THE DYNAMICS OF A BROWNIAN PARTICLE IN A HOOKEAN TYPE POTENTIAL AND ITS EFFECTIVE DIFFUSION COEFFICIENT IN A RATCHET POTENTIAL

A Thesis Submitted to

the School of Graduate Studies
Addis Ababa University

In Partial Fulfilment

of the Requirement for the Degree
of Master of Science in Physics

by

Yigezu Mulugeta

Addis Ababa, Ethiopia
July 2007

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

THE DYNAMICS OF A BROWNIAN PARTICLE IN A HOOKEAN TYPE POTENTIAL AND ITS EFFECTIVE DIFFUSION COEFFICIENT IN A RATCHET POTENTIAL

by

Yigezu Mulugeta

Department of Physics
Faculty of Science

Approved by the Examination Committee

Dr. Mulugeta Bekele, Advisor: ___________________________

Dr. Esayas Belay, Examiner: ___________________________

Dr. Ahmed Mustefa, Examiner: ___________________________

To my mother and sisters.

Abstract

In the first part of this work, we use the one dimensional random walk model to simulate the tracings, the autocorrelation function and the Gaussian distribution of the positions of a Brownian particle (a bead of radius $R_{bead} = 240$ nm) tethered by a DNA tether of persistence length, $l_p = 45$ nm, whose other end is anchored to a microscope slid. And in the second part, we derive the effective diffusion coefficient analytically and numerically for the one dimensional motion of the Brownian particle in a region where there is a periodic (ratchet) potential profile of period L. To derive the effective diffusion coefficient analytically, we use the known first passage time (FPT) method. For the simulation part, we use the one dimensional random walk model as in the first part of our work. The effective diffusion coefficient of the bead obtained both analytically and numerically vanishes at large potential barrier height. However, at the low barrier limit the analytical solution takes the value $\frac{2}{3}D_0$ (D_0 is the free thermal diffusion of the bead), while the numerical solution takes the expected value, D_0. Understanding these physical situations is a practical necessity in many experimental contexts, for instance in single biomolecules.

Acknowledgements

I would like to express my deepest gratitude to my advisor Dr. Mulugeta Bekele for his continuous support, follow up, advise and friendly approach. I would like to acknowledge also Mr. Berhanu Woldemichael and Mr. Fikadu Legesse for their invaluable comments on every contents of this work. I am extermly great full to my mother W/o Tiringo Wandimhun for her support throughout my educational carrier. Finally, I wish to thank all my friends, relatives and statistical physics group who are involved directly or indirectly to this work.

Chapter 1

Introduction

Most of us probably remember hearing about Brownian motion in high school, when we are taught that pollen grains jiggle around randomly in water due to the impacts of millions of invisible molecules. Brown came up with this discovery in Summer of 1827 when he began to make microscopic observation of suspension of grains released from pollen sacks taken from a type of evening promises called clarkia pulchella [1]. What Brown saw surprised him: the tiny grains, which were suspended in water, appeared to be in constant motion never to slow or stop. Moreover, as Brown verified, it was not caused by external influences such as light or temperature. He also quickly ruled out his first idea - that the grains were somehow alive - by examining grains from inorganic minerals. So Brown had shown that whatever it was, this incessant dance was not biology after all: it was physics.

But the theory of Brownian motion was developed after Einstein's famous theory of Brownian motion which was published in the Journal Annalen der Physik in 1905 [2]. Einstein's theory demonstrated how Brownian motion offered experimentalists the possibility to prove that molecules existed, despite the fact that molecules themselves were too small to be seen directly [3].

Brownian motion was one of the three fundamental advances that Einstein made in 1905, the others being special relativity and the idea of light quanta. Of these three great works, Einstein's analysis of Brownian motion remains the least well known. But this part of Einstein's scientific legacy was the key to a revolution that is at least as important as relativity or quantum physics. One century later, Brownian motion continues to be of immeasurable importance in modern science, from physics through biology to the latest wonders of nanotechnology.

Sometime after Einstein's original derivation of the dynamics of a Brownian particle in a fluid, the prominent French physicist Paul Langevin (1872 - 1946) independently presented a new method of description of the Brownian motion [4]. His reasoning was as follows. From statistical mechanics, it was known that the mean kinetic energy of the Brownian particle in one dimension should, in equilibrium, reach a value

$$\langle \frac{1}{2} m v^2 \rangle = \frac{1}{2} k_B T. \tag{1.1}$$

Here T is absolute temperature of the medium, k_B is Boltzmann's constant, m and v are mass and speed of the Brownian particle respectively. Einstein had also used this fact. According to Langevin the force on the Brownian particle due to the fluid medium it is moving through is split into two, which are not actually independent of each other. These are:

i) a drag viscous force which Langevin assumed to be expressed by the same formula as in a macroscopic hydrodynamics, i.e $-6\pi\eta a\frac{dx}{dt}$, η being the viscosity and a is the diameter of the particle, assumed spherical.

ii) another fluctuating force $X(t)$ which represents the irregular impacts of the molecules of the fluid on the Brownian particle. All that is known about this fluctuating force is the above fact, and that it should be positive and negative with equal probability. Thus, the equation of motion of the particle is given by Newton's second law as:

$$m\frac{d^2x}{dt^2} = -6\pi\eta a\frac{dx(t)}{dt} + X(t). \tag{1.2}$$

The above equation is called Langevin's equation of motion. To describe the dynamics of small suspended particles in a fluid, Langevin included the above two forces (the viscous drag and the fluctuating force $X(t)$) to the ordinary Newton's equation of motion. Using his reasoning Langevin has got the same result for the mean squared deviation of the position of the Brownian particle after time t, as Einstein independently deduced.

Langevin's equation was the first example of a stochastic differential equation - a differential equation with a random term $X(t)$ - and hence whose solution is, in some sense, a random function. Each solution of the Langevin's equation represents a different random trajectory and, using only rather simple properties of $X(t)$ (the fluctuating force), measurable results can be derived.

This thesis work has two parts. In the first part we simulate the motion of a bead of radius $R_{bead} \approx 240$nm tethered by a DNA tether whose other end is anchored to a microscope slide. Besides tracking position, the other outputs of the simulation are the autocorrelation function and the probability distribution of the beads's positions. In the second part of our work we obtain analytical and computer simulation results for the effective diffusion coefficient of the one dimensional motion of a Brownian particle (the bead considered above) in an external potential. To obtain the simulation result for the effective diffusion of the bead we explicitly use Langevin's equation of motion. While for the analytical result we use the known method of the mean first passage time (FPT) [4].

The rest of this thesis is organized in the following way. In Chapter two we present a detailed discussion of elementary simulation of tethered particle motion and report the actual simulation we did for a realistic particle (a bead tethered to a DNA molecule of known persistence length) [5]. In Chapter three we extend the simulation technique used in Chapter two to obtain the simulation result for the effective diffusion coefficient of the Brownian particle moving in the medium described above. We also obtain the result analytically for the same Brownian particle under similar conditions. In Chapter four we compare the analytical and simulation results. Finally, in Chapter five we summarize our findings and conclude.

