Effective Vacancy Diffusion in NiAl Binary Alloy

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The undersigned hereby certify that they have read and recommend to the School of Graduate Studies for acceptance a thesis entitled "**Effective Vacanacy Diffusion in NiAl Binary Alloy**" by **Yoseph Abebe** in partial fulfillment of the requirements for the degree of Master of Science (MSc) in physics.

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Abstract

We considered three different types of mechanisms by which a vacancy diffuses: next nearest neighbor(NNN) jumps, triple defect mechanism and two variants of six-jumps cycles([110] and [100] bent directions). This is investigated by considering the vacancy diffusion as motion of a Brownian particle in a potential field. We used the migration energy profile for the three types of mechanisms simulated by Kristen *et al* [1] to evaluate the effective vacancy diffusion coefficient at two high temperature values. We have found that their effective vacancy diffusion coefficient depends on migration energy and temperature for the three vacancy diffusion mechanisms. We compared the effective vacancy diffusion coefficient for the three vacancy diffusion mechanisms and identified that the triple defect path is the fastest than the other two diffusion mechanisms.

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Chapter 1

Introduction

1.1 Binary Alloy

An alloy is a solid solution composed of two or more metals, or of a metal(s) with one or more nonmetals [2, 3]. Metals and alloys are virtually everywhere in our daily lives. Alloys usually have different properties from those of the component elements. Alloys are used to make aircraft engines, automobiles, bridges, buildings and even paper clips. Most alloys are created to change the elemental metals' physical properties, such as conductivity, density, ductility, hardness, luster, malleability, melting point, tensile strength, and/or chemical properties, such as resistance to corrosion. Alloys often exhibit increased strength and hardness. Various treatments can be used such as cold-working or heat treatment followed by quenching and tempering a metal. In the 1930's, scientists only had the ability to characterize large(macro) properties of metals; however, now they have the ability to characterize both the structure and chemistry of alloys [4].
Examples of binary alloys are alloys of Nickel, Aluminum, Bismuth, Cobalt, Copper, Iron etc.

The binary alloy(B2) intermetallic compounds are of a great interest from scientific and technological points of view. They exhibit physical and mechanical properties that have been applied in many different areas including the aerospace and the microelectronic industries. Diffusion in these intermetallic compounds has been the subject of many

theoretical and experimental studies over the past 50 years. The theoretical interest lies in the understanding of the different mechanisms of diffusion that can occur through the bulk or the grain boundary. From a technological point of view, many creep and sintering studies in intermetallic compounds are intimately connected with diffusion [3].

1.1.1 Bulk Diffusion of NiAl Binary Alloy

Bulk NiAl adopts a B2 structure, which consists of two inter-penetrating simple-cubic lattices. The unit cell consists of two atoms: Ni and Al. NiAl compound binary alloy below melting temperature would have equilibrium structure and the compound maintains crystal structure [1]. But if it is above the melting temperature the compound is in disordered state without crystal structure. Usually, a crystalline solid 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, and oxidation. All crystalline defects and imperfections are classified in to four basic categories: point defects, line defects, plane defects, volume defects. The common point defects are: vacancy (atom sites normally occupied in the perfect crystal, from which the atom are missed), interstitial atoms (atoms in a wrong site) and extrinsic point defects (point defects involving foreign atoms). Atomic diffusion in crystal is usually mediated by point defects. The two basic mechanisms of atomic diffusion are vacancy mechanism and interstitial mechanism [5]. In this thesis we will deal with the mechanism of vacancy diffusion in NiAl binary alloy.

There are two types of point defect vacancy diffusion: Schottky and Frenkel defect. In Frenkel defect the atom vacates its position in the lattice and transfer to an interstitial position in the crystal creating two defects within the lattice, a vacancy and an interstitial. On the other hand, in Schottky defect the atom leaves its site thereby creating a vacancy and moves to the surface of the crystal. Schottky defect leaves only one defect within the

lattice, a vacancy. The vacancy diffusion in B2 compounds is much more complex. This complexity arises because of the ordered structure and the additional energy involved in any mechanism that would destroy order, even if only temporarily [4]. Three main categories of vacancy diffusion mechanism have been postulated to characterize the diffusion of vacancy in B2 compounds. [4, 1]

1. Next Nearest Neighbor (NNN) jump vacancy diffusion mechanism
2. Triple defect jump vacancy diffusion mechanism
3. Six-jump cycle jump vacancy diffusion mechanism

In the next nearest neighbor jump mechanism the atom jumps in its own sub lattice in the second neighbor site exchanging site with the vacancy. This mechanism can be expected to be energetically favorable due to the fact that there is no disorder created during the process [4]. The simplest Ni diffusion mechanism one could imagine occurs only on the Ni sublattice. NNN jumps requiring prior formation of a Ni vacancy as seen in Fig 1.1.

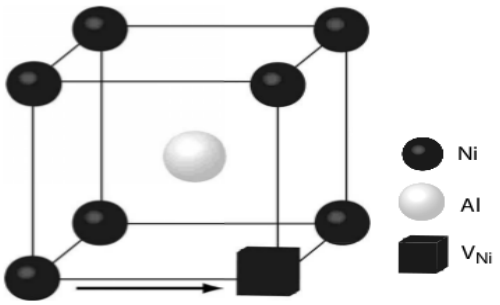


Figure 1.1: NNN jump diffusion pathway of NiAl binary alloy

In the triple defect mechanism Fig. 1.2 was first postulated by N. A. Stolwijk, M. van Gend [6] as a mechanism of diffusion in B2 intermetallics in their work studying diffusion in CoGa. The mechanism consists of four NN jumps initiated by a triple defect cluster comprised in the case of NiAl of two Ni vacancies and a Ni antisite atom. The first step moves the Ni antisite atom to a Ni vacancy, creating an Al vacancy and a Ni vacancy. Next, an Al atom moves into the Ni vacancy, leaving a defect cluster of two Al vacancies and an Al antisite atom. The Al antisite atom then moves onto the Al sub- lattice, recreating a

Ni vacancy and an Al vacancy. Finally, a Ni atom moves onto the Al sublattice, leaving the final configuration of a translated Ni triple defect. Through this mechanism, two Ni atoms shift in the same direction by a lattice vector and one Al atom moves by a lattice vector in the opposite direction.

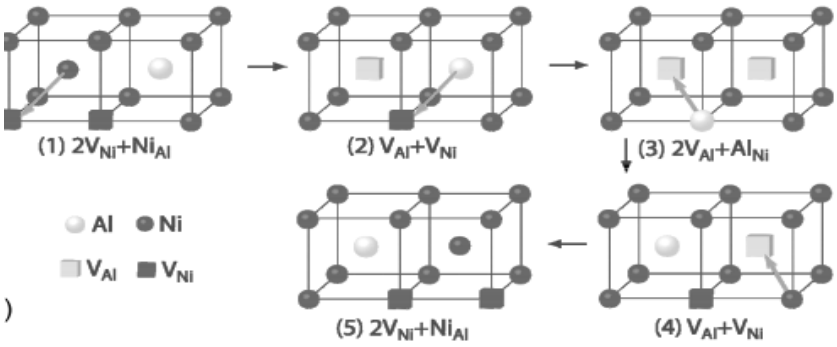


Figure 1.2: Triple deffect mechanism diffusion pathway of NiAl binary alloy

In the six-jump cycle proposed as a mechanism for diffusion in B2 intermetallics by Elcock and McCombie [7]. The six-jump cycle in principle can occur by three different pathways, one of which results in a Ni atom moving in the [110] direction whereas the other two paths move a Ni atom in the [100] direction for straight and bent. All three cycles are proposed to start with a Ni vacancy into which an Al atom jumps, forming a defect cluster of an Al vacancy and an Al antisite atom. Then a Ni atom moves into the Al vacancy creating a defect cluster of an Al antisite, a Ni antisite, and a Ni vacancy. An Al atom fills the Ni vacancy forming a cluster of two Al antisite, a Ni antisite, and an Al vacancy. Because of symmetry, the second half of the cycle consists of the same NN jumps but in reverse order. Types of six-jump cycle vacancy diffusion mechanisms are:

1. [110] six jump cycle vacancy diffusion mechanism
2. [100] bent and straight six jump cycle vacancy diffusion mechanism

We will deal on the two vacancy diffusion mechanisms of [110] and [100] bent vacancy diffusion.

The [110] six-jump cycle vacancy diffusion mechanism as shown in Fig 1.3.

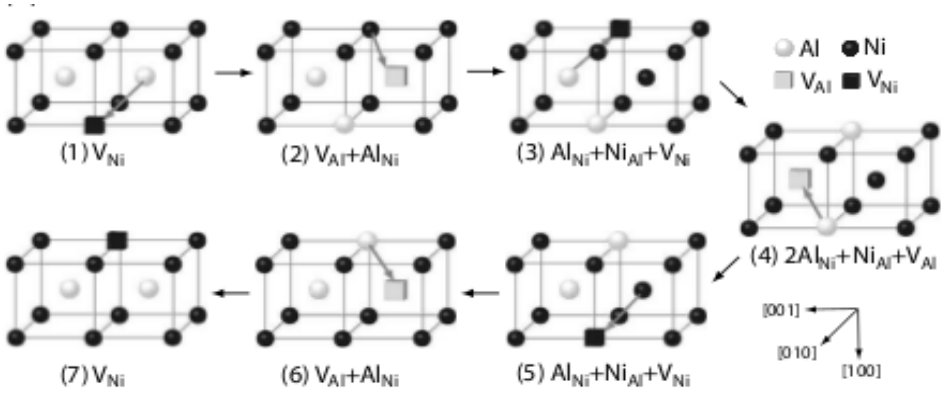


Figure 1.3: Diffusion path way for [110] six-jump cycle of NiAl binary alloy

The [100] 'bent' six-jump cycle vacancy diffusion mechanism as shown in Fig 1.4.

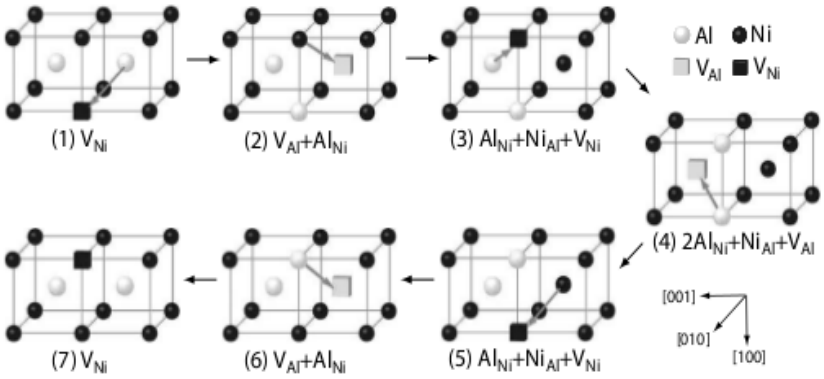


Figure 1.4: Diffusion pathway for [100] 'bent' six-jump cycle of NiAl binary alloy

Kristen *et al* [1] carried out simulations for the three kinds of vacancy diffusion mechanisms for NiAl binary alloy. For each path way, they found migration energy and the pre-exponetial factors D_0 at high temperature. They found that the [100] six-jump cycle has the high migration energy and while the triple defect mechanism has the least migration energy. From their result they predict that the NNN jump, triple defect and [110] six-jump cycles are the plausible mechanisms for the Ni diffusion in NiAl since their migration energy and D_0 are in very good agreement with experimental data. On the other hand, they found that the [100] bent and straight six-jump cycle are $1ev$ higher than the experimental value and they excluded [100] six-jump cycle as a possible diffusion mechanisms.

The main purpose of this thesis is to evaluate the effective vacancy diffusion coefficient (D_{eff}), for the three kinds of diffusion mechanisms. In order to evaluate D_{eff} we use the result of Kristen *et al* [1] as an input and apply the techniques developed by P. Reimann on how to evaluate diffusion coefficient in a periodic potential. One assumption we use to evaluate D_{eff}, is to consider vacancy motion as that of a Brownian dynamics.

