\phi) = T_{AB}(\phi)$

and

$Q^1_A(\phi) = Q^2_A(\phi) = Q^3_A(\phi) = Q^4_A(\phi) = Q^5_A(\phi) = Q^6_A(\phi) = Q^7_A(\phi) = Q^8_A(\phi) = Q_A(\phi)$ Equation (2.27) takes a simple form:

$$G_{AB68}(\phi) = \frac{8\chi_A(\phi)T_{AB}(\phi}{1-8\chi_A(\phi)Q_A(\phi)}, \tag{2.35}$$

where,

$$\chi_A = [1 - (1 - 4p)\exp(i\phi)]^{-1} \tag{2.36}$$

and $T_{AB}(\phi)$, $Q_A(\phi)$, χ_c and $\chi_D = \chi_E = \chi_F = \chi_G$ are terms already defined in subsection 2.3.2. After substituting all the appropriate expressions stated in the above model (sub section 2.3.2), we find the final expressions of G_{AB68} and $\frac{dG_{AB68}}{di\phi}$ at $\phi = 0$ as,

$$G_{AB68}|_{\phi=0} = \frac{-p}{q(p+q)} \tag{2.37}$$

and

$$\frac{dG_{AB68}}{di\phi}|_{\phi=0} = \frac{p}{4}(\frac{2p^3}{q^5} + \frac{-7p^2 - 9pq + q^2}{q^2(p+q)^2}). \tag{2.38}$$

From Eqs. (2.37) and (2.38), we get,

$$MFPT = T68 = \frac{-q(p+q)}{4p}(\frac{2p^3}{q^5} + \frac{-7p^2 - 9pq + q^2}{q^2(p+q)^2}). \tag{2.39}$$

2.3 Calculation of MFPT for a Vacancy Diffusing in a One-Jump Cycle

It is pointed out that a vacancy initially at point A can jump to the next nearest neighbor site of the same species with less probability at sufficiently low temperature. Models that we considered in the previous section are still applicable for this type of jump too. The ϕ probability controlling the motion of a vacancy in $One - Jump$ cycle through a single path is simply calculated as

$$G(\phi) = \chi_A(\phi) T_{AM}(\phi). = \chi(\phi) p_o \exp(i\phi), \tag{2.40}$$

where,

$$\chi_A = \frac{1}{1 - (1 - p_o)\exp(i\phi)}. \tag{2.41}$$

From Eqs. (2.40) and (2.41), one obtains:

$$G(\phi) = \frac{p_o \exp(i\phi)}{1 - (1 - p_o)\exp(i\phi)}. \tag{2.42}$$

The mean first passage time to jump from point A to point M, T_{11} is expressed as,

$$T_{11} = \frac{1}{G(\phi)} \frac{dG(\phi)}{di\phi}|_{\phi=0} = \frac{1}{p_o}. \tag{2.43}$$

Similarly, the MFPT for the vacancy in a $one-jump$ cycle moving through all possible paths (four paths) can be expressed (except, $\chi_A = \frac{1}{1-(1-4p_o)\exp(i\phi)}$ in this case) as

$$T_{14} = \frac{1}{G(\phi)} \frac{dG(\phi)}{di\phi}|_{\phi=0} = \frac{1}{4p_o}. \tag{2.44}$$

We find the expressions of MFPT's as the functions of local jump probabilities for the two proposed models both in $Six - Jump$ and $One - Jump$ cycles. Our goal is to find the expression of MFPT in terms of the model parameters, energy barrier height, the temperature and the lattice distance. Next, we are going to calculate the local jump probabilities, p, q and p_0 as the functions model parameters.

Chapter 3

THE DYNAMICS OF A VACANCY AS A BROWNIAN MOTION IN A BISTABLE POTENTIAL

Our main objective in this work is to determine one of the diffusion properties, MFPT, a Brownian particle (a vacancy) in a given potential profile shown in the Fig. 1.4. We consider an ideal system, i. e, no interaction of a vacancy with the neighboring atoms. The potential barrier height that the vacancy has to cross in jumping from one state to the other is taken to be the same throughout the system. The local jump probabilities, p and q are constant in all jumps. To determine the expression for p and q interms of energy barrier height, it is sufficient to take only a single double well potential (see Fig.3.1) of the potential profile in the Fig. 1.4. Calculating the average time for the vacancy to jump from one well to another in a double well potential shown in the Fig. 3.1 is the main task to have the general expression for MFPT. From the inverse relation of average time in a local jump and local jump probabilities, we can obtain the expressions for p, q and p_0.

3.1 Brownian Particle (a Vacancy) in a Double Well Potential

Consider a vacancy moving in a double well potential as shown Fig. 3.1. Let our Brownian particle with mass m be under the influence of external total potential, $V(x)$ in a one dimensional highly viscous medium of constant friction coefficient γ and temperature T. The Langevin Equation governing the dynamics of such a particle is given by:

$$m\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} - V'(x) + \sqrt{2k_BT\gamma}\xi(t). \tag{3.1}$$

The above differential equation takes account of all the three possible forces acted on a given Brownian particle. These are:

1. A velocity dependent friction force due to the viscosity of a medium, $-\gamma\frac{dx}{dt}$.
2. The force due to the external potential $V(x)$, $-V'(x)$.
3. A random force acquired from a random thermal kick, $\sqrt{2k_BT\gamma}\xi(t)$. Here,

x- refers to the position of the particle at time t, m- is the mass of the particle, γ- is the friction coefficient of the medium on which the particle is moving, K_B- is the Boltzmann constant, T- is the constant background temperature of the medium, $V'(x)$- force derivable from some position dependent potential V(x) and $\xi(t)$- is the Gaussian white noise with two basic properties,

$$\langle\xi(t)\rangle = 0 \tag{3.2}$$

and

$$\langle\xi(t)\xi(t')\rangle = \sigma\delta(t-t'), \tag{3.3}$$

where σ is a constant equals to $\sqrt{2k_BT\gamma}$.

For viscous medium (very high friction medium) Eq. 3.1 can be reduced to

$$\frac{dx}{dt} = -\frac{V'(x)}{\gamma} + \xi(t)\sqrt{\frac{2k_BT}{\gamma}}. \tag{3.4}$$

For $dW(t) = \xi(t)(dt)$, one gets

$$dx = -\frac{1}{\gamma}V'(x)(dt) + \sqrt{\frac{2k_BT}{\gamma}}(dW(t)). \tag{3.5}$$

For the Langevin equation of the form

$$dx = A(x)dt + B(x)dW(t) \tag{3.6}$$

the corresponding forward and backward Fokker Plank equations respectively are

$$\partial_t p(x,t) = -\partial_x[A(x)p(x,t)] + \frac{1}{2}\partial_x^2[B(x)p(x,t)] \tag{3.7}$$

and

$$\partial_t p(x,t) = A(x)\partial_x p(x,t) + \frac{1}{2}B(x)\partial_x^2 p(x,t). \tag{3.8}$$

Inserting the values of $A(x)$ and $B(x)$ from Eq. (3.5) in to Eqs. (3.7) and (3.8), we get

$$\partial_t p(x,t) = \frac{1}{\gamma}\partial_x[V'(x)p(x,t)] + \frac{k_BT}{\gamma}\partial_x^2 p(x,t) \tag{3.9}$$

and

$$\partial_t p(x,t) = -\frac{V'(x)}{\gamma}\partial_x p(x,t) + \frac{k_BT}{\gamma}\partial_x^2 p(x,t), \tag{3.10}$$

respectively. Note that $p(x,t)$ is the probability of a particle to be found at the position x at time t.