Chapter 2

Elementary simulation of tethered particle motion

2.1 Introduction

In this Chapter we describe the basic properties of polymer chains and as a first practice we simulate the dynamics of a Brownian particle (a bead of radius R_{bead} = 240 nm) tethered to a DNA tether whose other end is anchored to a microscope slide.

2.2 Ideal(statistical) model of a polymer chain

A polymer chain is a sequence of chemical repeating units (called monomers) connected by covalent bonds. The simplest possible model of a polymer chain is a series of bonds which are linearly and freely jointed into a chain and may intersect itself any number of times. By freely jointed we mean that the angle between any two consecutive bonds is completely free and unhindered. If each bond is represented by the vector **a**, then the end to end vector, **R**, of such a freely jointed chain (FJC) model is

$$\mathbf{R} = \sum_{i=1}^{i=N} \mathbf{a}_i. \tag{2.1}$$

However, for a freely fluctuating chain the average end-to-end vector $\mathbf{R}$, will be zero. Thus, $\langle \mathbf{R} \rangle$ doesn't serve as a good measure of the chain size as it is zero irrespective of the number of monomers, N, in the chain. Another measure of the size of a chain is the mean of the square of the end-to-end distance denoted by $R^2 = \langle \mathbf{R}.\mathbf{R} \rangle$. For consistency in dimensions, R will be referred as the polymer size, $R = \langle \mathbf{R}.\mathbf{R} \rangle^{\frac{1}{2}}$. The mean squared end-to-end distance of a chain, R^2 is given by

$$R^2 = Na^2 + 2 \sum_{i=1}^{N} \sum_{j>i} \langle \mathbf{a}_i.\mathbf{a}_j \rangle. \tag{2.2}$$

For a FJC the second term of the above equation vanishes. Therefore, the size of such a chain scales as a square root of the number of monomers, i.e $R \sim \sqrt{N}$.

For a jointed chain whose consecutive bonds are correlated, Eq.(2.2) provides us with a simple expression for the chain size. The orientational correlation between bonds which are widely separated along the backbone of a chain is lost, i.e., in the limit of bonds located far apart, i.e., $\langle \mathbf{a}_i.\mathbf{a}_{i\pm m} \rangle = 0$ for large m. Thus, the distance along the backbone over which the bonds are correlated is simply the distance that is spanned by $2m$ consecutive bonds, where m is the smallest number for which $\langle \mathbf{a}_i.\mathbf{a}_{i\pm m} \rangle = 0$. This distance over which a 2- or 3-dimensional chain is inflexible or "stiff" is called the persistence length of a chain, l_p, and defined by

$$l_p = a + \frac{1}{a} \sum_{j>i} \langle \mathbf{a}_i.\mathbf{a}_j \rangle. \tag{2.3}$$

Here one could see that for FJC, the persistence length is simply the length of a single bond, a. The persistence length of a chain is determined by the chemistry of individual chemical monomers as well as how these monomers interact with the surrounding small solvent molecules. For example, the persistence length of polystyrene is roughly a nanometer and corresponds to the length of 4 to 5 backbone bonds. In contrast, $ds - DNA$ has a persistence length on the order of 50nms, corresponding to about 150 base pairs [6]. In terms of the persistence length, the mean squared end-to-end distance of a chain is expressed as

$$R^2 = Na^2(\frac{2l_p}{a} - 1). \tag{2.4}$$

Eq.(2.4) conveys much information. It shows that for the general model of a jointed chain with orientational correlation, $R^2 \sim Na^2$. This means that any ideal chain has a size which can be described using a formula similar to $R^2 = Na^2$, whether it is freely jointed or is a jointed chain with orientational correlation. This can be done by defining N_{stat} and a_{stat} as the number and size of statistical units within the chain and representing a chain of N bonds of size a by these statistical units. The size of the statistical unit is simply twice of the persistence length, $a_{stat} = 2l_p$. These statistical segments are linked in a freely jointed manner and consequently, the size of the chain is $R^2 = N_{stat}a_{stat}^2$. The size of a statistical segment, a_{stat}, is often referred to as the "Kuhn step length" and N_{stat} as number of Kuhn step lengths in the chain. In the remaining part of this thesis, we drop the subscript and simply write $R^2 = Na^2$ by assuming that we are talking about Kuhn or statistical units.

2.3 Thermodynamics and force-extension relation of an ideal chain

From thermodynamics the Helmoltz free energy at constant temperature is expressed as

$$\Delta F = \Delta U - T\Delta S, \tag{2.5}$$

where U is the internal energy of the chain, T is the temperature and S is the entropy. Examples of energies which contribute to U range from Lennard-Jones interactions to complex interactions which scientists might propose, all of which are of the form $U = f(r_{ij})$, where r_{ij} is a vector of distances between monomers, solvent, or other particle or surface which might be included in the system. By definition, an ideal chain suffers no interactions and contributes nothing to the internal energy at a constant temperature, i.e., $\Delta U = 0$. On the other hand, the chain has considerable disorder, measured by the number of configurations that it can adopt and quantified by the thermodynamic quantity entropy. If we were to hold the two ends of the chain a distance Na apart so that the chain is taut, we would considerably decrease the number of configurations that the chain could adopt, which means in stretching the chain to its taut state we perform work on the system to increase the free energy of the system. In order to describe the thermodynamics of an ideal chain, therefore, one needs only to quantify the entropy of the chain.

From Boltzmann's principle the entropy of a system is $S = k_B \ln \Omega$, where Ω is the number of configurations of the system and k_B is the Boltzmann's constant. In terms of the end-to-end distance, the entropy is expressed as

$$S = k_B \ln[\Omega_0 P(R)], \tag{2.6}$$

where Ω_0 is the total number of configurations of the chain, and $P(R)$ is the probability of finding the end-to-end distance to be R which is mathematically expressed as

$$P(R) = (\frac{3}{2\pi N a^2})^{\frac{-3}{2}} \exp(-\frac{3R^2}{2Na^2}). \tag{2.7}$$

Since for an ideal chain $dF = -TdS$, the force $\mathbf{f}$ needed to stretch the chain is given by

$$\mathbf{f} = -\frac{dF}{dR}\hat{\mathbf{R}} = T\frac{dS}{dR}\hat{\mathbf{R}}. \tag{2.8}$$

Upon substituting the value of S from Eqn.(2.6) one could get the value of $\mathbf{f}$ to be

$$\mathbf{f} = -3k_B T\frac{\mathbf{R}}{Na^2}, \tag{2.9}$$

and it could be written in terms of the persistence length as

$$\mathbf{f} = -3k_B T\frac{\mathbf{R}}{2l_{tot}l_p}, \tag{2.10}$$

where l_{tot} is the contour length of the chain. As we can see from Eqn.(2.10) above $\mathbf{f}$ is a vector quantity, and in the direction opposite to the end-to-end vector. In other words, $\mathbf{f}$ is a restoring force.