The rest of this thesis is organized as follows. In Chapter Two we derive the effective diffusion coefficient for the Brownian particle as done by P.Reimann [9] and illustration of its use. In Chapter Three we will evaluate the effective vacancy diffusion coefficient for three diffusion mechanisms. Finally, in Chapter Four we summarize our results and give conclusions.

Chapter 2

Effective Diffusion

2.1 Einstein diffusion coefficient

We consider the following model for the overdamped Brownian motion of a particle with coordinate $x(t)$ [9]. The corresponding Langevin dynamics is governed by the equation

$$m\ddot{x}(t) + V'(x) = -\eta\dot{x}(t) + \sigma\xi(t), \tag{2.1}$$

where η is the viscous frictional constant and σ is amplitude of the noise force; m is the mass of the particle; x is the position of the particle with time; $V(x)$ is the periodic potential with period L. Thermal fluctuations are modeled as usual [11, 12] by Gaussian white noise with zero average.

$$\langle\xi(t)\rangle = 0, \tag{2.2}$$

and satisfying the fluctuation disspation theorem

$$\langle\xi(t)\xi(s)\rangle = 2\eta k_B T\delta(t-s), \tag{2.3}$$

Here T is background temperature and k_B is the Boltzmann's constant and $\langle ...\rangle$ indicates average over the statistical ensemble of a quantity, In the limit of strong friction the amplitude of friction force is much larger than the magnitude of force of inertia.

$$\mid \eta\dot{x} \mid \gg \mid m\ddot{x} \mid, \tag{2.4}$$

So, the inertial term $m\ddot{x}$ can be neglected and the dynamics of Eq. (2.1) becomes

$$\eta\dot{x} = -V'(x) + \sigma\xi(t), \tag{2.5}$$

If we consider the system under the influence of only random force with zero external force Eq. (2.1) is reduced to

$$\eta\dot{x} = \sigma\xi(t). \tag{2.6}$$

The corresponding Fokker-Plank equation for this dynamics is

$$\partial_t P(x,t \mid x_0,t_0) = \frac{\sigma^2}{2\eta^2}\frac{\partial^2}{\partial_x^2}P(x,t \mid x_0,t_0), \tag{2.7}$$

where $P(x,t \mid x_0,t_0)$ is the conditional probability of finding particle at x at time t given that it was at x_0 at time $t = t_0$.

This equation which is Einstein Diffusion equation, describes microscopic transport of a material and heat [13]. Now let as consider the diffusive behavior of particles, thus the mean square displacement can be defined as

$$\langle (x(t) - x(t_0))^2 \rangle = \int_{\Omega_\infty} (x(t) - x(t_0))^2 P(x,t \mid x_0,t_0) d^3r, \tag{2.8}$$

Solving Eq. (2.7) gives the solution of Einstein Diffusion Equation as the $P(x,t \mid x_0,t_0)$ can be

$$P(x,t \mid x_0,t_0) = \frac{1}{\sqrt{4\pi D_0 \Delta t}} exp[\frac{-(x-x_0)^2}{4D_0\Delta t}], \tag{2.9}$$

Evaluating Eq. (2.8), the mean square displacement can be calculated using Eq. (2.9) as follows

$$\langle (x(t) - x(t_0))^2 \rangle = 2D_0\Delta t. \tag{2.10}$$

Then the effective diffusion coefficient defined by [9]

$$D_{eff} = lim_{t\to\infty}\frac{\langle x^2(t)\rangle - \langle x(t)\rangle^2}{2t}, \tag{2.11}$$

Substituting Eq. (2.10) in Eq. (2.11) we get the so called effective diffusion coefficient and the Einstein Diffusion coefficient D_0 is equivalent. When $V'(x) = 0$ and $F = 0$ the diffusion coefficient is given by Einstein result $D_0 = \frac{k_B T}{\eta}$

$$D_{eff} = k_B T/\eta = D_0. \tag{2.12}$$

2.2 Effective Diffusion Coefficient

In this section we take a Brownian particle in an external periodic potential V(x) and background noise and evaluate its effective diffusion coefficient D_{eff}. This has been done by P. Reimann [9]. However, since this thesis is based on utilizing the P. Reimann method of we think it is important to derive it here.

$$\eta\dot{x} = -V'(x) + \sigma\xi(t), \tag{2.13}$$

where η is viscous friction coefficient and $V(x)$ is periodic potential with period L,

$$V(x + L) = V(x),$$

the first basic quantity of interests is the particle current

$$\langle\dot{x}\rangle = lim_{t\to\infty}\frac{\langle x(t)\rangle}{t} = 0. \tag{2.14}$$

We defined the effective diffusion coefficient as follows

$$D_{eff} = lim_{t\to\infty}\frac{\langle x(t)^2\rangle - \langle x(t)\rangle^2}{2t}. \tag{2.15}$$

From [9] we defined the particle current and the effective diffusion coefficient

$$\langle\dot{x}\rangle = \frac{L}{\langle t(x_0 \to x_0 + L)\rangle}. \tag{2.16}$$

$$D_{eff} = \frac{L^2}{2}\frac{\langle t^2(x_0 \to x_0 + L)\rangle - \langle t(x_0 \to x_0 + L)\rangle^2}{\langle t(x_0 \to x_0 + L)\rangle^3}. \tag{2.17}$$

where x_0 is the initial point and $\langle t^n(a \to b)\rangle$ is the nth moment of the first passage time a to $b > a$ for stochastic trajectory obeying Eq. (2.1). And the general form of the Mean First Passage Time, the stochastic processes Eq. (2.1) an arbitrary point but fixed $x(0) = x_0$ and we have $\langle t(x_0 \to b)\rangle$ from [9, 14]

$$T_n(x_0 \to b) = \langle t^n(x_0 \to b)\rangle = \frac{n}{D_0}\int_{x_0}^{b} dx exp(\frac{V(x)}{k_BT})\int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_BT}) * T_{n-1}(y \to b) \tag{2.18}$$

Where $T_0(y \to b) = \langle t^0(y \to b) \rangle = 1$.

We now come to our main point which is working by P.Reimann derivation reported in [9] for the effective diffusion coefficient. Using Eq. (2.18) the general formula of mean first passage time, we calculate the effective diffusion for Eq. (2.17).

Let as define

$$\Delta T_2(x_0 \to b) = \langle t^2(x_0 \to b) \rangle - \langle t(x_0 \to b) \rangle^2 = T_2(x_0 \to b) - [T_1(x_0 \to b)]^2, \tag{2.19}$$

where $b = x_0 + L$

$$\Delta T_2(x_0 \to x_0+L) = \langle t^2(x_0 \to x_0+L) \rangle - \langle t(x_0 \to x_0+L) \rangle^2 = T_2(x_0 \to x_0+L) - [T_1(x_0 \to x_0+L)]^2,$$

substituting Eq. (2.19) in Eq. (2.17) then D_{eff},

$$D_{eff} = \frac{L^2}{2} \frac{\Delta T_2(x_0 \to x_0 + L)}{[T_1(x_0 \to x_0 + L)]^3}, \tag{2.20}$$

Let as solve for $T_1(x_0 \to b), T_2(x_0 \to b)$, from Eq. (2.18),

where n=1

$$T_1(x_0 \to b) = \frac{1}{D_0} \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}) * T_0(y \to b), \tag{2.21}$$

where $T_0(y \to b) = 1$ then the above equation is

$$T_1(x_0 \to b) = \frac{1}{D_0} \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}),$$

where we have introduced

$$I_+(x) = \frac{1}{D_0} exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}). \tag{2.22}$$

$$I_-(x) = \frac{1}{D_0} exp(\frac{-V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{V(y)}{k_B T}). \tag{2.23}$$

So,

$$T_1(x_0 \to b) = \int_{x_0}^{b} dx I_+(x), \tag{2.24}$$

then squaring of $T_1(x_0 \to b)$

$$[T_1(x_0 \to b)]^2 = [\int_{x_0}^{b} dx I_+(x)]^2, \tag{2.25}$$

and when $b{=}x_0 + L$

$$[T_1(x_0 \to x_0 + L)]^2 = [\int_{x_0}^{b} dx I_+(x)]^2.$$

Calculating for $T_2(x_0 \to b)$ where $n = 2$ will also lead

$$T_2(x_0 \to b) = \frac{2}{D_0} \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}) * T_1(y \to b), \tag{2.26}$$

Finding for $T_1(y \to b)$

$$T_1(y \to b) = \frac{1}{D_0} \int_{y}^{b} dz exp(\frac{V(z)}{k_B T}) \int_{-\infty}^{z} dx exp(\frac{-V(x)}{k_B T}),$$

where $I_+(z) = \frac{1}{D_0} exp(\frac{V(z)}{k_B T}) \int_{-\infty}^{z} dx exp(\frac{-V(x)}{k_B T})$.

$$T_1(y \to b) = \int_{y}^{b} dz I_+(z), \tag{2.27}$$

Substituting $T_1(y \to b)$ in Eq. (2.26)

$$T_2(x_0 \to b) = \frac{2}{D_0} \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}) \int_{y}^{b} dz I_+(z), \tag{2.28}$$

now let us split the integral $\int_y^b = \int_y^x + \int_x^b$

$$T_2(x_0 \to b) = \frac{2}{D_0} \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{V(x)}{k_B T}) * [\int_{y}^{x} dz I_+(z) + \int_{x}^{b} dz I_+(z)],$$

$$= \frac{2}{D_0} (\int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}) * \int_{y}^{x} dz I_+(z) + Y, \tag{2.29}$$

where Y is given by

$$Y = \frac{2}{D_0} (\int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}) * \int_{x}^{b} dz I_+(z), \tag{2.30}$$

from Eq. (2.22) we have

$$I_+(x) = \frac{1}{D_0} exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}).$$

and substituting Eq. (2.22) in Eq. (2.30) we have the following expression

$$= 2\int_{x_0}^{b} dxI_+(x)\int_{x}^{b} dzI_+(z), \tag{2.31}$$

again we also split the integral of $\int_x^b = \int_{x_0}^b + \int_x^{x_0}$ from Eq. (2.31)

$$= 2\int_{x_0}^{b} dxI_+(x)[\int_{x_0}^{b} dzI_+(z) + \int_{x}^{x_0} dzI_+(z)], \tag{2.32}$$

$$= 2\int_{x_0}^{b} dxI_+(x)\int_{x_0}^{b} dzI_+(z) - 2\int_{x_0}^{b} dxI_+(x)\int_{x_0}^{x} dzI_+(z),$$

$$= 2[\int_{x_0}^{b} dxI_+(x)]^2 - 2\int_{x_0}^{b} dxI_+(x)\int_{x_0}^{x} dzI_+(z), \tag{2.33}$$

From Eq. (2.25) $[T_1(x_0 \to b)]^2 = [\int_{x_0}^{b} dxI_+(x)]^2$, then substituting in E.q 2.33

$$Y = 2[T_1(x_0 \to b)]^2 - 2\int_{x_0}^{b} dxI_+(x)\int_{x_0}^{x} dzI_+(z),$$

Exchanging of x and z where $x \to z$

$$= 2[T_1(x_0 \to b)]^2 - 2\int_{x_0}^{b} dzI_+(z)\int_{x_0}^{z} dxI_+(x), \tag{2.34}$$

we can rearrange or fix the interval because the system are homogeneous $z = b$

$$Y = 2[T_1(x_0 \to b)]^2 - 2\int_{x_0}^{b} dzI_+(z)\int_{x_0}^{b} dxI_+(x),$$

from Eq. (2.31)

$$Y = 2[T_1(x_0 \to b)]^2 - 2Y, \tag{2.35}$$

Finally we get for Y

$$Y = [T_1(x_0 \to b)]^2. \tag{2.36}$$

let as substitute Eq. (2.36) in Eq. (2.29)

$$T_2(x_0 \to b) = \frac{2}{D_0}(\int_{x_0}^{b} dxexp(\frac{V(x)}{k_BT})\int_{-\infty}^{x} dyexp(\frac{-V(y)}{k_BT}) * \int_{y}^{x} dzI_+(z) + Y,$$

$$T_2(x_0 \to b) = \frac{2}{D_0}(\int_{x_0}^{b} dxexp(\frac{V(x)}{k_BT})\int_{-\infty}^{x} dyexp(\frac{-V(y)}{k_BT}) * \int_{y}^{x} dzI_+(z) + [T_1(x_0 \to b)]^2. \tag{2.37}$$

