Effect of an intermediate metastable state

on the escape rate of a Brownian particle

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ABSTRACT

We considered a Brownian particle trying to escape from a single-well potential with a run away on one side aided by the thermal energy of the medium in which it is moving. The analytical expression of escape rate of a Brownian particle is calculated for a model original potential (inverted N) and for a modified model potential having an intermediate metastable state using supersymmetric and mean first passage time methods. The modified model potential is parameterized by location and slope of the intermediate metastable state. We compared the escape rate for the modified model potential with that for the original a model potential and found that their ratio takes optimum value at a particular position of the intermediate state. In addition, this ratio takes optimum value at a particular slope value of the intermediate state.

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CHAPTER 1

Introduction

Consider a Brownian particle in one dimension trying to escape from a single-well potential with a runaway on one side aided by the thermal energy of the medium in which it is moving. The rate of escape of the particle for a high barrier, low noise limit (U >>k_B T) is proportional to Exp$\left[\frac{-U}{k_B T}\right]$ where k_B is Boltzmann's constant, T is temperature of the medium and U is height of the barrier over which the particle attempts to escape. Other parameters affecting the escape rate and which enter as part of the proportionality constant are friction of the medium (γ), distance between the potential minimum A and potential maximum B as well as the potential profile around points A and B [see Fig. 1.1].

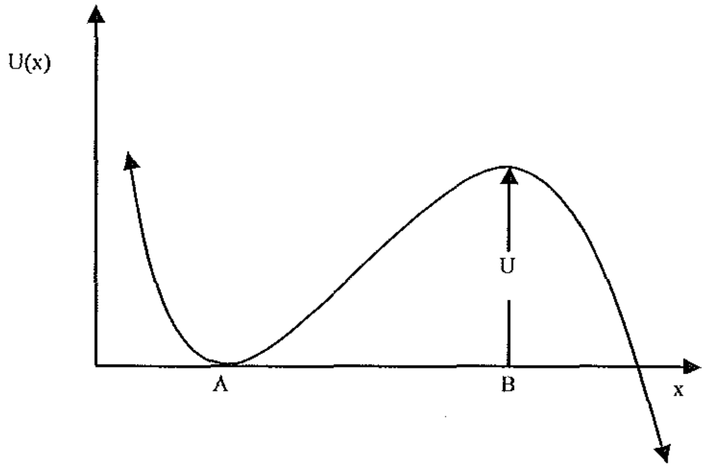

Figure 1.1: Original potential: single-well potential with a runaway on one side

This is a classic problem that appears in all processes having thermally activated kinetics such as chemical reactions and phase transitions. It was first addressed and tackled by Kramers almost sixty years ago [1] and is still being refined and extended. A large amount of literature exists on this classic problem and its extensions [2,3].

Recently, it is found that changing the smooth potential profile between points A and B so as to have one or more metastable states in between, while maintaining U and the distance between A and B fixed, increases the escape rate [4]. Our work aims at carefully studying this fact. In particular, we want to see how having a single metastable sate between points A and B affects the escape rate [see Fig. 1.2]. In other words, we want to compare the escape rate for the modified potential with that of the escape rate for the original potential.

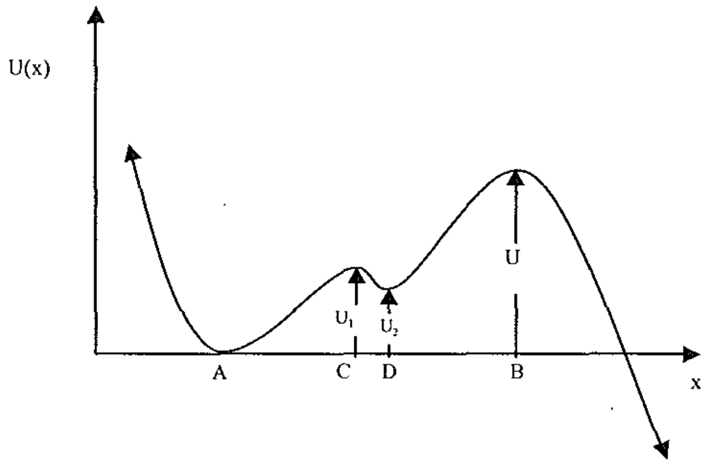

Figure 1.2: Modified potential having a single intermediate metastable state

Two quantities describing the intermediate metastable state of the modified potential are the two parameters characterizing it. One is location of the metastable state with respect to the point A or B. The other is the parameter that controls the local barrier height of the metastable state.

In order to get analytical expressions for the two escape rates, we take piecewise linear potentials. The parameter characterizing the location of the metastable state will be taken as the distance of its minimum from B. On the other hand, the parameter characterizing the local barrier height of the metastable state will be related to the magnitude of the slope of the piecewise linear potential profile found between points A and B. Eventhough these model potentials are very simple and idealized, the essential results one gets will not be different from those when one takes realistic model potentials.

The rest of this thesis is organized as follows. Chapter 2 introduces two methods of finding escape rate: the supersymmetric (SUSY) method and the mean first passage time (MFPT) method. Using these two methods, chapter 3 finds the expressions for the escape rate for the model original potential; i.e. an inverted N-shaped potential. In chapter 4, the escape rate for the modified potential is found once again using the two methods. In chapter 5, the expression for the factor by which the escape rate has improved due to the presence of the intermediate metastable state is analyzed as a function of the two parameters. Chapter 6 gives a summary of the results and a conclusion.

CHAPTER 2

Two Methods of Finding Escape Rate

In the next two sections we will present two methods of finding the escape rate of a Brownian particle in trying to cross a potential barrier. In the first section we will present the supersymmetric method that has been recently introduced [5] while in the second section we will present a method of finding mean first passage time to cross the barrier which is equal to the inverse of the escape rate. In both cases we start from the Fokker-Planck (FP) equation which governs the particle's motion. We confine our problem to the high friction limit where the FP equation takes the familiar Smoluchowski equation,

$$\frac{\partial p(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x} + \beta U'(x)\right] p(x,t), \tag{2.1}$$

where, p(x,t) is the time dependent probability density associated with the particle position, D is the diffusion coefficient, $\beta = \frac{1}{k_B T}$ and $U' = \frac{dU}{dx}$.

2.1 The Supersymmetric (SUSY) Method

The SUSY method is one of the methods by which we can calculate the escape rate for idealized potentials. The method involves converting the Smoluchowski equation (SE) to Euclidean Schrodinger equation and solve an eigenvalue equation to get the escape rate. We briefly summarize the method similar to that presented by Schonhammer [6].

We use the ansatz which puts the spacial and the time components of the probability density as a product

$$p(x,t) = \varphi(x) e^{\frac{-\beta U(x)}{2}} e^{-\lambda t} \tag{2.2}$$

and convert the SE, Eq. (2.1), to a time independent Euclidean Schrodinger equation for $\varphi(x)$:

$$H_+ \varphi_+(x) = E_+ \varphi_+(x) \tag{2.3}$$

with, $H_+ = A^+ A$ being positive semi-definite, where $E_+ = \frac{\lambda}{D}$

$$A = \frac{d}{dx} + \frac{1}{2}\beta U'(x), \tag{2.4}$$

and

$$A^+ = -\frac{d}{dx} + \frac{1}{2}\beta U'(x). \tag{2.5}$$

Here $\varphi_+(x)$ is the same as $\varphi(x)$.