2.4 The size of a chain in a good and poor solvent conditions

If a FJC is placed in a poor solvent, the monomer-monomer interactions are favored over monomer-solvent interactions. Thus, the chain will adopt a configuration that minimizes contact with the poor solvent and maximizes self-contact. Very simply, a long, flexible chain will collapse upon itself, forming a dense monomer mass that excludes solvent molecules from its interior. In its collapsed state, the chain cannot completely avoid contact with the solvent, but if it adopts a spherical collapsed state, then it will minimize its solvent-monomer interactions. In collapsed state the chain will lower ΔU simply because $U_{monomer-solvet} > U_{monomer-monomer}$. However, when the chain goes from a solvated, fully flexible chain to a collapsed chain with a dense core, the chain will lose entropy, i.e., $\Delta S < 0$. Thus there are two competing effects: the interaction with the solvent will promote collapse i.e., the interactions contribute to a lowering of the free energy, but the loss of entropy will actually suppress the chain collapse i.e., entropy contributes to an increase in the free energy. Indeed, the balance of these two effects is determined by the temperature. If the temperature of the chain is low so that the chain adopts a collapsed configuration, in a poor solvent the size of the chain scales with the cubed root of the number of monomers, i.e., $R \sim N^{\frac{1}{3}}a$ [6].

If, on the other hand, the chain is placed in a good solvent it will adopt a configuration that maximizes contact with the solvent. That is, the chain will adopt a random walk configuration, with the exception that it will not self-intersect. In a good solvent the size of the chain scales with $N^{\frac{3}{5}}a$, i.e., $R \sim N^{\frac{3}{5}}a$ [6].

2.5 Simulation of tethered particle

The manipulation of single polymer chains, adsorbed into a surface has received considerable attention in the past decade from both theoreticians as well as experimentalists. With the advent of the Atomic Force Microscope (AFM) and optical tweezers (OT), scientists are capable to impose nanometer scale deformations and measure the resulting forces on the scale of picoNewtons [6]. Here is the schematic diagram of AFM.

Figure 2.1: This is schematic diagram of Atomic Force Microscope. It is taken from [6]

Here, we wish to simulate the motion of a bead of radius R_{bead}, attached to a tether of length L_{tot} whose other end is anchored to a microscope slide as shown in Fig. below. To perform the simulation suppose that the only external forces acting on the bead are: the hard wall repulsion from the microscope slide, the tension force from the tether and random collisions with the surrounding water molecules. With these assumptions, the equation of motion of the bead is governed by the Langevin dynamics which is given by

$$m\ddot{x} = -\gamma\dot{x} - \kappa x + \sqrt{2k_B T\gamma}\zeta(t), \tag{2.11}$$

where, κ is the spring constant of the tether, $k_B T = 4.1 * 10^{-21} J$ is the thermal energy at room temperature, γ is the friction constant of the medium, m, x, $\dot{x}$ and $\ddot{x}$ are the mass, the position, the speed and the acceleration of the bead respectively and $\zeta(t)$ is a Gaussian white noise whose mean is zero and variance one. In a high friction limit Eqn.(2.11) reduces to [4]

$$\gamma\dot{x} = -\kappa x + \sqrt{2k_B T\gamma}\zeta(t). \tag{2.12}$$

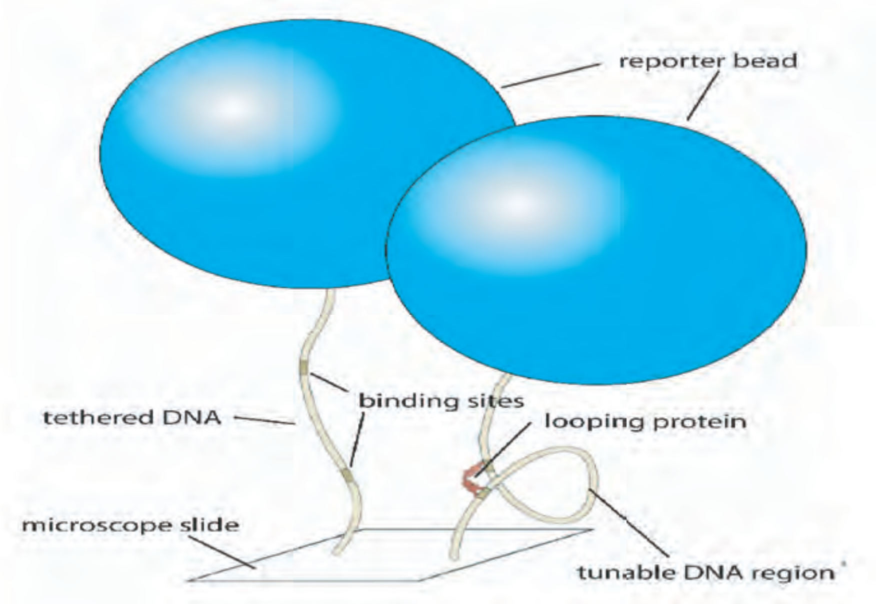


Figure 2.2: A bead tethered by a DNA whose other end is anchored to a microscope slide. This is taken from http://www.rpgroup.caltech.edu/courses/PBL/index.html

Using the same reasoning as in [5] we approximate the system (bead + DNA tether) by a single Hookean spring with effective length L_{tot} $=L_{tether}+$ R_{bead} and effective persistence length l_{peff} slightly larger than l_p. In the data L_{tether} is taken to be 1200 nm [5]. Taking the above approximation into account, from Eqn.(2.10) we get the spring constant, κ, of the DNA tether to be

$$\kappa = \frac{3k_B T}{2l_{peff}L_{tot}}. \tag{2.13}$$

If the tether is not there Eqn.(2.12) reduces to

$$dx = \sqrt{\frac{2k_B T}{\gamma}}\zeta(t)dt. \tag{2.14}$$

Suppose we observe the bead in time intervals of Δt, then in the absence of the tether the discrete form of Eqn.(2.14) becomes

$$\Delta x = \sqrt{\frac{2k_B T}{\gamma}}\zeta(t)\Delta t, \tag{2.15}$$

while the variance of the random steps Δx of the bead is given by

$$\langle(\Delta x)^2\rangle - \langle\Delta x\rangle^2 = \frac{2k_B T}{\gamma}\langle(\Delta t\zeta(t))^2\rangle - \frac{2k_B T}{\gamma} * \langle\Delta t\zeta(t)\rangle^2. \tag{2.16}$$

From the fact that $\zeta(t)$ is a Gaussian distributed white noise with mean zero and variance one and $(\Delta t\zeta(t))^2$ is the square of the Wiener path [4], we get

$$\langle(\Delta x)^2\rangle = \frac{2k_B T\Delta t}{\gamma}. \tag{2.17}$$

Applying the Einstein-Stokes relation in Eqn.(2.17), we get

$$\langle(\Delta x)^2\rangle = 2D_0\Delta t, \tag{2.18}$$

where, D_0 is the free thermal diffusion of the bead. From Eqn.(2.18) we see that without the tether, the bead would take independent random steps, each a displacement drawn from a Gaussian random distribution with mean squared step length of