3.2 Mean First Passage Time For a Local Jump

We are interested to know the duration of a Brownian particle whose motion is described by the Fokker Plank equations Eq. (3.9) or (3.10) remains in a certain region of x. The solution of this problem can be achieved by use of the backward FPE [4].

3.2.1 Two Absorbing Barriers

Let the particle be initially at x at time $t = 0$ within the interval (a, b), $a \leq x \leq b$. It is assumed that the particle leaves the region when it touches the absorbing boundaries erected at $x = a$ and $x = b$. We define a function $G(x, t)$ as the probability that the particle to stay in the interval (a, b) up to time t. Here, $G(x, t)$ can be easily expressed as

$$G(x,t) = \int_a^b dx' p(x', t|x, 0) \tag{3.11}$$

where $p(x', t|x, 0)$ is the conditional probability of finding the particle at x' at time t given that it was at x at time $t = 0$.

Let $f(t)dt$ be the probability that the particle leaves the interval (a, b) within the time dt (between t and $t + dt$), the same as the probability of being in the interval (a, b) up to time t and then leave the interval between t and $t + dt$. Hence

$$f(t)dt = G(x,t) \int_a^b dy p(y, t + \Delta t|z, t). \tag{3.12}$$

Note that y is out of the interval. In the time interval t and $t + dt$, the particle has only two possibilities, either to leave the interval (a, b) or even to stay in the interval. Mathematically, one can rewrite the above statement as

$$\int_a^b dy p(y, t + \Delta t|z, t) + \int_a^b dx' p(x', t + \Delta t|z, t) = 1. \tag{3.13}$$

The first term of Eq. (3.13) stands for the probability that the particle leaves the interval in the time interval dt, where as the second term is that of staying in the interval up to time $t + dt$. Thus, Eq (3.12) becomes

$$f(t)dt = G(x,t)[1 - \textstyle\int_a^b dx' p(x', t + \Delta t|z, t) = G(x,t) - \int_a^b dz p(z, t|x, 0) \int_a^b dx' p(x', t + \Delta t|z, t). \tag{3.14}$$

Rearranging Eq. (3.14) gives us

$$f(t)dt = G(x,t) - \int_a^b dx' \int_a^b dz p(x', t + \Delta t|z, t) p(z, t|x, 0) \tag{3.15}$$

By Chapman-Kolmogorov Equation:

$$\int_a^b dzp(x', t + \Delta t|z, t)p(z, t|x, 0) = p(x', t + \Delta t|x, 0). \tag{3.16}$$

Then, Eq. (3.15) will be:

$$f(t)dt = G(x, t) - \int_a^b dx'p(x', t + \Delta t|x, 0). \tag{3.17}$$

By analogy of Eq. (3.11), we get

$$\int_a^b dx'p(x', t + \Delta t|x, 0) = G(x, t + \Delta t). \tag{3.18}$$

Note that the function $G(x, t + \Delta t)$ is the probability of getting the particle in the interval at time $t + dt$. Hence

$$f(t)dt = G(x, t) - G(x, t + \Delta t) = -\partial_t G(x, t)dt. \tag{3.19}$$

The mean first passage time (average time) can be described as,

$$\langle t \rangle = \int_0^\infty tdtf(t). \tag{3.20}$$

Putting Eq. (3.19) in Eq. (3.20) and integrating it by part, we find

$$\langle t \rangle = t(x) = \int_0^\infty dtG(x, t). \tag{3.21}$$

Noting that $G(x, t)$ at $t = \infty$ is zero, that is equivalent to say that the particle should leave the interval as time goes to infinity. Assuming that our system is time homogenous, Eq. (3.11) will be of the form,

$$G(x, t) = \int_a^b dx'p(x', 0|x, -t) \tag{3.22}$$

with the corresponding backward FPE:

$$\partial_t p(x', 0|x, -t) = A(x)\partial_x p(x', 0|x, -t) + \frac{B(x)}{2}\partial_x^2 p(x', 0|x, -t). \tag{3.23}$$

Differentiating Eq. (3.22), with respect to time once and with respect to x once and twice, we find

$$\partial_t G(x,t) = \int_a^b dx' \partial_t p(x',0|x,-t), \tag{3.24}$$

$$\partial_x G(x,t) = \int_a^b dx' \partial_x p(x',0|x,-t) \tag{3.25}$$

and

$$\partial_x^2 G(x,t) = \int_a^b dx' \partial_x^2 p(x',0|x,-t). \tag{3.26}$$

After integrating both sides of Eq. (3.23) over dx', we arrive at

$$\int_a^b \partial_t dx' p(x',0|x,-t) = A(x) \int_a^b dx' \partial_x p(x',0|x,-t) + \frac{B(x)}{2} \int_a^b dx' \partial_x^2 p(x',0|x,-t). \tag{3.27}$$

Comparing Eqs. (3.24), (3.25) and (3.26) with Eq. (3.27), we find:

$$\partial_t G(x,t) = A(x)\partial_x G(x,t) + \frac{B(x)}{2}\partial_x^2 G(x,t). \tag{3.28}$$

Integrating Eq. (3.28) over dt in the interval $(0,\infty)$ leads to

$$\int_0^\infty dt \partial_t G(x,t) = \int_0^\infty dt[A(x)\partial_x G(x,t)] + \frac{1}{2}\int_0^\infty dt[B(x)\partial_x^2 G(x,t)] \tag{3.29}$$

which results to a simplified expression of a form:

$$G(x,\infty) - G(x,0) = A(x)\partial_x \int_0^\infty dt G(x,t) + \frac{1}{2}B(x)\partial_x^2 \int_0^\infty dt G(x,t) \tag{3.30}$$

where, $G(,\infty) = 0$ and $G(x,0) = \int_a^b dx' p(x',0|x,0) = \int_a^b dx' \delta(x'-x) = 1$. Eq. (3.29) turns out to be,

$$A(x)\partial_x \int_0^\infty dt G(x,t) + \frac{1}{2}B(x)\partial_x^2 \int_0^\infty dt G(x,t) = -1. \tag{3.31}$$

Eq. (3.31) can be reduced to:

$$A(x)\partial_x t(x) + \frac{1}{2}B(x)\partial_x^2 t(x) = -1. \tag{3.32}$$

Eq. (3.32) is the ordinary differential equation for t(x) with the boundary condition:

$$t(a) = t(b) = 0. \tag{3.33}$$

Equation (3.33) tells us that the particle initially at a or at b will stay in the interval for zero time. The solution of Eq. (3.32) gives us the general expression for the first passage time. Rearranging Eq. (3.32) gives us,

$$\frac{d^2t(x)}{dx^2} + \frac{2A(x)}{B(x)}\frac{dt(x)}{dx} = \frac{-2}{B(x)} \tag{3.34}$$

Denoting $h(x) = \frac{dt(x)}{dx}$, Eq. (3.34) can be rewritten as

$$\frac{dh(x)}{dx} + \frac{2A(x)}{B(x)}h(x) = -\frac{2}{B(x)}, \tag{3.35}$$

whose homogenous differential equation is

$$\frac{dh(x)}{dx} + \frac{2A(x)}{B(x)}h(x) = 0, \tag{3.36}$$

with solution

$$h(x) = \frac{h(a)}{\psi(x)}, \tag{3.37}$$

where $\psi(x) = \exp(\int_a^x dx' \frac{2A(x')}{B(x')})$.