Inserting Eq. (2.37) and Eq. (2.25) in Eq. (2.19) for $\Delta T_2(x_0 \to b)$

$$\Delta T_2(x_0 \to b) = T_2(x_0 \to b) - [T(x_0 \to b)]^2,$$

$$\Delta T_2(x_0 \to b) = \frac{2}{D_0}(\int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}) * \int_{y}^{x} dz I_+(z), \tag{2.38}$$

split the integral $\int_y^x = \int_{-\infty}^x + \int_y^{-\infty}$ then inserting in Eq. (2.38). where $\int_y^{-\infty}$. This interval are out of observation so we don't need because the system are periodic.

$$= \frac{2}{D_0} \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dy exp(\frac{-V(y)}{k_B T}) \int_{-\infty}^{x} dz I_+(z), \tag{2.39}$$

we can interchange this integral expression $\int_{-\infty}^{x} dy = \int_{-\infty}^{z} dy$ because the integral doesn't affect by the interval so,

$$= \frac{2}{D_0} \int_{x_0}^{b} exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{z} dy exp(\frac{-V(y)}{k_B T}) \int_{-\infty}^{x} dz I_+(z), \tag{2.40}$$

$I_+(z) = \frac{1}{D_0} exp(\frac{V(z)}{k_B T}) \int_{-\infty}^{z} dy exp(\frac{-V(y)}{k_B T})$. using this

where

$$\frac{1}{D_0} \int_{-\infty}^{z} dy exp(\frac{-V(y)}{k_B T}) = I_+(z) exp(\frac{-V(z)}{k_B T}), \tag{2.41}$$

Substituting Eq. (2.41) in Eq. (2.40)

$$= 2 \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dz I_+(z)[I_+(z) exp(\frac{-V(z)}{k_B T})],$$

$$= 2 \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{-\infty}^{x} dz exp(\frac{-V(z)}{k_B T}) I_+^2(z), \tag{2.42}$$

where we are working on the periodic boundary condition L. The integral from $-\infty$ to x changes $x - L$ to x then we have.

$$= 2 \int_{x_0}^{b} dx exp(\frac{V(x)}{k_B T}) \int_{x-L}^{x} dz exp(\frac{-V(z)}{k_B T}) I_+^2(z), \tag{2.43}$$

inter changing the order of the integral for dx and dz we get

$$= 2 \int_{x_0}^{b} dz exp(\frac{-V(z)}{k_B T}) \int_{z-L}^{z} dx exp(\frac{V(x)}{k_B T}) I_+^2(z), \tag{2.44}$$

$$I_+(z) = \frac{1}{D_0} exp(\frac{V(z)}{k_B T}) \int_0^L dx exp(\frac{-V(x)}{k_B T}). \tag{2.45}$$

$$I_-(z) = \frac{1}{D_0} exp(\frac{-V(z)}{k_B T}) \int_0^L dx exp(\frac{V(x)}{k_B T}). \tag{2.46}$$

use the the interval for $b \to x_0 + L$ and $z \to L$

$$= 2 \int_{x_0}^{x_0+L} dz exp(\frac{-V(z)}{k_B T}) \int_0^L dx exp(\frac{V(x)}{k_B T}) I_+^2(z), \tag{2.47}$$

substituting Eq. (2.46) in Eq. (2.47)

$$\Delta T_2(x_0 \to x_0 + L) = 2D_0 \int_{x_0}^{x_0+L} dz I_-(z)[I_+^2(z)], \tag{2.48}$$

we can interchange $z \to x$

$$\Delta T_2(x_0 \to x_0 + L) = 2D_0 \int_{x_0}^{x_0+L} dx I_-(x)[I_+^2(x)]. \tag{2.49}$$

Finally the Effective Diffusion Coefficient can be calculated from Eq. (2.20) we have

$$D_{eff} = \frac{L^2}{2} \frac{\Delta T_2(x_0 \to x_0 + L)}{[T_1(x_0 \to x_0 + L)]^3},$$

then substituting Eq. (2.49) in Eq. (2.20)

$$D_{eff} = L^2 \frac{D_0 \int_{x_0}^{x_0+L} dx I_-(x)[I_+^2(x)]}{[\int_{x_0}^{x_0+L} I_+(x)]^3}. \tag{2.50}$$

When their is external potential and the force is zero $F = 0$, by substituting I_- and I_+ in Eq. (2.50) the generalized effective diffusion coefficient is

$$D_{eff} = \frac{L^2 D_0}{\int_0^L dx exp(\frac{V(x)}{k_B T}) \int_0^L dy exp(\frac{-V(y)}{k_B T})}. \tag{2.51}$$

This is the expression that was derived by P. Reimann [9]. As an illustration, taking a rachet periodic potential we will evaluate D_{eff} in the following section.

2.2.1 Finding effective diffusion coefficient along a periodic piece wise linear Potential

The periodic potential over the period, 0 and L along the rachet potential, and the potential $V(x) = U_0$

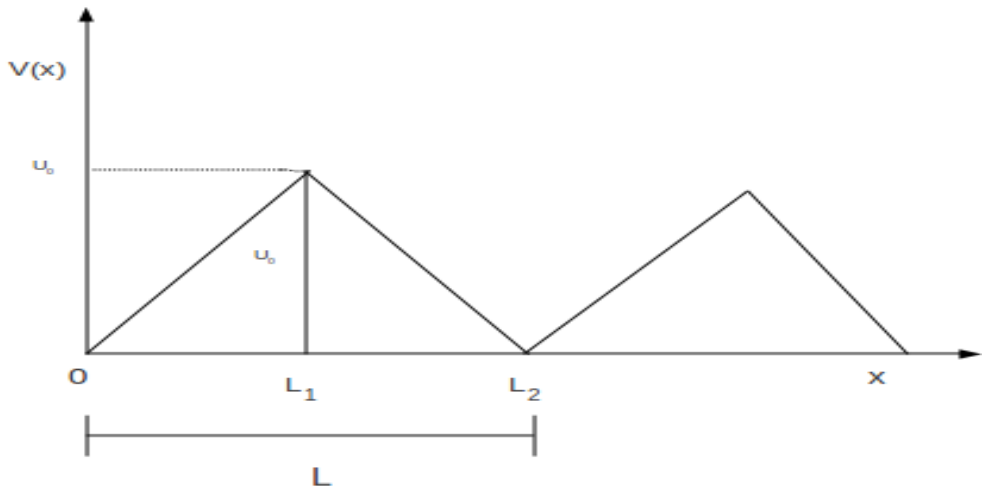


Figure 2.1: The periodic potential of rachet path

which is mathematically expressed as

$$V(x) = \begin{cases} \frac{U_0 x}{L_1} & for \quad 0 < x < L_1 \\ 2U_0 - \frac{U_0 x}{L_1} & for \quad L_1 < x < L_2 \end{cases} \tag{2.52}$$

The potential is symmetric and periodic. And using Eq. (2.51) P. Reimann derivation and which is given by Eq. (2.52) of the potential. we can evaluate the effective diffusion coefficient.

$$D_{eff} = \frac{D_0}{\int_0^L \frac{dx}{L} exp(\frac{V(x)}{k_B T} \int_0^L \frac{dy}{L} exp(\frac{-V(y)}{k_B T})}, \tag{2.53}$$

using Eq. (2.53) solve for D_{eff} and let us integrate $\int_0^L dx exp(\frac{V(x)}{k_B T})$, inserting the value of $V(x)$ for the two interval $L_1 = \frac{L}{2}$ and $L_2 = L$

$$\int_0^L dx exp(\frac{V(x)}{k_B T}) = \int_0^{L_1} dx exp(\frac{U_0 x}{k_B T L_1}) + \int_{L_1}^{L_2} dx exp(\frac{2U_0}{k_B T} - \frac{U_0 x}{k_B T L_1}), \tag{2.54}$$

$$\int_0^L dx exp(\frac{V(x)}{k_B T}) = \frac{k_B T}{U_0}[exp(\frac{U_0}{k_B T}) - 1], \tag{2.55}$$

and also integrate $\int_0^L dy exp(\frac{-V(y)}{k_B T})$ and inserting the value of $V(y)$ for the two intervals L_1 and L_2

$$\int_0^L dy exp(\frac{-V(y)}{k_B T}) = \int_0^{L_1} dy exp(\frac{-U_0 x}{k_B T L_1}) + \int_{L_1}^{L_2} dy exp(\frac{-2U_0}{k_B T} + \frac{U_0 x}{k_B T L_1}), \tag{2.56}$$

$$\int_0^L dy exp(\frac{-V(y)}{k_BT}) = \frac{k_BT}{U_0}[1 - exp(\frac{-U_0}{k_BT})], \tag{2.57}$$

substituting Eq. (2.55) and Eq. (2.57) in Eq. (2.53) we get

$$D_{eff} = \frac{D_0}{[\frac{k_BT}{U_0}]^2[exp(\frac{U_0}{k_BT}) + exp(\frac{-U_0}{k_BT}) - 2]}. \tag{2.58}$$

From Eq. (2.58) we see that D_{eff} satisfy the Einstein diffusion coefficient $D_{eff} = D_0$ when the potential $V(x) \to 0$. Expanding the exponetial term $exp(\frac{U_0}{k_BT}) = 1 + \frac{U_0}{k_BT}$ and $exp(\frac{-U_0}{k_BT}) = 1 - \frac{U_0}{k_BT}$

$$D_{eff} = \lim_{U_0 \to 0} \frac{D_0}{[\frac{k_BT}{U_0}]^2[exp(\frac{U_0}{k_BT}) + exp(\frac{-U_0}{k_BT}) - 2]}, \tag{2.59}$$

substituting the expanding term

$$D_{eff} = \lim_{U_0 \to 0} \frac{D_0 \frac{[U_0]^2}{[k_BT]^2}}{[(1 + \frac{U_0}{k_BT}) + (1 - \frac{U_0}{k_BT}) - 2]},$$

Then, finally we have found that the equation of the effective diffusion coefficient is equivalent to the Einstein diffusion coefficient

$$D_{eff} = D_0. \tag{2.60}$$

We have proved that the effective diffusion coefficient is equivalent to the Einstein diffusion coefficient when $V(x) \to 0$. Which is every system under zero potential exhibit it's effective diffusion coefficient is equal to the Einstein diffusion coefficient. It means that the equation we have found is valid because zero potential always follows Einstein diffusion coefficient,

$$D_{eff} = \frac{D_0[\frac{U_0}{k_BT}]^2 exp(\frac{-U_0}{k_BT})}{[1 + exp(\frac{-2U_0}{k_BT}) - 2exp(\frac{-U_0}{k_BT})]}. \tag{2.61}$$

So, the above result is the D_{eff} for simple rachet potential problem for Fig. 2.1 and for a given potential in Eq. (2.52).

In the following Chapter, we will take a binary alloy (NiAl) and we will evaluate the effective vacancy diffusion coefficient for the three kinds of vacancy diffusion mechanisms for NiAl binary alloy.

Chapter 3

Bulk NiAl Binary Alloy Effective Vacancy Diffusion Coefficient

The mechanism by which a single vacancy diffuses in mono-atomic crystalline material is basically through site exchange with one of its nearest-neighbor atoms. The vacancy diffusion continues through the material successively in a random way such that each new site occupied is usually energetically identical to any other earlier occupied site. As such, in homogeneous vacancy diffusion order is maintained throughout the vacancy diffusion.

