EFFECT OF LOCAL HEATING ON ESCAPE AND EQUILIBRATION RATES IN A BISTABLE POTENTIAL

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Dedication

This thesis is dedicated to my father **Ato Fekade Duki** and my mother **W/o Aster Zeleke** for their invaluable support, encouragement and educating not only me but also all their children.

ABSTRACT

The detailed kinetic aspect of the Landauer's *blow-torch* theorem is investigated for two models of non-homogeneous media, proposed by Landauer and by van Kampen. For both models, we considered a symmetric W-potential with hot locality temperature profile and applied the Brinkman's method to obtain analytic expressions for the escape and equilibration rates. The escape and equilibration rates are functions of strength, position and width of the hot locality, and the barrier height. We find that the presence of the hot locality has improved the equilibration rates for both models. The calculation also reveals that the equilibration rate for Landauer's model has an optimal position where it gets its maximum value while for the van Kampen's model it is an increasing function of position.

CONTENTS

Chapter 1

INTRODUCTION

In equilibrium statistical mechanics, we study the macroscopic properties of a system on the bases of the general arguments of molecular-kinetic concepts. To study such equilibrium system, one need not investigate how the system is relaxed to the equilibrium state. The general arguments are quite sufficient to describe systems without knowing the detailed processes which bring about the final equilibrium state. For example in an isolated system, a state with lowest energy is the most probable state at equilibrium and in general the relative occupation of higher-energy states are described by the Boltzmann distribution $e^{-\frac{E}{k_B T}}$ where E is the energy, T is the absolute temperature and k_B is the Boltzmann constant. However many macroscopic systems of practical interest are non-homogeneous, non-linear and operate far from equilibrium. Hence the general arguments of the equilibrium statistical mechanics may not work and one has to study the non-equilibrium nature of the system.

To illustrate the implications of this idea, Landauer raised the question of relative stability of a competing local energy minima for a system far from equilibrium and discussed what we now call the blow torch theorem [1]. His point was that relative stability of a multistable system could be altered by path-dependent diffusion even when localized to the neighbourhoods of the potential barriers separating the deterministically stable or metastable states. That is, the most probable state of such a system can not be determined from the information about local minima alone and hence one has to see the detailed kinetics of the system to talk about the stability. In fact his idea generalizes the problem of Kramers reaction rate [2] in equilibrium thermal fluctuation to the case of non-uniform temperature along the reaction coordinate.

To justify Landauer's blow torch theorem, van Kampen [3,4] derived the equations that are appropriate for the description of diffusion in non-homogeneous media, by considering two models, where he developed a thermally activated diffusion equations for the media from stochastic point of view. He also showed [3] that there could be a net current when particles are allowed to pass through an alternative route by passing the hot region. Using computer simulation, Sinha and Moss [5] have also verified Landauer's argument. Experimental work was also done in a thermally activated superconducting ring with a weak link where transitions produce temperature changes [6].

Most of the works on this problem were confined to the studies of the influence of space-dependent temperature on the steady state relative occupations of energy minima. The only work on the detailed kinetic aspect of the problem is the work by Mulugeta Bekele *et.al.* [7]. Using supersymmetric method, they have calculated the lowest relaxation time in a bistable potential in the presence of a hot locality, for the model proposed by van Kampen. In this thesis we address the same problem. We want to calculate the relaxation time for the slow equilibration process for two models, that are proposed by Landauer [8] and by van Kampen [3] using Brikman's method [9].

The rest of the thesis is organized as follows. In chapter 2, we first introduce the two types of non-homogeneous media and then develop the Fokker-Planck equations that govern the evolution of the diffusion processes for these models. In chapter 3, we discuss the dynamics for the two types of non-homogeneous media in a bistable potential in detail and obtain the general expressions for the escape rates and the equilibration rates. By choosing a particular W-potential with a peciewise constant hot locality in one of the wells of the potential, we obtain analytic expressions for the escape rates and the equilibration rate for each medium in chapter 4. These results are discussed in detail including from physical point of view in chapter 5. Finally, we summarize our results and conclude in chapter 6.

Chapter 2

DIFFUSION IN TWO TYPES OF NON-HOMOGENEOUS MEDIA

In this chapter, we present two types of non-homogeneous media under which diffusion processes take place. We will find that, unlike homogeneous medium, the equations governing motion of Brownian particles in non-homogeneous media are model specific. Consequences of and comparisons between the governing equations will be indicated.

2.1 LANDAUER'S PIPE MODEL

We discuss the model proposed by Rolf Landauer [8] to study the diffusion of Brownian particles in a non-homogeneous temperature background. The model considers a very thin straight pipe of circular cross-section with inner radius ϵ. The axis of the pipe serves as x axis and the wall of the pipe has a temperature of T which depends on the position x. The pipe is filled with non-interacting Brownian particles each of mass m. The medium inside the pipe is assumed to be vacuum so that there is no interaction between the medium and the particles. The particles are subjected to an external force field whose potential is given by $V(x)$.

Because of the applied external field and the random thermal fluctuation of the background, the particles will diffuse in the tube. Moreover, if the diameter of the tube is very small compared to the length of the pipe, the diffusion of the particles can be approximated by a one dimensional diffusion equation.

To study the dynamics of these non-interacting Brownian particles it is sufficient to consider the motion of a single particle in a viscous medium in one dimension. The state of the particle in phase space is described by its position x and velocity v. The equation of motion for the particle is given by the Langevin equations of the form

$$m\frac{dv}{dt} = -V'(x) - bv + \sqrt{2bk_BT}\xi(t) \tag{2.1.1}$$

and

$$\frac{dx}{dt} = v \tag{2.1.2}$$

where b is the damping constant of the medium and $\sqrt{2bk_BT}\xi(t)$ is the random force on the particle due to the thermal kick of the environment. The prime on the potential denotes derivative with respect to the position x. The random force is assumed to be a Gaussian white noise whose mean is zero and is delta correlated. That is,

$$\langle\xi(t)\rangle = 0 \tag{2.1.3}$$

and

$$2bk_BT\left\langle\xi(t)\xi(t')\right\rangle = \delta(t-t'), \tag{2.1.4}$$

where k_B is the Boltzmann's constant.

By taking an assumption that the physical fluctuating force $\xi(t)$ is to be interpreted as

$$\xi(t)dt = dW(t), \tag{2.1.5}$$

the Langevin equations (2.1.1) and (2.1.2) can be transformed to the following stochastic differential equations:

$$dx = vdt \tag{2.1.6}$$

and

$$mdv = -(V'(x) + bv)dt + \sqrt{2bk_BT}dW(t). \qquad (2.1.7)$$

Through Ito calculus [10], these stochastic differential equations can be transformed to the corresponding Fokker-Planck equation of the form

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}(vp) + \frac{1}{m}\frac{\partial}{\partial v}\left[(V'(x) + bv)\,p\right] + \frac{bk_BT}{m^2}\frac{\partial^2 p}{\partial v^2}, \qquad (2.1.8)$$

where $p(x, v, t)$ is the probability density of finding the particle at position x with velocity v at time t in phase space. This Fokker-Planck equation can slightly be simplified by introducing new scaled variables

$$y = x\sqrt{\frac{m}{k_BT}}, \qquad (2.1.9)$$

$$u = v\sqrt{\frac{m}{k_BT}}, \qquad (2.1.10)$$

$$U = \frac{V(x)}{k_BT}, \qquad (2.1.11)$$

and

$$\gamma = \frac{b}{m}. \qquad (2.1.12)$$

In terms of these scaled variables, the corresponding Fokker-Planck equation takes the form

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial y}(up) + \frac{\partial}{\partial u}\left(U'(y)p\right) + \gamma\frac{\partial}{\partial u}\left(up + \frac{\partial p}{\partial u}\right). \qquad (2.1.13)$$

This is the celebrated Kramers' equation. At steady state its solution is given by

$$p_{ss}(y, u) = NExp\left[-U(y) - \frac{u^2}{2}\right], \qquad (2.1.14)$$

where N is the normalizing constant. In terms of the original variables (x, t) the steady state solution is

$$p_{ss}(x, v) = NExp\left[-\frac{V(x)}{k_BT} - \frac{mv^2}{2k_BT}\right] \qquad (2.1.15)$$

which is the familiar Boltzmann distribution in equilibrium statistical mechanics. The denominator k_BT in the exponent arises from the assumed coefficient $\sqrt{2bk_BT}$ of the fluctuating force.

For three dimensional case where the position of the particle is $\vec{r} \equiv (x_1, x_2, x_3)$ and its velocity is $\vec{v} \equiv (v_1, v_2, v_3)$, the Kramers' equation is given by

$$\frac{\partial f(\vec{r};\vec{v};t)}{\partial t} = -\vec{v}.\frac{\partial f}{\partial \vec{r}} + \vec{\nabla}U(\vec{r}).\frac{\partial f}{\partial \vec{v}} + \gamma\sum_{i=0}^{3}\frac{\partial}{\partial v_i}\left(\frac{\partial}{\partial v_i} + v_i\right) f \qquad (2.1.16)$$

where $f(\vec{r};\vec{v};t)$ is the probability density of finding the particle at position $\vec{r}$ with velocity $\vec{v}$ at time t. In a system where there is no viscous force, the damping term becomes zero and the Kramers equation takes the form

$$\frac{\partial f}{\partial t} = -\vec{v}.\frac{\partial f}{\partial \vec{r}} + \vec{\nabla}U(\vec{r}).\frac{\partial f}{\partial \vec{v}}. \qquad (2.1.17)$$

For Landauer's pipe model this equation holds for $y^2 + z^2 < \epsilon^2$; i.e, inside the tube. As a boundary condition we assume that the particle, on colliding with the wall of the tube, gets thermalized with the wall of the pipe at the instance it collides with the wall and then gets reflected with equal probability in all directions. That is, the particle satisfies the Maxwell velocity distribution corresponding to the local temperature $T(x)$. Mathematically this boundary condition can be written as

$$f = \tilde{N}Exp\left[-\frac{V(\vec{r})}{k_BT} - \frac{mv^2}{2k_BT}\right] \qquad (2.1.18)$$

for $\mid \vec{r} \mid = \epsilon$ and $\vec{v}.\vec{r} < 0$. $\tilde{N}$ is the normalizing constant and is determined by considering that, per second, as many particles leave the wall of the pipe as arrive at it.

To discuss the one dimensional diffusion of particles in the tube one has to consider the limiting case where $\epsilon \rightarrow 0$. In this limit almost all the particles at a given point x on the axis of the pipe have undergone their last collision in the neghibourhood of this point. Hence, to lowest order approximation in ϵ, every particle satisfies the Maxwell velocity distribution corresponding to the local temperature $T(x)$. A slight deviation from this distribution is obtained by taking the next order of approximation in ϵ . This deviation causes the particle to diffuse along the pipe. To obtain the equation that governs the dynamics of the system from the Kramers' equation, one has to apply a singular perturbation technique and integrate the distribution function f over the velocity components. van Kampen [6] showed that the appropriate Fokker-Planck equation for such Landauer's pipe is

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\mu(x)V'(x)P(x,t) + \frac{\partial}{\partial x}(D(x)P(x,t))\right], \qquad (2.1.19)$$

where $\mu(x) = \frac{8\epsilon}{3\sqrt{2\pi T(x)}}$ is the mobility of the particle, $V(x)$ the applied potential and $D(x)$ is the diffusion coefficient. Such Fokker-Planck equation as Eq. (2.1.19) where velocity variable does not appear is usually called Smoluchowski equation.