Let the general solution to the non-homogenous differential Eq. (3.35) be,

$$h(x) = \frac{H(x)}{\psi(x)} \tag{3.38}$$

Substituting Eq (3.38) in to Eq. (3.35), we get,

$$\frac{dH(x)}{dx} = -\frac{2\psi(x)}{B(x)} \tag{3.39}$$

and

$$H(x) = H(a) - 2\int_a^x dx' \frac{\psi(x')}{B(x')}. \tag{3.40}$$

At the same time Eq. (3.38) becomes,

$$h(x) = \frac{H(a)}{\psi(x)} - \frac{2}{\psi(x)}\int_a^x dx' \frac{\psi(x')}{B(x')}. \tag{3.41}$$

Subsequently,

$$t(x) - t(a) = \int_a^x dx' [\frac{H(a)}{\psi(x')} - \frac{2}{\psi(x')}\int_a^{x'} dy \frac{\psi(y)}{B(y)}]. \tag{3.42}$$

Applying the boundary conditions of Eq. (3.33), one obtains

$$H(a) = \frac{2[\int_a^x \frac{dx'}{\psi(x')}\int_a^{x'} dy \frac{\psi(y)}{B(y)} + \int_x^b \frac{dx'}{\psi(x')}\int_a^{x'} dy \frac{\psi(y)}{B(y)}]}{\int_a^b \frac{dx'}{\psi(x')}}. \tag{3.43}$$

Finally, we get a simple expression of the form,

$$t(x) = 2\frac{[(\int_a^x \frac{dx'}{\psi(x')})\int_x^b \frac{dy}{\psi(y)}\int_a^y dz \frac{\psi(z)}{B(z)} - (\int_x^b \frac{dx'}{\psi(x')})\int_a^x \frac{dy}{\psi(y)}\int_a^y dz \frac{\psi(z)}{B(z)}]}{\int_a^b \frac{dy}{\psi(y)}}. \tag{3.44}$$

3.2.2 One Absorbing Barrier

Let us consider the again motion of the Brownian particle in the interval (a,b), where at $x = a$ and $x = b$ are the reflecting and absorbing barriers, respectively. The two boundary conditions imposed here are

$$\partial_x G(a,t) = G(b,t) = 0. \tag{3.45}$$

Applying the above boundary conditions in Eq. (3.42), we get,

$$H(a) = 0. \tag{3.46}$$

After some algebra, we obtain

$$t(x) = 2\int_x^b \frac{dy}{\psi(y}\int_a^y dz \frac{\psi(z)}{B(z)}. \tag{3.47}$$

For $x = b$ reflecting and $x = a$ absorbing, the boundary conditions are

$$\partial_x G(b,t) = G(a,t) = 0. \tag{3.48}$$

Putting the above boundary conditions in Eq. 3.42, we get

$$H(a) = 2\int_a^b dy \frac{\psi(y)}{B(y)}. \tag{3.49}$$

Then the expression of mean first passage time of the particle is

$$t(x) = 2\int_a^x \frac{dy}{\psi(y} \int_x^b dz \frac{\psi(z)}{B(z)}. \tag{3.50}$$

To find the expression for the MFPT in a local jump, we have to take the potential profile shown in the Fig. 1.4, which is assumed to be symmetric, piecewise linear and the same slope in magnitude (see Fig. 3.2).

For our simplified model, taking only a single asymmetric double well potential, like Fig. 3.1 is sufficient to calculate the MFPT taken by the particle to jump from one well to another. It is proved that for arbitrary time homogenous stochastic process, Kramer's flux-over barrier (escape) rate is identical to the inverse of the associated mean first passage time as shown in Fig. 3.3. Using equality of the magnitude of the slope,

$$\frac{E_1}{a} = \frac{E_1 - E_2}{b - a}. \tag{3.51}$$

Equations governing the potential profile shown in the Fig. 3.3 are given by

$$V(x) = \begin{cases} \frac{-E_1 x}{a}, & x \leq 0 \\ \frac{E_1 x}{a}, & 0 \leq x \leq a \\ \frac{-E_1 x}{a} + 2E_1, & a \leq x \leq b \\ \frac{E_1(x-b)}{a} + E_1 - E_2, & x > b. \end{cases} \tag{3.52}$$

Using Eqs. (3.47) and (3.50), we can calculate MFPT taken by the vacancy from $x = 0$ to $x = L$ and from $x = L$ to $x = 0$, respectively.

3.3 MFPT From x=0 to x=L

To calculate the MFPT from $x = 0$ to $x = L$, first we have to assume that our reflecting boundary is to the left of $x = 0$ in the limit $x \longrightarrow \infty$ and the vacancy is considered to be absorbed at $x = L$. The dynamics of the vacancy in a six - jump is fully governed by by the backward FPE, clearly stated in the beginning of this chapter. i. e,

$$\partial_t p(x,t) = -\frac{V'(x)}{\gamma}\partial_x p(x,t) + \frac{k_B T}{\gamma}\partial_x^2 p(x,t). \tag{3.53}$$

From the definition of $\psi(x)$, we find

$$\psi(x) = \exp(-\frac{-V(x)}{k_B T}). \tag{3.54}$$

Inserting Eq. (3.54) and using the value of B(x) in Eq. (3.47) and (3.50) give us

$$t(x) = \frac{\gamma}{k_B T}\int_x^b dy \exp(\frac{V(y)}{k_B T})\ int_a^y dz \exp(-\frac{V(z)}{k_B T}). \tag{3.55}$$

Similarly, for the case when the reflecting boundary is to the right of $x = b$ and the absorbing boundary is at $x = 0$, the MFPT will be

$$t(x) = \frac{\gamma}{k_B T}\int_a^x dy \exp(\frac{V(y)}{k_B T})\int_x^L dz \exp(-\frac{V(z)}{k_B T}). \tag{3.56}$$

Thus,

$$t(0 \longrightarrow L) = \frac{\gamma}{k_B T}\int_x^L \exp(\frac{V(y)}{k_B T}\int_a^y dz \exp(-\frac{V(z)}{k_B T}). \tag{3.57}$$

Substituting $x = 0$ and taking the limit $a \longrightarrow -\infty$, we have

$$t(0 \longrightarrow L) = \frac{\gamma}{k_B T}\int_0^L \exp(\frac{V(y)}{k_B T})\int_{-\infty}^y dz \exp(-\frac{V(z)}{k_B T}) = \frac{\gamma}{k_B T}[h_1 + h_2] \tag{3.58}$$

where

$$h_1 = \int_0^a dy \exp(\frac{V(y)}{k_B T})\int_{-\infty}^y dz \exp(-\frac{V(z)}{k_B T}) \tag{3.59}$$

and

$$h_2 = \int_a^L dy \exp(\frac{V(y)}{k_B T}) \int_{-\infty}^{y} dz \exp(-\frac{V(z)}{k_B T}). \tag{3.60}$$