This Hamiltonian H_+ corresponds to the motion of a particle in the potential $V_+(x)$

$$V_+(x) = \left[\frac{1}{2}\beta U'(x)\right]^2 - \frac{1}{2}\beta U''(x). \tag{2.6}$$

For a high potential barrier, the escape rate is determined by the smallest non-zero eigenvalue, $\lambda_1 = DE_+^1$, of the SE where E_+^1 is the eigenvalue of the first excited state of Eq. (2.3). The first excited state $\varphi_+^1(x)$ of the Hamiltonian H_+ is degenerate with the ground state $\varphi_-^0(x)$ of the Hamiltonian $H_- = AA^+$ so that

$H_-\varphi_-^0 = E_-^0\varphi_-^0$ with $E_-^0 = E_+^1$ and the 'supersymmetric partner potential', $V_-(x)$, is given by

$$V_-(x) = \left[\frac{1}{2}\beta U'(x)\right] + \frac{1}{2}\beta U''(x). \tag{2.7}$$

The problem thus boils down to finding the ground state eigenvalue E_-^0 of this 'partner' potential, so that the escape rate becomes

$$\lambda_1 = DE_-^0 \tag{2.8}$$

2.2 The Mean First Passage Time (MFPT) Method

This method poses the problem of escape rate of a Brownian particle in an inverse way. Consider the particle placed at $x_1$in the single-well potential with a runaway on one side as shown in Fig. 2.1. The problem is to find the mean time, T(1→ 2), taken by the particle to reach point 2 for the first time. This time is usually called *mean first passage time* (MFPT). Point 2 is taken to be far away from the barrier top point 0. Once this value is found, the escape rate is simply equivalent to its inverse. To find T(1→ 2) we use the backward FP equation. (Since the backward FP equation is not commonly encountered, its derivation is given in the Appendix A). We more or less follow Gardiner's approach to the problem of mean first passage time [7].

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

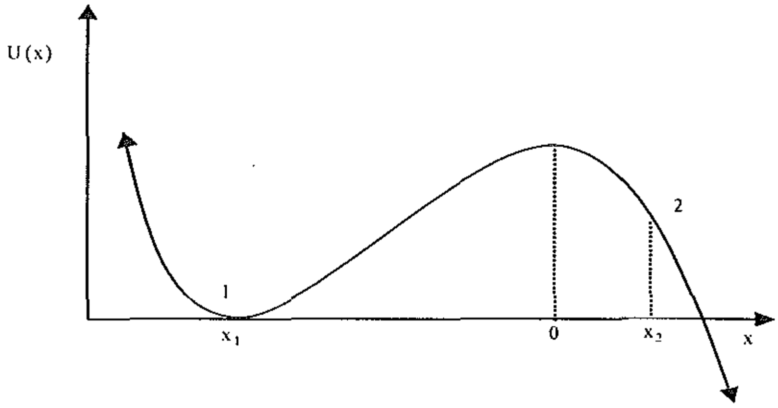

Figure 2.1: Original potential with a runaway on one side

x_1. That is,

$$F(x_1, t) = \int_{-\infty}^{x_2} p(x, t \mid x_1, 0) dx \tag{2.9}$$

where $p(x, t \mid x_1, 0)$ is the probability density of finding the particle at position x at time t given that it was initially at position x_1. $p(x, t \mid x_1, 0)$ is governed by the Smoluchowski equation, Eq.(2.1), and its corresponding backward Fokker-Planck equation can be written as

$$\frac{\partial p(x, t \mid x_1, 0)}{\partial t} = D \frac{\partial}{\partial x_1} \left[\frac{\partial}{\partial x_1} - \beta U'(x_1) \right] p(x, t \mid x_1, 0). \tag{2.10}$$

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

$$\frac{\partial F(x_1, t)}{\partial t} = D \frac{\partial}{\partial x_1} \left[\frac{\partial}{\partial x_1} - \beta U'(x_1) \right] F(x_1, t). \tag{2.11}$$

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

$$T(1 \to 2) = \int_{0}^{\infty} t P_{x_1}(t) dt. \tag{2.12}$$

On the other hand,

$$P_{x_1}(t)dt = F(x_1, t) \int_{x_2}^{\infty} dy \int_{-\infty}^{x_2} p(y, t + dt \mid x, t) dx \tag{2.13}$$

which implies,

$$P_{x_1}(t)dt = F(x_1, t) \left[1 - \int_{-\infty}^{x_2} dy \int_{-\infty}^{x_2} p(y, t + dt \mid x, t) dx \right] \tag{2.14}$$

or

$$P_{x_1}(t)dt = F(x_1, t) - F(x_1, t + dt) = \frac{-\partial F(x_1, t)}{\partial t} dt. \tag{2.15}$$

Hence,

$$T(1 \to 2) = -\int_{0}^{\infty} t \frac{\partial F(x_1, t)}{\partial t} dt = \int_{0}^{\infty} F(x_1, t) dt, \tag{2.16}$$

since $F(x_1, \infty) = 0$. Noting also that $F(x_1, 0) = 1$. This implies

$$\int_{0}^{\infty} \frac{\partial F(x_1, t)}{\partial t} dt = F(x_1, \infty) - F(x_1, 0) = -1. \tag{2.17}$$

From Eqs.(2.11), (2.16) and (2.17) we get

$$D \frac{\partial}{\partial x_1} \left[\frac{\partial}{\partial x_1} - \beta U'(x_1) \right] T(1 \to 2) = -1. \tag{2.18}$$

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

$$T(1 \to 2) = \frac{1}{D}\int_{x_1}^{x_2} dx \exp[\beta U(x)] \int_{-\infty}^{x} \exp[-\beta U(y)]dy. \qquad (2.19)$$

When the barrier separating the two states is high compared to the thermal energy, Eq. (2.19) approximately becomes,

$$T(1 \to 2) \cong \frac{1}{D}\left[\int_{-\infty}^{x} \exp[-\beta U(y)]dy\right]\int_{x_1}^{x_2} \exp[\beta U(x)]dx. \qquad (2.20)$$

Since the escape rate λ of the particle is the inverse of its mean first passage time, the expression for the escape rate is then given by

$$\lambda = \frac{D}{\left[\int_{-\infty}^{0} \exp[-\beta U(y)]dy\right]\int_{x_1}^{x_2} \exp[\beta U(x)]dx}. \qquad (2.21)$$

The two definite integrals appearing in the expression for λ can be evaluated when the potential is simple. In the next two chapters we will use these two methods to get analytic expression for the escape rates for the original model potential as well as for the corresponding modified potential.

CHAPTER 3

Escape rate for a model potential

In this chapter we take a simple model potential for a single-well potential with a runaway on one side. The escape rate of a Brownian particle from the potential well will be evaluated using both methods presented in the previous chapter.

The model potential is a piecewise linear having a shape of an inverted N (see Fig.3.1). We take the slope of the straight lines to have the same magnitude. The model potential can then be characterized by the magnitude of the barrier height, U_0 and by the width of the potential, L.

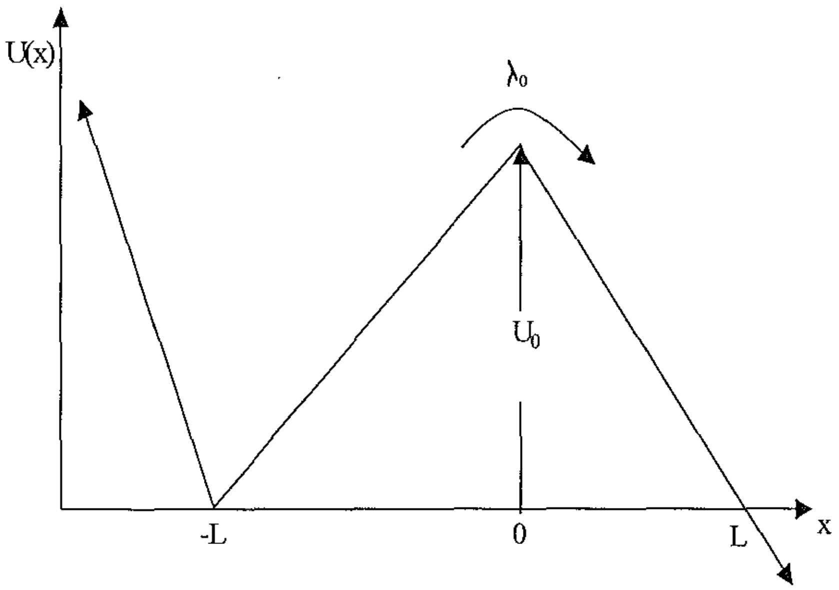

Figure 3.1: Model of original potential: single-well potential with a runaway on one side (inverted N), λ_0 is the escape rate