$2D_0\Delta t$. Let us assume that the magnitude of the independent steps of the bead due to the random collision with the molecules of water to be $\sqrt{2D_0\Delta t}$. In addition to the random collision with the molecules of water, if the bead is subjected to a constant force f Eqn.(2.15) becomes

$$\Delta x = \sqrt{2D_0\Delta t}\zeta(t) + \frac{f\Delta t}{\gamma}. \tag{2.19}$$

We see from Eqn.(2.19) above that the net motion of the bead is obtained by superimposing an additional deterministic drift term, $\Delta_{drift}x = \frac{f\Delta t}{\gamma}$ on the random steps. But for the case of a tethered particle motion the additional external force is $f = -\kappa\mathrm{x}$ coming from the tether is not constant but rather position dependent. Using the same reasoning as in [5], in small time intervals of Δt (perhaps smaller than the actual video frame rate which is around 30 - 40 fps) the force f is assumed constant. So substituting f by -κx and using the fact that $\gamma = \frac{k_BT}{D_0}$, Eqn.(2.19) becomes

$$\Delta x = \sqrt{2D_0\Delta t}\zeta(t) + \frac{-\kappa x D_0\Delta t}{k_BT}. \tag{2.20}$$

By taking Markov's assumption into account from Eqn. (2.20), we get the expression for each independent discrete steps to be

$$\Delta x_i = \sqrt{2D_0\Delta t}\zeta(t) + \frac{-\kappa x_i D_0\Delta t}{k_BT}, \tag{2.21}$$

where ,x_i is the initial position of the bead and $\Delta x_i = x_{i+1} - x_i$, i.e.

$$x_{i+1} = x_i + \Delta x_i. \tag{2.22}$$

To obtain computer simulation results of the motion of the tethered bead we model $\zeta(t)$ by a random number generator, 'randn', which is a built in function in Matlab software. This random number generator 'randn' generates a Gaussian distributed random numbers with mean zero and variance one. With this substitution Eqn.(2.21) reduces to

$$\Delta x_i = (\sqrt{2D_0\Delta t})randn - \frac{\kappa D_0 \Delta t}{k_B T} x_i. \tag{2.23}$$

Denoting $\sqrt{2D_0\Delta t}$ by LDiff and $\frac{-\kappa D\Delta t}{k_B T}$ by mu we get

$$\Delta x_i = LDiff * randn + mu x_i. \tag{2.24}$$

In our simulation we took $\Delta t = 0.63ms$, for a total of about a million steps. A subroutine in the program records the position of the bead, which is initially at the origin, at each time step of Δt. Then, the other subroutines of the program computes and plot the autocorrelation and the one sided Gaussian fit of the positions recorded and the the probability of finding the bead at these positions. For further information interested reader could see the matlab code in [5].

$$\log(Autocorr) = \log\langle x_i x_j \rangle, \tag{2.25}$$

where x_i and x_j are the positions of the bead at different times. Interested reader could see the matlab code in [5].

Accumulating about a million data points of the position of the bead for a single time step of Δt, we obtained the autocorrelation and the one sided Gaussian distribution of the bead's positions that could be compared to experimental results. Fig.(2.3) corresponds to the simulated result of the position of the center of the bead. One could see from the graph that the mean of the beads displacement is zero as expected and it is in a very good agreement to its experimental counter part in [5].

Fig.(2.4) is the plot of the autocorrelation of the bead's positions. As one would expect our simulation result of the autocorrelation function tells us that the positions of the bead widely separated in time are uncorrelated. By comparing with the autocorrelation of the bead's positions obtained by experiment we found that our simulation result is in a very good agreement.

Finally, Fig.(2.5) is the plot of the one sided Gaussian fit to the distribution of the bead's position with the same normalization and variance as the recorded bead's position. As it could be seen from the graph the sample positions of the bead coincides with the Gaussian fit and again in a very good agreement to its experimental counter part as other results of our simulation do.

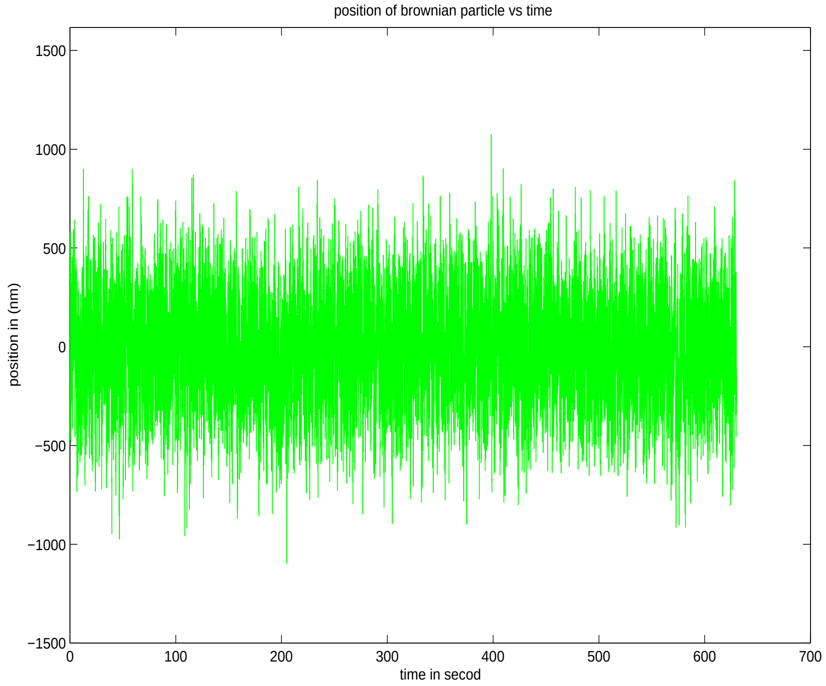


Figure 2.3: Sample simulation data for the x-component of the motion a bead of radius $R_{bead} \approx 240$nm,attached to a DNA tether of length $L_{tether} \approx 3500$ base pairs, or ≈ 1200nm.