After putting appropriate potential functions in Eqs. (3.60) and (3.61), we get

$$h_1 = \frac{-(k_B T)^2 L^2 (2 - 2\exp(\frac{E_1}{k_B T}) + \frac{E_1}{k_B T})}{(E_1 + E_2)^2} \tag{3.61}$$

and

$$h_2 = \frac{(k_B T)^2 L^2 \exp(-\frac{E_2}{k_2 T})(2 - 2\exp(\frac{E_1}{k_B T}) + \exp(\frac{E_2}{k_B T})(-2 + \frac{E_1}{k_B T}) + 2\exp(\frac{E_1+E_2}{k_B T}))}{(E_1 + E_2)^2}. \tag{3.62}$$

Hence,

$$t(0 \longrightarrow b) = \frac{4L^2 (k_B T)^2 \gamma \exp(\frac{E_1}{k_B T})}{(E_1 + E_2)^2}. \tag{3.63}$$

As it is already stated in section (3.54), the local jump probability, p is equal to the inverse of $t(0 \longrightarrow b)$. i.e

$$p = \frac{1}{t(0 \longrightarrow L)} = \frac{(E_1 + E_2)^2 \exp(-\frac{E_1}{k_B T})}{4L^2 \gamma (k_B T)^2}. \tag{3.64}$$

3.4 MFPT from $x = L$ to $x = 0$

In this case, our reflecting boundary is to the right of $x = b$ and the particle considered to be absorbed at $x = 0$. The appropriate expression of MFPT for such a situation is Eq. (3.56)$with$a=0,x=L$andthelimit$L$\longrightarrow \infty$, we find,

$$t(L \longrightarrow 0) = \frac{\gamma}{k_B T} \int_L^0 \exp(\frac{V(y)}{k_B T}) \int_{\infty}^{b} dz \exp(-\frac{V(z)}{k_B T}) \tag{3.65}$$

which can be reduced to

$$t(b \longrightarrow 0) = \frac{\gamma}{k_B T}[f_1 + f_2] \tag{3.66}$$

where,

$$f_1 = \int_L^a dy \exp(\frac{V(y)}{k_B T}) \int_\infty^b dz \exp(-\frac{V(z)}{k_B T}) \tag{3.67}$$

and

$$f_2 = \int_a^0 dy \exp(\frac{V(y)}{k_B T}) \int_\infty^b dz \exp(-\frac{V(z)}{k_B T}). \tag{3.68}$$

After some algebra, we get

$$f_1 = \frac{-(k_B T)^2 L^2 (2 - 2\exp(\frac{E_2}{k_B T}) + \frac{E_2}{k_B T})}{(E_1 + E_2)^2} \tag{3.69}$$

and

$$f_2 = \frac{(k_B T)^2 L^2 \exp(-\frac{E_1}{k_2 T})(2 - 2\exp(\frac{E_2}{k_B T}) + \exp(\frac{E_1}{k_B T})(-2 + \frac{E_1}{k_B T}) + 2\exp(\frac{E_1+E_2}{k_B T}))}{(E_1 + E_2)^2}. \tag{3.70}$$

Substitution of Eqs. (3.70) and (3.71) in Eq. (3.67), we get

$$t(L \longrightarrow 0) = \frac{4L^2 (k_B T)^2 \gamma \exp(\frac{E_2}{k_B T})}{(E_1 + E_2)^2}. \tag{3.71}$$

The associated local jump probability, q will be:

$$q = \frac{1}{t(L \longrightarrow 0)} = \frac{(E_1 + E_2)^2 \exp(-\frac{E_2}{k_B T})}{4L^2 \gamma (k_B T)^2}. \tag{3.72}$$

3.5 MFPT from $x = 0$ to $x = c$

In the case of $One - Jump$ cycle, MFPT from $x = 0$ to $x = c$ and MFPT from $x = c$ to $x = 0$ are equal, as a result p_o and q_o are the same. To find the expression of T_1 in terms of E_o, b and T, we have to look for the expression of MFPT from $x = 0$ to $x = c$ and then p_o. Finally, we substitute expression of p_o in Eq. (2.42). The potential energy equation associated with Fig. 3.4 is given by

$$V(x) = \begin{cases} \frac{-E_o x}{a}, & x \leq 0 \\ \frac{E_o x}{a}, & 0 \leq x \leq a \\ \frac{-E_o x}{a}, & a \leq x \leq c \\ \frac{E_o}{a}, & x > c. \end{cases} \tag{3.73}$$

Considering the reflecting boundary to be to the left of $x = 0$, we apply Eq: (3.37) to calculate the mean first passage time for a vacancy in a $One - Jump$ cycle. I.e

$$t(x) = 2\int_x^b \frac{dy}{\psi(y} \int_a^y dz \frac{\psi(z)}{B(z)} \tag{3.74}$$

which can be expressed as

$$t(x) = \frac{\gamma}{k_B T}\int_x^c \exp(\frac{V(y)}{k_B T})\int_a^y dz \exp(-\frac{V(z)}{k_B T}). \tag{3.75}$$

Using the limit $x = b$, $x = 0$ and limit $b \longrightarrow \infty$, we arrive at

$$t(x) = \frac{\gamma}{k_B T}\int_0^c \exp(\frac{V(y)}{k_B T})\int_{-\infty}^y dz \exp(-\frac{V(z)}{k_B T}) \tag{3.76}$$

which can be squeezed to

$$t(0 \longrightarrow c) = \frac{\gamma}{k_B T}[g_1 + g_2] \tag{3.77}$$

where, $g_1 = \int_0^a \exp(\frac{V(y)}{k_B T} \int_{-\infty}^y dz \exp(-\frac{V(z)}{k_B T})$. and $g_2 = \int_a^c \exp(\frac{V(y)}{k_B T} \int_{-\infty}^y dz \exp(-\frac{V(z)}{k_B T})$.

Putting the appropriate values of $V(x)$ in g_1 and g_2 and integrate them, we get

$$g_1 = \frac{c^2 k_B T[E_o - 2(-1 + \exp(\frac{E_o}{k_B T}))]}{4E_o^2} \tag{3.78}$$

and

$$g_2 = \frac{c^2 \exp(-3E_o k_B T)kT(kT - 3\exp(E_o k_B T) + 3\exp(2E_o k_B T) + \exp(3E_o k_B T)(E_o - kT)}{4E_o^2}. \tag{3.79}$$

From Eq. (3.77), we get,

$$T_1 = t(0 \longrightarrow c) \approx \frac{c^2 \gamma kT \exp(E_o kT)}{2E_o^2}. \tag{3.80}$$

The corresponding local jump probability, p_o will be:

$$p_o = \frac{1}{T_1} = \frac{4E_o^2}{L^2 \gamma k_B T(-3 + 2\exp(\frac{E_o}{kT}))}. \tag{3.81}$$