3.1 Evaluation of escape rate using SUSY method

As discussed in the previous chapter, we need to construct the supersymmetric partner potential and obtain its ground state eigenvalue. The SUSY partner potential defined as

$$V_-(x) = \left[\frac{\beta U'(x)}{2}\right]^2 + \frac{1}{2}\beta U''(x), \tag{3.1}$$

takes the following form for our model potential:

$$V_-(x) = \nu_0^2 + 2\nu_0[\delta(x+L) - \delta(x)] \tag{3.2}$$

where $\nu_0 = \frac{\beta U_0}{2L}$. Note that the potential $V_-(x)$ has one repulsive and one attractive delta-potential superimposed over a constant potential (see Fig. 3.2).

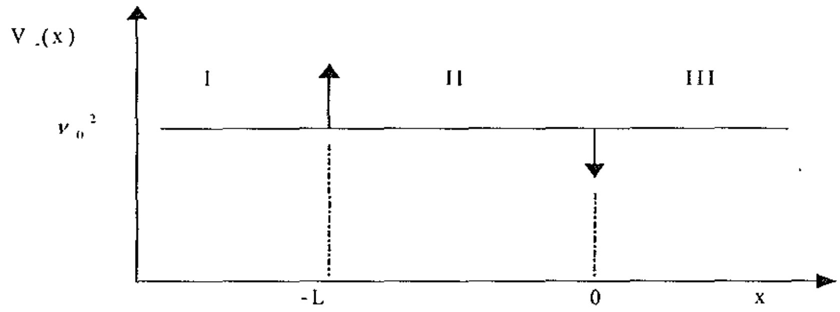

Figure 3.2: Plot of partner potential V_(x)

The corresponding Hamiltonian, H_-, is given by

$$H_- = -\frac{d^2}{dx^2} + \nu_0^2 + 2\nu_0[\delta(x+L) - \delta(x)] \tag{3.3}$$

so that the Schrodinger equation corresponding to the ground state wave function, $\varphi_-^0(x)$, is

$$H_{-}\varphi_{-}^{0}(x) = E_{-}^{0}\varphi_{-}^{0}(x). \tag{3.4}$$

The ground state wave function is of the form $ae^{-kx} + be^{kx}$ peaked around the positions of the delta potentials. We identify three regions I, II and III demarcated by the two delta potentials (see Fig.3.2) and express the ground state wave function in each region as follows :

$$\varphi_{-}^{(0)}(x) = \begin{cases} \textit{Region I}, \ \varphi_{I}(x) = Ae^{-k(x+L)} + Be^{k(x+L)}, & \text{for x} \leq -L \\ \textit{Region II}, \ \varphi_{II}(x) = Ce^{-kx} + De^{kx}, & \text{for -L } \leq x \leq 0 \\ \textit{Region III}, \ \varphi_{III}(x) = Fe^{-kx} + Ge^{kx}, & \text{for x} \geq 0 \end{cases} \tag{3.5}$$

To relate the coefficients, A, B, ..., we use boundary conditions. Let us first start relating coefficients C, D of $\varphi_{II}(x)$ with coefficients A, B $\varphi_{I}(x)$. First of all, since the wave function is single valued

$$\varphi_{II}(-L) = \varphi_{I}(-L). \tag{3.6}$$

This implies that

$$Ce^{kL} + De^{-kL} = A + B. \tag{3.7}$$

Next, integrating the Schrodinger equation, Eq.(3.4), over an infinitesimal interval ε around x = -L and taking the limit as $\varepsilon \rightarrow 0$, we get

$$\varphi_{II}'(-L) - \varphi_{I}'(-L) = 2\nu_{0}\varphi_{I}(-L), \tag{3.8}$$

where prime stands for derivative with respect to x. This implies that

$$-kCe^{kL} + kDe^{-kL} + Ak - Bk = 2\nu_0 (A + B) . \tag{3.9}$$

From Eqs.(3.7) and (3.9) we solve for C and D in terms of A and B and put the result as a matrix equation:

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} \left(1 - \frac{\nu_0}{k}\right) e^{-kL} & \left(-\frac{\nu_0}{k}\right) e^{-kL} \\ \left(\frac{\nu_0}{k}\right) e^{kL} & \left(1 + \frac{\nu_0}{k}\right) e^{kL} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} . \tag{3.10}$$

Using the same procedure as above to relate coefficients F, G of $\varphi_{III}(x)$ with coefficients C, D of $\varphi_{II}(x)$, we get

$$\begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} 1 + \frac{\nu_0}{k} & \frac{\nu_0}{k} \\ -\frac{\nu_0}{k} & 1 - \frac{\nu_0}{k} \end{pmatrix} \begin{pmatrix} C \\ D \end{pmatrix} . \tag{3.11}$$

Using Eq.(3.10) in (3.11) coefficients F, G are related to the coefficients A, B by the matrix equation

$$\begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} \left(1 - \frac{\nu_0^2}{k^2}\right) e^{-kL} + \left(\frac{\nu_0}{k}\right)^2 e^{kL} & \frac{\nu_0}{k}\left(1 + \frac{\nu_0}{k}\right)\left(e^{kL} - e^{-kL}\right) \\ \frac{\nu_0}{k}\left(1 - \frac{\nu_0}{k}\right)\left(e^{kL} - e^{-kL}\right) & \left(\frac{\nu_0}{k}\right)^2 e^{-kL} + \left(1 - \frac{\nu_0^2}{k^2}\right) e^{kL} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} . \tag{3.12}$$

Since the ground state wave function is *bounded*, then, the coefficients A and G must be equal to zero. Hence, the matrix equation Eq.(3.12) can be written as

$$\begin{pmatrix} F \\ 0 \end{pmatrix} = \begin{pmatrix} \omega_{11} & \omega_{12} \\ \omega_{21} & \omega_{22} \end{pmatrix} \begin{pmatrix} 0 \\ B \end{pmatrix} . \tag{3.13}$$

This implies that

$$0 = \omega_{22} B . \tag{3.14}$$

This equation has nontrivial solution provided $\omega_{22} = 0$. That is,

$$\omega_{22} = \left(\frac{\nu_0}{k}\right)^2 e^{-kL} + \left(1 + \frac{\nu_0}{k}\right)\left(1 - \frac{\nu_0}{k}\right) e^{kL} = 0. \tag{3.15}$$

Rearranging Eq. (3.15), we get

$$k^2 = \nu_0^2 \left(1 - e^{2kL}\right). \tag{3.16}$$

On the other hand, substituting one of the expressions for the ground state wave function from Eq. (3.5) in the Schrodinger equation, Eq. (3.4), we find that

$$k^2 = \nu_0^2 - E_-^0. \tag{3.17}$$

Using Eq.(3.17) in Eq.(3.16) and noting that for high barrier ($U_0 >> k_B T$) $kL \sim \frac{\beta U_0}{2}$, we find the ground state eigenvalue E_-^0 to be

$$E_-^0 = \left(\frac{\beta U_0}{2L}\right)^2 e^{-\beta U_0}. \tag{3.18}$$

Hence, the escape rate which is (see Eq.(2.8)), $\lambda_0 = DE_-^0$, will then be given by

$$\lambda_0 = D\left(\frac{\beta U_0}{2L}\right)^2 e^{-\beta U_0}. \tag{3.19}$$

3.2 Evaluation of Escape Rate Using MFPT Method

In this section we will use the method of mean first passage time to find, once again, the value for the escape rate for the model potential shown in Fig. 3.1.