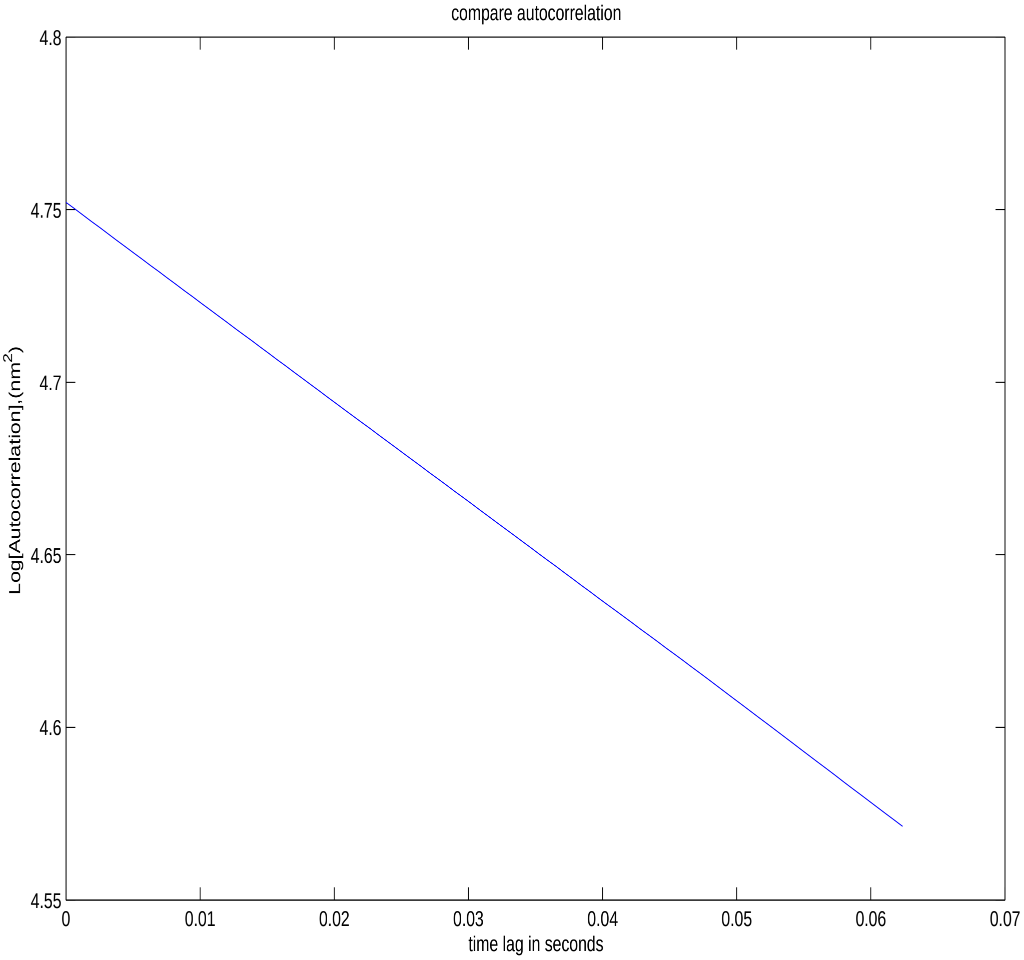
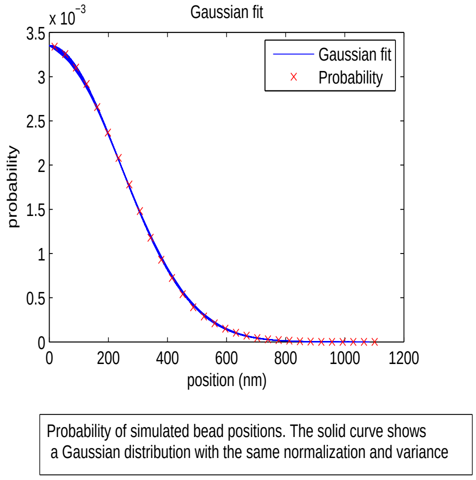


Figure 2.4: Simulated result of the logarithm of the autocorrelation function of x expressed in nm^2 using parameters l_{peff}= 72nm and effective viscosity 2.4 times that of water in bulk



Probability of simulated bead positions. The solid curve shows a Gaussian distribution with the same normalization and variance

Figure 2.5: Two times of probability of the bead positions.The solid curve shows a Gaussian distribution with the same normalization and variance.

Chapter 3

Effective diffusion coefficient of a bead in a ratchet potential

3.1 Introduction

Diffusion is the phenomenon of random motion causing a system to decay towards its equilibrium condition. For example, diffusion of particles causes a net movement of particles from areas of high concentration to areas of lower concentration until equilibrium is reached. It is spontaneous process (more familiarly known as "passive" form of transport rather than "active"). Diffusion can affect a variety of different quantities. Examples include diffusion of concentration, heat or momentum.

In this Chapter we first carry out a computer simulation of a Brownian particle diffusing in a medium with an external ratchet potential of the form shown in Fig.(3.1) below and determine the way the effective diffusion coefficient, D_{eff}, depends on the barrier height of the ratchet potential. This will be followed by analytically finding D_{eff} for the same particle in the same environment.

The reason that we take this model is because it has physical significance to understand processes of life. For example, with some modification our model could be used to study the dynamics of molecular motors. One particular example of such a molecular motor is Kinesin-1 enzyme, or motor protein. It is a force generating enzyme which converts the free energy of the gamma phosphate bond of ATP into mechanical work. This work is used to power transport of intercellular organelles along microtubules which are thin cylindrical tubes made up of proteins that are used to make structures involved in cellular movement such as flagella. As Kinesin-1 molecule moves over the microtubules, it gets trapped because of the polarity of the microtubules. This trap potential could be best approximated by a sawtooth type potential profile [7].

3.2 The simulation

The diffusion coefficient, which could be called the effective diffusion coefficient, D_{eff}, of particles is defined by [8]:

$$D_{eff} = limit_{t\to\infty} \frac{\langle (x(t))^2 \rangle - \langle x(t) \rangle^2}{2t}, \tag{3.1}$$

where, x(t) is the particle position at time t and $\langle ... \rangle$ is the statistical average of the physical quantity in the angular bracket.

The forces acting on the bead are the random collisions with the molecules of the environment, the force that arises due to potential difference and the viscous drag force. Thus the equation of motion of the bead in the high friction limit is given by

$$\dot{x} = -\frac{\partial U(x)}{\gamma \partial x} + \sqrt{\frac{2k_B T}{\gamma}} \zeta(t). \tag{3.2}$$

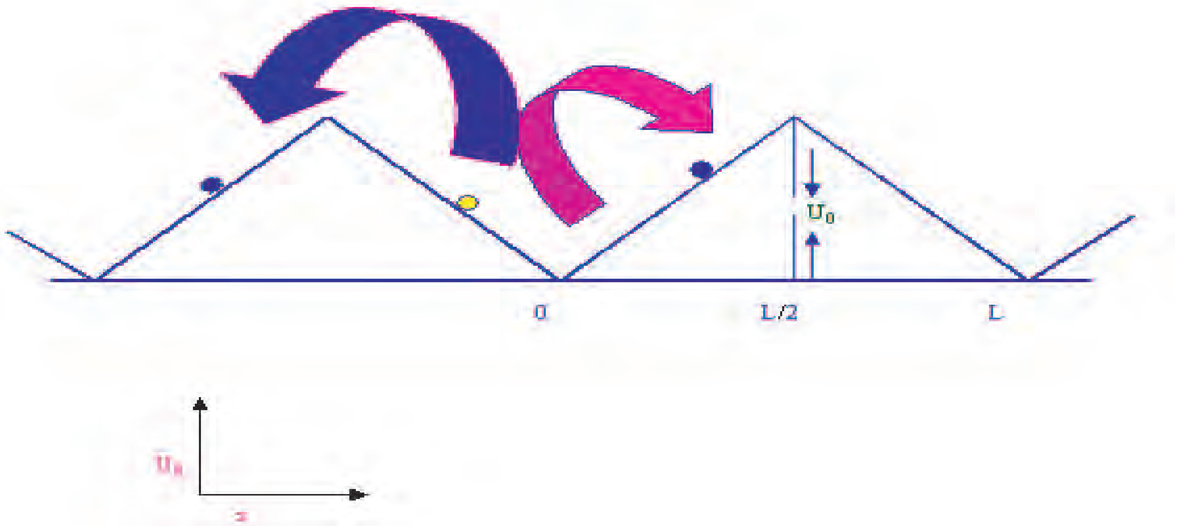


Figure 3.1: Symmetric ratchet potential profile with period L and barrier height 'U_0' which is a constant 'u' times that of thermal energy at room temperature T, i.e., U_0=u k_B T