The stationary solution of Eq. (2.1.19) in the absence of the applied potential is

$$P_{ss}(x) = \frac{const}{\sqrt{T(x)}}, \qquad (2.1.20)$$

which arises because of the thermal kick from the background. The dependence of $P_{ss}(x)$ on the temperature; i.e, $P_{ss} \propto \frac{1}{\sqrt{T(x)}}$ explains the fact that the speed of the particles is proportional to the $\sqrt{T(x)}$. Such equilibration process is usually called temperature equilibration. This tells us that the particle spends less time in hot regions. In general, the stationary solution in the presence of the external field is

$$P_{ss}(x) = \frac{const}{\sqrt{T(x)}} exp\left[-\int^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right]. \tag{2.1.21}$$

The effect of the external potential $V(x)$ on the steady state distribution of the system is fully accounted for by the factor

$$exp\left[-\int^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right]. \tag{2.1.22}$$

To see the meaning of this exponent in Eq. (2.1.21) from thermodynamics point of view, we consider a bistable potential whose minima are located at $x = x_a$ and at $x = x_c$ while its maxima is at $x = 0$ as shown in Fig. 2.1.

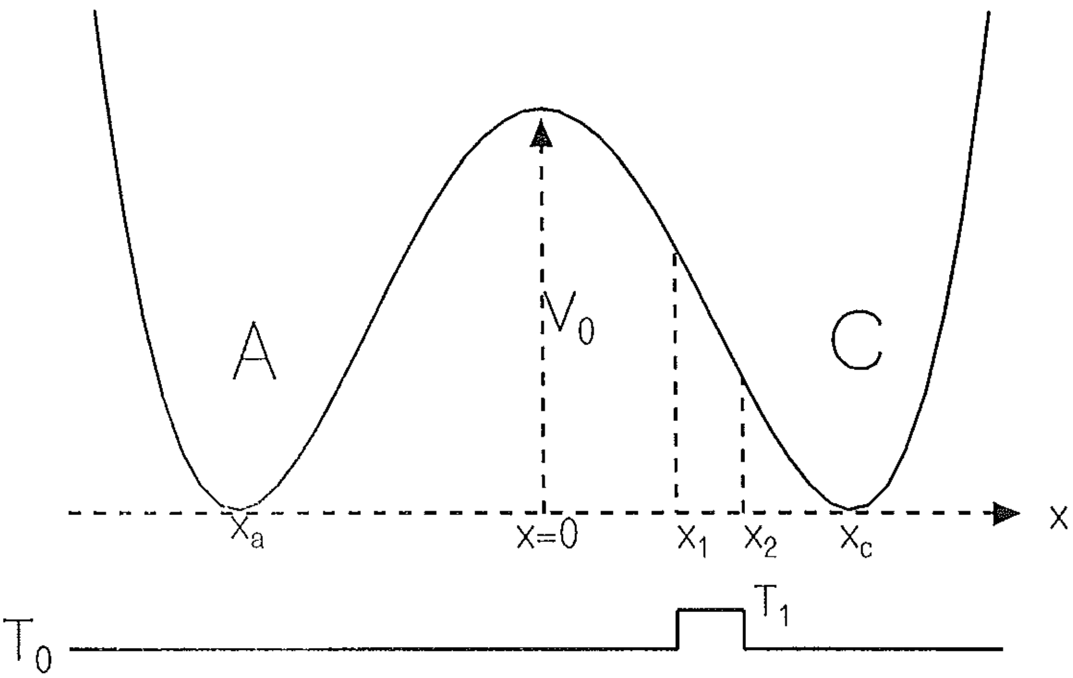

Fig. 2.1 A symmetric bistable potential

First we consider an isolated system whose background has a uniform temperature. For high friction limit, because of the isolation of the system, the energy of the heat bath (the background) plus the energy of the particle is always constant, E_0. If the particle is at position x, then its energy will be $V(x)$, so that the energy, E, of the heat bath is $E_0 - V(x)$. Thus the entropy, S, of the heat bath is dependent on $E_0 - V(x)$. Expanding the entropy in powers of $V(x)$ and neglecting the higher order terms, we get

$$S[E_0 - V(x)] = S(E_0) - \frac{dS}{dE}V(x) = S(E_0) - \frac{V(x)}{k_B T_0}. \qquad (2.1.23)$$

Then the probability density of finding the particle with energy $V(x)$ becomes

$$P^e(x) = C' Exp\left[-\frac{V(x)}{k_B T_0}\right] \qquad (2.1.24)$$

where C' is the normalizing constant and the superscript e stands for the equilibrium distribution. This is the familiar canonical distribution in equilibrium statistical mechanics.

If we consider the two wells as two distinct regions, then the probability of finding the particle in the left well is

$$N^e(A) = C' \int_{-\infty}^{0} Exp\left[-\frac{V(x)}{k_B T_0}\right] dx \qquad (2.1.25)$$

while the probability of finding the particle in the right well is

$$N^e(C) = C' \int_{0}^{\infty} Exp\left[-\frac{V(x)}{k_B T_0}\right] dx \qquad (2.1.26)$$

where A and C denote the left and right well regions, respectively.

Now let us consider a non-homogeneous temperature background for the system. Let the temperature in the region (x_1, x_2) be raised to T_1 as shown in Fig. 2.1. This means that we have an additional heat bath with temperature T_1 which the particle interacts whenever it enters the region (x_1, x_2). Suppose the particle enters the region at point x_1 and leaves it at x_2. During the time it stays in the region, it gains an energy of $V(x_2) - V(x_1)$. As a result the heat bath with temperature T_1 loses the same amount of energy so that its entropy decreases by

$$\triangle S_1 = -\frac{V(x_2) - V(x_1)}{k_B T_1}. \tag{2.1.27}$$

When the particle leaves that region, it thermalizes with the heat bath at temperature T_0 so that its temperature decreases to T_0. Thus the entropy of the heat bath with temperature T_0 increases by

$$\triangle S_0 = \frac{V(x_2) - V(x_1)}{k_B T_0}. \tag{2.1.28}$$

Thus the passage of a particle through the interval (x_1, x_2) has the effect of transfering the energy $V(x_2) - V(x_1)$ from the hot heat bath to the cold heat bath. This exchange of heat increases the entropy of the total system by an amount of

$$\triangle S = \triangle S_1 + \triangle S_0. \tag{2.1.29a}$$

That is,

$$\triangle S = \left(\frac{V(x_2) - V(x_1)}{k_B}\right)\left(\frac{1}{T_0} - \frac{1}{T_1}\right) \tag{2.1.29b}$$

$e^{\triangle S}$ is the factor by which the probability for the particle to be in the left well is enhanced. Hence, in the non-homogeneous temperature background at steady state the ratio of the probabilities of finding the particle in the two wells is

$$\frac{N^s(A)}{N^s(C)} = \frac{N^e(A)}{N^e(C)} Exp\left[\left(\frac{V(x_2) - V(x_1)}{k_B}\right)\left(\frac{1}{T_0} - \frac{1}{T_1}\right)\right]. \tag{2.1.30}$$

This is what we call the Landauer's blow torch effect [1].

To obtain the explicit expression for the relative stability, one has to expand the potential about its minima. Near the minima the potential

$V(x)$ can be approximated by a parabola so that

$$N^e(A) \simeq C' \int_{-\infty}^{0} Exp\Big[-\frac{\big(V(x_a)+\frac{1}{2}(x-x_a)^2 V''(x_a)\big)}{k_B T_0}\Big] dx. \qquad (2.1.31)$$

Considering that the potential in region A is approximately parabolic and wide enough, upon integration one gets

$$N^e(A) \simeq C' \sqrt{\frac{2\pi T_0}{V''(x_a)}} Exp\Big[-\frac{V(x_a)}{k_B T_0}\Big]. \qquad (2.1.32)$$

Similarly,

$$N^e(C) \simeq C' \sqrt{\frac{2\pi T_0}{V''(x_c)}} Exp\Big[-\frac{V(x_c)}{k_B T_0}\Big]. \qquad (2.1.33)$$

Hence

$$\frac{N^s(A)}{N^s(C)} = \sqrt{\frac{V''(x_c)}{V''(x_a)}}\, e^{\left[-\left(\frac{V(x_c)-V(x_2)}{k_B T_0}\right)-\left(\frac{V(x_2)-V(x_1)}{k_B T_1}\right)-\left(\frac{V(x_1)-V(x_a)}{k_B T_0}\right)\right]}. \qquad (2.1.34)$$

This expression can be written as

$$\frac{N^s(A)}{N^s(C)} = \sqrt{\frac{V''(x_c)}{V''(x_a)}} Exp\Big[-\int_{x_a}^{x_c} \frac{V'(x)}{k_B T(x)} dx\Big]. \qquad (2.1.35)$$

This form represents the general temperature profile. Therefore, the factor

$$Exp\Big[-\int^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\Big] \qquad (2.1.36)$$

in the steady state solution of the Landauer's pipe model determines the relative stability of the particle in the potential and it has a pumping effect.

2.2 van KAMPEN'S MODEL

This is a model proposed by van Kampen [3]. He considers a pipe filled with a non-homogeneous medium. In this model the medium acts as a heat reservoir and hence it takes the temperature of the pipe which varies in position along the axis of the pipe. The existence of a viscous medium in the pipe causes the particle's motion to be damped by a resistive force whose magnitude is proportional to the velocity of the Brownian particle. Since the medium temperature is position dependent, the damping coefficient, γ, is in general non-homogeneous in space.

The motion of a Brownian particle in such a medium in phase space is governed by the Kramers' equation Eq. (2.1.8), which is

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x}(vf) + \frac{1}{m}\frac{\partial}{\partial v}\left[\left(V'(x) + \gamma(x)v\right) f\right] + \frac{\gamma(x)k_B T(x)}{m^2}\frac{\partial^2 f}{\partial v^2} \quad (2.2.1)$$

where $f(x, v, t)$ is the probability distribution function in phase space and γ is the damping coefficient. For a particle with unit mass, Eq.(2.2.1) can be reduce to the form

$$\frac{\partial f}{\partial t} = -v\frac{\partial f}{\partial x} + V'(x)\frac{\partial f}{\partial v} + \gamma(x)\frac{\partial}{\partial v}\left(vf + k_B T(x)\frac{\partial f}{\partial v}\right). \quad (2.2.2)$$

In a case where the damping coefficient γ and the background temperature T are constant, it is well known [2,11] how to derive the Smoluchowski equation of the system for high friction limit. But when both γ and T are non-homogeneous, one has to apply singular perturbation technique and the general method of eliminating fast variables [10] on the above Kramers' equation to get the corresponding Smoluchowski equation. The resulting equation, first derived by van Kampen [4], is given by

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\mu(x)V'(x)P(x,t) + \mu(x)\frac{\partial}{\partial x}\left(k_B T(x) P(x,t)\right)\right] \quad (2.2.3)$$

where $\mu(x) = \frac{1}{\gamma(x)}$ is the mobility of the particle in the viscous medium.

The steady state probability distribution of this system is given by

$$P_{ss} = \frac{C}{T(x)} Exp\left[-\int^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right] \quad (2.2.4)$$

where C is the the normalizing constant. Here again the exponential part is the contribution of the potential and it has a pumping effect.

The factor $\frac{1}{T(x)}$ can roughly be explained from thermodynamics point of view as follows. The particles that we considered in the pipe are non-interacting and hence the system can be considered as an ideal gas system. Moreover we know, from equilibrium statistical mechanics, that for an ideal gas system pressure is constant on a horizontal plane, say, located at a distance z from see level. This means that there is pressure equilibration on that plane; i.e., the ideal gas equation is satisfied. Hence,

$$\tilde{p} = \tilde{n}RT = \text{constant} \quad (2.2.5a)$$

on that plane surface; where $\tilde{p}$ is the pressure, $\tilde{n}$ is the number density and R is the universal gas constant. But for an ideal gas, it is sufficient to study the dynamics of the probability distribution of a representative particle. In that case one can replace the number density $\tilde{n}$ in Eq. (2.2.5a) by the probability density distribution P. Therefore Eq. (2.2.5a) can be written in the form

$$\tilde{p} = PRT = \text{constant} \quad (2.2.5b)$$

which shows us that the probability distribution is inversely proportional to the temperature $T(x)$. This means that the probability of finding the particle in a hot region is less than in a cold region. As a result the particle will spend less time in the hot region.

In this chapter, we have indicated two main points. The first one is that steady state solutions for non-homogeneous media are drastically different from that for homogeneous medium and the second is that there are similarities and differences between the steady state state solutions of the two models.