In Chapter two, we have already derived the expression for the escape rate (see Eq. (2.20)). For our model potential shown in Fig. 3.1, the expression for the escape rate becomes

$$\lambda_0' = \frac{D}{\left[\int\limits_{-\infty}^{0} \exp[-\beta U(y)]dy\right] \int\limits_{-L}^{\infty} \exp[\beta U(x)]dx}. \tag{3.20}$$

The potential profile for our model potential is given as

$$U(x) = \begin{cases} -S_0 x - U_0 \,, & for \quad x \leq -L \\ S_0 x + U_0 \,, & for \quad -L \leq \ x \leq 0 \\ -S_0 x + U_0 \,, & for \quad x \geq 0 \end{cases} \tag{3.21}$$

where $S_0 = \frac{U_0}{L}$. Let us evaluate the two definite integrals. That is,

$$\begin{aligned} \int\limits_{-\infty}^{0} e^{-\beta U(x)}dx &= \int\limits_{-\infty}^{-L} e^{\beta(S_0 x + U_0)}dx + \int\limits_{-L}^{0} e^{-\beta(S_0 x + U_0)}dx \\ &= \frac{2L}{\beta U_0} - \left(\frac{L}{\beta U_0}\right) e^{-\beta U_0}, \end{aligned} \tag{3.22}$$

while

$$\begin{aligned} \int\limits_{-L}^{\infty} e^{\beta U(x)}dx &= \int\limits_{-L}^{0} e^{\beta(S_0 x + U_0)}dx + \int\limits_{0}^{\infty} e^{\beta(-S_0 x + U_0)}dx \\ &= \frac{2L}{\beta U_0} e^{\beta U_0} - \frac{L}{\beta U_0}. \end{aligned} \tag{3.23}$$

The product of the two integrals is

$$\left(\frac{2L}{\beta U_0}\right) e^{\beta U_0} \left(1 - e^{-\beta U_0} + e^{-2\beta U_0}\right). \tag{3.24}$$

For high barrier

$$\left[\int\limits_{-\infty}^{0} \exp[-\beta U(y)]dy\right] \int\limits_{-L}^{\infty} \exp[\beta U(x)]dx = \left(\frac{2L}{\beta U_0}\right)^2 e^{\beta U_0}. \tag{3.25}$$

Hence, the escape rate becomes

$$\lambda_0' = D \left(\frac{\beta U_0}{2L} \right)^2 e^{-\beta U_0} \tag{3.26}$$

In the next chapter we take a modified model potential and evaluate the escape rate using the two methods.

CHAPTER 4

Escape Rate For a Modified Model Potential

In chapter 3 we calculated the escape rate of a Brownian particle from a model potential using supersymmetric and mean first passage time methods. In this chapter we consider a modified model potential having an intermediate metastable state between the potential minimum (*at* $x = -L$) and the potential maximum (*at* $x = 0$) of the well as shown in Fig. 4.1. The escape rate of a Brownian particle from the modified model potential well will be evaluated using both methods presented in chapter two.

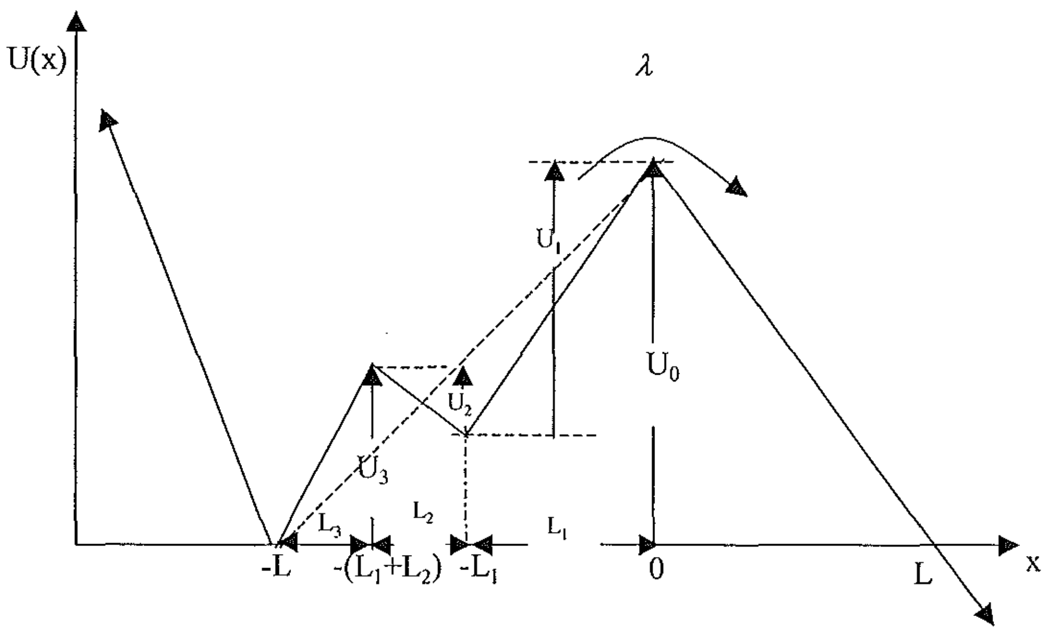

Figure 4.1: Modified model potential with a single intermediate metastable state

The modified model potential is a piecewise linear, characterized by the magnitude of the potential barriers U_0, U_1, U_2, U_3, and by the widths of the potential barriers L, L_1, L_2, L_3,. We simplify the model by taking the three straight lines found between $x = -L$ and $x = 0$ to have the same magnitude of slope.

So, $L_1 + L_2 + L_3 = L$

$U_1 - U_2 + U_3 = U_0$

and $\frac{U_1}{L_1} = \frac{U_2}{L_2} = \frac{U_3}{L_3}$.

We specify the position of the *intermediate* state interms of the scaled L_1, i.e. $L_1 = yL$. On the other hand, the slope S can also be scaled such that $S = zS_0$ where $S_0 = \frac{U_0}{L}$. Hence, y and z are the parameter characterizing the modified model potential. In terms of these parameters y and z,

$$\begin{aligned} L_1 &= Ly \\ L_2 &= \tfrac{L}{2}(1 - \tfrac{1}{z}) \\ L_3 &= \tfrac{L}{2}(1 + \tfrac{1}{z}) - Ly, \end{aligned} \tag{4.1}$$

while

$$\begin{aligned} U_1 &= U_o zy \\ U_2 &= \tfrac{U_0}{2}(z - 1) \\ U_3 &= \tfrac{U_0}{2}(z + 1) - U_o zy, \end{aligned} \tag{4.2}$$

4.1 Escape rate from a modified model potential using SUSY Method

As discussed in chapter 2, we need to construct the supersymmetric partner potential and obtain its ground state eigenvalue. The SUSY partner potential defined as

$$V_{-}(x) = \left[\frac{\beta U'(x)}{2}\right]^2 + \frac{1}{2}\beta U''(x), \tag{4.3}$$

takes the following form for our modified model potential:

$$V_{-}(x) = \begin{cases} \nu_0^2 \ , & for, x < -L \ and \ x > 0 \\ \nu^2 + (\nu+\nu_0)\,\delta\,(x+L) - 2\nu\delta\,(x+L_1+L_2) & \\ +2\nu\delta\,(x+L_1) - (\nu+\nu_0)\,\delta\,(x)\ , & \text{for -L} \leq \text{ x } \leq \ 0 \end{cases} \tag{4.4}$$

where $\nu_0 = \frac{\beta U_0}{2L}$, $\nu = \frac{\beta S}{2}$, $S = \frac{U_1}{L_1} = \frac{U_2}{L_2} = \frac{U_3}{L_3}$. The potential V$_{-}(x)$ has two repulsive and two attractive delta-potentials superimposed over a constant potential (see Fig. 4.2).