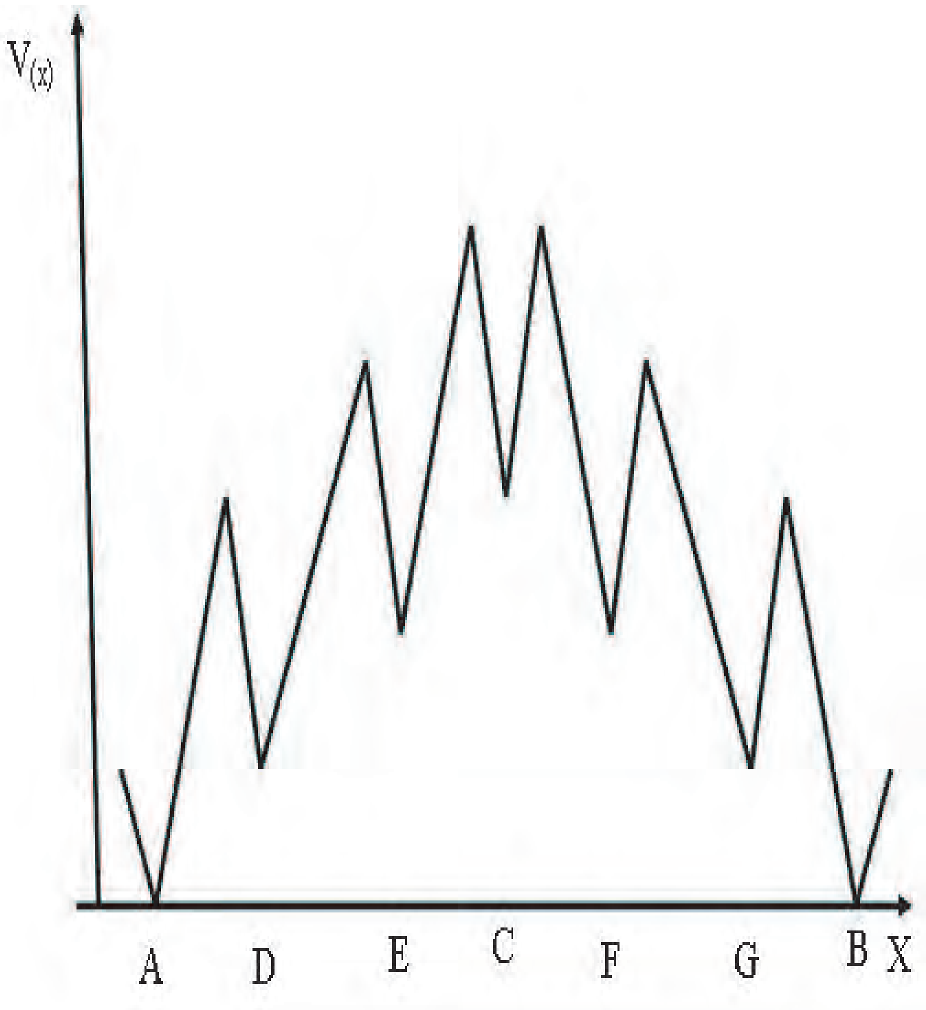

Figure 3.1: Plot of V(x) versus x.

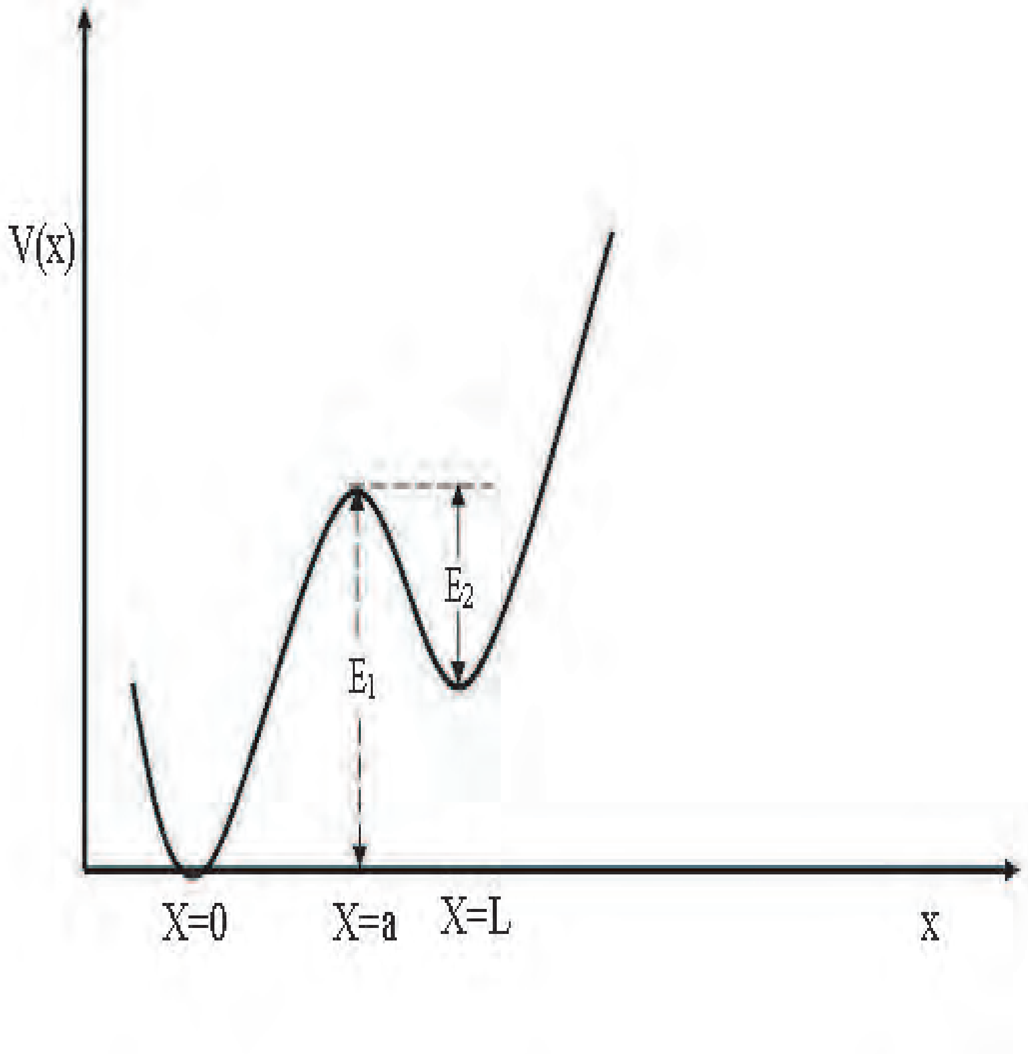

Figure 3.2: Asymmetric double well potential.