In the next chapter we will study the slow dynamics of the Brownian particle in a bistable potential with non-homogeneous temperature background for the models presented in this chapter.

Chapter 3

RATE EQUATIONS IN A BISTABLE POTENTIAL FOR NON-HOMOGENEOUS MEDIA

Brownian motion in a bistable potential has two time scales in its evolution. One is the fast time scale which is of the order of time required for local equilibration in one of the wells. The other time scale is associated with the slow process of escaping from one well to the other or vice versa. This slow time scale is of the order of time required for global equilibration.

In this chapter, we are interested in the slow dynamic of the Brownian particle as it approaches to the steady state in a bistable potential. Identifying the two wells as two regions we formulate the rate equations governing the late stage dynamics of the Brownian particle. This is done for the two types of non-homogeneous media.

3.1 RATE EQUATIONS FOR LANDAUER'S PIPE MODEL

In this section we study the dynamics of the Brownian particle in Landauer's pipe model, where temperature is non-homogeneous. As a particular example we consider a double well potential $V(x)$, whose barrier height is V_0 as shown in the Fig. 3.1. The peak of the barrier is located at $x = 0$ and the two minima are located at $x = -L$ and at $x = L$. The non-homogeneous temperature of the medium is obtained by locally heating a certain portion of the pipe in one of the wells.

A particle that moves in this double well potential is subjected to the random force of the background. Originally the particle is assumed to be caught in one of the potential wells and as time advances it gets a continuous kick from the background and as a result it may escape from the well by passing over the potential barrier V_0.

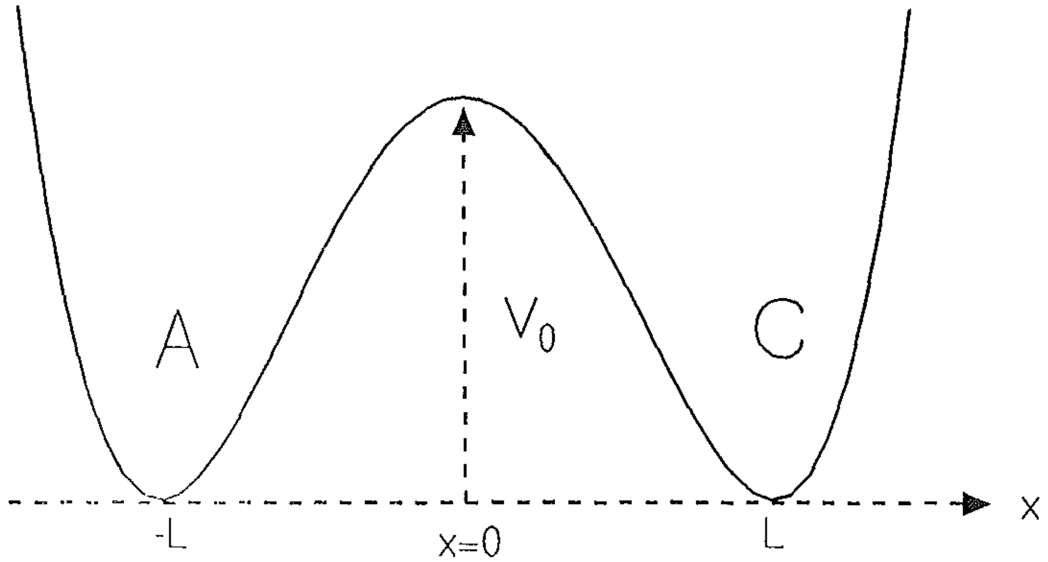

Fig. 3.1 A symmetric bistable potential

The dynamics of the particle is governed by the Smoluchowski equation

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\mu(x)\frac{dV}{dx}P(x,t) + \frac{\partial}{\partial x}(D(x)P(x,t))\right] \qquad (3.1.1)$$

where $\mu(x)$ is the mobility of the particle and $D(x)$ is the diffusion coefficient. In this equation the mass of the particle is assumed to be unity.

Following Brinkman's [9] approach to solve the problem, we define $n_A(t)$ and $n_C(t)$ to be the probabilities of getting the particle in the left well and the the right well at time t, respectively. Then

$$n_A(t) = \int_{-\infty}^{0} P(x,t)dx$$

and

$$n_C(t) = \int_0^\infty P(x,t)dx.$$

If we integrate Eq. (3.1.1) from $-\infty$ to zero over x we get the differential equation for $n_A(t)$. That is,

$$\int_{-\infty}^0 \frac{\partial P(x,t)}{\partial t}dx = \int_{-\infty}^0 \frac{\partial}{\partial x}\left[\mu(x)\frac{dV}{dx}P(x,t) + \frac{\partial}{\partial x}(D(x)P(x,t))\right] dx$$

$$= -\int_{-\infty}^0 \frac{\partial J(x,t)}{\partial x}dx$$

$$= -J(0,t)$$

where

$$J(x,t) = -\mu(x)\frac{dV}{dx}P(x,t) - \frac{\partial}{\partial x}(D(x)P(x,t))$$

is the probability current density and the point $x = -\infty$ is assumed to be a reflecting barrier. Hence,

$$\frac{\partial n_A(t)}{\partial t} = -J(0,t). \tag{3.1.2}$$

But the probability density is normalized so that we have

$$\int_{-\infty}^\infty P(x,t)dx = 1$$

or

$$n_A(t) + n_C(t) = 1.$$

This implies that

$$\frac{\partial n_A(t)}{\partial t} = -\frac{\partial n_C(t)}{\partial t}. \tag{3.1.3}$$

As far as the particle motion is concerned, the two wells in the potential can be considered as two regions where two kinds of processes take place. The first one is the local equilibration process in each well of the potential and the other is the global equilibration in which the two wells exchange the particle. The local equilibration process is a very fast process compared to the time required for the global equilibration. The detailed comparison between the time scales of these two processes is discussed in the Appendix. The equilibration time for the fast process (τ_f) is of the order of

$$\tau_f \sim \frac{\gamma}{\eta} \tag{3.1.4}$$

while the equilibration time for the slow process (τ_s) in a homogeneous background is of the order of

$$\tau_s \sim \frac{\gamma}{\eta} e^{\frac{V_0}{k_B T_0}} \tag{3.1.5}$$

where γ is the damping coefficient of the force that the particle experiences from the medium or from collision with the wall of the pipe and η is the measure of the curvature of the potential wells. These approximate values of time scales show that the global process is indeed a very slow process compared to the local process.

In this thesis our main goal is to study the dynamics of the slow process or the global equilibration process. For slow process, the contribution of the current at the peak of the barrier is mainly from the neghibouring points of $x = 0$, that is from the region $(-L, L)$. To find the current density $J(0,t)$ at the pick of the barrier height, we express Eq. (3.1.1) as

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}, \tag{3.1.6}$$

where $J(x,t)$ is the current density. The expression for the current density $J(x,t)$, given by

$$J(x,t) = -\mu(x)\frac{dV}{dx}P(x,t) - \frac{\partial}{\partial x}(D(x)P(x,t))$$

can be rearranged as follows:

$$\frac{\partial}{\partial x}(D(x)P(x,t)Q(x)) = -J(x,t)Q(x) \tag{3.1.7}$$

where

$$Q(x) \equiv Exp\left[\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right]. \tag{3.1.8}$$

Note that we have used the Einstein relation

$$D(x) = \mu(x) k_B T(x). \tag{3.1.9}$$

Integrating Eq. (3.1.7) from $-L$ to L we get

$$P(L,t)D(L)Q(L) - P(-L,t)D(-L) = -\int_{-L}^{L} J(x,t)Q(x)dx. \tag{3.1.10}$$

For high barrier $V_0(\gg k_B T)$ the integral on the right side of Eq. (3.1.10) can be simplified. For such condition, as Brinkman [9] assumed, the region near the top of the barrier gives major contribution to the integral. On the other hand, $J(x,t)$ is very nearly constant in this region so that we can replace its value by $J(0,t)$. Hence, we get

$$-J(0,t) = \frac{P(L,t)D(L)Q(L) - P(-L,t)D(-L)}{\int_{-L}^{L} Q(x)dx}. \tag{3.1.11}$$

Now let us find the non-steady state probability density $P(x,t)$ to calculate $P(L,t)$ and $P(-L,t)$. To do this we consider the steady state current density $J_{ss}(x,t)$. At steady state, $J_{ss}(x,t) = 0$ so that

$$\mu(x)\frac{dV}{dx}P_{ss}(x) + \frac{d}{dx}(D(x)P_{ss}(x)) = 0.$$

This implies that the steady state solution of the probability density is given by

$$P_{ss}(x) = \frac{C}{D(x)}Exp\left(-\int_{-L}^{x}\frac{V'(\tilde{x})}{k_B T(\tilde{x})}d\tilde{x}\right), \tag{3.1.12}$$

where C is the normalization constant. Since $D(x) = \mu(x)k_B T(x)$ and the mobility is proportional to the inverse of the square root of the temperature, $\mu(x) \propto \frac{1}{\sqrt{T(x)}}$, as shown in Eq. (2.1.19), we get

$$P_{ss}(x) = \frac{C_0}{\sqrt{T(x)}}Exp\left(-\int_{-L}^{x}\frac{V'(\tilde{x})}{k_B T(\tilde{x})}d\tilde{x}\right). \tag{3.1.13}$$

The equilibration process in each well is very fast compared to the global equilibration process which require escape over the barrier. This means that for global equilibration process the probability distribution $P(x,t)$ in each well is not very far away from the steady state distribution and can be approximated by

$$P(x,t) = \chi(t)P_{ss}(x) \tag{3.1.14}$$

where $\chi(t)$ is essentially constant within each well, and changes only in the vicinity of the peak of the barrier height. The function $\chi(t)$ is obtained by integrating $P(x,t)$. That is,

$$\int_{-\infty}^{0} P(x,t)dx = \int_{-\infty}^{0} \chi(t)P_{ss}(x)dx = n_A(t)$$

and

$$\int_{0}^{\infty} P(x,t)dx = \int_{0}^{\infty} \chi(t)P_{ss}(x)dx = n_C(t)$$

From these two relations, the correction factor for the non-equilibrium distribution function, $\chi(t)$ can be written as

$$\chi(t) = \frac{n_A(t)}{\int_{-\infty}^{0} P_{ss}(x)dx} \qquad \text{for} \quad x < 0 \tag{3.1.15a}$$

and

$$\chi(t) = \frac{n_C(t)}{\int_{0}^{\infty} P_{ss}(x)dx} \qquad \text{for} \quad x \geq 0. \tag{3.1.15b}$$

Substituting the expression of steady state solution P_{ss}, we get the following expression for $\chi(t)$. For $x < 0$

$$\chi(t) = \frac{n_A(t)}{C_0 \int_{-\infty}^{0} \frac{1}{\sqrt{T(x)}} Exp\left(-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right) dx}, \tag{3.1.16a}$$

and for $x \geq 0$

$$\chi(t) = \frac{n_C(t)}{C_0 \int_{0}^{\infty} \frac{1}{\sqrt{T(x)}} Exp\left(-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right) dx}. \tag{3.1.16b}$$

Inserting Eqs. (3.1.16a) and (3.1.16b) in Eq. (3.1.14) one gets the values of $P(L,t)$ and $P(-L,t)$ as

$$P(-L,t) = \frac{n_A(t)}{\sqrt{T(-L)} \int_{-\infty}^{0} \frac{1}{\sqrt{T(x)}} Exp\left(-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right) dx}, \tag{3.1.17}$$

and

$$P(L,t) = \frac{n_C(t) Exp\left(-\int_{-L}^{L} \frac{V'(x)}{k_B T(x)} dx\right)}{\sqrt{T(L)} \int_{0}^{\infty} \frac{1}{\sqrt{T(x)}} Exp\left(-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right) dx}. \tag{3.1.18}.$$

Combining the Eqs. (3.1.2), (3.1.3), (3.1.11), (3.1.17) and (3.1.18) and arranging some of the terms we get an equation that describes the transfer of the particle between the two wells or the *rate equation* for the probabilities of finding the particle in the two wells. That is,

$$\frac{\partial n_A}{\partial t} = -\lambda_A n_A(t) + \lambda_C n_C(t) \tag{3.1.19}$$

and

$$\frac{\partial n_C}{\partial t} = \lambda_A n_A(t) - \lambda_C n_C(t) \tag{3.1.20}$$

where

$$\lambda_A = \frac{D(-L)}{\sqrt{T(-L)}\left(\int_{-L}^{L} Q(x)dx\right)\left(\int_{-\infty}^{0} \frac{dx}{\sqrt{T(x)}Q(x)}\right)} \tag{3.1.21}$$

and

$$\lambda_C = \frac{D(L)}{\sqrt{T(L)}\left(\int_{-L}^{L} Q(x)dx\right)\left(\int_{0}^{\infty} \frac{dx}{\sqrt{T(x)}Q(x)}\right)} \tag{3.1.22}$$

with $Q(x)$ is given by Eq. (3.1.8).