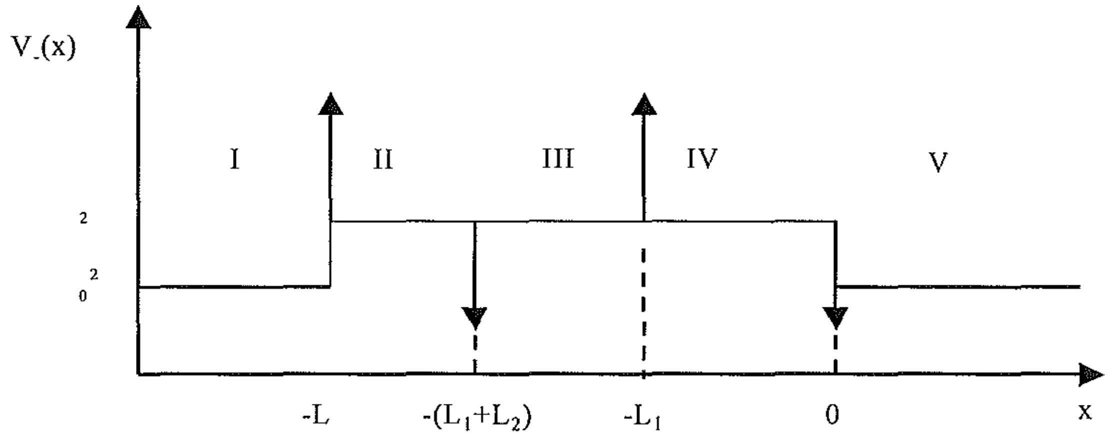

Figure 4.2: Plot of partner potential

The corresponding Hamiltonian, H$_{-}$, is given by

$$H_{-} = -\frac{d^2}{dx^2} + \nu_0^2 \ , \qquad for, x < -L \ and \ x > 0 \tag{4.5}$$

and

$$H_{-}=\begin{cases} -\frac{d^2}{dx^2}+\nu^2+(\nu+\nu_0)\,\delta\,(x+L)-2\nu\delta\,(x+L_1+L_2) \\ +2\nu\delta\,(x+L_1)-(\nu+\nu_0)\,\delta\,(x)\,, \quad for-L\leq x\leq 0 \end{cases} \tag{4.6}$$

so that the Schrodinger equation corresponding to the ground state wave function, $\varphi_{-}^{0}(x)$, is

$$H_{-}\varphi_{-}^{0}(x)=E_{-}^{0}\varphi_{-}^{0}(x) \tag{4.7}$$

The ground state wave function is of the form $ae^{-qx}+be^{qx}$ peaked around the position of delta-potentials. We identify five regions I, II, III, IV, and V demarcated by the four delta potentials (see Fig. 4.2) and express the ground state wave function in each region as follows:

$$\varphi_{-}^{0}(x)=\begin{cases} RegionI,\varphi_{I}(x)=Ae^{-k(x+L)}+Be^{k(x+L)} \\ RegionII,\varphi_{II}(x)=Ce^{-q(x+L_1+L_2)}+De^{q(x+L_1+L_2)} \\ RegionIII,\varphi_{III}(x)=Fe^{-q(x+L_1)}+Ge^{q(x+L_1)} \\ RegionIV,\varphi_{IV}(x)=Ie^{-qx}+Je^{qx} \\ RegionV,\varphi_{V}(x)=Pe^{-kx}+Qe^{kx} \end{cases} \tag{4.8}$$

where $k=\left(\nu_0^2-E_{-}^{0}\right)^{\frac{1}{2}}$ and $q=\left(\nu^2-E_{-}^{0}\right)^{\frac{1}{2}}$. To relate the coefficients, A, B, ..., we use boundary conditions. Let us first start relating coefficients C, D of $\varphi_{II}(x)$ with coefficients A, B of $\varphi_{I}(x)$. First of all, since the wave function is single valued

$$\varphi_{II}(-L)=\varphi_{I}(-L). \tag{4.9}$$

This implies that

$$Ce^{qL_3}+De^{-qL_3}=A+B. \tag{4.10}$$

Next, integrating the Schrodinger equation, Eq.(4.7), over an infinitesimal interval ε around x = -L and taking the limit as $\varepsilon \to 0$, we get

$$\varphi'_{II}(-L) - \varphi'_{I}(-L) = (\nu + \nu_0)\, \varphi_I(-L). \tag{4.11}$$

This implies that

$$-Cqe^{qL_3} + Dqe^{-qL_3} + Ak - kB = (\nu + \nu_0)\,(A + B)\,. \tag{4.12}$$

From Eq.(4.10) and Eq.(4.12) we solve for C and D in terms of A and B and put the result as a matrix equation:

$$\begin{pmatrix} C \\ D \end{pmatrix} = \mathrm{M}_1 \begin{pmatrix} A \\ B \end{pmatrix}, \tag{4.13}$$

where

$$\mathrm{M}_1 = \begin{pmatrix} \left(\frac{1}{2} + \frac{k}{2q} - \frac{\nu}{2q} - \frac{\nu_0}{2q}\right) e^{-qL_3} & \left(\frac{1}{2} - \frac{k}{2q} - \frac{\nu}{2q} - \frac{\nu_0}{2q}\right) e^{-qL_3} \\ \left(\frac{1}{2} - \frac{k}{2q} + \frac{\nu}{2q} + \frac{\nu_0}{2q}\right) e^{qL_3} & \left(\frac{1}{2} + \frac{k}{2q} + \frac{\nu}{2q} + \frac{\nu_0}{2q}\right) e^{qL_3} \end{pmatrix}. \tag{4.14}$$

Next we relate coefficients F, G of $\varphi_{III}(x)$ with coefficients C, D of $\varphi_{II}(x)$. Since the wave function is single valued,

$$\varphi_{III}(-L_1 - L_2) = \varphi_{II}(-L_1 - L_2). \tag{4.15}$$

This implies that

$$Fe^{qL_2} + Ge^{-qL_2} = C + D. \tag{4.16}$$

Integrating the Schrodinger equation, Eq.(4.7), over an infinitesimal interval ε around x $=-L_1 - L_2$ and taking the limit as $\varepsilon \to 0$, and the delta function is negative we get

$$\varphi'_{III}(-L_1 - L_2) - \varphi'_{II}(-L_1 - L_2) = -2\nu\varphi_{II}(-L_1 - L_2). \tag{4.17}$$

This implies that

$$-Fqe^{qL_2} + Gqe^{-qL_2} + qC - qD = -2\nu\,(C + D)\,. \tag{4.18}$$

From Eq.(4.16) and Eq.(4.18) we solve for F and G in terms of C and D and put the result as a matrix equation:

$$\begin{pmatrix} F \\ G \end{pmatrix} = \mathrm{M}_2 \begin{pmatrix} C \\ D \end{pmatrix} \tag{4.19}$$

where

$$\mathrm{M}_2 = \begin{pmatrix} \left(1+\frac{\nu}{q}\right)e^{-qL_2} & \left(\frac{\nu}{q}\right)e^{-qL_2} \\ \left(-\frac{\nu}{q}\right)e^{qL_2} & \left(1-\frac{\nu}{q}\right)e^{qL_2} \end{pmatrix}. \tag{4.20}$$