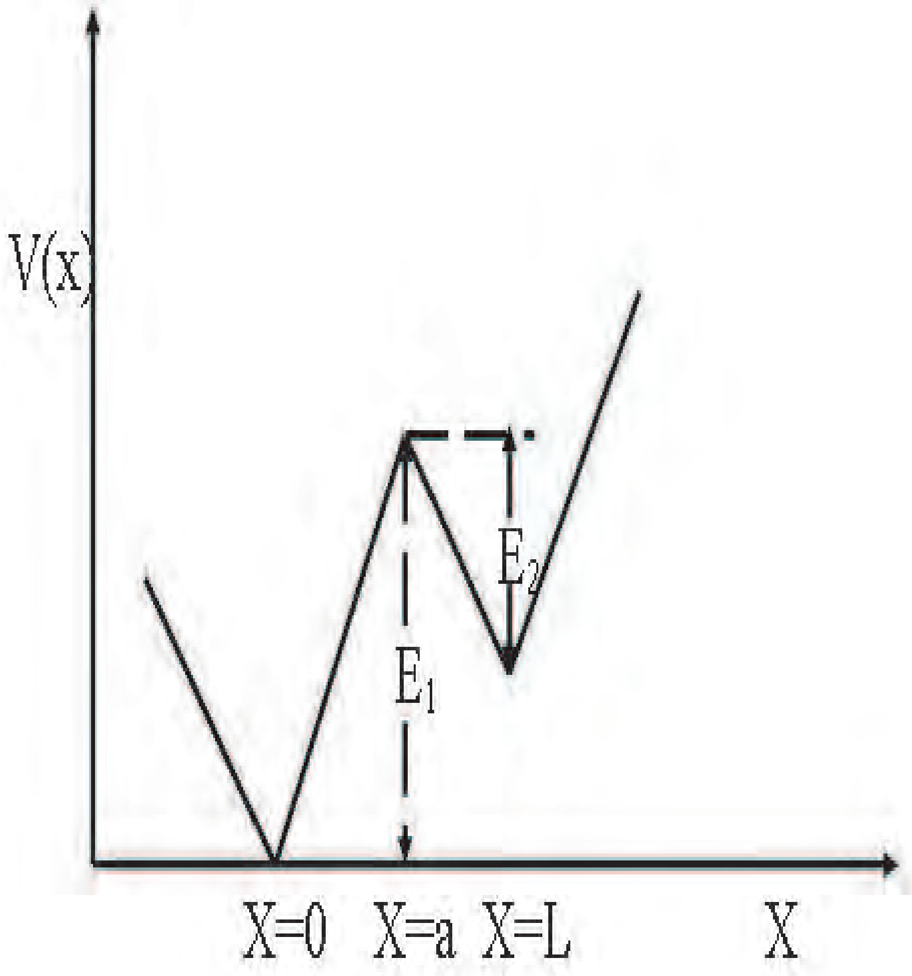

Figure 3.3: Asymmetric piecewise linear double well potential.

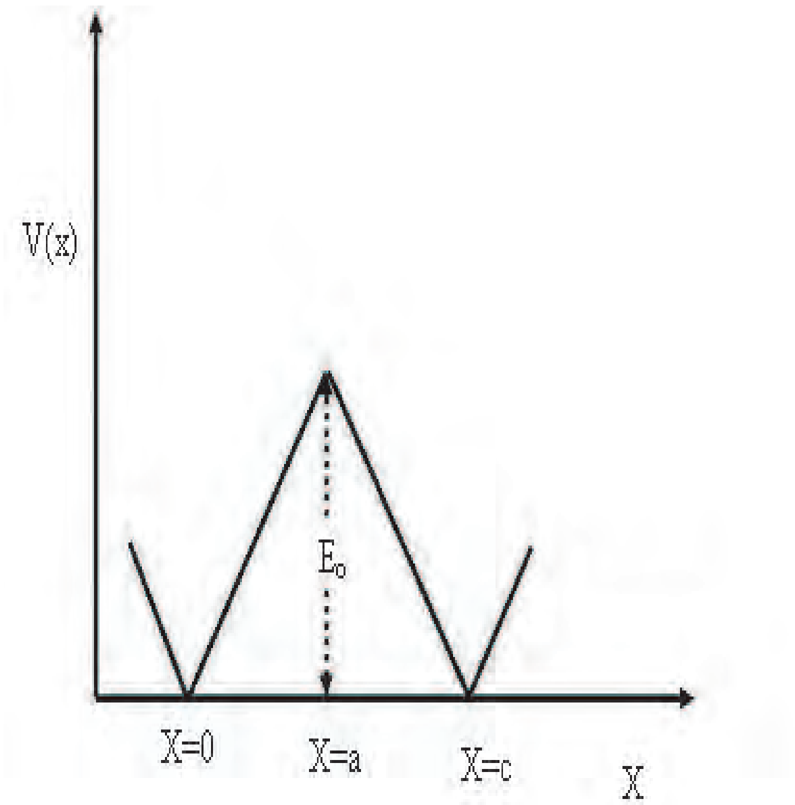

Figure 3.4: Schematic diagram for symmetric and pieces wise linear potential profile during $One - Jump$ cycle.

Chapter 4

Result and Discussion

In Chapter three, we obtained analytical expressions for the mean first passage time of a vacancy diffusing in a binary alloy via $One-Jump$ and $Six-Jump$ cycles taking two different models for both type of jumps (i. e, a single path and all possible paths models). We find the values of T_{11}, T_{14}, T_{61} and T_{68} in terms of E_1, E_0, T and L (E_2 is substituted by $\frac{E_1}{2}$). For the sake of simplicity, we have introduced the dimensionless quantities, m and r, whose expressions are $m = \frac{E_1}{kT}$ and $r = \frac{E_0}{2E_1}$. To investigate how T_{11}, T_{14}, T_{61} and T_{68} behave as the functions of m and r and to identify which model is dominant over the other, we have diverted our attention in exploring the ratios $\frac{T_{11}}{T_{61}}$, $\frac{T_{14}}{T_{68}}$ and $\frac{T_{61}}{T_{68}}$.

First we examine how $\frac{T_{11}}{T_{61}}$, and $\frac{T_{14}}{T_{68}}$ behave as the functions of m for fixed r. Figure 4.1 shows the plot of $\frac{T_{11}}{T_{61}}$ *versus* m for $r = 0.8$ and 1.0. This figure demonstrates that for high temperature regime, the mean first passage time for $One-Jump$ cycle is shorter compared to the $Six-Jump$ cycle. For $r = 0.8$, the same figure shows that, $\frac{T_{11}}{T_{61}}$ takes a maximum value at certain temperature, T. For $r = 1.6$, the $One-Jump$ cycle is dominant over the $Six-Jump$ cycle at high temperature regime where as at low temperature regime the reverse is true as shown in the Fig. 4.2. The figure certainly reveals that the ratio $\frac{T_{11}}{T_{61}}$ has the point at which it becomes unity. This value tells us that the mean first passage time for a vacancy diffusing through $One-Jump$ cycle equal to the mean first passage time for a vacancy diffusing through $Six-Jump$ cycle through a single path (i.e the two paths are equally likely to be completed). Figure 4.3 is the plot of $\frac{T_{14}}{T_{68}}$ $versus$ m for fixed $r = 0.8, 1.0$ and 1.2. The figure demonstrates the result having similar behavior as the previous one. The $Six-Jump$ cycle through all possible paths is favored over the $One-Jump$ cycle through all possible paths at low temperature zone and vice versa.

We further investigate how the ratios $\frac{T_{11}}{T_{61}}$ and $\frac{T_{14}}{T_{68}}$ behave as we vary r for fixed m. One should note that when $r = 1$, the barrier height for both $One-Jump$ and $Six-Jump$ cycles take the same value. Here as shown in Fig. 4.4, the ratio $\frac{T_{11}}{T_{61}}$ is less than one for small values of r and greater than one for relatively large values of r. This clearly illustrates that, if the barrier height (E_0) is less than the barrier height for the $Six-Jump$ cycle, T_{11} will be shorter than T_{61}. For the reveres case, T_{11} will be longer than T_{61}. Figure 4.5 also shows the same behavior as that of Fig. 4.4.

We also compared the mean first passage time of the $Six-Jump$ cycle for only one possible path to that of all possible paths. The mean first passage time for the $Six-Jump$ cycle through all possible paths model is always significantly shorter than the $Six-Jump$ cycle through a single path model.

Finally, the result that we found is physically meaningful and one can extract sense out of it. But, it is not yet counter checked by the previously done experimental or theoretical results on this area using this technique.