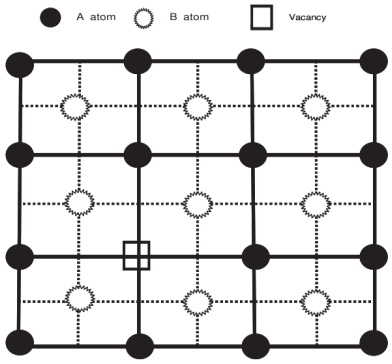


Figure 3.1: A binary alloy on two-dimensional lattice with a single vacancy occupying a site on sublattice A.

The situation is not so simple if the crystalline material is, for instance, composed of a binary alloy which consists of two interpenetrating simple cubic sub-lattices that are

predominantly occupied by two different atoms, A and B. Figure 3.1 is an illustration of a binary alloy in two-dimensional lattice with a single vacancy. Whenever the vacancy on site A exchanges its site with one of its nearest-neighbor atoms, the process leads to disorder in the crystalline structure. If the vacancy randomly moves successively via nearest-neighbor jumps, a string of anti-structure atoms would lead to disorder in the material. To avoid this problem of disordering, two alternative diffusion mechanisms are likely to take place: either jumps of the vacancy to further distant sites on the same sublattice or a cycle of successive intermediate jumps to nearest-neighbor in which the atomic disorder appearing during the earlier part of one cycle is followed by successive healing during the later part of the cycle [15]. There are three mechanisms for vacancy diffusion in binary alloy:

1. Next Nearest Neighbor (NNN) jump mechanism
2. Triple Defect mechanism
3. Six-jump cycle mechanism

In this chapter we use the method derived in chapter two to find the effective diffusion coefficient for the three mechanisms of Ni vacancy motion in NiAl alloy.

3.1 Next Nearest Neighbor (NNN) jump in NiAl

One could imagine a single vacancy formed on Ni sublattice as it diffuse by hopping to nearest site on the same sublattice. NNN-jump requiring prior formation of a Ni vacancy as shown in Fig. 1.1. Fig. 3.2 gives the energy profile of the vacancy (migration energy) jumps to the NNN site as reported in [1]. The MEP Fig. 3.2 indicates that the maximum migration energy is $2.58ev$ at a temperature of 1200K and 1500K along the reaction coordinate.

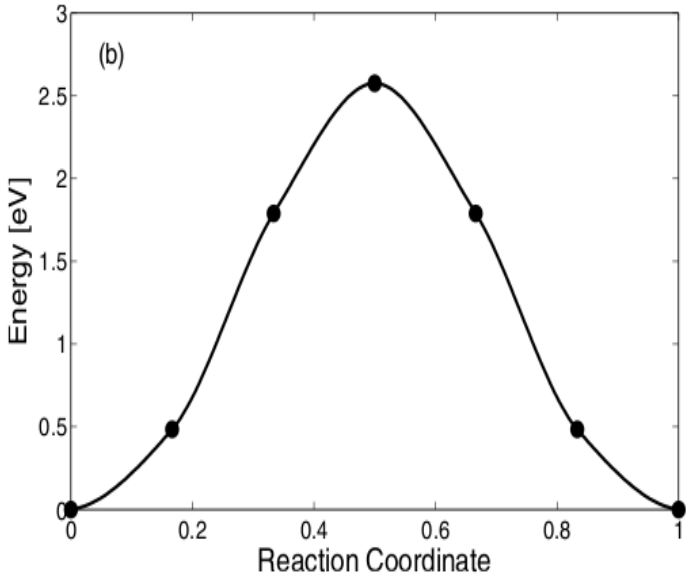


Figure 3.2: MEP of vacancy diffusion path of the NNN Ni jump [1]

Then our aim is to evaluate the effective vacancy diffusion coefficient (D_{eff}), using Eq. (2.51) for the potential of Fig. 3.2 and repeating periodically. Inorder to evaluate D_{eff} we simplify the potential energy curve to piece-wise linear potential energy curve as depicted in Fig. 3.3.

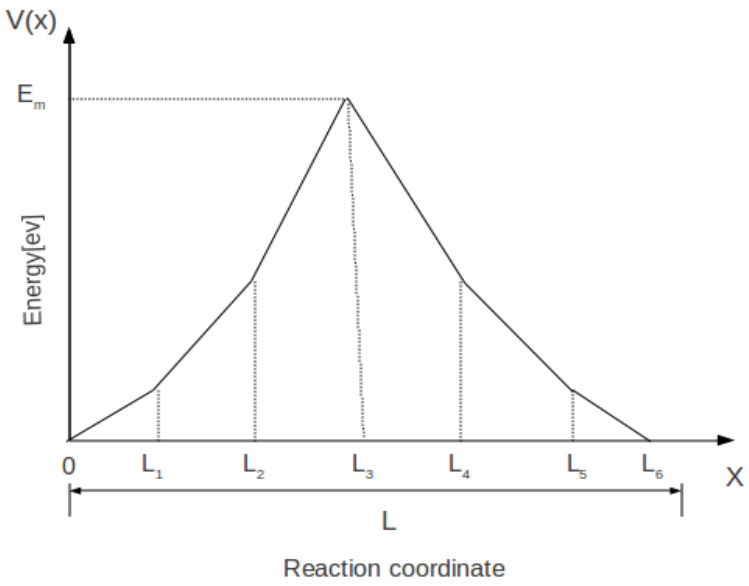


Figure 3.3: MEP of the NNN jump mechanism vacancy diffusion along a periodic piece wise linear potential energy

So, now our assumption in the NiAl binary alloy vacancy diffusion mechanism have periodic and symmetric potential through the atom diffusion to the vacant space, we are followed fully the NiAl binary vacancy diffusion mechanism as the Brownian dynamics of the system and the length of our system, let as take L for the over all process and the length of L_1 up to L_6 have the same lattice spacing length which is $\frac{L}{6}$ but the length from L_1 up to L_6 is as follows

$$L_1 = \frac{L}{6}, \qquad L_2 = \frac{L}{3},$$
$$L_3 = \frac{L}{2}, \qquad L_4 = \frac{4L}{6},$$
$$L_5 = \frac{5L}{6}, \qquad L_6 = L,$$

The piece-wise linear potential profile within the interval $0 < x < L$ is given by

$$V(x) = \begin{cases} \frac{U_0 x}{L_1} & for \quad 0 < x < L_1 \\ U_0 + \frac{U_0 L_1}{L_2} - \frac{U_0 x}{L_2} & for \quad L_1 < x < L_2 \\ \frac{U_0 L_1}{L_2} + \frac{U_0 L_2}{L_3} - \frac{U_0 x}{L_3} & for \quad L_2 < x < L_3 \\ \frac{U_0 L_1}{L_2} + \frac{U_0 L_2}{L_3} - U_0 - \frac{U_0 L_3}{L_4} + \frac{U_0 x}{L_4} & for \quad L_3 < x < L_4 \\ \frac{U_0 L_1}{L_2} + \frac{U_0 L_2}{L_3} - \frac{U_0 L_3}{L_4} + \frac{U_0 L_4}{L_5} - \frac{U_0 x}{L_5} & for \quad L_4 < x < L_5 \\ \frac{U_0 L_1}{L_2} + \frac{U_0 L_2}{L_3} - \frac{U_0 L_3}{L_4} + \frac{U_0 L_4}{L_5} - U_0 + \frac{U_0 L_5}{L_6} - \frac{U_0 x}{L_6} & for \quad L_5 < x < L_6 \end{cases} \tag{3.1}$$

Note that the potential profile is symmetric, then we only use the potential equation for L_1, L_2, L_3, because after this interval it is periodic $0 < x < L_1$, $L_1 < x < L_2$, $L_2 < x < L_3$. Then we use Eq. (2.50) to evaluate D_{eff} for NNN Ni jump

$$D_{eff} = \frac{L^2 D_0}{\int_0^L dx exp(\frac{V(x)}{k_B T}) \int_0^L dy exp(\frac{-V(y)}{k_B T})}, \tag{3.2}$$

To carry out the integration found in the denominator of Eq. (3.2) for $\int_0^L dx exp(\frac{V(x)}{k_B T})$, we note that

$$\begin{aligned} \int_0^L dx exp(\frac{V(x)}{k_B T}) \quad &= \int_0^{L_1} dx exp(\frac{V(x)}{k_B T}) + \int_{L_1}^{L_2} dx exp(\frac{V(x)}{k_B T}) + \int_{L_2}^{L_3} dx exp(\frac{V(x)}{k_B T}) \\ &+ \int_{L_3}^{L_4} dx exp(\frac{V(x)}{k_B T}) + \int_{L_4}^{L_5} dx exp(\frac{V(x)}{k_B T}) + \int_{L_5}^{L_6} dx exp(\frac{V(x)}{k_B T}), \end{aligned} \tag{3.3}$$

Utilizing the symmetric property of the potential, the above integration turns out to be

$$= 2[\int_0^{L_1} dx exp(\frac{V(x)}{k_B T}) + \int_{L_1}^{L_2} dx exp(\frac{V(x)}{k_B T}) + \int_{L_2}^{L_3} dx exp(\frac{V(x)}{k_B T})], \tag{3.4}$$

We next use the expressions for the piece-wise linear potential in the evaluation of the integration which we found to be

$$\begin{aligned} \int_0^L dx exp(\frac{V(x)}{k_B T}) \quad &= [\frac{2k_B TL}{6U_0}[exp(\frac{U_0}{k_B T}) - 1] - \frac{2k_B TL}{3U_0}[exp(\frac{U_0}{2k_B T}) - exp(\frac{U_0}{k_B T})] \\ &- \frac{k_B TL}{U_0}[exp(\frac{U_0}{6k_B T}) - exp(\frac{U_0}{2k_B T})]], \end{aligned} \tag{3.5}$$

$$= [\frac{k_B TL}{U_0}][exp(\frac{U_0}{k_B T}) + \frac{1}{3} exp(\frac{U_0}{2k_B T}) - exp(\frac{U_0}{6k_B T}) - \frac{1}{3}], \tag{3.6}$$

and carry out the integration found in the denominator of Eq. (3.2) for $\int_0^L dyexp(\frac{-V(y)}{k_BT})$, we note that

$$\begin{aligned}\int_0^L dyexp(\frac{-V(y)}{k_BT}) \quad &= \int_0^{L_1} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_1}^{L_2} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_2}^{L_3} dyexp(\frac{-V(y)}{k_BT}) \\ &+ \int_{L_3}^{L_4} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_4}^{L_5} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_5}^{L_6} dyexp(\frac{-V(y)}{k_BT}),\end{aligned} \tag{3.7}$$

Utilizing the symmetric property of the potential, the above integration turns out to be

$$= 2[\int_0^{L_1} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_1}^{L_2} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_2}^{L_3} dyexp(\frac{-V(y)}{k_BT})], \tag{3.8}$$

We next use the expressions for the piece-wise linear potential in the evaluation of the integration which we found to be

$$\begin{aligned}\int_0^L dyexp(-\frac{V(y)}{k_BT}) \quad &= [\frac{-2k_BTL}{6U_0}[exp(\frac{-U_0}{k_BT}) - 1] + \frac{2k_BTL}{3U_0}[exp(\frac{-U_0}{2k_BT}) - exp(\frac{-U_0}{k_BT})] \\ &+ \frac{k_BTL}{U_0}[exp(\frac{-U_0}{6k_BT}) - exp(\frac{-U_0}{2k_BT})]],\end{aligned} \tag{3.9}$$

$$= [\frac{k_BTL}{U_0}][-exp(\frac{-U_0}{k_BT}) - \frac{1}{3}exp(\frac{-U_0}{2k_BT}) + exp(\frac{-U_0}{6k_BT}) + \frac{1}{3}], \tag{3.10}$$