We now relate coefficients I, J of $\varphi_{IV}(x)$ with coefficients F, G of $\varphi_{III}(x)$. Single valuedness of the wave function leads to the relation

$$\varphi_{IV}(-L_1) = \varphi_{III}(-L_1), \tag{4.21}$$

which implies that

$$Ie^{qL_1} + Je^{-qL_1} = F + G. \tag{4.22}$$

Integrating the Schrodinger equation, Eq.(4.7), over an infinitesimal interval ε around x $=-L_1$ and taking the limit as $\varepsilon \to 0$, we get

$$\varphi'_{IV}(-L_1) - \varphi'_{III}(-L_1) = 2\nu\varphi_{III}(-L_1). \tag{4.23}$$

This implies that

$$-Iqe^{qL_1} + Jqe^{-qL_1} + Fq - Gq = 2\nu\,(F + G)\,. \tag{4.24}$$

From Eq.(4.22) and Eq.(4.24) we solve for I and J in terms of F and D and put the result as a matrix equation:

$$\begin{pmatrix} I \\ J \end{pmatrix} = \mathrm{M}_3 \begin{pmatrix} F \\ G \end{pmatrix} \tag{4.25}$$

where,

$$\mathrm{M}_3 = \begin{pmatrix} \left(1 - \frac{\nu}{q}\right) e^{-qL_1} & \left(-\frac{\nu}{q}\right) e^{-qL_1} \\ \left(\frac{\nu}{q}\right) e^{qL_1} & \left(1 + \frac{\nu}{q}\right) e^{qL_1} \end{pmatrix}. \tag{4.26}$$

Considering coefficients P, Q of $\varphi_V(x)$ and coefficients I, J of $\varphi_{IV}(x)$ and relating them at point x = 0 due to the single-valuedness of the wave function we get

$$P + Q = I + J. \tag{4.27}$$

Next, integrating the Schrodinger equation, Eq.(4.7), over an infinitesimal interval ε around x = 0 and taking the limit as $\varepsilon \to 0$, we get

$$\varphi_V'(0) - \varphi_{IV}'(0) = -(\nu + \nu_0)\, \varphi_{IV}(0). \tag{4.28}$$

This implies that

$$-kP + kQ + qI - qJ = -(\nu + \nu_0)(I + J). \tag{4.29}$$

From Eq.(4.27) and Eq.(4.29) we solve for I and J in terms of F and D and put the result as a matrix equation:

$$\begin{pmatrix} P \\ Q \end{pmatrix} = \mathrm{M}_4 \begin{pmatrix} I \\ J \end{pmatrix} \tag{4.30}$$

where,

$$\mathrm{M}_4 = \begin{pmatrix} \frac{1}{2} + \frac{q}{2k} + \frac{\nu}{2k} + \frac{\nu_0}{2k} & \frac{1}{2} - \frac{q}{2k} + \frac{\nu}{2k} + \frac{\nu_0}{2k} \\ \frac{1}{2} - \frac{q}{2k} - \frac{\nu}{2k} - \frac{\nu_0}{2k} & \frac{1}{2} + \frac{q}{2k} - \frac{\nu}{2k} - \frac{\nu_0}{2k} \end{pmatrix} \tag{4.31}$$

Using Eq.(4.14), Eq.(4.20), and Eq.(4.26) in Eq.(4.31) we at last relate coefficients P, Q with coefficients A, B by the matrix equation

$$\begin{pmatrix} P \\ Q \end{pmatrix} = \mathrm{M} \begin{pmatrix} A \\ B \end{pmatrix}. \tag{4.32}$$

where $\mathrm{M} = \mathrm{M}_4\mathrm{M}_3\mathrm{M}_2\mathrm{M}_1$ Since the ground state wave function is *bounded*, then, the coefficients A and Q must be equal to zero. Hence, the matrix equation Eq.(4.32) can be written as

$$\begin{pmatrix} P \\ 0 \end{pmatrix} = \begin{pmatrix} \mathrm{M}_{11} & \mathrm{M}_{12} \\ \mathrm{M}_{21} & \mathrm{M}_{22} \end{pmatrix} \begin{pmatrix} 0 \\ B \end{pmatrix}. \tag{4.33}$$

This implies that

$$\mathrm{M}_{22} B = 0. \tag{4.34}$$

This equation has nontrivial solution provided

$$\mathrm{M}_{22} = 0. \tag{4.35}$$

M_{22} is basically a function of y, z and E_{-}^{0} for a given βU_0 and L. It is made up of products of exponentials (such as e^{kL}, e^{qL}...) and factors that are functions of k, q, ν, and ν_0. To evaluate the root, E_{-}^{0}, of M_{22} we exploit the high barrier limit as we have done in the previous chapter:

(i) Take $\mathrm{e}^{kL} \sim \mathrm{e}^{\frac{\beta U_0}{2}}$ and $\mathrm{e}^{qL} \sim \mathrm{e}^{\frac{z\beta U_0}{2}}$

and (ii) Expand k and q terms appearing in the factors up to first order in E_{-}^{0}. The details of finding this root is done in Appendix B. The result is

$$E_{-}^{0}\left(y,z\right)=\frac{4\nu_{0}^{2}z^{2}t_{4}}{4t_{2}+\left(1+z\right)^{2}t_{3}+\left(1-z\right)^{2}t_{4}+2\left(1+z\right)t_{11}}. \tag{4.36}$$

Hence, the escape rate

$$\lambda=DE_{-}^{0}\left(y,z\right), \tag{4.37}$$

is given by

$$\lambda=\frac{4D\nu_{0}^{2}z^{2}t_{4}}{4t_{2}+\left(1+z\right)^{2}t_{3}+\left(1-z\right)^{2}t_{4}+2\left(1+z\right)t_{11}}. \tag{4.38}$$

The expressions for the t's are given in Appendix B.

4.2 Escape rate from a modified model potential using MFPT method

In this section we will use the method of mean first passage time to find, once again, the value for the escape rate of a Brownian particle from a modified model potential shown in Fig. 4.1.

In chapter two, we have already derived the expression for the escape rate (see Eq.(2.20)). For our modified model potential shown in Fig.4.1, the expression for the escape rate becomes

$$\lambda' = \frac{D}{\left[\int\limits_{-\infty}^{0}\exp[-\beta U(y)]dy\right]\int\limits_{-L}^{\infty}\exp[\beta U(x)]dx}. \tag{4.39}$$

The potential profile for our modified model potential is given as

$$U(x)=\begin{cases} -S_0 x-U_0, & \text{for } x \le -L \\ S_0 z x+U_0, & \text{for } -L\le x \le -(L_1+L_2) \\ -(S_0+2U_0)Zx+U_0, & \text{for } -(L_1+L_2)\le x \le -L_1 \\ S_0 Z x+U_0, & \text{for } -L_1 \le x \le 0 \\ -S_0 x+U_0, & \text{for } x \ge 0 \end{cases} \tag{4.40}$$

where $S_0 = \frac{U_0}{L}$, $z = \frac{S}{S_0}$, and y has the value $0 \leq y \leq 1$. Let us evaluate the two definite integrals. That is,

$$\int_{-\infty}^{0} e^{-\beta U(x)} dx = \left(\frac{1}{\beta S}\right) e^{-\beta U_3} \left[-2 + 2e^{\beta U_2} + (1+Z)e^{\beta U_3} - e^{\beta(U_2-U_1)}\right], \tag{4.41}$$

while

$$\int_{-L}^{\infty} e^{\beta U(x)} dx = \left(\frac{1}{\beta S}\right) e^{\beta U_3} \left[2 - 2e^{-\beta U_2} - e^{-\beta U_3} + (1+Z)e^{\beta(U_0-U_3)}\right]. \tag{4.42}$$

The product of the two integrals of Eq. (4.41) and Eq. (4.42) is given as using Appendix B Eq.(B.2)

$$\frac{1}{z^2}\left(\frac{1}{\beta S_0}\right)^2 \left[-8 - 2(1+z) + 4t_{17} + t_4^2 + (1+z)^2 t_3^2 + 2t_{11}((1+z)t_3 - t_4)\right] \tag{4.43}$$

Hence, the escape rate becomes

$$\lambda' = \frac{Dz^2(\beta S_0)^2}{-8 - 2(1+z) + 4t_{17} + t_4^2 + (1+z)^2 t_3^2 + 2t_{11}((1+z)t_3 - t_4)} \tag{4.44}$$

In the next chapter we will compare this value of the escape rate for the modified model potential with the value of the escape rate for the original model potential which we have calculated in chapter 3.