Here $U(x)$ is the external potential in which the bead is moving. If one observes the bead in small time intervals of Δt, in the absence of the external potential the bead takes independent steps with mean square deviation $\langle(\Delta x)^2\rangle$ given by

$$\langle(\Delta x)^2\rangle = 2D_0\Delta t, \tag{3.3}$$

where D_0 is the free thermal diffusion of the bead. To obtain our simulation result we took Δt=0.00063s which is very small compared to the actual time required for a small bead to go from the top of the potential field whose height $U_0 = k_BT$ and period L=2000 nms down to the nearest zero level. For example, a bead of silica of radius R_{bead}=240nm takes around 0.08 seconds to travel from the top of the potential field down to the nearest zero level due to only the potential profile. In addition to the random collisions, if the bead is subjected to the ratchet potential, its net motion is obtained by superimposing an additional deterministic drift on the random steps;

$$\Delta_{drift}x = \frac{-\partial U(x)\Delta t}{\gamma \partial x}. \tag{3.4}$$

Similar to the tethered particle motion case of the previous Chapter, we assume the magnitude of the independent random jumps to be $\sqrt{2D_0\Delta t}$ and the net displacement Δx of the bead in time Δt becomes

$$\Delta x = \sqrt{2D_0\Delta t}\zeta(t) - \frac{D_0\Delta t}{k_BT}\frac{\partial U(x)}{\partial x}. \tag{3.5}$$

By taking the Markov's assumption into account, Eqn.(3.4) reduces to:

$$\Delta x_i = \sqrt{2D_0\Delta t}\zeta(t) - \frac{D_0\Delta t}{k_BT}\frac{\partial U(x)}{\partial x}|_{x=x_i}, \tag{3.6}$$

where, $\Delta x_i = x_{i+1} - x_i$, i.e.,

$$x_{i+1} = \Delta x_i + x_i. \tag{3.7}$$

To obtain computer simulation result of Eqn.(3.5) we modelled $\zeta(t)$ by a random number generator $R1$ given as in [9] by

$$R1 = U1\sqrt{-2\frac{\ln W}{W}}, \tag{3.8}$$

where, $W = (U1)^2 + (U2)^2$ and $U1$ and $U2$ are random numbers between 0 and 1. This random number generator $R1$ similar to the builtin function 'randn' in matlab software generates a Gaussian distributed random numbers with mean squared deviation of one about the value zero. By substituting $\zeta(t)$ by $R1$ in Eqn.(3.5) we get

$$\Delta x_i = \sqrt{2D_0\Delta t}R1 - \frac{D_0\Delta t}{k_BT}\frac{\partial U(x)}{\partial x}|_{x=x_i}. \tag{3.9}$$

Denoting $\sqrt{2D_0\Delta t}$ by $LDiff$ the above equation reduces to

$$\Delta x_i = LDiff * R1 - \frac{D_0\Delta t}{k_BT}\frac{\partial U(x)}{\partial x}|_{x=x_i}. \tag{3.10}$$

To perform the simulation, the program is designed to compute the position of the bead after each time interval, $\Delta t = 0.00063s$, using Eq.(3.10) for N iterations and records the last position of the bead. Starting from the same initial condition under the same potential, the program is repeated N times having N values for the last position of the bead. This will be used to evaluate D_{eff} corresponding to the particular value of the barrier height. Next, we change the value of the barrier height and repeat the same procedures above to evaluate the value of D_{eff}. We have chosen N to be 10^5 and we change the barrier height in steps of 0.1 k_BT starting from U_0=0 to U_0=$10k_BT$. To obtain the simulated result we run our program in a single personal computer. The computer takes about one and half an hour to compute the effective diffusion coefficient of the bead for a single value of the barrier height when $N = 10^5$. For further information one could see the Fortran code found in the appendix.

3.3 Analytical derivation of the effective diffusion coefficient

As in Eqn.(3.1) the effective diffusion constant of particles is expressed as:

$$D_{eff} = Lim_{t\to\infty}\frac{\langle(x(t))^2\rangle - \langle x(t)\rangle^2}{2t}. \tag{3.11}$$

Our aim here is to derive the analytic expression for the effective diffusion coefficient D_{eff}. To do so we start from the following exact expression of the effective diffusion coefficient [10] .

$$D_{eff} = \frac{L^2}{2} \frac{\langle t^2(x_0 \to x_0 + L)\rangle - \langle t(x_0 \to x_0 + L)\rangle^2}{\langle t(x_0 \to x_0 + L)\rangle^3}, \tag{3.12}$$

where x_0 is an arbitrary reference point and $\langle t^n(a \to b)\rangle$ is the n^{th} order moment of the first passage time from a to $b > a$. For a stochastic trajectory obeying Eqn.(3.2), the moments of the first passage time are related by the well known closed analytical recursion relation as in [10] by

$$\langle t^n(a \to b)\rangle = \int_a^b dx \int_{-\infty}^x \frac{ndy}{D_0} \langle t^{n-1}(y \to b)\rangle \exp \frac{[U(x) - U(y)]}{k_B T}. \tag{3.13}$$

If we take the arbitrary initial point x_0 to be at the origin, Eqn.(3.12) becomes

$$D_{eff} = \frac{L^2}{2} \frac{\langle t^2(0 \to L)\rangle - \langle t(0 \to L)\rangle^2}{\langle t(0 \to L)\rangle^3}. \tag{3.14}$$

As one could see from Eqn.(3.14), to find an explicit expression for the effective diffusion D_{eff} we need to find the first and the second order moments of the first passage time (FPT) from 0 to L. Using the fact that the zeroth order moment of FPT is one, the first and the second order moments of FPT are expressed as

$$\langle t(0 \to L)\rangle = \int_0^L dx \int_{-\infty}^x \frac{dy}{D_0} \exp(\frac{[U(x) - U(y)]}{k_B T}), \tag{3.15}$$

and

$$\langle t^2(0 \to L)\rangle = \int_0^L dx \int_{-\infty}^x \frac{2dy}{D_0} \langle t(y \to L)\rangle \exp(\frac{[U(x) - U(y)]}{k_B T}). \tag{3.16}$$