Then substituting Eq. (3.6) and Eq. (3.10) in Eq. (3.2) we find that D_{eff}

$$D_{eff} = \frac{D_0}{[\frac{k_BT}{U_0}]^2[exp(\frac{U_0}{k_BT}) + \frac{1}{3}exp(\frac{U_0}{2k_BT}) - exp(\frac{U_0}{6k_BT}) - \frac{1}{3}] * [-exp(\frac{-U_0}{k_BT}) - \frac{1}{3}exp(\frac{-U_0}{2k_BT}) + exp(\frac{-U_0}{6k_BT}) + \frac{1}{3}]}, \tag{3.11}$$

$$\frac{D_{eff}}{D_0} = \frac{\frac{U_0^2}{[k_BT]^2}}{[exp(\frac{U_0}{k_BT}) + \frac{1}{3}exp(\frac{U_0}{2k_BT}) - exp(\frac{U_0}{6k_BT}) - \frac{1}{3}] * [-exp(\frac{-U_0}{k_BT}) - \frac{1}{3}exp(\frac{-U_0}{2k_BT}) + exp(\frac{-U_0}{6k_BT}) + \frac{1}{3}]} \tag{3.12}$$

Then let as check the solution of D_{eff} when $V(x) \to 0$, D_{eff} is equivalent to the Einstein diffusion coefficient D_0

$$\frac{D_{eff}}{D_0} = \lim_{U_0 \to 0} \frac{\frac{U_0^2}{[k_BT]^2}}{[exp(\frac{U_0}{k_BT}) + \frac{1}{3}exp(\frac{U_0}{2k_BT}) - exp(\frac{U_0}{6k_BT}) - \frac{1}{3}] * [-exp(\frac{-U_0}{k_BT}) - \frac{1}{3}exp(\frac{-U_0}{2k_BT}) + exp(\frac{-U_0}{6k_BT}) + \frac{1}{3}]} \tag{3.13}$$

when $U_0 \to 0$ we must expand the exponential terms which is

$$exp(\frac{U_0}{k_BT}) = 1 + \frac{U_0}{k_BT}, \qquad exp(\frac{-U_0}{k_BT}) = 1 - \frac{U_0}{k_BT}, \tag{3.14}$$

$$exp(\frac{U_0}{2k_BT}) = 1 + \frac{U_0}{2k_BT}, \qquad exp(\frac{-U_0}{2k_BT}) = 1 - \frac{U_0}{2k_BT}, \tag{3.15}$$

$$exp(\frac{U_0}{6k_BT}) = 1 + \frac{U_0}{6k_BT}, \qquad exp(\frac{-U_0}{6k_BT}) = 1 - \frac{U_0}{6k_BT}, \tag{3.16}$$

After inserting Eq. (3.14), Eq. (3.15) and Eq. (3.16) in Eq. (3.13) then finally we find

$$D_{eff} = D_0. \tag{3.17}$$

Our result of Eq. (3.17) shows that D_{eff} and the Einstein diffusion coefficient D_0 are equal for the NNN Ni-jump binary alloy. Eq. (2.12) shows as for every system under zero potential $D_{eff} = D_0$. So, then we can say that D_{eff} for the NNN Ni-jump binary alloy is valid solution. Then the simplified form of our result for D_{eff}.

$$D_{eff} = \frac{D_0 \frac{U_0^2}{[k_BT]^2}}{[exp(\frac{U_0}{k_BT}) + \frac{1}{3}exp(\frac{U_0}{2k_BT}) - exp(\frac{U_0}{6k_BT}) - \frac{1}{3}] * [-exp(\frac{-U_0}{k_BT}) - \frac{1}{3}exp(\frac{-U_0}{2k_BT}) + exp(\frac{-U_0}{6k_BT}) + \frac{1}{3}]} \tag{3.18}$$

From Kristen A. Marino and Emily A. Carter [1] paper in Table I, we are taking the value for D_0, migration energy E_m for two different temperature and substituting in Eq. (3.18). The migration energy must be converted from electron volt to Joule(J) where $1ev = 1.602176487 \times 10^{-19}$J

$$U_0 = 2.58ev = 4.13 \times 10^{-19}J,$$

then we can find effective vacancy diffusion coefficient D_{eff} for NNN Ni-jump vacancy diffusion mechanism as follows

Table 3.1: NNN Ni jump vacancy diffusion mechanism: migration energies(E_m), pre-exponential factors D_0 for 1200K and 1500 K. and our result D_{eff}

	T=1200k	T=1500k
U_0	4.13×10^{-19}J	4.13×10^{-19}J
D_0	$0.64 \times 10^{-5}\ m^2\ s^{-1}$	$0.79 \times 10^{-5}\ m^2\ s^{-1}$
$\frac{D_{eff}}{D_0}$	2.66×10^{-8}	2.35×10^{-6}
D_{eff}	$1.70 \times 10^{-13}\ m^2\ s^{-1}$	$1.86 \times 10^{-11}\ m^2\ s^{-1}$

3.2 Triple defect jump mechanism

The transition state in the triple defect mechanism is more complex than that of a NNN Ni jump. NiAl vacancy as shown in Fig. 1.2 through this mechanism, two Ni atoms shift in the same direction by a lattice vector and one Al atom moves by a lattice vector in the opposite direction. Fig. 3.4 gives the energy profile of the vacancy(migration energy) jump to the triple defect mechanism reported in [1]. The MEP Fig. 3.4 indicates that the migration energy at a temperature of 1200K and 1500K along the reaction coordinate.

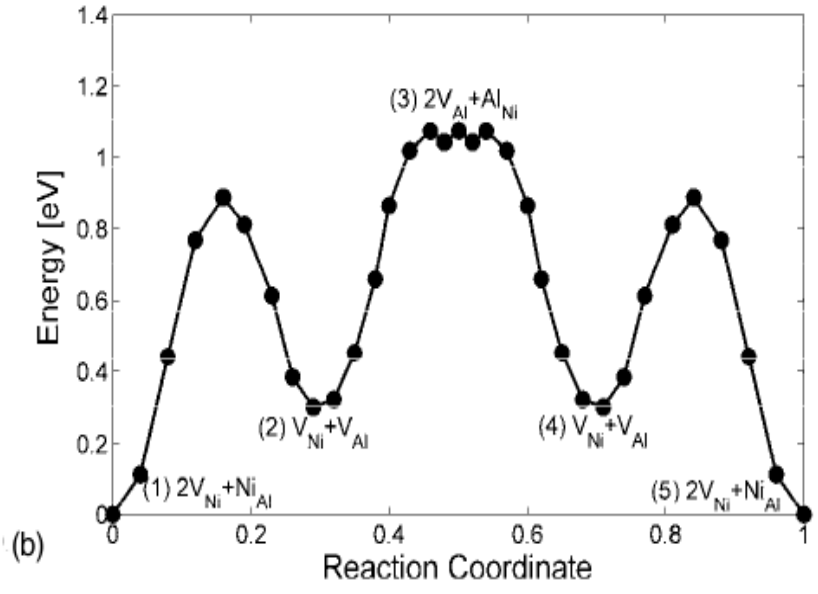


Figure 3.4: MEP of vacancy diffusion for triple defect mechanism for NiAl binary alloy [1]

In this mechanism our aim is also to evaluate the effective vacancy diffusion for the triple defect vacancy diffusion mechanism, using Eq. (2.51) for the potential of Fig. 3.4 and repeating periodically. Inorder to evaluate D_{eff} of the triple defect vacancy diffusion mechanism we are following the same kind of techniques from NNN Ni-jump mechanism just taking the plot of migration energy E_m Fig. 3.4 and simplify the potential curve to piece-wise linear potential curve depicted Fig. 3.5. The assumption also the same, now our assumption is the NiAl binary alloy vacancy diffusion have symmetric potential through the atom diffusion to the vacant space. We follow the same kind of the Brownian dynamics to the NiAl vacancy diffusion.

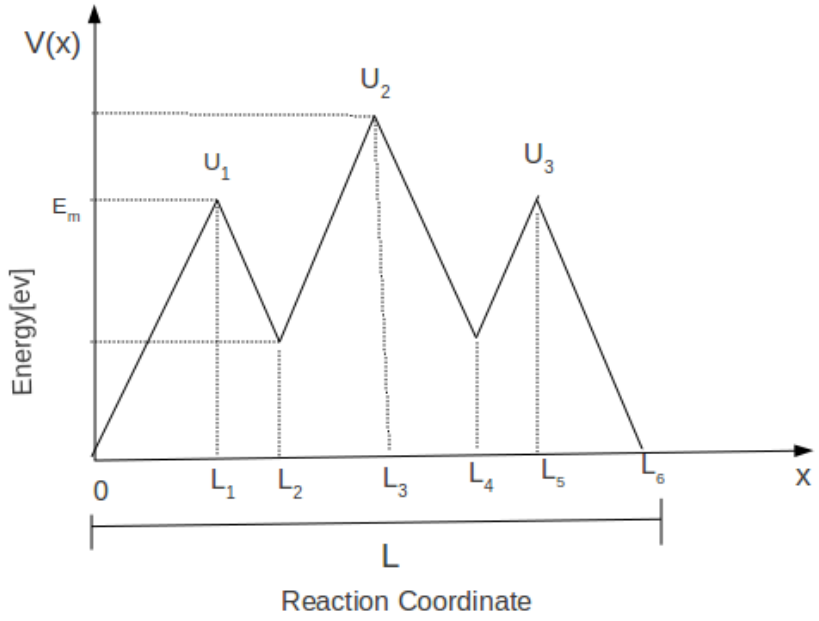


Figure 3.5: MEP of the triple defect mechanism vacancy diffusion along a periodic piece wise linear potential energy

The total length we measure for the reaction coordinate lattice spacing but we must scale this measurement from the plot to make equivalent measurement. Where $L = 6.8$ and taking the spacing for each distance. Then our a measurement for all length as

follows:

$$L_1 = \frac{1.1L}{6.8}, \qquad L_2 = \frac{2L}{6.8},$$
$$L_3 = \frac{3.4L}{6.8}, \qquad L_4 = \frac{4.8L}{6.8},$$
$$L_5 = \frac{5.7L}{6.8}, \qquad L_6 = L,$$

From the above we see that the potential are symmetric. The piece-wise linear potential within the interval of $0 < x < L$ is given by

$$V(x) = \begin{cases} \frac{U_1 x}{L_1} & for \quad 0 < x < L_1 = L_5 < x < L_6 \\ U_2 + \frac{U_2 L_1}{L_2} - \frac{U_2 x}{L_2} & for \quad L_1 < x < L_2 = L_4 < x < L_5 \\ \frac{U_3 L_1}{L_2} + \frac{U_3 L_2}{L_3} - \frac{U_3 x}{L_3} & for \quad L_2 < x < L_3 = L_3 < x < L_4 \end{cases} \tag{3.19}$$

We use Eq. (2.51) to evaluate D_{eff} for triple defect mechanism

$$D_{eff} = \frac{L^2 D_0}{\int_0^L dx exp(\frac{V(x)}{k_B T}) \int_0^L dy exp(\frac{-V(y)}{k_B T})}, \tag{3.20}$$

and to carry out the integration found in the denominator of Eq. (3.20), we note that

$$\begin{aligned} \int_0^L dx exp(\frac{V(x)}{k_B T}) \quad &= \int_0^{L_1} dx exp(\frac{V(x)}{k_B T}) + \int_{L_1}^{L_2} dx exp(\frac{V(x)}{k_B T}) + \int_{L_2}^{L_3} dx exp(\frac{V(x)}{k_B T}) \\ &+ \int_{L_3}^{L_4} dx exp(\frac{V(x)}{k_B T}) + \int_{L_4}^{L_5} dx exp(\frac{V(x)}{k_B T}) + \int_{L_5}^{L_6} dx exp(\frac{V(x)}{k_B T}), \end{aligned} \tag{3.21}$$