λ_A and λ_C are the rate at which the particle jumps from left to right and from right to left, respectively. The above rate equations are exactly the same as the equations that one gets in chemical reactions. In fact, in chemical reaction processes, λ_A and λ_C are called the reaction rates.

For Landauer's pipe model, the escape rates λ_A and λ_C depend on the form of the potential and the temperature profile.

The eigenvalues of the coefficient matrix for the rate equations (3.1.19) and (3.1.20) are $\lambda = 0$ and $\lambda = -(\lambda_A + \lambda_C)$. This tells us that the relaxation time or the equilibration time for the global process is

$$\tau_s = \frac{1}{|\lambda|} = \frac{1}{\lambda_A + \lambda_C} \tag{3.1.23}$$

This is the typical time one has to wait to see the steady state distribution of the Brownian particle in a double well potential. In chemical reaction, we call this time τ_s as the time scale one has to wait to see the product after the reaction started.

3.2 RATE EQUATIONS FOR van KAMPEN'S MODEL

In this section we discuss the dynamics of a Brownian particle in a bistable potential when there exists a medium inside the Landauer's pipe. As we discussed in the second chapter, this model assumes the medium to be non-homogeneous and have a temperature $T(x)$ which varies in space along the pipe. The probability distribution function of a particle in such a medium evolves according to the Smoluchowski equation

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} \tag{3.2.1}$$

where the current density $J(x,t)$ is given by

$$J(x,t) = -\mu(x)\left[V'(x)P(x,t) + \frac{\partial}{\partial x}\left(k_B T(x)P(x,t)\right)\right] \tag{3.2.2}$$

In this model, we again, consider the double well potential shown in Fig.[3.1] and calculate the equilibration rate for the system by applying the same technique as we used in the previous Landauer's pipe model.

The expression in Eq. (3.2.2) can be written in the form

$$-\frac{J(x,t)}{\mu(x)k_B}Q(x) = \frac{\partial}{\partial x}\left(P(x,t)T(x)Q(x)\right). \tag{3.2.3}$$

where $Q(x)$ is given by Eq. (3.1.8). Since we are interested in the escape rates over the barrier height, we can integrating Eq. (3.2.3) from $-L$ to L to get an approximate value for the current density at the origin; i.e.,

$$-\int_{-L}^{L} \frac{J(x,t)Q(x)}{\mu(x)k_B}dx = P(L,t)T(L)Q(L) - P(-L,t)T(-L). \tag{3.2.4}$$

For high barrier $V_0(\gg k_B T_0)$, one can replace $J(x,t)$ by $J(0,t)$. Hence

$$-J(0,t) = k_B \frac{P(L,t)T(L)Q(L) - P(-L,t)T(-L)}{\int_{-L}^{L} \frac{Q(x)}{\mu(x)}dx} \tag{3.2.5}$$

The non-steady state distributions at the minima points can be obtained by using Eq. (3.1.14); i.e,

$$P(x,t) = \chi(t) P_{ss}(x)$$

where $P_{ss}(x)$ is the steady state distribution of the system and $\chi(t)$ is the correction factor as discussed in the previous section. The steady state distribution is obtained by solving the equation $J_{ss}(x,t) = 0$. That is,

$$\mu \left[V'(x) P_{ss}(x) + \frac{\partial}{\partial x} \left(k_B T(x) P_{ss}(x) \right) \right] = 0.$$

The solution of this equation is given by

$$P_{ss}(x) = \frac{C}{T(x)} Exp\left[- \int^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x} \right]. \tag{3.2.6}$$

Combining Eqs. (3.1.15a), (3.1.15b), (3.1.14) and (3.2.6) one gets the distributions $P(-L,t)$ and $P(L,t)$ as

$$P(-L,t) = \frac{n_A(t)}{T(-L) \int_{-\infty}^{0} \frac{dx}{T(x) Q(x)}} \tag{3.2.7}$$

and

$$P(L,t) = \frac{n_C(t)}{T(L) \int_{0}^{\infty} \frac{dx}{T(x) Q(x)}}. \tag{3.2.8}$$

Substitution of the distributions at the minima points in Eq. (3.2.5) and combining the resulting equation with Eqs. (3.1.2) and (3.1.3), one gets therate equations

$$\frac{\partial n_A}{\partial t} = -\lambda_A^{(v)} n_A(t) + \lambda_C^{(v)} n_C(t) \tag{3.2.9}$$

and

$$\frac{\partial n_C}{\partial t} = \lambda_A^{(v)} n_A(t) - \lambda_C^{(v)} n_C(t) \tag{3.2.10}$$

where the escape rates $\lambda_A^{(v)}$ and $\lambda_C^{(v)}$ for this model are given by

$$\lambda_A^{(v)} = \frac{k_B}{\int_{-L}^{L} \frac{Q(x)}{\mu(x)}dx \int_{-\infty}^{0} \frac{dx}{T(x)Q(x)}} \tag{3.2.11}$$

and

$$\lambda_C^{(v)} = \frac{k_B}{\int_{-L}^{L} \frac{Q(x)}{\mu(x)}dx \int_{0}^{\infty} \frac{dx}{T(x)Q(x)}}. \tag{3.2.12}$$

The time scale that it takes for the system to equilibrate globally is

$$\tau_s^{(v)} = \frac{1}{\lambda_A^{(v)} + \lambda_C^{(v)}} \tag{3.2.11}$$

We have obtained general expressions for the escape rates of the Brownian particle in a bistable potential for both models. In the next chapter we will consider a simple W-potential and a piecewise constant temperature profile for both models to get analytic expressions for the escape rates as well as for the equilibration rates.

Chapter 4

EVALUATION OF THE ESCAPE RATES

In chapter three we have obtained general expressions for the escape rates for the two models. There we considered a general double well potential and a general position dependent temperature profile. We now consider a specific type of double well potential along with a certain temperature profile and evaluate the rates at which the Brownian particle escapes from one well to the other for both models.

For the bistable potential we take a simple symmetric W-potential which is piecewise linear and having the same magnitude in slope as shown in the Fig. 4.1. It is described by the barrier height V_0 and the distance $2L$ between the two minima located at $x = \pm\, L$ on the either side of the origin.

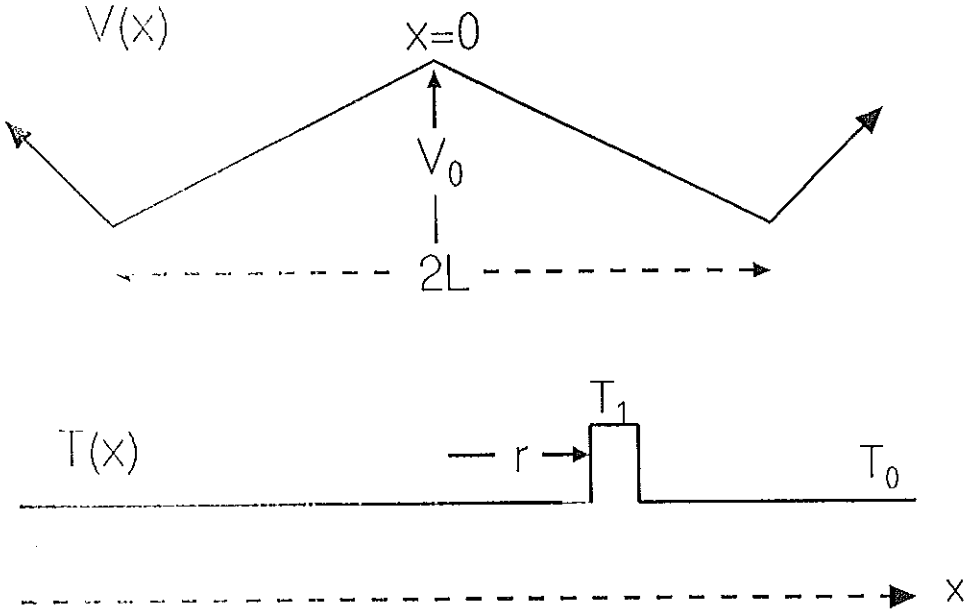

Fig. 4.1 The plot of the symmetric potential with the hot temperature profile.

The W-potential that we consider for both models is described by the following sets of equations:

$$V(x) = \begin{cases} -V_0\left(\frac{x}{L}+1\right) & \text{if} \quad x \leq -L \\ V_0\left(\frac{x}{L}+1\right) & \text{if} \quad -L \leq x \leq 0 \\ V_0\left(-\frac{x}{L}+1\right) & \text{if} \quad 0 \leq x \leq L \\ V_0\left(\frac{x}{L}-1\right) & \text{if} \quad x \geq L \end{cases} \tag{4.1}$$

The non-homogeneous temperature background is taken to be piecewise constant with the hot locality placed somewhere in the right well of the potential. This hot locality is parameterized by the quantities α, δ and s which describe the position from the potential maxima, width and the strength of the hot region, respectively. We define these parameters as follows:

$$\text{position } = r = \alpha L, \tag{4.2}$$

$$\text{width} = W = \delta L. \tag{4.3}$$

$$\text{strength} = s = \frac{\Delta T}{T_0} = \frac{T_1 - T_0}{T_0}, \tag{4.4}$$

where r is the position of the left side of the hot zone from $x = 0$, L is the distance between the center and one of the minima points, T_1 is the temperature of the hot zone and T_0 is the temperature of the rest of the background. Mathematically the temperature profile is described by the function

$$T(x) = T_0 + \Delta T[\Theta(x - \alpha L) - \Theta(x - (\alpha + \delta)L)] \tag{4.5}$$

where $\Theta(x)$ is the Heaviside function.

In the following two sections we find the analytic expressions for the escape rates for the two models.