The external ratchet potential, $U(x)$, over a period, i.e., between 0 and L is mathematically expressed as

$$U(x) = \begin{cases} \frac{2uk_BTx}{L} & \text{if } 0 < x \leq \frac{L}{2}, \\ \frac{-2uk_BTx}{L} + 2uk_BT & \text{otherwise.} \end{cases} \tag{3.17}$$

After some mathematical manipulation, we get the values of $\langle t(0 \to L)\rangle$ and $\langle t^2(0 \to L)\rangle$ to be

$$\langle t(0 \to L)\rangle = \frac{e^{-u}[-1+e^u]^2 L^2}{2u^2 D_0}, \tag{3.18}$$

and

$$\langle t^2(0 \to L)\rangle = \frac{L^4 e^{-2u}(e^u - 1)}{2u^4 D_0^2}[A+B], \tag{3.19}$$

where,

$A = [-1-(-1+u)e^u]$,

and

$B = e^{3u} - (1+u)e^{2u}$.

Upon substituting the values for $\langle t(0 \to L)\rangle$ and $\langle t^2(0 \to L)\rangle$ from equations (3.18) and (3.19) respectively into Eqn.(3.14), we obtained the exact expression for D_{eff} to be

$$D_{eff} = \frac{u^2 D_0 e^u(1+e^u)}{(-1+e^u)^5}[-1-2ue^u+e^{2u}], \tag{3.20}$$

Hence,

$$\frac{D_{eff}}{D_0} = \frac{u^2 e^u(1+e^u)}{(-1+e^u)^5}[-1-2ue^u+e^{2u}]. \tag{3.21}$$

In this chapter we have explained the procedure of how to compute the effective diffusion coefficient as a function of the barrier height of the ratchet potential. We have also found analytical expression for D_{eff} as a function of its barrier height U_0. In the following Chapter, we present a detailed discussion of our results.

Chapter 4

Result and discussions

With out going in to detailed calculation, one could expect that the effective diffusion coefficient, D_{eff}, of particles moving in a region where there is a potential barrier of height, U_0, (for our case $U_0 = uk_BT$) to satisfy two limiting results. These are:
a) The effective diffusion coefficient has to vanish at a very large barrier height, i.e.,

$$Limit_{u \to \infty} D_{eff} = 0, \tag{4.1}$$

and

b) The effective diffusion coefficient has to approach the value D_0, free thermal diffusion constant of particles, if the barrier height approaches zero, i.e.,

$$Limit_{u \to 0} D_{eff} = D_0. \tag{4.2}$$

Our numerical simulation result for the effective diffusion coefficient, D_{eff}, confirms these results. However, the analytic solution of the effective diffusion coefficient satisfies the following limiting results. These are:
a) The effective diffusion coefficient vanishes at a very large barrier height, i.e.,

$$Limit_{u \to \infty} D_{eff} = 0, \tag{4.3}$$

and

b) The effective diffusion coefficient approach the value, $\frac{2}{3}D_0$, as the barrier height approaches zero, i.e.,

$$Limit_{u\to 0}D_{eff} = \frac{2}{3}D_0. \tag{4.4}$$

The dependence of the effective diffusion coefficient on the value of u, hence on the value of the barrier height, is shown in Fig.(4.1) below. One could see from the graph that the numerical simulation result for the effective diffusion coefficient takes the value D_0 when u is near zero and then decays to zero when u becomes large. However, the analytical solution for the effective diffusion coefficient takes the value, $\frac{2}{3}D_0$, when u approaches zero and the decays to zero when u is becoming larger and larger.

Though, the simulated and analytical results for the effective diffusion take the same pattern there is an observed difference. To deal with these results let us consider two regions in the graph shown in Fig.(4.1).

a) In the low barrier limit, in the region where the the height of the ratchet potential is less than $4k_BT$, a significant deviation between the numerical and analytical results of the effective diffusion, D_{eff}, of the bead is observed.

b) In the high barrier region of the ratchet potential, i.e., in a region where the barrier height is between $4k_BT$ and $10k_BT$, the numerical simulation result and the analytical solution of the effective diffusion coefficient are in a very good agreement. We would expect that the difference between the numerical simulation result and the analytical solution to the effective diffusion coefficient at a low barrier limit is the combined effect of the small number of data points we take for the simulated result

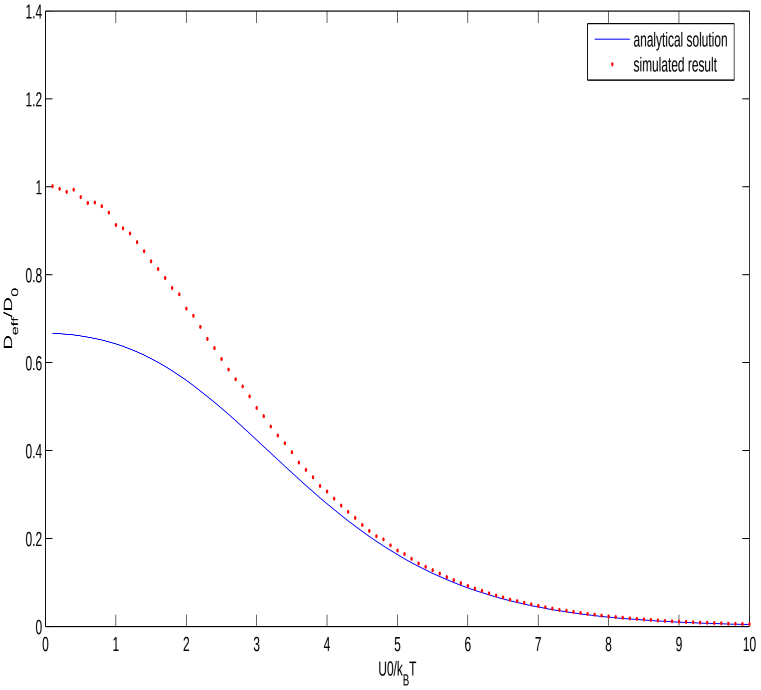


Figure 4.1: Effective diffusion coefficient versus barrier height measured in the units of D_0 and k_B T respectively. The solid line shows the analytical solution of the effective diffusion while the doted one shows the corresponding simulated result for a bead of radius ($R_{bead} = 240$ nms) moving along the x - axis.

because of limited machine capacity and the reflecting boundary approximation taken to solve for the first and the second order moments of the first passage time of the bead from 0 to L.

Chapter 5

Summary and Conclusion

In this thesis we have used the one dimensional random walk model to simulate the dynamics of a Brownian particle (a bead of radius $R_{bead} = 240$ nms) for two different external potential profiles. In the first part of our work, we simulated the dynamics of the bead which is tethered by a DNA tether of persistence length, $l_p = 45$ nms, whose other end is anchored to a microscope slide. The results of this simulation were the tracking, the autocorrelation and the Gaussian distributions of positions of the bead. These results are found to be in a good agreement with their experimental counter parts.