Utilizing the symmetric property of the potential, the above integration turns out to be

$$= 2[\int_0^{L_1} dx exp(\frac{V(x)}{k_B T}) + \int_{L_1}^{L_2} dx exp(\frac{V(x)}{k_B T}) + \int_{L_2}^{L_3} dx exp(\frac{V(x)}{k_B T})], \tag{3.22}$$

By using the expression for the piece-wise linear potential in Eq. (3.19) in the evaluation of the integration which we found to be

$$\begin{aligned} \int_0^L dx exp(\frac{V(x)}{k_B T}) \quad &= 2[\frac{1.1 k_B T}{6.8 U_1} L[exp(\frac{U_1}{k_B T}) - 1] - \frac{2 k_B T}{6.8 U_2} L[exp(\frac{1.1 U_2}{2 k_B T}) - exp(\frac{U_2}{k_B T})] \\ &- \frac{3.4 k_B T}{6.8 U_3} L[exp(\frac{0.9 U_3}{6.8 k_B T}) - exp(\frac{1.1 U_3}{2 k_B T})]], \end{aligned} \tag{3.23}$$

and to carry out the integration found in the denominator of Eq. (3.20) for $\int_0^L dyexp(\frac{-V(y)}{k_BT})$, we note that

$$\begin{aligned}\int_0^L dyexp(\frac{-V(y)}{k_BT}) \quad &= \int_0^{L_1} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_1}^{L_2} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_2}^{L_3} dyexp(\frac{-V(y)}{k_BT}) \\ &+ \int_{L_3}^{L_4} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_4}^{L_5} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_5}^{L_6} dyexp(\frac{-V(y)}{k_BT}),\end{aligned} \tag{3.24}$$

Utilizing the symmetric property of the potential, the above integration turns out to be

$$= 2[\int_0^{L_1} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_1}^{L_2} dyexp(\frac{-V(y)}{k_BT}) + \int_{L_2}^{L_3} dyexp(\frac{-V(y)}{k_BT})], \tag{3.25}$$

By using the expression for the piece-wise linear potential in Eq. (3.19) we found to be

$$\begin{aligned}\int_0^L dyexp(\frac{-V(y)}{k_BT}) \quad &= 2[\frac{-1.1k_BT}{6.8U_1}L[exp(\frac{-U_1}{k_BT}) - 1] + \frac{2k_BT}{6.8U_2}L[exp(\frac{-1.1U_2}{2k_BT}) - exp(\frac{-U_2}{k_BT})] \\ &+ \frac{3.4k_BT}{6.8U_3}L[exp(\frac{-0.9U_3}{6.8k_BT}) - exp(\frac{-1.1U_3}{2k_BT})]],\end{aligned} \tag{3.26}$$

Finally substituting Eq. (3.23) and Eq. (3.26) in Eq. (3.2) we found D_{eff}. Then the general solution for the effective vacancy diffusion coefficient for triple defect vacancy diffusion mechanism.

$$\begin{aligned}D_{eff} = \quad &\frac{D_0}{[k_BT]^2[2[\frac{1.1}{6.8U_1}[exp(\frac{U_1}{k_BT}) - 1] - \frac{2}{6.8U_2}[exp(\frac{1.1U_2}{6.8k_BT}) - exp(\frac{U_2}{k_BT})] - \frac{3.4}{6.8U_3}[exp(\frac{0.94U_3}{6.8k_BT}) - exp(\frac{1.1U_3}{2k_BT})]]} \\ *&\frac{1}{[2[\frac{-1.1}{6.8U_1}[exp(\frac{-U_1}{k_BT}) - 1] + \frac{2}{6.8U_2}[exp(\frac{-1.1U_2}{6.8k_BT}) - exp(\frac{-U_2}{k_BT})] + \frac{3.4}{6.8U_3}[exp(\frac{-0.94U_3}{6.8k_BT}) - exp(\frac{-1.1U_3}{2k_BT})]]},\end{aligned} \tag{3.27}$$

We have to check the solution when $V(x) \to 0$ is equal to $D_{eff} = D_0$.

$$\begin{aligned}\frac{D_{eff}}{D_0} = \lim_{U_{1,2,3}\to 0} \quad &\frac{\frac{1}{[k_BT]^2}}{[2[\frac{1.1}{6.8U_1}[exp(\frac{U_1}{k_BT}) - 1] - \frac{2}{6.8U_2}[exp(\frac{1.1U_2}{6.8k_BT}) - exp(\frac{U_2}{k_BT})] - \frac{3.4}{6.8U_3}[exp(\frac{0.94U_3}{6.8k_BT}) - exp(\frac{1.1U_3}{2k_BT})]]} \\ *&\frac{1}{[2[\frac{-1.1}{6.8U_1}[exp(\frac{-U_1}{k_BT}) - 1] + \frac{2}{6.8U_2}[exp(\frac{-1.1U_2}{6.8k_BT}) - exp(\frac{-U_2}{k_BT})] + \frac{3.4}{6.8U_3}[exp(\frac{-0.94U_3}{6.8k_BT}) - exp(\frac{-1.1U_3}{2k_BT})]]},\end{aligned} \tag{3.28}$$

Expanding the exponetial terms and inserting in Eq. (3.28) which is

$$exp(\frac{U_1}{k_BT}) = 1 + \frac{U_1}{k_BT}, \qquad exp(-\frac{U_1}{k_BT}) = 1 - \frac{U_1}{k_BT} \tag{3.29}$$

$$exp(\frac{1.1U_2}{2k_BT}) = 1 + \frac{1.1U_2}{2k_BT}, \qquad exp(\frac{U_2}{k_BT}) = 1 + \frac{U_2}{k_BT}, \tag{3.30}$$

$$exp(-\frac{1.1U_2}{2k_BT}) = 1 - \frac{1.1U_2}{2k_BT}, \qquad exp(-\frac{U_2}{k_BT}) = 1 - \frac{U_2}{k_BT} \tag{3.31}$$

$$exp(\frac{0.94U_3}{6.8k_BT}) = 1 + \frac{0.94U_3}{6.8k_BT}, \qquad exp(\frac{1.1U_3}{2k_BT}) = 1 + \frac{1.1U_3}{2k_BT}, \tag{3.32}$$

$$exp(-\frac{0.94U_3}{6.8k_BT}) = 1 - \frac{0.94U_3}{6.8k_BT}, \qquad exp(-\frac{1.1U_3}{2k_BT}) = 1 - \frac{1.1U_3}{2k_BT}, \tag{3.33}$$

Substitute Eq. (3.29-3.33) in Eq. (3.28) then finally we note that,

$$D_{eff} = D_0. \tag{3.34}$$

$D_{eff} = D_0$ also true for triple defect mechanism binary alloy when the potential goes to zero. So, then we can say that our result for effective diffusion coefficient D_{eff} for triple defect binary alloy is valid solution. Then we found D_{eff}

$$D_{eff} = \frac{\frac{D_0}{[k_BT]^2}}{[2[\frac{1.1}{6.8U_1}[exp(\frac{U_1}{k_BT}) - 1] - \frac{2}{6.8U_2}[exp(\frac{1.1U_2}{6.8k_BT}) - exp(\frac{U_2}{k_BT})] - \frac{3.4}{6.8U_3}[exp(\frac{0.94U_3}{6.8k_BT}) - exp(\frac{1.1U_3}{2k_BT})]]} * \frac{1}{[2[\frac{-1.1}{6.8U_1}[exp(\frac{-U_1}{k_BT}) - 1] + \frac{2}{6.8U_2}[exp(\frac{-1.1U_2}{6.8k_BT}) - exp(\frac{-U_2}{k_BT})] + \frac{3.4}{6.8U_3}[exp(\frac{-0.94U_3}{6.8k_BT}) - exp(\frac{-1.1U_3}{2k_BT})]]}, \tag{3.35}$$

Eq. (3.35) is the result of effective vacancy diffusion coefficient for triple defect vacancy diffusion mechanism. So, now let as substitute some parameters from Kristen A. Marino and Emily A. Carter [1] paper in Table II, we are taking the value for D_0, Migration Energy E_m for two different temperature 1200K and 1500K and substituting in Eq. (3.35) .The migration Energy must be converted to electron volt(ev) to joule(J) so,$1ev = 1.602176487 \times 10^{-19}$J.

$$U_1 = 0.89ev = 1.43 \times 10^{-19}J,$$

$$U_2 = 0.74ev = 1.19 \times 10^{-19}J,$$

$$U_3 = 0.59ev = 9.45 \times 10^{-20}J,$$

then we found for effective vacancy diffusion coefficient for triple defect vacancy diffusion mechanism(D_{eff}) as follows.

Table 3.2: Triple defect vacancy diffusion mechanism: migration energies(E_m), pre-exponential factors D_0 for 1200K and 1500 K.and our result D_{eff}

	T=1200K	T=1500K
U_1	$1.43 \times 10^{-19} J$	$1.43 \times 10^{-19} J$
U_2	$1.19 \times 10^{-19} J$	$1.19 \times 10^{-19} J$
U_3	$9.45 \times 10^{-20} J$	$9.45 \times 10^{-20} J$
D_0	$0.43 \times 10^{-5}\ m^2\ s^{-1}$	$0.46 \times 10^{-5}\ m^2\ s^{-1}$
$\frac{D_{eff}}{D_0}$	0.03	0.09
D_{eff}	$1.22 \times 10^{-7}\ m^2\ s^{-1}$	$3.91 \times 10^{-7}\ m^2\ s^{-1}$

3.3 Six-jump cycle vacancy diffusion mechanism

This mechanism occurs in three different pathways, one a Ni atom moving in the [110] direction whereas the other two paths move a Ni atom in the [100] direction. In [100] in this direction two ways 'straight' and 'bent'. We are working in the [110] and [100]'bent' direction movement of the Ni vacancy diffusion mechanism. For the [100]'straight' mechanisms we didn't do it because the same technique to solve D_{eff}.

In this mechanism also we are applying the same technique from the two vacancy diffusion mechanism, NNN Ni-jump and triple defect to solve the effective vacancy diffusion coefficient. Let us follow the P.Reimann equation Eq. (2.51) and inorder to evaluate D_{eff} we simplify the potential curve to piece-wise linear potential curve as depicted Fig. 3.7 and Fig. 3.9. Our assumption also the NiAl binary alloy vacancy diffusion periodic and symmetric potential for the vacancy diffusion processes and by applying the Brownian dynamics to the NiAl vacancy diffusion.

We work on two types six jump cycle vacancy diffusion:

1. six-jump cycle for [100] bent direction vacancy diffusion mechanism
2. six-jump cycle for [110] direction vacancy diffusion mechanism

3.3.1 six-jump cycle for [100] 'bent' vacancy diffusion mechanism

In [100] bent direction six-jump cycle vacancy diffusion mechanism as shown in Fig 1.4. Kristen group found that for Fig. 3.6 the energy profile of vacancy(migration energy E_m) jump for the three potential picks reported in [1]. The MEP Fig. 3.6 indicates that the migration energy at a temperature of 1200K and 1500K along the reaction coordinate.