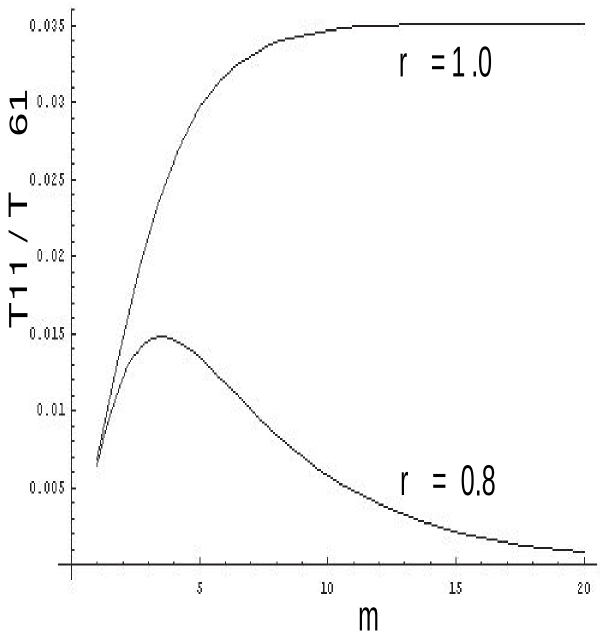

Figure 4.1: Plot of T_{11}/T_{61} *versus* m for $r = 0.8$ and 1.

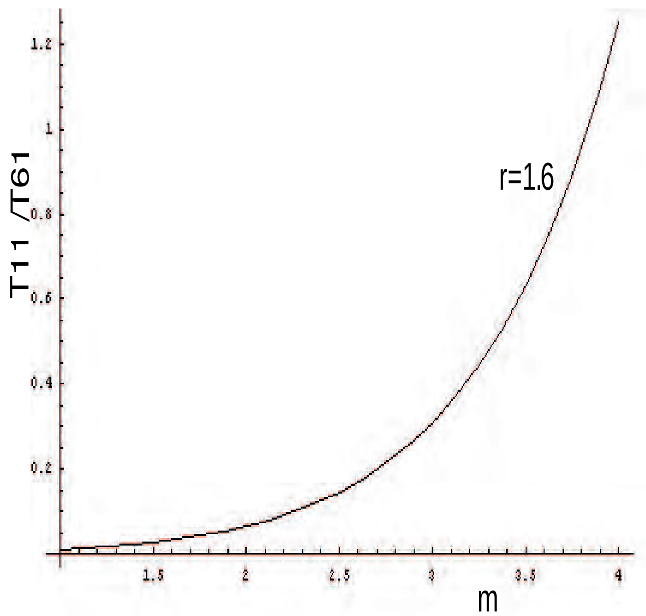

Figure 4.2: Plot of T_{11}/T_{61} *versus* m for $r = 1.6$.

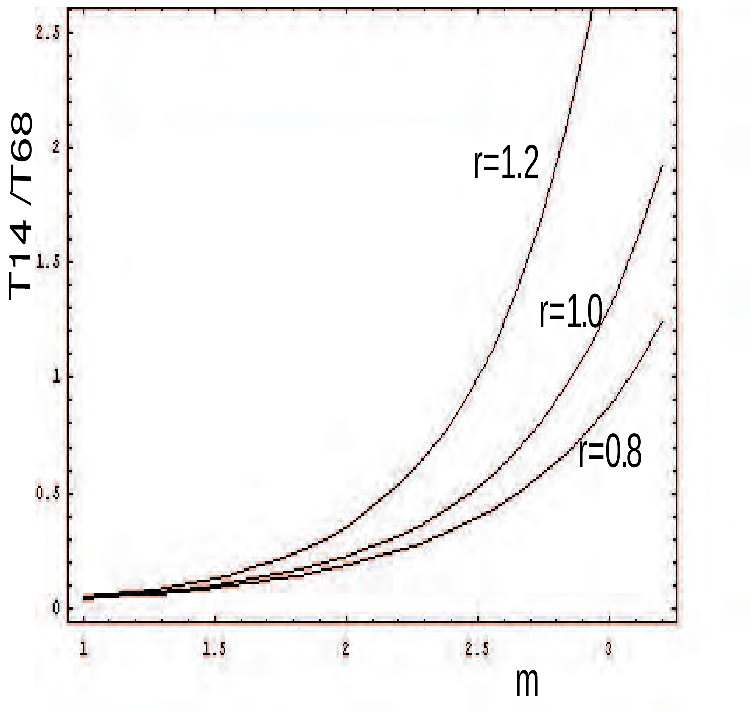

Figure 4.3: Plot of T_{14}/T_{68} *versus* m for $r = 0.8, 1$ and 1.2.

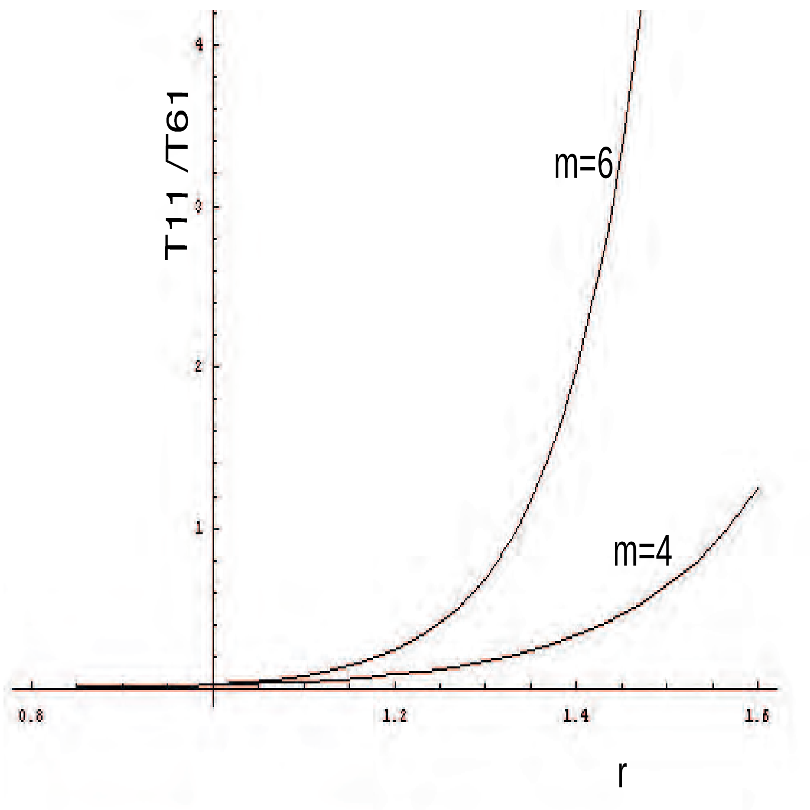

Figure 4.4: Plot of T_{11}/T_{61} *versus* r for $m = 4$ and 6.