4.1 EVALUATION OF THE ESCAPE RATES FOR LANDAUER'S PIPE MODEL

The general expressions for the escape rates from right to left and vice versa of the Brownian particle in the Landauer's pipe case, are given by Eqs. (3.1.21) and (3.1.22). Let us write them once again:

$$\lambda_A = \frac{D(-L)}{\sqrt{T(-L)}\int_{-L}^{L} e^{\int_{-L}^{x}\frac{V'(\tilde{x})}{k_BT(\tilde{x})}d\tilde{x}}dx\int_{-\infty}^{0}\frac{1}{\sqrt{T(x)}}e^{-\int_{-L}^{x}\frac{V'(\tilde{x})}{k_BT(\tilde{x})}d\tilde{x}}dx}$$

and

$$\lambda_C = \frac{D(L)}{\sqrt{T(L)}\int_{-L}^{L} e^{\int_{-L}^{x}\frac{V'(\tilde{x})}{k_BT(\tilde{x})}d\tilde{x}}dx\int_{0}^{\infty}\frac{1}{\sqrt{T(x)}}e^{-\int_{-L}^{x}\frac{V'(\tilde{x})}{k_BT(\tilde{x})}d\tilde{x}}dx}.$$

We first evaluate the integrals that appear in the escape rates λ_A and λ_C. The first integral in the escape rate expressions is

$$\int_{-L}^{L} Q(x)dx = \int_{-L}^{L} Exp\left[\int_{-L}^{x}\frac{V'(\tilde{x})}{k_BT(\tilde{x})}d\tilde{x}\right]dx.$$

Since both the potential and the temperature of the system are position dependent, we have to divide the integral in four parts. Hence, we have

$$\int_{-L}^{0} Q(x)dx + \int_{0}^{\alpha L} Q(x)dx + \int_{\alpha L}^{(\alpha+\delta)L} Q(x)dx + \int_{(\alpha+\delta)L}^{L} Q(x)dx.$$

The value of each of these integrals is

$$\int_{-L}^{0} Q(x)dx = \frac{k_BT_0L}{V_0}\left(e^{\frac{V_0}{k_BT_0}} - 1\right),$$

$$\int_{0}^{\alpha L} Q(x)dx = \frac{k_BT_0L}{V_0}\left(e^{\frac{V_0}{k_BT_0}} - e^{\frac{(1-\alpha)V_0}{k_BT_0}}\right),$$

$$\int_{\alpha L}^{(\alpha+\delta)L} Q(x)dx = \frac{k_B T_1 L}{V_0} e^{\frac{(1-\alpha)V_0}{k_B T_0}} \left(1 - e^{-\frac{\delta V_0}{k_B T_1}}\right) \qquad \text{and,}$$

$$\int_{(\alpha+\delta)L}^{L} Q(x)dx = \frac{k_B T_0 L}{V_0} e^{-\frac{\delta V_0}{k_B T_1}} \left(e^{\frac{(1-\alpha)V_0}{k_B T_0}} - e^{\frac{\delta V_0}{k_B T_0}}\right).$$

Therefore,

$$\int_{-L}^{L} Q(x)dx = \frac{k_B T_0 L}{V_0} e^{\frac{V_0}{k_B T_0}} G \tag{4.1.1}$$

where G is given by

$$G = 2 + s\left(e^{-\alpha u_0} - e^{-\left[\alpha + \frac{\delta}{1+s}\right]u_0}\right) - e^{\left[\frac{\delta s}{1+s} - 1\right]u_0} - e^{-u_0}$$

with $u_0 = \frac{V_0}{k_B T_0}$. But the contribution of the last two terms is negligible as compared to the other terms since we consider high barrier case ($V_0 \gg k_B T_0$). Hence we can neglect them and write G as

$$G \simeq 2 + s\left(e^{-\alpha u_0} - e^{-\left[\alpha + \frac{\delta}{1+s}\right]u_0}\right) \tag{4.1.2}$$

Next we evaluate the other two integrals that appear in the expression for the escape rates. These are,

$$\int_{-\infty}^{0} \frac{dx}{\sqrt{T(x)}Q(x)} \qquad \text{and} \qquad \int_{0}^{\infty} \frac{dx}{\sqrt{T(x)}Q(x)}.$$

The first integral can be written as

$$\int_{-\infty}^{0} \frac{dx}{\sqrt{T(x)}Q(x)} = \int_{-\infty}^{-L} \frac{dx}{\sqrt{T(x)}Q(x)} + \int_{-L}^{0} \frac{dx}{\sqrt{T(x)}Q(x)}$$

Its value is

$$\int_{-\infty}^{0} \frac{dx}{\sqrt{T(x)}Q(x)} = \frac{k_B\sqrt{T_0}L}{V_0} He^{-\frac{V_0}{k_BT_0}} \tag{4.1.3}$$

where H is given by

$$H = 2e^{u_0} - 1. \tag{4.1.4}$$

Similarly the second integral can be written as

$$\int_0^{\infty} \frac{dx}{\sqrt{T(x)}Q(x)} = \int_0^{\alpha L} \ldots + \int_{\alpha L}^{(\alpha+\delta)L} \ldots + \int_{(\alpha+\delta)L}^{L} \ldots + \int_L^{\infty} \ldots$$

The values of each of these integrals is given by the following expressions:

$$\int_0^{\alpha L} \frac{dx}{\sqrt{T(x)}Q(x)} = \frac{k_B\sqrt{T_0}L}{V_0}\left(e^{\frac{(\alpha-1)V_0}{k_BT_0}} - e^{-\frac{V_0}{k_BT_0}}\right),$$

$$\int_{\alpha L}^{(\alpha+\delta)L} \frac{dx}{\sqrt{T(x)}Q(x)} = \frac{k_B\sqrt{T_1}L}{V_0} e^{\frac{(\alpha-1)V_0}{k_BT_0}}\left(e^{\frac{\delta V_0}{k_BT_1}} - 1\right),$$

$$\int_{(\alpha+\delta)L}^{L} \frac{dx}{\sqrt{T(x)}Q(x)} = \frac{k_B\sqrt{T_0}L}{V_0} e^{\frac{\delta V_0}{k_BT_1}}\left(e^{\frac{-\delta V_0}{k_BT_0}} - e^{\frac{(\alpha-1)V_0}{k_BT_0}}\right) \qquad \text{and}$$

$$\int_L^{\infty} \frac{dx}{\sqrt{T(x)}Q(x)} = \frac{k_B\sqrt{T_0}L}{V_0} e^{\frac{\delta V_0}{k_B}\left[\frac{1}{T_1}-\frac{1}{T_0}\right]}.$$

Hence we have

$$\int_0^{\infty} \frac{dx}{\sqrt{T(x)}Q(x)} = \frac{k_B\sqrt{T_0}L}{V_0} Ke^{\frac{-V_0}{k_BT_0}} \tag{4.1.5}$$

where K is given by

$$K = -1 + 2e^{\left[1-\frac{\delta s}{1+s}\right]u_0} + (\sqrt{1+s} - 1)\left(e^{\frac{\delta u_0}{(1+s)}} - 1\right)e^{\alpha u_0}.$$

But compared to the other terms, -1 can be neglected and we can write K as

$$K = 2e^{\left[1-\frac{\delta s}{1+s}\right]u_0} + (\sqrt{1+s} - 1)\left(e^{\frac{\delta u_0}{(1+s)}} - 1\right) e^{\alpha u_0}. \tag{4.1.6}$$

Finally, the rate at which the Brownian particle escapes from the left well to the right well of the W-potential in the Landauer's pipe model under a locally heated temperature background is

$$\lambda_A = \left(\frac{u_0}{L}\right)^2 \frac{D(-L)}{GH} \tag{4.1.7}$$

while the escape rate of the particle from right well to the left well is

$$\lambda_C = \left(\frac{u_0}{L}\right)^2 \frac{D(L)}{GK} \tag{4.1.8}$$

where G, H and K are given by Eqs. (4.1.2), (4.1.4) and (4.1.6), respectively. The equilibration rate of the slow process for such system is

$$\frac{1}{\tau_s} = \lambda_A + \lambda_C = \left(\frac{u_0}{L}\right)^2 \left(\frac{D(L)}{GH} + \frac{D(-L)}{GK}\right)$$

Since the temperature at the two minima points is the same in our model; i.e, $T(-L) = T(L)$, $D(-L) = D(L)$ and the equilibration rate can be written as

$$\frac{1}{\tau_s} = D_0 \left(\frac{u_0}{L}\right)^2 \left(\frac{1}{H} + \frac{1}{K}\right) \frac{1}{G} \tag{4.1.9}$$

where

$$D_0 = D(-L) = D(L).$$

4.2 EVALUATION OF THE ESCAPE RATES FOR van KAMPEN'S MODEL

We now evaluate the escape rates and the equilibration rate for the symmetric W-potential and piecewise constant temperature profile for van Kampen's model. This evaluation considers the mobility of the particle to be homogeneous; i.e., $\mu(x) = \mu_0 =$ constant. Hence the general expressions for the escape rates for such model take the following form:

$$\lambda_A^{(v)} = \frac{D^{(v)}(-L)}{T(-L)\int_{-L}^{L} e^{\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx \int_{-\infty}^{0} \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx} \tag{4.2.1}$$

and

$$\lambda_C^{(v)} = \frac{D^{(v)}(L)}{T(L)\int_{-L}^{L} e^{\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx \int_{0}^{\infty} \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx} \tag{4.2.2}$$

where we have used the Einstein relation, Eq. (3.1.9). The first integral in these expressions is already calculated and is given by Eq. (4.1.1); i.e,

$$\int_{-L}^{L} e^{\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \frac{L}{u_0} e^{u_0} G$$

where G is given by Eq. (4.1.2).

We now evaluate the other integrals.

$$\int_{-\infty}^{0} \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \int_{-\infty}^{-L} \ldots + \int_{-L}^{0} \ldots$$

This is equal to

$$\int_{-\infty}^{0} \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \left(\frac{k_B L}{V_0}\right) H e^{-u_0} \tag{4.2.3}$$

where H is given by Eq. (4.1.4).

Similarly

$$\int_0^\infty \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \int_0^{\alpha L} \ldots + \int_{\alpha L}^{(\alpha+\delta)L} \ldots + \int_{(\alpha+\delta)L}^{L} \ldots + \int_L^\infty \ldots$$

The value of each of these integrals is given as follows.

$$\int_0^{\alpha L} \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \left(\frac{k_B L}{V_0}\right) \left(e^{\frac{(\alpha-1)V_0}{k_B T_0}} - e^{-\frac{V_0}{k_B T_0}}\right),$$

$$\int_{\alpha L}^{(\alpha+\delta)L} \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \left(\frac{k_B L}{V_0}\right) e^{\frac{(\alpha-1)V_0}{k_B T_0}} \left(e^{\frac{\delta V_0}{k_B T_1}} - 1\right),$$

$$\int_{(\alpha+\delta)L}^{L} \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \left(\frac{k_B L}{V_0}\right) e^{\frac{\delta V_0}{k_B T_1}} \left(e^{\frac{-\delta V_0}{k_B T_0}} - e^{\frac{(\alpha-1)V_0}{k_B T_0}}\right) \qquad \text{and}$$

$$\int_L^\infty \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \left(\frac{k_B L}{V_0}\right) e^{\frac{\delta V_0}{k_B}\left[\frac{1}{T_1} - \frac{1}{T_0}\right]}.$$

Therefore

$$\int_0^\infty \frac{1}{T(x)} e^{-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx = \frac{k_B L}{V_0} e^{-u_0} I,$$

where I is given by

$$I = 2e^{\left[1 - \frac{\delta s}{1+s}\right] u_0} - 1. \tag{4.2.4}$$

The escape rates of the Brownian particle in this type model are, therefore, given as

$$\lambda_A^{(v)} = \left(\frac{u_0}{L}\right)^2 \frac{D^{(v))_0}(-L)}{GH}, \tag{4.2.5}$$

and

$$\lambda_C^{(v)} = \left(\frac{u_0}{L}\right)^2 \frac{D^{(v)}(L)}{GI} \tag{4.2.6}$$

where G and I are given by Eqs. (4.1.3) and (4.2.2), respectively. The equilibration rate of the slow process in this model is

$$\frac{1}{\tau_s} = \lambda_A + \lambda_C = \left(\frac{u_0}{L}\right)^2 D_0^{(v)} \left(\frac{1}{I} + \frac{1}{H}\right) \frac{1}{G}. \tag{4.2.7}$$

We obtained analytic expressions for the escape rates of the Brownian particle for both models *because* we have chosen a simple W-potential along with piecewise constant temperature profile. Otherwise it would have been impossible to get analytic expression and one has to numerically evaluate the general expressions for the escape rates Eqs. (3.1.21) and (3.1.22) for specific type of potential and temperature profile. Although this selection of W-potential and temperature profile may not be realistic, the essential information about the effect of the local heating on the escape rates and the equilibration rates is obtained without any loss of generality.

The escape rates that we obtained in this chapter are functions of the parameter of α, δ and s. In the next chapter we discuss the behaviour of the escape rates and the equilibration rates as the parameters α, δ or s varies.