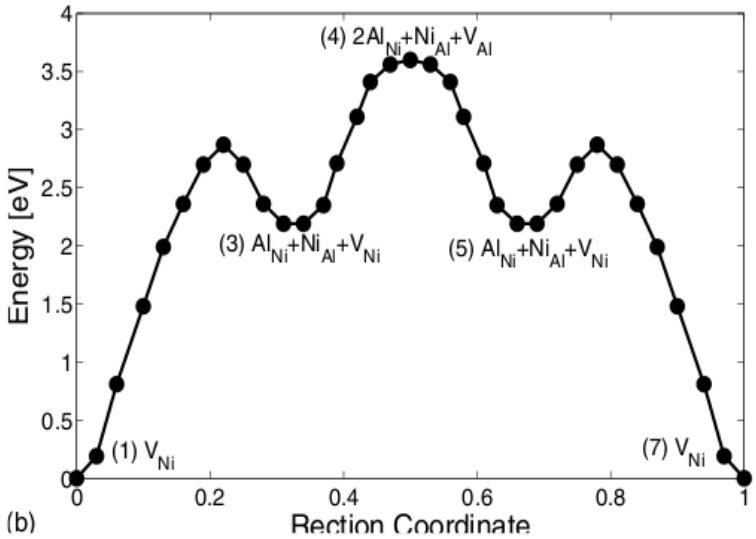
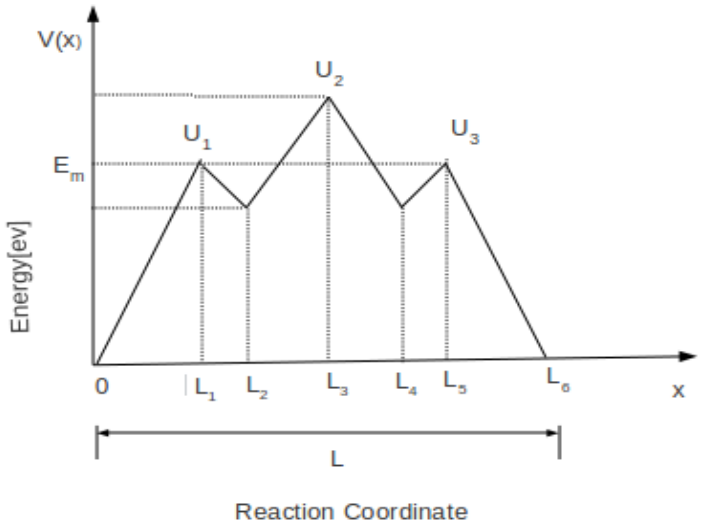


Figure 3.6: MEP for the six-jump cycle to [100] 'bent' direction vacancy diffusion for the NiAl binary alloy [1]

The total length of Fig. 3.6 is L=7.6 lattice spacing and to make equivalent with their measurement we must take their ratio. The over all measurement for each spacing distance for $L_1, L_2, L_3, L_4, L_5, L_6$

$$L_1 = \frac{1.7}{7.6}L, \qquad L_2 = \frac{2.5}{7.6}L,$$
$$L_3 = \frac{3.8}{7.6}L, \qquad L_4 = \frac{5.1}{7.6}L,$$
$$L_5 = \frac{5.9}{7.6}L, \qquad L_6 = L,$$

The MEP Fig. 3.6 indicates that the migration energy at a temperature of 1200K and



1500K.

Figure 3.7: MEP of the six-jump cycle [100] 'bent' vacancy diffusion along a periodic piece wise linear potential energy

The piece-wise linear potential with in the interval of $0 < x < L$ is given

$$V(x) = \begin{cases} \frac{U_1 x}{L_1} & for \quad 0 < x < L_1 = L_5 < x < L_6 \\ U_2 + \frac{U_2 L_1}{L_2} - \frac{U_2 x}{L_2} & for \quad L_1 < x < L_2 = L_4 < x > L_5 \\ \frac{U_3 L_1}{L_2} + \frac{U_3 L_2}{L_3} - \frac{U_3 x}{L_3} & for \quad L_2 < x < L_3 = L_3 < x > L_4 \end{cases} \tag{3.36}$$

We use Eq. (2.51) to evaluate D_{eff} for six-jump cycle [100] 'bent' direction vacancy diffusion and by recalling Eq. (3.2) we have

$$D_{eff} = \frac{L^2 D_0}{\int_0^L dx exp(\frac{V(x)}{k_B T}) \int_0^L dy exp(-\frac{V(y)}{k_B T})}.$$

and to carry out the integration found in the denominator of Eq. (3.2) for $\int_0^L dx exp(\frac{V(x)}{k_B T})$we note

$$\begin{aligned} \int_0^L dx exp(\frac{V(x)}{k_B T}) \quad &= \int_0^{L_1} dx exp(\frac{V(x)}{k_B T}) + \int_{L_1}^{L_2} dx exp(\frac{V(x)}{k_B T}) + \int_{L_2}^{L_3} dx exp(\frac{V(x)}{k_B T}) \\ &+ \int_{L_3}^{L_4} dx exp(\frac{V(x)}{k_B T}) + \int_{L_4}^{L_5} dx exp(\frac{V(x)}{k_B T}) + \int_{L_5}^{L_6} dx exp(\frac{V(x)}{k_B T}), \end{aligned} \tag{3.37}$$

Utilizing the symmetric property of the potential, the above integration turns out to be

$$\int_0^L dx exp(\frac{V(x)}{k_BT}) = 2[\int_0^{L_0} dx exp(\frac{V(x)}{k_BT}) + \int_{L_1}^{L_2} dx exp(\frac{V(x)}{k_BT}) + \int_{L_2}^{L_3} dx exp(\frac{V(x)}{k_BT})], \quad (3.38)$$

We next use the expression for the piece-wise linear potential in the evaluation of the integration which we found to be

$$\begin{aligned}\int_0^L dx exp(\frac{V(x)}{k_BT}) \quad &= 2[\frac{1.7k_BT}{7.6U_1}L[exp(\frac{U_1}{k_BT}) - 1] - \frac{2.5k_BT}{7.6U_2}L[exp(\frac{1.7U_2}{2.5k_BT}) - exp(\frac{U_2}{k_BT})] \\ &\quad - \frac{3.8k_BT}{7.6U_3}L[exp(\frac{3.2U_3}{9.5k_BT}) - exp(\frac{1.7U_3}{2.5k_BT})]],\end{aligned} \quad (3.39)$$

and to carry out the integration found in the denominator of Eq. (3.2) for $\int_0^L dx exp(-\frac{V(y)}{k_BT})$we note

$$\begin{aligned}\int_0^L dy exp(\frac{-V(y)}{k_BT}) \quad &= \int_0^{L_1} dy exp(\frac{-V(y)}{k_BT}) + \int_{L_1}^{L_2} dy exp(\frac{-V(y)}{k_BT}) + \int_{L_2}^{L_3} dy exp(\frac{-V(y)}{k_BT}) \\ &\quad + \int_{L_3}^{L_4} dy exp(\frac{-V(y)}{k_BT}) + \int_{L_4}^{L_5} dy exp(\frac{-V(y)}{k_BT}) + \int_{L_5}^{L_6} dy exp(\frac{-V(y)}{k_BT}),\end{aligned} \quad (3.40)$$

Utilizing the symmetric property of the potential, the above integration turns out to be

$$\int_0^L dy exp(\frac{-V(y)}{k_BT}) = 2[\int_0^{L_0} dy exp(\frac{-V(y)}{k_BT}) + \int_{L_1}^{L_2} dy exp(\frac{-V(y)}{k_BT}) + \int_{L_2}^{L_3} dy exp(\frac{-V(y)}{k_BT})], \quad (3.41)$$

We next use the expression for the piece-wise linear potential in the evaluation of the integration which we found to be

$$\begin{aligned}\int_0^L dy exp(\frac{-V(y)}{k_BT}) \quad &= 2[\frac{-1.7k_BT}{7.6U_1}L[exp(\frac{-U_1}{k_BT}) - 1] + \frac{2.5k_BT}{7.6U_2}L[exp(\frac{-1.7U_2}{2.5k_BT}) - exp(-\frac{U_2}{k_BT})] \\ &\quad + \frac{3.8k_BT}{7.6U_3}L[exp(\frac{-3.2U_3}{9.5k_BT}) - exp(\frac{-1.7U_3}{2.5k_BT})]],\end{aligned} \quad (3.42)$$

Substitute Eq. (3.39) and Eq. (3.42) in Eq. (3.2) then D_{eff} will be

$$\begin{aligned}D_{eff} = &\frac{D_0}{[2[\frac{1.7k_BT}{7.6U_1}[exp(\frac{U_1}{k_BT}) - 1] - \frac{2.5k_BT}{7.6U_2}[exp(\frac{1.7U_2}{2.5k_BT}) - exp(\frac{U_2}{k_BT})] - \frac{3.8k_BT}{7.6U_3}[exp(\frac{3.2U_3}{9.5k_BT}) - exp(\frac{1.7U_3}{2.5k_BT})]]} \\ &* \frac{1}{[2[\frac{-1.7k_BT}{7.6U_1}[exp(\frac{-U_1}{k_BT}) - 1] + \frac{2.5k_BT}{7.6U_2}[exp(\frac{-1.7U_2}{2.5k_BT}) - exp(\frac{-U_2}{k_BT})] + \frac{3.8k_BT}{7.6U_3}[exp(\frac{-3.2U_3}{9.5k_BT}) - exp(\frac{-1.7U_3}{2.5k_BT})]]}.\end{aligned} \quad (3.43)$$

Now when the system potential goes to zero D_{eff} for [100]'bent' six-jump cycle must be equivalent to Einstein diffusion coefficient.

$$\frac{D_{eff}}{D_0} = \lim_{U_{1,2,3}\to 0} \frac{\frac{1}{[k_BT]^2}}{[2[\frac{1.7}{7.6U_1}[exp(\frac{U_1}{k_BT})-1]-\frac{2.5}{7.6U_2}[exp(\frac{1.7U_2}{2.5k_BT})-exp(\frac{U_2}{k_BT})]-\frac{3.8}{7.6U_3}[exp(\frac{3.2U_3}{9.5k_BT})-exp(\frac{1.7U_3}{2.5k_BT})]]} * \frac{1}{[2[\frac{-1.7}{7.6U_1}[exp(\frac{-U_1}{k_BT})-1]+\frac{2.5}{7.6U_2}[exp(\frac{-1.7U_2}{2.5k_BT})-exp(\frac{-U_2}{k_BT})]+\frac{3.8}{7.6U_3}[exp(\frac{-3.2U_3}{9.5k_BT})-exp(\frac{-1.7U_3}{2.5k_BT})]]}, \tag{3.44}$$

so, when $U_{1,2,3} \to 0$ then expanding exponetial terms

$$exp(\frac{U_1}{k_BT}) = 1+\frac{U_1}{k_BT}, \quad exp(\frac{-U_1}{k_BT}) = 1-\frac{U_1}{k_BT} \tag{3.45}$$

$$exp(\frac{1.7U_2}{2.5k_BT}) = 1+\frac{1.7U_2}{2.5k_BT}, \quad exp(\frac{U_2}{k_BT}) = 1+\frac{U_2}{k_BT}, \tag{3.46}$$

$$exp(\frac{-1.7U_2}{2.5k_BT}) = 1-\frac{1.7U_2}{2.5k_BT}, \quad exp(\frac{-U_2}{k_BT}) = 1-\frac{U_2}{k_BT}, \tag{3.47}$$

$$exp(\frac{3.2U_3}{9.5k_BT}) = 1+\frac{3.2U_3}{9.5k_BT}, \quad exp(\frac{1.7U_3}{2.5k_BT}) = 1+\frac{1.7U_3}{2.5k_BT}, \tag{3.48}$$

$$exp(\frac{-3.2U_3}{9.5k_BT}) = 1-\frac{3.2U_3}{9.5k_BT}, \quad exp(\frac{-1.7U_3}{2.5k_BT}) = 1-\frac{1.7U_3}{2.5k_BT}, \tag{3.49}$$

substituting this expanded term Eq. (3.45-3.49) in Eq. (3.44) after substitution finally we found,

$$D_{eff} = D_0. \tag{3.50}$$

Eq. (3.50) shows as under zero potential the effective vacancy diffusion coefficient and Einstein diffusion coefficient are equal then we can say that equation Eq. (3.43) is effective vacancy diffusion coefficient for six-jump cycle to [100]'bent' vacancy diffusion mechanism to NiAl binary alloy.