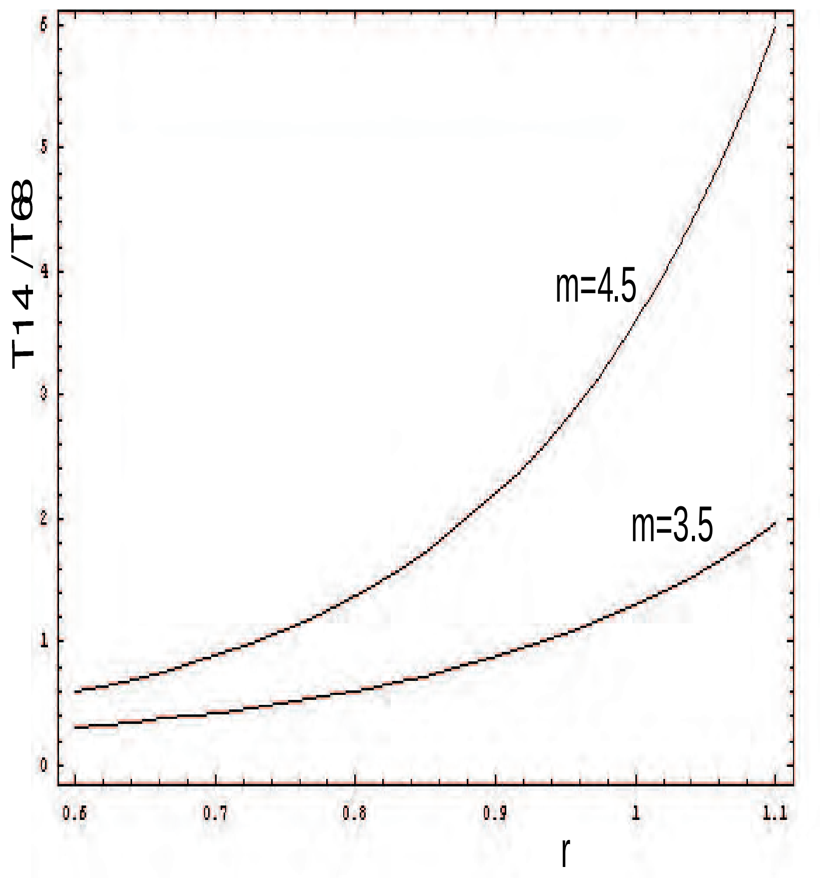

Figure 4.5: Plot of T_{14}/T_{68} *versus* r for $m = 3.5$ and 4.5.

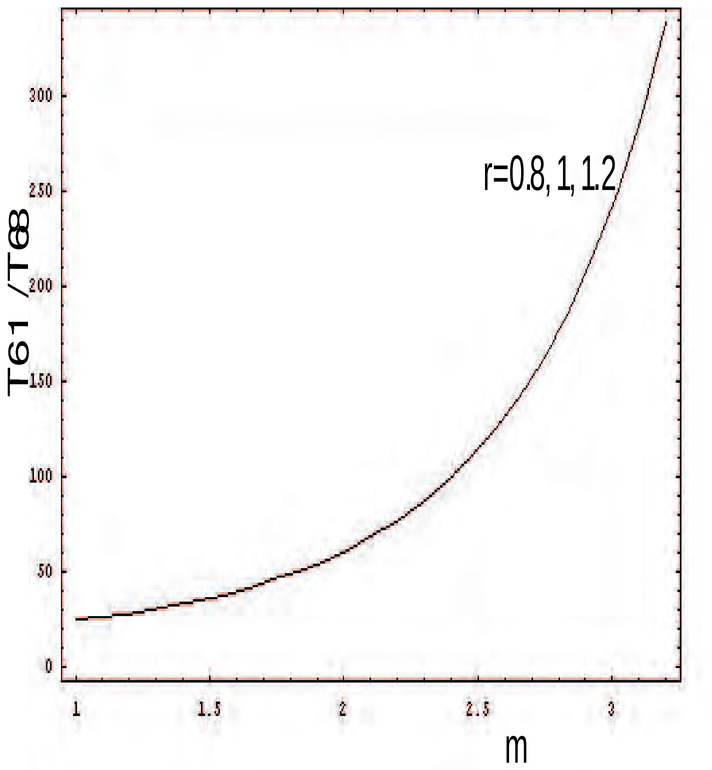

Figure 4.6: Plot of T_{61}/T_{68} *versus* m for $r = 0.8, 1$ and 1.2.

Chapter 5

Summary and conclusion

In this work, we considered two models to study the Mean First Passage Time for a vacancy diffusing in a two dimensional ordered Binary Alloy by using " Random Walk on Network" technique. The first model is $One - Jump$ cycle model, a model which describes a single hoping of a vacancy from initial stable state to the next nearest site of the same atomic species. The second one is $Six - Jump$ cycle model, which explains the six successive jumps of a vacancy to reach its most stable state. Each models are also divided into two sub models, a single path and eight path models. All these our models are applicable for the determination of mean first passage time of a vacancy under consideration together with some assumptions. These assumptions are:

1. the medium through which a vacancy is diffusing (the lattice structure of ordered binary alloy) is assumed to be with low concentration of thermal defects and close to stoichiometry,

2. a vacancy under consideration is supposed to be isolated (no external interaction with the surrounding atoms or other vacancies),

3. the diffusion coefficients of both types of atoms involved in binary alloy formation are assumed to be equal and

4. a vacancy itself is not actually a particle but it is quasi-particle assumed to be a

Brownian particle performing a Brownian motion, random walk on the lattice sites of a crystal structure. By making use of all these assumptions, we have found different analytic expression of mean first passage times for different models. These expressions are found to be functions of the local jump probabilities, p, q and p_0. Furthermore, the local jump probabilities, p , q and p_o are also calculated from the concept of the mean first passage time for the Brownian particle under the double well potential. They are expressed as the functions of model parameters, E_1, E_2, the background temperature of the system, T and the lattice spacing, L. The MFPT can then be expressed in terms of energy barrier heights, E_1, E_2, the background temperature of the system, T and the lattice spacing, L.

We have also identified which model is favored over the other and we have shown that the temperature of the medium on which a vacancy is diffusing has a prominent impact on the dominance of one model over the other. We did this comparison by plotting the ratios of different mean first passage times describing their models ($\frac{T_{11}}{T61}$, $\frac{T_{14}}{T68}$ and $\frac{T_{61}}{T68}$) as the functions of the dimensionless quantities, $m = \frac{E_1}{kT}$ and $r = \frac{E_0}{2E_1}$ keeping one of them constant at a time. As a result, we have found at relatively lower temperature region, the $Six - Jump$ cycle is dominant over the $One - Jump$ cycle except in the case $\frac{T_{11}}{T61}$ $versus$ m for $r = 0.8$ and 1.0. However, the $One - Jump$ cycle is favored over the $Six - Jump$ cycle at higher temperature.

To sum up, this work can be extended to the study of MFPT for a vacancy in three dimensional ordered binary alloys as most alloys in nature exist in three dimensions. It can also be studied in $non - stoichiometric$ cases and considering all the complicated jumps of a vacancy through the lattice by using Monte Carlo Simulation method. Finally, the problem that we solved can also be resolved by using other techniques, like supper symmetric method and we hope that experiments can be done to check the mechanism and the result we present in this thesis.

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DECLARATION

I hereby declare that this thesis is my original work and has not been presented for a degree in any other University. All sources of material used for the thesis have been duly acknowledged.

Name: ***Zerihun Getahun***
Signature:_______________

This thesis has been submitted for examination with my approval as University advisor.

Name: ***Dr. Mulugeta Bekele***
Signature:_______________

Addis Ababa University
Department of Physics
June, 2006.