Chapter 5

RESULT AND DISCUSSION

The explicit expressions for the escape rates are obtained in the last chapter. These escape rates are functions of the parameters α, δ and s and hence, the effect of the hot locality on these rates and also on the equilibration rate can be studied in terms of these parameters. Since the hot locality is placed between the peak of the barrier height and the right minima, the parameters α and δ take positive value between 0 and 1. On the other hand s takes positive values for a hot locality and negative values between -1 and 0, if one considers a cold locality.

The change in escape rates due to the presence of the hot locality is better studied in terms of the factor by which the escape rate has improved. We call this factor as the *improvement factor*, Λ, which is defined as

$$\Lambda = \frac{\lambda}{\lambda^0} \tag{5.1}$$

where λ is the escape rate in the presence of the hot locality and λ^0 is the escape rate in the absence of the hot locality. In the Landauer's pipe model, the improvement factors for the escape rates are

$$\Lambda_A = \frac{\lambda_A}{\lambda_A^0} \qquad \text{and} \qquad \Lambda_C = \frac{\lambda_C}{\lambda_C^0}. \tag{5.2}$$

Since the W-potential that we considered is symmetric, the escape rate to the right and to the left of the barrier height are identical when there is no hot locality. That is, for $s = 0$

$$\lambda_A^0 = \lambda_C^0 = \frac{D_0}{2}\left(\frac{u_0}{L}\right)^2 \frac{1}{(1 - e^{-u_0})(2e^{u_0} - 1)}.$$

For high barrier $V_0(\gg k_B T_0)$, e^{-u_0} can be neglected compared to 1 and the escape rates become

$$\lambda_A^0 = \lambda_C^0 = \frac{D_0}{4}\left(\frac{u_0}{L}\right)^2 e^{-u_0}. \tag{5.3}$$

Using these results, the expressions for the improvement factors Λ_A and Λ_C, for the Landauer's pipe model are given by

$$\Lambda_A = \frac{2}{2 + se^{-\alpha u_0}\left(1 - e^{-\frac{\delta u_0}{1+s}}\right)} \tag{5.4}$$

and

$$\Lambda_C = \frac{2e^{u_0}}{\left[2 + s\left(1 - e^{-\frac{\delta u_0}{1+s}}\right)e^{-\alpha u_0}\right]\left[2e^{\left(1-\frac{\delta s}{1+s}\right)u_0} + \left(\sqrt{1+s} - 1\right)\left(e^{\frac{\delta u_0}{1+s}} - 1\right)e^{\alpha u_0}\right]}. \tag{5.5}$$

Now let us see the dependence of the improvement factor on the parameters α, δ and s. First we consider Λ_A. For a given α and δ, the exponential term that contains s in the denominator of Eq. (5.4) increases as s increases and therefore the term in the bracket decreases. But the coefficient of the bracket in this denominator, s, is dominant for large value of s. Therefore the escape rate to the right well decreases as s increases.

Next we take fixed values of s and α to see the dependence of the improvement factor Λ_A on the width of the hot locality. As δ increases the exponential $e^{-\frac{\delta s}{1+s}u_0}$ term in the bracket weakly decreases and hence Λ_A decreases also weakly. We can argue in the same way to see decreasing effect of α on Λ_A as it increases.

The dependence of the improvement factor Λ_C on the parameters s, α and δ can also be discussed in the same way. For constant values of s and δ one can see how the escape rate behave when α varies. In the denominator of Λ_C there are two competing terms that contain α; i.e $e^{\pm\alpha u_0}$. Hence for small values of α the term which contains $e^{-\alpha u_0}$ is dominant and for large values of α the term with $e^{\alpha u_0}$ dominates. That means there is an optimal value α at which the escape rate takes maximum value.

Variation of the width of the hot zone also has an effect on the escape rate. To see that we fix s and α. Then, as we have seen for the discussion of Λ_A, the term having δ in the first square bracket in the denominator of Eq. (5.5) increases as δ increases. The other square bracket has two terms having δ whose combined effect is to decrease the denominator by a large amount. Therefore, the escape rate will increase by a large factor as the width of the hot locality increases.

Finally, we consider the effect of the strength s on the improvement factor Λ_C. Again, as we saw in the argument for Λ_A, the first square bracket term in the denominator of Λ_C increases as s increases. But the other square bracket term decreases significantly as s increases. Hence the escape rate increases by a large factor as the strength of the hot region increases.

The above arguments can be checked by observing the plots of the escape rates Λ_A and Λ_C as a functions of the parameters s, α and δ. We have drawn the graph of $\Lambda_A(s)$ and $\Lambda_C(s)$ using Mathematica. The results are shown in Figs. 5.1 and 5.2. The graphs show that the escape rate of the Brownian particle to the right of the potential barrier decreases very weakly. On the other hand, the escape rate to the left of the potential barrier increases significantly as the hot locality gets stronger and stronger.

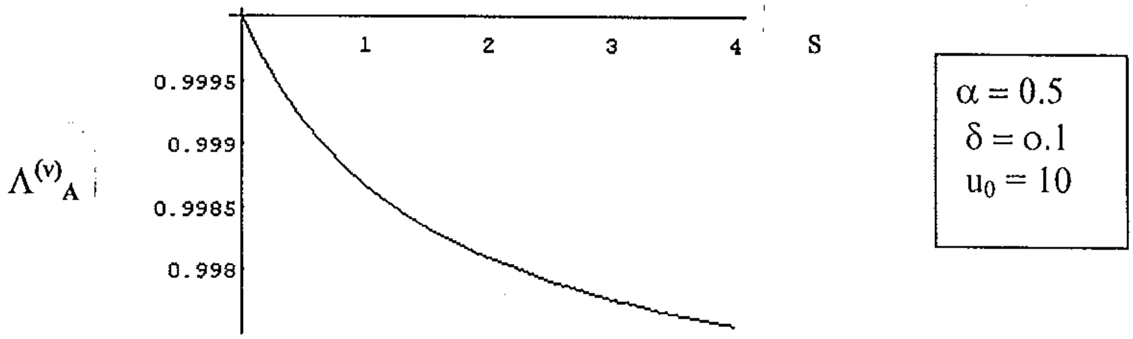

Fig. 5.1 Plot of Λ_A as a function of strength, s.

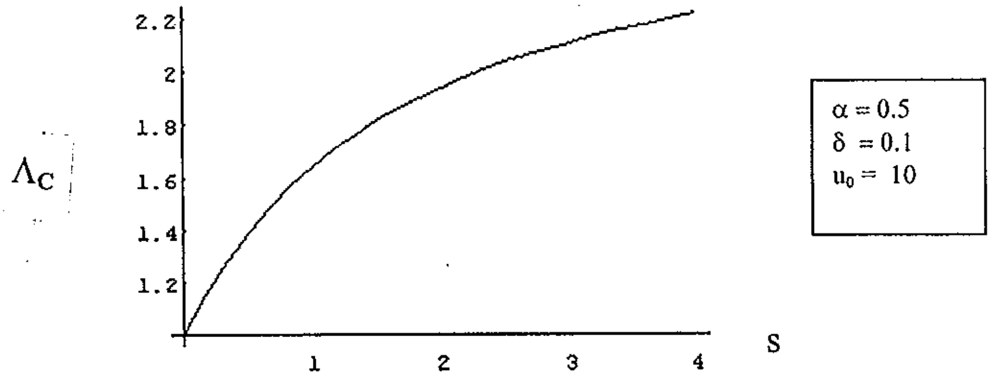

Fig. 5.2 Plot of Λ_C as a function of strength, s.

From physical point of view, these results can be explained as follows. The escape rate to the left well, λ_C, increases as s increases because the hot reservoir gives the particle a strong thermal kick and as a result the particle easily jumps over the barrier. On the other hand, the escape rate to the right of the barrier decreases as s increases. That is because of the bouncing back effect that arises due to the hot locality. Whenever there is a jump from left to right, there is a strong thermal kick to the particle from the hot locality and that causes the particle to bounce back to the left well. Due to this, the particle will spend more time in the left well than that without hot locality. Therefore, the escape rate to the right well decrease as s increases.

We can also define the improvement factor associated with the equilibration rate as

$$\Lambda = \frac{\lambda_A + \lambda_C}{\lambda_A^0 + \lambda_C^0}. \tag{5.6}$$

The graph of $\Lambda(s)$ is shown in Fig. 5.3. It tells us that the hot locality has indeed a strong effect on the equilibration rate. This implies locally heating Landauer's pipe decreases the equilibration time of the system.

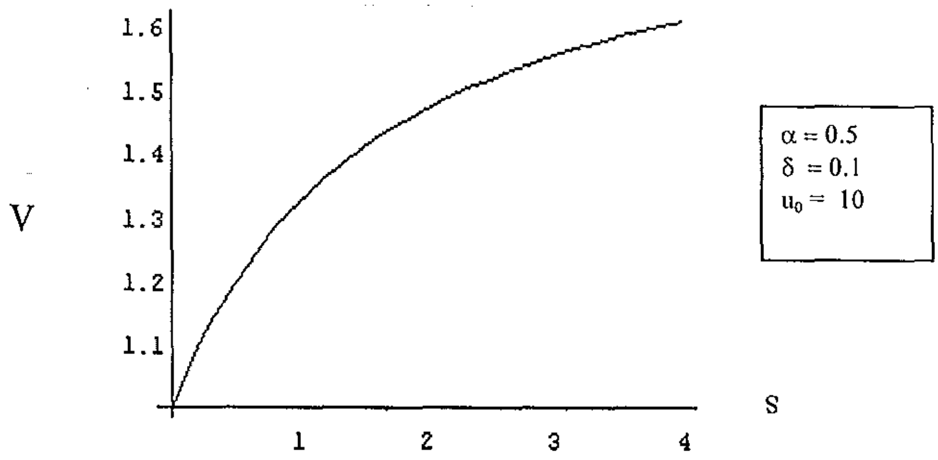

Fig. 5.3 Plot of Λ as a function of strength, s.

The variation of the escape rates and the equilibration rate for variable width of the hot locality is shown in Figs. 5.4, 5.5 and 5.6. As we argued in our earlier discussion, these graphs show that the improvement factor Λ_C increases by a large factor as δ increases while Λ_A decreases very gently as δ increases. This is because of the fact that as the width of the hot zone increases, both the pumping and bouncing effects on the particle increase. This makes the right well less stable and hence the particle prefers to stay in the left well. That means the escape rate to the left well increases as the width of the hot region increases. The equilibration rate of the system will also be improved when we increase the width of the hot locality.

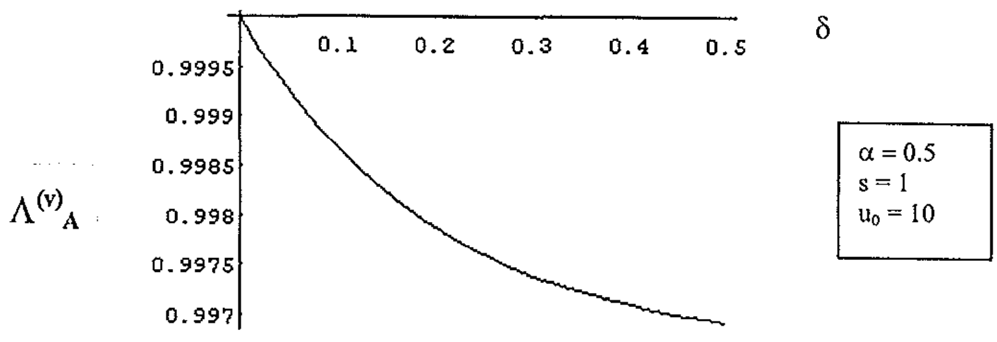

Fig. 5.4 Plot of Λ_A as a function of width, δ.