Then D_{eff} will be

$$D_{eff} = \frac{D_0\frac{U_0^2}{[k_BT]^2}}{[2[\frac{1.7}{7.6U_1}[exp(\frac{U_1}{k_BT})-1]-\frac{2.5}{7.6U_2}[exp(\frac{1.7U_2}{2.5k_BT})-exp(\frac{U_2}{k_BT})]-\frac{3.8}{7.6U_3}[exp(\frac{3.2U_3}{9.5k_BT})-exp(\frac{1.7U_3}{2.5}k_BT)]]} * \frac{1}{[2[\frac{-1.7}{7.6U_1}[exp(\frac{-U_1}{k_BT})-1]+\frac{2.5}{7.6U_2}[exp(\frac{-1.7U_2}{2.5k_BT})-exp(\frac{-U_2}{k_BT})]+\frac{3.8}{7.6U_3}[exp(\frac{-3.2U_3}{9.5k_BT})-exp(\frac{-1.7U_3}{2.5k_BT})]]}. \tag{3.51}$$

Generally we find that Eq. (3.51) is D_{eff} for six jump cycle to [100]'bent' direction Vacancy diffusion mechanism of NiAl binary alloy. Now let as insert some parameters in

Eq. (3.51) from Kristen A. Marino and Emily A. Carter paper from Table IV, and we are taking the value of D_0 and the migration energy for the given two temperature for 1200K and 1500K. The migration energy must be convert from electron volt to Joule(J). so, $1e = 1.602176487 \times 10^{-19}$J

$$U_1 = 2.87ev = 4.60 \times 10^{-19}J,$$
$$U_2 = 1.14ev = 2.26 \times 10^{-19}J,$$
$$U_3 = 0.68ev = 1.09 \times 10^{-19}J,$$

and also using the above energies we can find the effective vacancy diffusion coefficient for [100]'bent' six-jump cycle vacancy diffusion mechanism of NiAl binary alloy(D_{eff}).

Table 3.3: Six-jump cycle to [100] 'bent' vacancy diffusion mechanism: migration energies(E_m), pre-exponential factors D_0 for 1200K and 1500 K.and our result D_{eff}

	$T = 1200K$	$T = 1500K$
U_1	4.60×10^{-19}J	4.60×10^{-19}J
U_2	2.26×10^{-19}J	2.26×10^{-19}J
U_3	1.09×10^{-19}J	1.09×10^{-19}J
D_0	$1.21 \times 10^{-5}\ m^2\ s^{-1}$	$1.49 \times 10^{-5}\ m^2\ s^{-1}$
$\frac{D_{eff}}{D_0}$	1.75×10^{-9}	2.38×10^{-7}
D_{eff}	$2.12 \times 10^{-14}\ m^2\ s^{-1}$	$3.54 \times 10^{-12}\ m^2\ s^{-1}$

3.3.2 six-jump cycle for [110] vacancy diffusion Mechanism

In [110] six-jump cycle vacancy diffusion mechanism as shown in Fig 1.3. Kristen group found that Fig. 3.8 the energy profile of vacancy(migration energy E_m) jump for the three potential picks reported in [1]. The MEP Fig. 3.6 indicates that the migration energy at a temperature of 1200K and 1500K along the reaction coordinate.

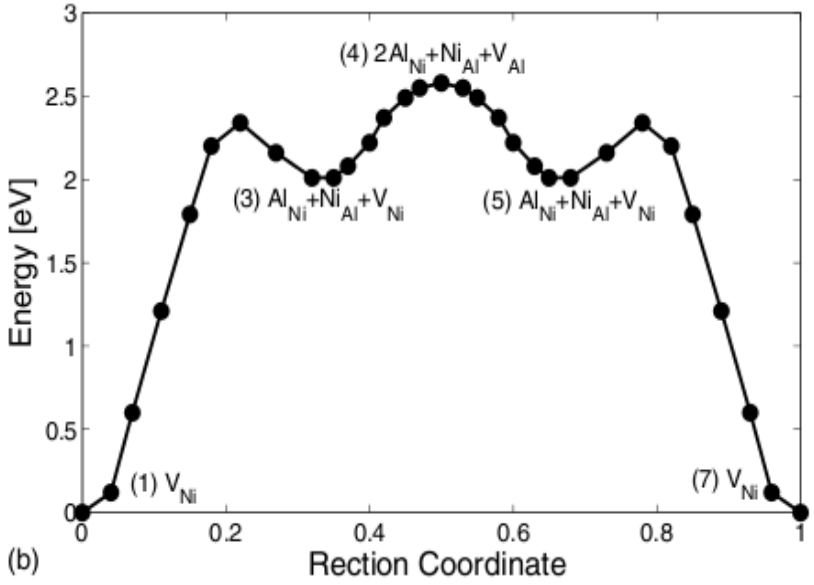


Figure 3.8: MEP for the six-jump cycle to [110] direction vacancy diffusion for the NiAl binary alloy [1]

The total length $L = 7.6$ lattice spacing for six-jump cycle to [110] vacancy diffusion mechanism for Fig. 3.7 and the spacing length for each length $L_1, L_2, L_3, L_4, L_5, L_6$ are identical to the [100] bent direction vacancy diffusion.

so, the spacing length for $L_1, L_2, L_3, L_4, L_5, L_6$ as follows:

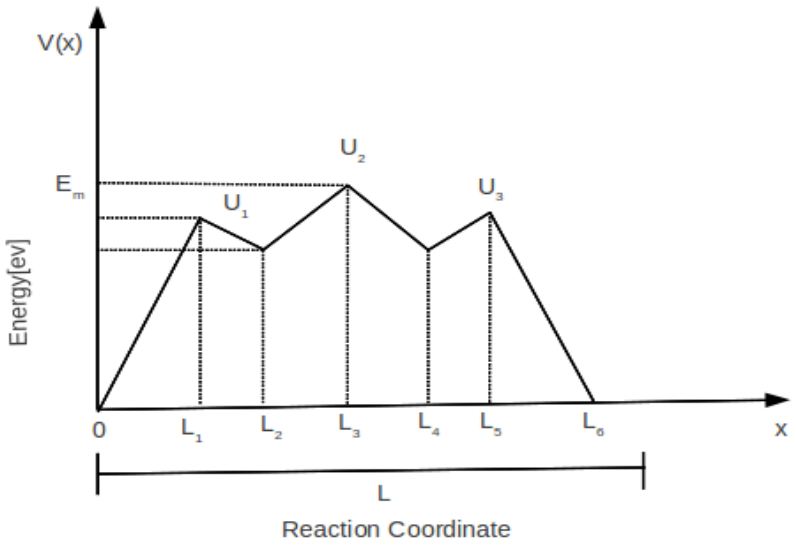


Figure 3.9: MEP of the six-jump cycle [110] vacancy diffusion along a periodic piece wise linear potential energy

$$L_1 = \frac{1.7}{7.6}L, \qquad L_2 = \frac{2.5}{7.6}L,$$
$$L_3 = \frac{3.8}{7.6}L, \qquad L_4 = \frac{5.1}{7.6}L,$$
$$L_5 = \frac{5.9}{7.6}L, \qquad L_6 = L,$$

The piece-wise linear potential with in the interval of $0 < x < L$ is given

$$V(x) = \begin{cases} \frac{U_1 x}{L_1} & for \quad 0 < x < L_1 = L_5 < x < L_6 \\ U_2 + \frac{U_2 L_1}{L_2} - \frac{U_2 x}{L_2} & for \quad L_1 < x < L_2 = L_4 < x > L_5 \\ \frac{U_3 L_1}{L_2} + \frac{U_3 L_2}{L_3} - \frac{U_3 x}{L_3} & for \quad L_2 < x < L_3 = L_3 < x > L_4 \end{cases} \tag{3.52}$$

The over all calculation for the effective vacancy diffusion coefficient to six-jump cycle [110] direction vacancy diffusion for NiAl binary alloy is the same as for the six-jump cycle [100] bent direction vacancy diffusion for NiAl binary alloy. So, it is enough putting the result of D_{eff}. The only difference is their migration energy E_m and preexponential

factor D_0.

$$D_{eff} = \frac{D_0 \frac{U_0^2}{[k_B T]^2}}{[2[\frac{1.7}{7.6U_1}[exp(\frac{U_1}{k_B T}) - 1] - \frac{2.5}{7.6U_2}[exp(\frac{1.7U_2}{2.5k_B T}) - exp(\frac{U_2}{k_B T})] - \frac{3.8}{7.6U_3}[exp(\frac{3.2U_3}{9.5k_B T}) - exp(\frac{1.7U_3}{2.5k_B T})]]} * \frac{1}{[2[\frac{-1.7}{7.6U_1}[exp(\frac{-U_1}{k_B T}) - 1] + \frac{2.5}{7.6U_2}[exp(\frac{-1.7U_2}{2.5k_B T}) - exp(\frac{-U_2}{k_B T})] + \frac{3.8}{7.6U_3}[exp(\frac{-3.2U_3}{9.5k_B T}) - exp(\frac{-1.7U_3}{2.5k_B T})]]}. \tag{3.53}$$

Eq. (3.53) is the effective vacancy diffusion coefficient for six-jump cycle [110] direction vacancy diffusion for NiAl binary alloy. Inserting the value the migration energy and D_0 will find D_{eff}. First let as change the migration energy from Electron volt(ev) to the joule(J). $1ev = 1.602176487 \times 10^{-19}$J

$$U_1 = 2.34ev = 3.75 \times 10^{-19}J,$$
$$U_2 = 0.56ev = 8.97 \times 10^{-20}J,$$
$$U_3 = 0.33ev = 5.29 \times 10^{-20}J,$$

Using the above migration energy values and by substituting in Eq. (3.53) we can find the effective vacancy diffusion coefficient for six-jump cycle [110] direction vacancy diffusion mechanism at temperature of 1200K and 1500K.

Table 3.4: Six-jump cycle to [110] vacancy diffusion mechanism: migration energies(E_m), pre-exponential factors D_0 for 1200K and 1500 K.and our result D_{eff}

	$T = 1200K$	$T = 1500K$
U_1	3.75×10^{-19}J	3.75×10^{-19}J
U_2	8.97×10^{-20}J	8.97×10^{-20}J
U_3	5.29×10^{-20}J	5.29×10^{-20}J
D_0	$0.64 \times 10^{-5}\ m^2\ s^{-1}$	$0.74 \times 10^{-5}\ m^2\ s^{-1}$
$\frac{D_{eff}}{D_0}$	8.01×10^{-8}	4.35×10^{-6}
D_{eff}	$5.13 \times 10^{-13}\ m^2\ s^{-1}$	$3.22 \times 10^{-11}\ m^2\ s^{-1}$

Chapter 4

Summary And Conclusion

In this work, we have considered three types of vacancy diffusion mechanisms in the NiAl binary alloy. The first mechanism is next nearest neighbor(NNN), the second triple defect mechanism and the third one is six-jump cycle in [110] and [100]'bent' vacancy diffusion mechanism. We evaluated the diffusion coefficient along the three possible paths assuming each path separately at two high temperature values.

Accordingly, we summarized our results in tabular form in Table.4.1. The result vividly show that the triple defect path has the largest D_{eff} value of all the other while the six-jump cycle for [100]'bent' has least value. This variation manly occur due the different migration energy values. To the best of our knowledge this result is reported here for the first time. We hope this could be checked experimentally in the future.

Table 4.1: Comparison table for the three vacancy diffusion of NiAl binary alloy

Vacancy Diffusion type	Temperature(K)	$\frac{D_{eff}}{D_0}$	$D_{eff}(m^2\ s^{-1})$
Triple defect	1200K	0.03	1.22×10^{-7}
	1500K	0.09	3.91×10^{-7}
Six-jump cycle for[110] direction	1200K	8.01×10^{-8}	5.13×10^{-13}
	1500K	4.35×10^{-6}	3.22×10^{-11}
NNN Ni-jump	1200K	2.66×10^{-8}	1.70×10^{-13}
	1500K	2.35×10^{-6}	1.86×10^{-11}
Six-jump cycle for[100]'bent'	1200K	1.75×10^{-9}	2.12×10^{-14}
	1500K	2.38×10^{-7}	3.54×10^{-12}

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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.

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Place and time of submission: Addis Ababa University, June 2011

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

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