CHAPTER 5

Result and Discussion

In the previous two chapters we have evaluated the escape rates for the model potential (λ_0) as well as for the modified model potential (λ). We have used two methods to evaluate these escape rates. In the present chapter we are going to compare the two escape rates.

Let us take the ratio of the two escape rates, $\frac{\lambda}{\lambda_0}$. This quantity tells us the factor by which the escape rate has improved by taking the modified model potential instead of the original model potential. We call this factor, f, defined as

$$f = \frac{\lambda}{\lambda_0} \tag{5.1}$$

the *improvement factor*. Using the values of the escape rates found by supersymmetric method (Eq.(3.19) and (4.38)), the value of the improvement factor is given by

$$f = \frac{4z^2 t_3}{4t_2 + (1+z)^2 t_3 + (1-z)^2 t_4 + 2(1+z) t_{11}}. \tag{5.2}$$

On the other hand, the improvement factor found by the mean first passage time method (from Eqs. (3.26) and (4.44)) is

$$f' = \frac{4z^2 t_3^2}{-8 - 2(1+z) + 4t_{17} + t_4^2 + (1+z)^2 t_3^2 + 2t_{11}((1+z)t_3 - t_4)}. \tag{5.3}$$

The improvement factor is function of y, z and βU_0. Note that y is the (scaled) position of the intermediate metastable state from the barrier top, z is the (scaled) slope of the straight lines that form the intermediate metastable state while βU_0 is the (scaled) barrier height over which the particle escapes.

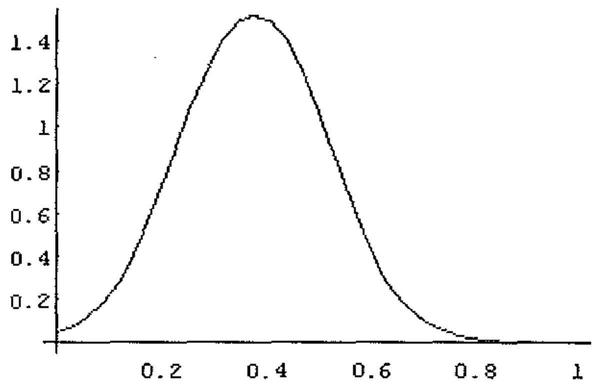

Figure 5.1: Plots of f (and f') versus y when $z = 2$ and $\beta U_0 = 8$.

Let us first see how f behaves as a function of y for fixed z and βU_0. Fig. (5.1) is a plot of f (and f') versus y for $z = 2$ and $\beta U_0 = 8$. This shows that f takes an optimum value at a particular value of y. In fact, the value of y at which f takes an optimum value can be found by equating the derivative of f with respect to y (for fixed z and βU_0)

$$\frac{\partial f}{\partial y} = 0. \tag{5.4}$$

We have found this to hold when

$$y = \frac{z+1}{4z}, \tag{5.5}$$

independent of the value of βU_0. Further, we note that this position corresponds to the situation when the mid-point of the intermediate straight line with negative slope *exactly* coincides with x=$\frac{-L}{2}$ (seeFig.5.2).

CHAPTER 6

Summary and Conclusion

In this thesis we took the problem of escape rate of a Brownian particle from a single-well potential with a runaway one side. Guided by a previous work that barrier subdivisions improves escape rates [4], we wanted to clearly see the effect of a *single* barrier subdivision on the escape rate. This barrier subdivision creates an intermediate metastable state between the potential minimum and potential maximum of the well. In order to get an explicit value for the escape rates, we considered model potentials both for the original as well as for the modified potential. We used two methods to calculate the escape rates for both model potentials.

The factor by which the escape rate improves due to the presence of the intermediate metastable state (improvement factor) is a function of 1) its position (y) relative to the barrier top 2) the steepness of the slope of the lines that form the state (z) and 3) the barrier height (βU_0).

We found out that there is a position y_0 of the intermediate state at which the improvement factor takes optimum value for a given z, *independent* of the *value of* βU_0. This position corresponds to having the barrier subdivision placed *exactly* around the mid point of the width (L) of the well. We also found that, fixing the position at y_0, the improvement factor takes optimum value at a given steepness value for a given βU_0.

In conclusion, we would like to add that further work in this direction could give a clue to the search for the potential profile that has the highest escape rate.

Using eq(A.10) in to eq(A.8)

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

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

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

Hence, we have

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

This is the backward Fokker-Planck equation.

Appendix B

In this appendix we will evaluate the root, E^0_-, of the matrix element M_{22}.

We start from the full expression of $M_{22} = 0$ which is

$$
\begin{aligned}
&\left[\frac{1}{2} - \frac{q}{4k} - \frac{k}{4q} + \frac{(\nu+\nu_0)^2}{4kq} - \frac{\nu^2}{2q^2} + \frac{\nu^2}{4kq} + \frac{q\nu^2}{4q^3} - \frac{\nu^2(\nu+\nu_0)^2}{4q^3k}\right] e^{-\nu L} \\
&+ \left[\frac{1}{2} + \frac{k}{4q} + \frac{q}{4k} - \frac{(\nu+\nu_0)^2}{4kq} - \frac{\nu^2}{2q^2} - \frac{\nu^2}{4kq} - \frac{k\nu^2}{4q^3} + \frac{\nu^2(\nu+\nu_0)^2}{4q^3k}\right] e^{\nu L} \\
&+ \left[\begin{array}{c} \frac{k\nu}{4q^2} - \frac{\nu}{4k} - \frac{\nu(\nu+\nu_0)}{2qk} - \frac{\nu(\nu+\nu_0)^2}{4q^2k} - \frac{k\nu^2}{4q^3} + \frac{\nu^2}{4kq} + \frac{\nu^2(\nu+\nu_0)}{2q^2k} \\ + \frac{\nu^2(\nu+\nu_0)^2}{4q^3k} \end{array}\right] e^{-\nu L\left(2x - \frac{S_0}{S}\right)} \\
&+ \left[\begin{array}{c} \frac{k\nu}{4q^2} - \frac{\nu}{4k} + \frac{\nu(\nu+\nu_0)}{2qk} - \frac{\nu(\nu+\nu_0)^2}{4q^2k} + \frac{k\nu^2}{4q^3} - \frac{\nu^2}{4kq} + \frac{\nu^2(\nu+\nu_0)}{2q^2k} \\ - \frac{\nu^2(\nu+\nu_0)^2}{4q^3k} \end{array}\right] e^{\nu L\left(2x - \frac{S_0}{S}\right)} \\
&+ \left[\begin{array}{c} -\frac{k\nu}{4q^2} + \frac{\nu}{4k} - \frac{\nu(\nu+\nu_0)}{2qk} + \frac{\nu(\nu+\nu_0)^2}{4q^2k} - \frac{k\nu^2}{4q^3} + \frac{\nu^2}{4kq} - \frac{\nu^2(\nu+\nu_0)}{2q^2k} \\ + \frac{\nu^2(\nu+\nu_0)^2}{4q^3k} \end{array}\right] e^{-\nu L(1-2x)} \\
&+ \left[\begin{array}{c} -\frac{k\nu}{4q^2} + \frac{\nu}{4k} + \frac{\nu(\nu+\nu_0)}{2qk} + \frac{\nu(\nu+\nu_0)^2}{4q^2k} + \frac{k\nu^2}{4q^3} - \frac{\nu^2}{4kq} - \frac{\nu^2(\nu+\nu_0)}{2q^2k} \\ - \frac{\nu^2(\nu+\nu_0)^2}{4q^3k} \end{array}\right] e^{\nu L(1-2x)} \\
&+ \left[\frac{\nu^2}{2q^2} + \frac{k\nu^2}{4q^3} + \frac{\nu^2}{4kq} - \frac{\nu^2(\nu+\nu_0)^2}{4q^3k}\right] e^{\nu L \frac{S_0}{S}} \\
&+ \left[\frac{\nu^2}{2q^2} - \frac{k\nu^2}{4q^3} - \frac{\nu^2}{4kq} + \frac{\nu^2(\nu+\nu_0)^2}{4q^3k}\right] e^{-\nu L \frac{S_0}{S}} = 0.
\end{aligned}
\tag{B.1}
$$