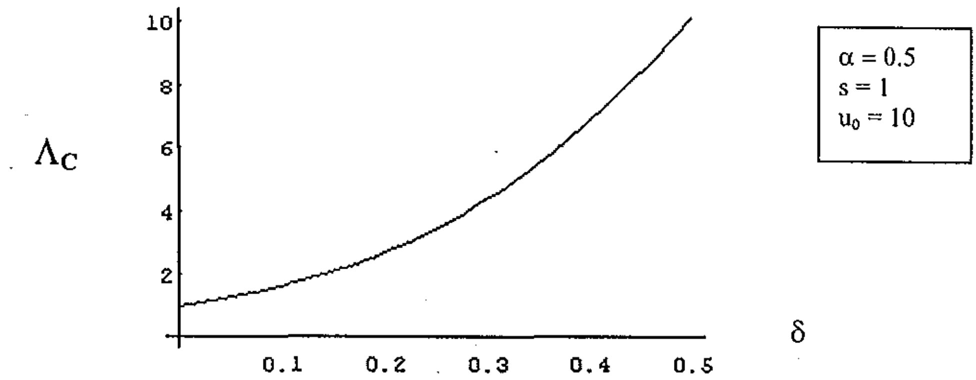

Fig. 5.5 Plot of Λ_C as a function of width, δ.

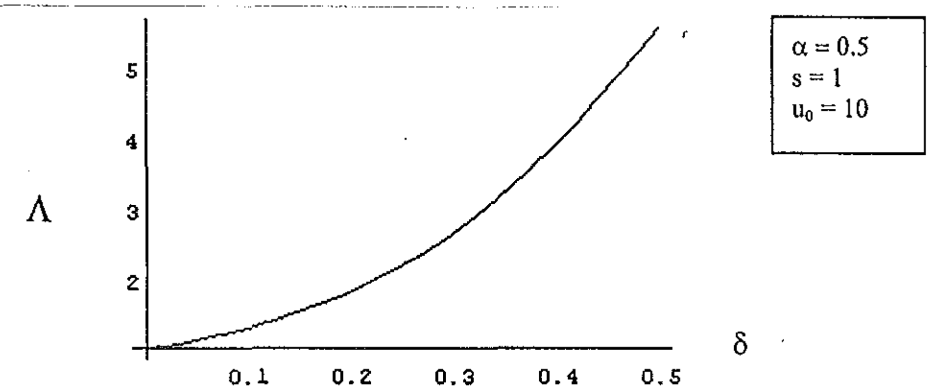

Fig. 5.6 Plot of Λ as a function of width, δ.

The dependence of the escape rates on the position of the hot locality is shown in Figs. 5.7 and 5.8. The graphs show that shifting the position of the hot locality further to the right decreases the bouncing effect of the hot locality. Hence we observe a slight improvement on the escape rate of the Brownian particle from left to right well. That means heating the pipe far away from the peak of the barrier height will not have any effect on the escape rate to the right. On the other hand we observe that Λ_C is highly dependent on the position of the hot locality. There is an optimal position of the hot locality at which Λ_C takes maximum value. The equilibration rate is also highly dependent on the position of the hot locality. As Fig. 5.9 shows, there is an optimal value of α at which the system's equilibration rate is maximum.

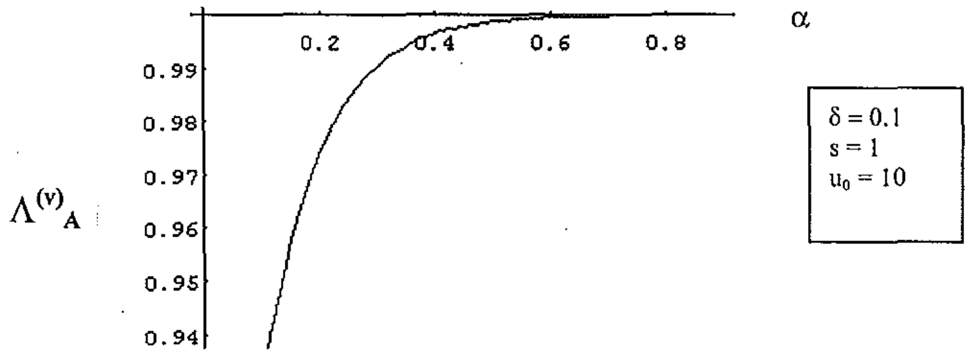

Fig. 5.7 The plot of Λ_A as a function of position, α.

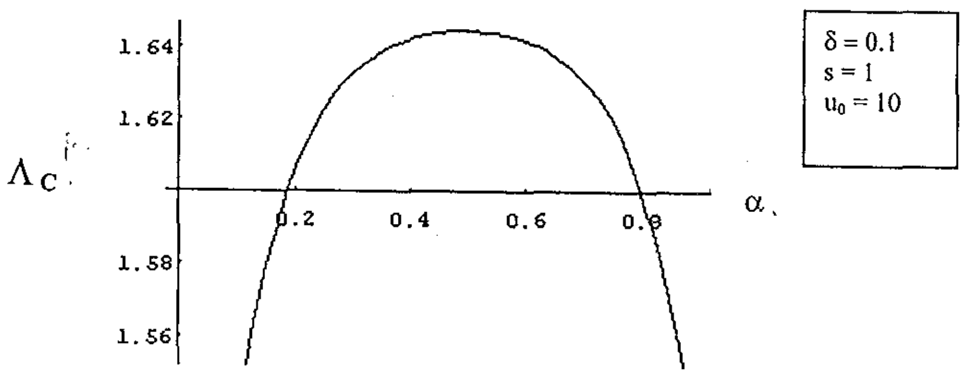

Fig. 5.8 The plot of Λ_C as a function of position, α.

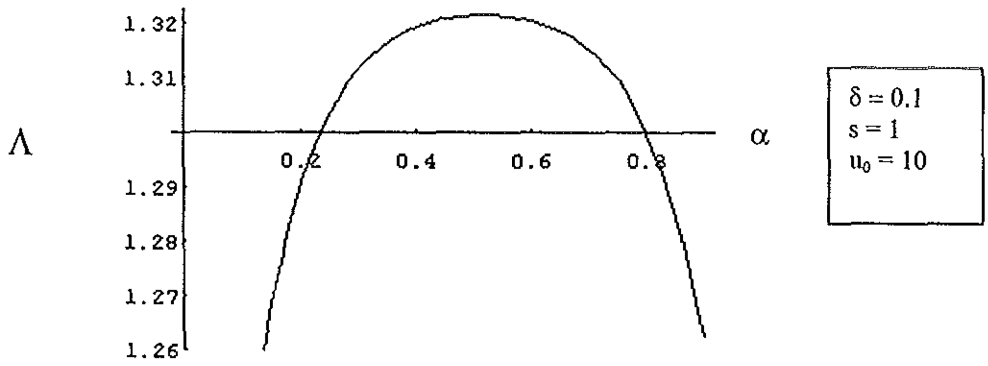

Fig. 5.9 The plot of Λ as a function of position, α.

Now we discuss the properties of the escape rates and the equilibration rate for the van Kampen's model of Brownian particle. Again here we define the improvement factor for this model as

$$\Lambda_A^{(v)} = \frac{\lambda_A^{(v)}}{\lambda_{A^0}^{(v)}} \qquad \text{and} \qquad \Lambda_C^{(v)} = \frac{\lambda_C^{(v)}}{\lambda_{C^0}^{(v)}} \tag{5.7}$$

where $\lambda_{A^0}^{(v)}$ and $\lambda_{C^0}^{(v)}$ are the escape rates of the particle when there is no hot locality. Actually the two escape rates have the same value in the absence of the hot locality because our W-potential is symmetric. Their value is give by

$$\lambda_{A^0}^{(v)} = \lambda_{C^0}^{(v)} = \frac{D_0^{(v)}}{4}\left(\frac{u_0}{L}\right)^2 e^{-u_0}. \tag{5.8}$$

Hence the relative escape rates are given by

$$\Lambda_A^{(v)} = \frac{2}{2 + se^{-\alpha u_0}\left(1 - e^{-\frac{\delta u_0}{1+s}}\right)} \tag{5.9}$$

and

$$\Lambda_C^{(v)} = \frac{2e^{u_0}}{\left[2 + s\left(1 - e^{-\frac{\delta u_0}{1+s}}\right)e^{-\alpha u_0}\right]\left[2e^{\left(1-\frac{\delta s}{1+s}\right)u_0} - 1\right]}. \tag{5.10}$$

The improvement factor of the Brownian particle to the right well in this model, $\Lambda_A^{(v)}$, is identical to the corresponding improvement factor of the particle in the Landauer's pipe model, Λ_A. This is because expressions for the escape rates λ_A and $\lambda_A^{(v)}$ are identical. On the other hand the expressions of the relative escape rates to the left well for the two models are totally different. In the van Kampen's model the relative escape rate $\Lambda_C^{(v)}$ is an increasing function of the position, width and strength. More over, in this model the relative escape rate has no optimal position at which the escape rate takes maximum value, which is not true for the Landauer's pipe case. Actually this difference arises because of the type of equilibration processes that the particle experiences during collision, with the wall of the pipe in the Landauer's case and with the medium in the case of the van Kampen's model.

The graph of the escape rate $\Lambda_C^{(v)}$ as a function of position, width and strength are, respectively, shown in Figs. 5.10, 5.11 and 5.12.

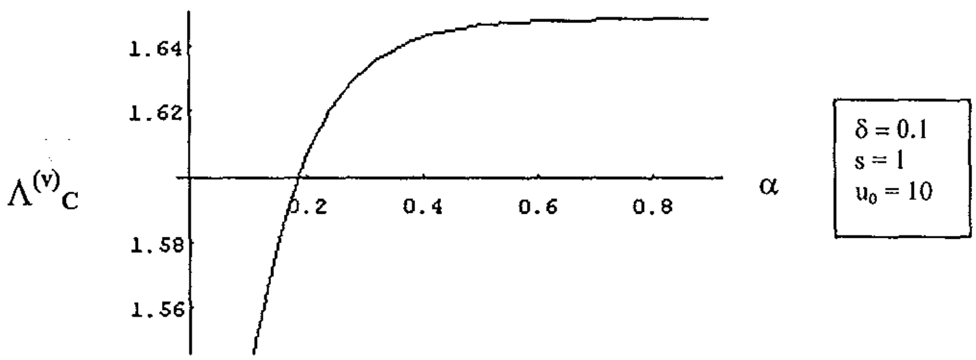

Fig. 5.10 Plot of $\Lambda^{(v)}{}_C$ as a function position, α.

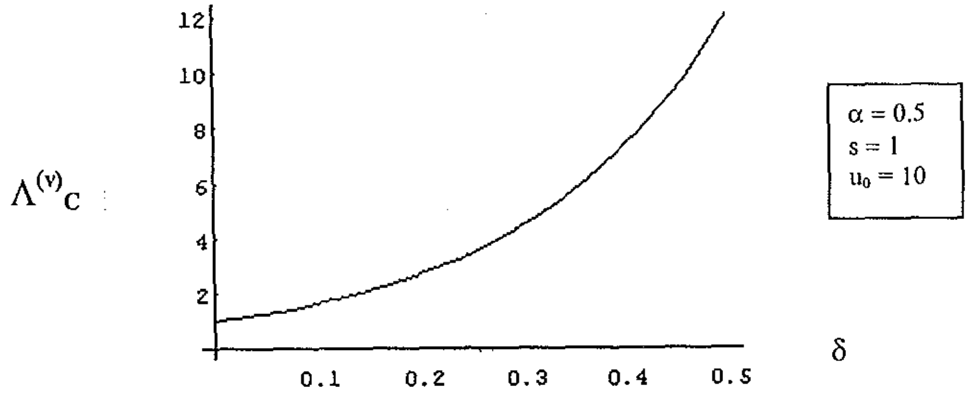

Fig. 5.11 Plot of $\Lambda^{(v)}{}_C$ as a function width, δ.