Let us use the following symbols to represent exponential terms appearing in Eq.(B.1)

$$
\begin{aligned}
t_1 &= e^{\frac{\beta U_0 z}{2}} & t_2 &= e^{\frac{-\beta U_0 z}{2}} \\
t_3 &= e^{\frac{\beta U_0}{2}} & t_4 &= e^{\frac{-\beta U_0}{2}} \\
t_5 &= e^{\frac{\beta U_0 z(1-2y)}{2}} & t_6 &= e^{\frac{-\beta U_0 z(1-2y)}{2}} \\
t_7 &= e^{\frac{\beta U_0 z(2y-\frac{1}{z})}{2}} & t_8 &= e^{\frac{-\beta U_0 z(2y-\frac{1}{z})}{2}} \\
t_9 &= t_1 - t_2 & t_{10} &= t_1 + t_2 \\
t_{11} &= -t_8 + t_7 - t_6 + t_5 & t_{12} &= t_9 - t_3 + t_4 - t_{11} \\
t_{13} &= -t_{12} & t_{14} &= -t_9 + t_3 - t_4 - t_{11} \\
t_{15} &= -t_{10} + t_3 + t_4 & t_{16} &= t_8 + t_7 - t_6 - t_5 \\
t_{17} &= t_{1.}t_2 + t_2.t_3.
\end{aligned} \tag{B.2}
$$

Using Eq. (B.2) in Eq. (B.1) and multiplying by the factor of $4q^3k$ we get

$$
\begin{aligned}
&\left[-(\nu+\nu_0)^2 q^2 + k^2q^2 + q^4\right] t_9 + \left[2q^3k\right] t_{10} + \left[2\nu(\nu+\nu_0) q^2\right] t_{11} + \\
&\left[\nu^2(\nu+\nu_0)^2\right] t_{12} + \left[\nu^2 k^2\right] t_{13} + \left[\nu^2 q^2\right] t_{14} + \left[2\nu^2 kq\right] t_{15} + \\
&\left[2\nu^2(\nu+\nu_0) q - \nu(\nu+\nu_0)^2 q - \nu q^3 + \nu q k^2\right] t_{16} = 0.
\end{aligned} \tag{B.3}
$$

Expanding k, q and their products up to order E_-^0, we have

$$
\begin{aligned}
q^3k &= \nu^3\nu_0\left(1 - \tfrac{3E_0}{2\nu^2} - \tfrac{E_0}{2\nu_0^2}\right), & q^2 &= \nu^2\left(1 - \tfrac{E_0}{\nu^2}\right), & k &= \nu_0\left(1 - \tfrac{E_0}{2\nu_0^2}\right), \\
q^4 &= \nu^4\left(1 - \tfrac{2E_0}{\nu^2}\right), & q^3 &= \nu^3\left(1 - \tfrac{3E_0}{2\nu^2}\right), & q &= \nu\left(1 - \tfrac{E_0}{2\nu^2}\right), \\
k^2q^2 &= \nu^2\nu_0^2\left(1 - \tfrac{E_0}{\nu_0^2} - \tfrac{E_0}{\nu^2}\right), & qk^2 &= \nu\nu_0^2\left(1 - \tfrac{E_0}{\nu_0^2} - \tfrac{E_0}{2\nu^2}\right), & k^2 &= \nu_0\left(1 - \tfrac{E_0}{\nu_0^2}\right), \\
kq &= \nu\nu_0\left(1 - \tfrac{E_0}{2\nu_0^2} - \tfrac{E_0}{2\nu^2}\right) & q &= \nu\left(1 - \tfrac{E_0}{2\nu^2}\right).
\end{aligned} \tag{B.4}
$$

Using Eq.(B.4) in Eq. (B.3),

$$\begin{aligned}
&\left[-(1+z)^2\left(1-\tfrac{E_0}{\nu^2}\right)+\left(1-\tfrac{E_0}{\nu^2}-\tfrac{E_0}{\nu_0^2}\right)+z^2\left(1-2\tfrac{E_0}{\nu^2}\right)\right]t_9\\
&+\left[2z\left(1-\tfrac{3E_0}{2\nu^2}-\tfrac{E_0}{2\nu_0^2}\right)\right]t_{10}+\left[2z\left(1+Z\right)\left(1-\tfrac{E_0}{\nu^2}\right)\right]t_{11}\\
&+\left[(1+z)^2\right]t_{12}+\left[1-\tfrac{E_0}{\nu_0^2}\right]t_{13}+\left[z^2\left(1-\tfrac{E_0}{\nu^2}\right)\right]t_{14}\\
&+\left[2z\left(1-\tfrac{E_0}{2\nu_0^2}-\tfrac{E_0}{2\nu^2}\right)\right]t_{15}\\
&+\left[\begin{array}{c}2z\left(1+z\right)\left(1-\tfrac{E_0}{2\nu^2}\right)-(1+z)^2\left(1-\tfrac{E_0}{2\nu^2}\right)-z^2\left(1-\tfrac{3E_0}{2\nu^2}\right)\\+\left(1-\tfrac{E_0}{2\nu^2}-\tfrac{E_0}{\nu_0^2}\right)\end{array}\right]t_{16}=0.
\end{aligned}\tag{B.5}$$

Bringing terms of order E_-^0 together, we get

$$\begin{aligned}
&-2zt_9+2zt_{10}+\left(2z+2z^2\right)t_{11}+\left(1+z\right)^2t_{12}+t_{13}+z^2t_{14}+2zt_{15}\\
&=\tfrac{E_0}{\nu_0^2}\left[\left(\tfrac{-2z+2z^2}{z^2}\right)t_9+\left(\tfrac{z^2+3}{Z}\right)t_{10}+\left(\tfrac{2z+2z^2}{z^2}\right)t_{11}+t_{13}+t_{14}+\left(\tfrac{z^2+3}{z}\right)t_{15}\right].
\end{aligned}\tag{B.6}$$

Then, we solve for the ground state eigenvalue E_-^0 and get is

$$E_-^0(y,z)=\frac{\nu_0^2\left(-2zt_9+2zt_{10}+\left(2z+2z^2\right)t_{11}+\left(1+z\right)^2t_{12}+t_{13}+z^2t_{14}+2zt_{15}\right)}{\left[\left(\frac{-2z+2z^2}{z^2}\right)t_9+\left(\frac{z^2+3}{z}\right)t_{10}+\left(\frac{2z+2z^2}{z^2}\right)t_{11}+t_{13}+t_{14}+\left(\frac{z^2+3}{z}\right)t_{15}\right]}.\tag{B.7}$$

Further simplification leads to

$$E_-^0(y,z)=\frac{4\nu_0^2z^2t_4}{4t_2+\left(1+z\right)^2t_3+\left(1-z\right)^2t_4+2\left(1+z\right)t_{11}}.\tag{B.8}$$

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