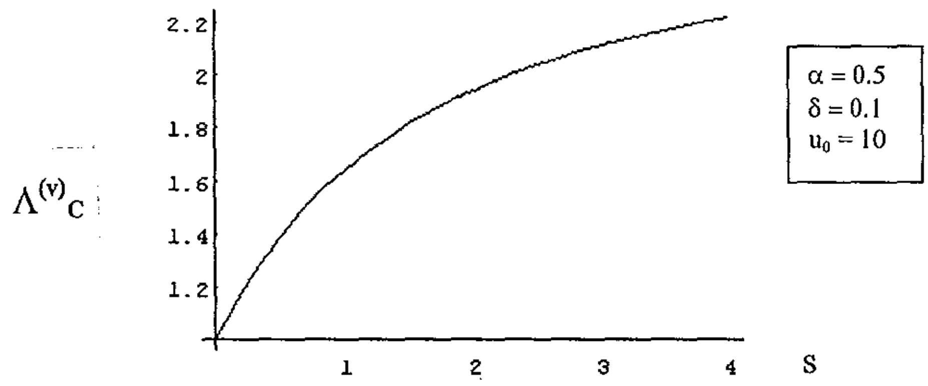

Fig. 5.12 Plot of $\Lambda^{(v)}{}_C$ as a function of strength, s.

Equilibration rate for this model has also improved by the presence of hot locality. In fact it is an increasing function of all the parameters α, δ and s. Unlike the Landauer's pipe model, this model has no optimal value of α at which the equilibration rate is maximum. The patterns of the improvement factor $\Lambda^{(v)}$ as a function of the parameters are shown in the Figs. 5.13, 5.14 and 5.15.

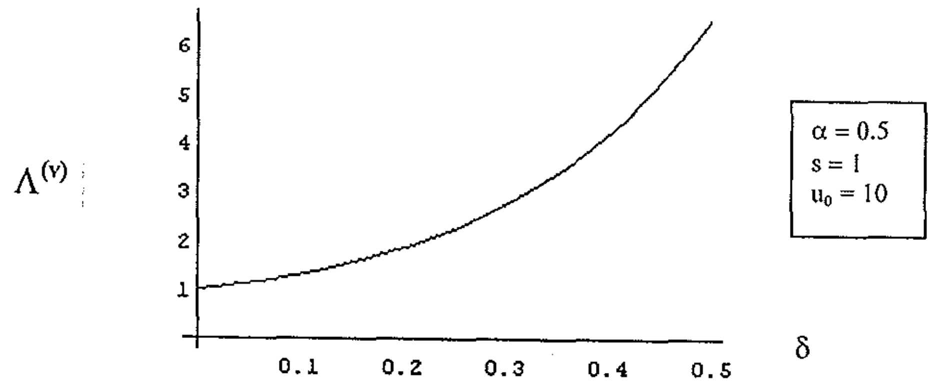

Fig. 5.13 Plot of $\Lambda^{(v)}$ as a function of width, δ.

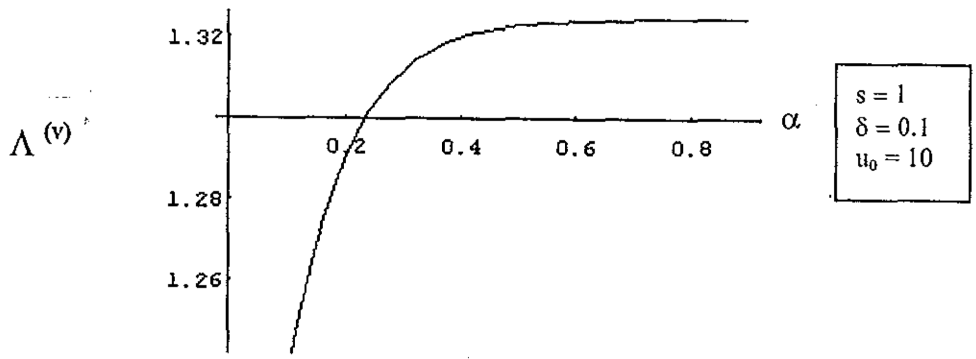

Fig. 5.14 Plot of $\Lambda^{(v)}$ as a function of position, α.

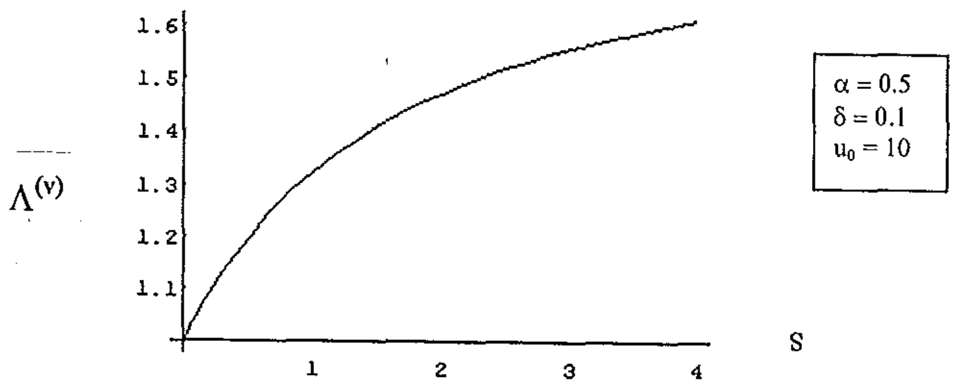

Fig. 5.15 Plot of $\Lambda^{(v)}$ as a function of strength, s.

Chapter 6

SUMMARY AND CONCLUSION

In this work, we considered two kinds of models for the study of diffusion in non-homogeneous media. For these models, we studied the dynamics of a Brownian particle in a bistable potential with non-uniform temperature background. In particular we considered a simple W-potential along with a piecewise constant temperature profile, where we put the hot locality somewhere within the right well. For this specific choice of potential and temperature profile, we obtained analytic expressions for the inter-well escape rates and the equilibration rates for both models by applying Brinkman's method.

These escape rates and the equilibration rates are functions of the strength, width and position of the hot locality, and the height of the potential barrier. In fact, the local heating has a strong pumping effect of particle to the left well while it has weak effect on retarding the escape rate of the the particle to the right well. As a result, for both models, we have found that the presence of the hot locality has improved both the equilibration rate of the systems and the escape rates to the left significantly as compared to that without hot locality.

An interesting result that we found in this work is that the escape rate of the particle to the left well and the equilibration rate of the system, for the Landauer's pipe model, have optimal positions at which they take their maximum values. Similar results are not observed for the van

Kampen's model where both the escape rate and the equilibration rate are increasing functions of the position. Even though this is due to the fact that the particle experiences different types of equilibration processes for the two models, the detailed reason of why it is so is yet to be explored.

Our results for the van Kampen's model are in agreement with the work of Mulugeta Bekele *et.al.* [7], which is done using supersymmetric and numerical methods. As an independent check, we finally recommend that, it is worth to do the problem of Landauer's pipe model using supersymmetric as well as numerical method.

Appendix

EQUILIBRATION TIMES FOR FAST AND SLOW PROCESSES

In this appendix we want to compare the time scales between the global equilibration process, τ_s, and the local equilibration process, τ_f. Let us first estimate τ_f .

The dynamics of the particle within the wells is governed by the Langevin equation

$$\frac{d^2x}{dt^2} = -V'(x) - \gamma\frac{dx}{dt} + \xi(t) \qquad (A.1)$$

where $-\gamma\frac{dx}{dt}$ is the friction force that the Brownian particle experiences from the medium or from collision with the wall of the pipe in the Landauer's pipe case. The coefficient γ is inversely proportional to the mobility of the particle μ; i.e, $\gamma \propto \frac{1}{\mu}$. For high friction limit, we can consider the particle to take a creeping motion so that

$$\frac{d^2x}{dt^2} \simeq 0.$$

Hence, the Langevin equation takes the form

$$\gamma\frac{dx}{dt} = -V'(x) + \xi(t). \qquad (A.2)$$

Taking the average of both sides of Eq. (A.2) eliminates the random force term. Hence we consider only the damping effect and we will keep track of the displacement of the mean value for $x(t)$; i.e,

$$\gamma\frac{dx}{dt} = -V'(x). \qquad (A.3)$$

If we approximate the potential near the minima points by a parabola of the form

$$\frac{1}{2}\eta(x \pm L)^2 \tag{A.4}$$

where $\eta = V''(\pm L)$, the Langevin equation takes the form

$$\frac{dx}{dt} = -\frac{\eta}{\gamma}(x \pm L). \tag{A.5}$$

The solution of this equation is

$$x(t) \pm L \sim Ce^{-\frac{\eta}{\gamma}t}, \tag{A.6}$$

where C is a constant which is determined from initial conditions. This tells us that any deviation of the particles position from equilibrium $\pm L$ point relaxes back within a time scale of

$$\tau_f = \frac{\gamma}{\eta}. \tag{A.7}$$

where this time scale τ_f depends on strength of the damping force and the shape of the potential.

Therefore any disturbed local process of the system relaxes to its equilibrium distribution within the order of time scale τ_f. At equilibrium, the probability distribution in each of the two wells can be approximated by the Boltzmann distribution whose peak is centered at the two points of the potential minima.

Now let us find an approximate value of the relaxation time for the global equilibration process, τ_s, and compare it with τ_f. We consider a uniform temperature background for the system; i.e, $T(x) = T_0$. Moreover, if the potential is approximated by parabola around the extrema points; i.e, around the points of minima we approximate by eq.(A.4) and for the curve around the barrier height, we consider

$$V(x) = V_0 - \frac{1}{2}\tilde{\eta}x^2 \tag{A.8}$$

with $\tilde{\eta} = V''^{(0)}$. Then,

$$\int_{-L}^{L} e^{\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}} dx \simeq \int_{-L}^{L} e^{\left(V_0 - \frac{\tilde{\eta}x^2}{2k_B T_0}\right)} dx. \tag{A.9}$$

But the contribution of the potential to the integral is significant only near the point $x = 0$; i.e as we go far away from $x = 0$ in both direction, the potential drops rapidly. Hence the limit of the integration can be stretched to the points at infinity which gives

$$\int_{-L}^{L} e^{\left(V_0 - \frac{\tilde{\eta}x^2}{2k_B T_0}\right)} dx \simeq \sqrt{\frac{2\pi k_B T_0}{\tilde{\eta}}} e^{\frac{V_0}{k_B T_0}}. \tag{A.10}$$

Similarly we have

$$\int_{-\infty(0)}^{0(\infty)} \frac{1}{\sqrt{T(x)}} e^{\left(-\int_{-L}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right)} dx = \frac{1}{2\sqrt{T_0}} \sqrt{\frac{2\pi k_B T_0}{\eta}} \tag{A.11}$$

Therefore substituting these results in to Eqs. (3.1.21) and (3.1.22), one gets the approximated values of the escape rates for a homogeneous background system as

$$\lambda_A = \lambda_C \sim \frac{1}{2} D(L) \frac{\sqrt{\eta\tilde{\eta}}}{2\pi k_B T_0} e^{-\frac{V_0}{k_B T_0}}. \tag{A.12}$$

Hence for such condition the approximated equilibration time for the global process is given by

$$\tau_s = \frac{1}{\lambda_A + \lambda_C} \sim \frac{2\pi k_B T_0}{\sqrt{\eta\tilde{\eta}} D(L)} e^{\frac{V_0}{k_B T_0}}. \tag{A.13}$$

Applying the Einstein relation (Eq. (3.1.9)) and the relation $\gamma = \frac{1}{\mu}$, τ_s, can be written as

$$\tau_s \sim \frac{2\pi\gamma}{\sqrt{\eta\tilde{\eta}}} e^{\frac{V_0}{k_B T_0}}. \tag{A.14}$$

If the approximated parabola at the minima points and at the maximum point for the potential are assumed to have the same shape, η and $\tilde{\eta}$ will have the same value, and therefore we can write the time scale τ_s as

$$\tau_s \sim \frac{2\pi\gamma}{\eta} e^{\frac{V_0}{k_B T_0}}$$

or we have

$$\frac{\tau_s}{\tau_f} \sim e^{\frac{V_0}{k_B T_0}} \qquad (A.14)$$

This result shows that the equilibration time for the global process is very much greater than the equilibration time for the local process, especially when the potential barrier height is much greater than the intensity of the thermal kick; i.e, $V_0 \gg k_B T_0$. We, therefore, conclude that the time it takes for global equilibration is extremely large compared to the time scale of the local equilibration. In other words, global processes are extremely slow as compared to the local processes.