In the second part of our work, we simulated the one dimensional motion of the bead in an external ratchet potential profile. The result of our simulation was the effective diffusion coefficient of the bead. The effective diffusion coefficient of the bead found using the numerical simulation method is in a good agreement with the corresponding analytical result in the region where the potential barrier height, U_0, is between $5k_BT$ and $10k_BT$. While for the other region, i.e., in the region where, U_0, is less than $5k_BT$, significant deviation is observed.

Since we recently got a parallel computing cluster of 15 nodes, in the future we could simulate physical problems that require a high capacity machine.

Finally, the simulation technique that we used to simulate the one dimensional motion of the bead could be extended to simulate the dynamics of small biological molecules, though it requires proper modelling, to understand the process of life.

Appendix

Here is the serial Fortran code that we used to simulate the effective diffusion of the bead's motion in a ratchet potential profile.

Serial code

```
PROGRAM RANDWALK ! This program simulates and analyzes the motion of 1D random
!walk confined in a rachet potential profile
IMPLICIT NONE
REAL::DELTAT , DELTAU ,XMEAN , VARX
INTEGER::N , M , L
REAL,ALLOCATABLE::XSIM (:) , XMAX (:) ,DIF (:) ,U0 (:) ,AB (:,:)
OPEN (10,FILE = 'YIG.DAT' , STATUS = 'UNKOWN' )
CALL ENPUTVALUES( DELTAU , DELTAT ,N , M )
ALLOCATE (XSIM(N)),(XMAX(N)) , (DIF(M)) ,( UO (M)) , ( AB (M ,2 ))
XMEAN = 0.0 , VARX = 0.0 ,XSIM = 0.0 , XMAX=0.0 , DIF=0.0, U0=0.0
CALL EVALUATE1(XSIM ,XMAX ,DELTAT , DELTAU , N , M , DIFF , U0 )
DO L=1,M
AB (L,1) = U0(L)
```

```
AB (L,2) = DIF(L)
END DO
DO L=1 , M
PRINT* , AB ( L,1:2)
WRITE (10,*) AB(L,1:2)
END DO
DEALLOCATE (AB),(XMAX),(XSIM),(DIF), (U0)
END PROGRAM RANDWALK
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
SUBROUTINE EVALUATE1(XSIM, XMAX , DELTAT , DELTAU, N, M, DIF, U0)
IMPLICIT NONE
INTEGER :: N, M, I, J , K, B
REAL :: XSIM(N), XMAX(N), DIF(M), U0(M), DELTAT, DELTAU
INTEGER , PARAMETER:: A = 1000 ! HALF OF THE PERIOD OF THE
RATCHET POTENTIAL(nm) .
REAL , PARAMETER :: KBT = 2.4E-21 ! THERMAL ENERGY (J)
REAL , PARAMETER ::ETA = 2.4E-30 !VISCOSITY OF WATER ($J * s/nm^3$)
INTEGER , PARAMETER :: $R_{bead}$ = 240 ! RADIUS OF BEAD (nm)
REAL :: DELTAX , F , XMEAN , VARX , MU , R1 ,D , LDIFF , TIME
REAL , PARAMETER :: PI = 22/7
D = KBT/(6*PI*ETA*$R_{bead}$) ! STOKES DIFFUSION CONSTANT($nm^2/s$)
LDIFF = SQRT(2*D*DELTAT) ! DIFFUSION (nm)
TIME = N*DELTAT
DO K = 1 , M
```

```
F = DELTAU * K * KBT /1000
U0(K) = DELTAU * K * DELTAT
MU = D * F /KBT * DELTAT ! DISPLACEMENT (nm)
DO J =1,N
DO I = 2 ,N
IF ( MOD (XSIM (I-1), REAL (A))==0.0) THEN
CALL RANDNUM (R1)
DELTAX = R1*LDIFF
XSIM (I) = XSIM (I-1) + DELTAX
ELSE
IF (XSIM(I-1)> 0.0 ) THEN
B = SIM(I-1)/A
IF ( MOD (B,2 )==0) THEN
CALL RANDNUM (R1)
DELTAX = R1 * LDIFF - MU
XSIM (I) = XSIM (I-1) + DELTAX
ELSE
CALL RANDNUM (R1)
DELTAX = R1 *LDIFF + MU
XSIM ( I ) = XSIM ( I-1 ) + DELTAX
END IF
ELSE
B = ABS ( XSIM ( I-1 )) /A
IF ( MOD( B , 2) == 0) THEN
```

```
CALL RANDNUM (R1) DELTAX = R1 * LDIFF + MU
XSIM ( I) = XSIM (I-1) + DELTAX
ELSE
CALL RANDNUM (R1)
DELTAX = R1 * LDIFF - MU
XSIM ( I) = XSIM (I-1) + DELTAX
END IF
END IF
END IF
END DO
XMAX ( J ) = XSIM ( N )
END DO
XMEAN = SUM ( XMAX ) /N
VARX = SUM ( ( XMEAN - XMAX )* ( XMEAN - XMAX ))/N
DIF ( K ) = VARX /(2.0 * TIME )
END DO
END SUBROUTINE EVALUATE1
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

   SUBROUTINE INPUTVALUES ( DELTAU , DELTAT , N , M )
IMPLICIT NONE
REAL :: DELTAU , DELTAT
INTEGER :: N , M
PRINT * , ' ENTER THE POTENTIAL STEP DELTAU = '
```

```
READ *,DELTAU
PRINT * , ' ENTER THE TIME STEP DELTAT = '
READ * , DELTAT
PRINT * , ' ENTER NUMBER OF DATA POINTS N = '
READ * , N
PRINT * , 'ENTER NUMBER OF POTENTIAL POINTS M = '
READ * , M
END SUBROUTINE INPUTVALUES

    !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

    SUBROUTINE RANDNUM ( A )
IMPLICIT NONE
REAL , PARAMETER :: PI = 22/7
REAL :: X , Y , U1 ,U2 , W ,A
DO
CALL RANDOM-NUMBER ( X )
CALL RANDOM-NUMBER ( Y )
U1 = 2 * X - 1
U2 = 2 * Y - 1
W = (U1)^2 + (U2)^2
IF ( W ¡1 ) THEN
A = U1 * SQRT ( -2 * ln(W) / W )
ELSE
```

```
CYCLE
END IF
EXIT
END DO
END SUBROUTINE RANDNUM
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
```

Bibliography

[1] J*ü*rgen Renn, Ann. Phys. (Leipzig) 14,Supplement,23-37 (2005) / DOI 10.1002/ andp. 2004/0131.

[2] Debashish Chowdhury, arXiv: Cond- mat/0504610.

[3] M D Haw, J. Phys. : Condens. Matter **14**(2005) 7769.

[4] C.W. Gardiner, *Handbook of Stochastic Processes*, 2^{nd} Edition (Springer,1985).

[5] John F. Beausang et al, arXiv:q-bio/0610007v1 [q-bio.BM].

[6] Edie Sevick, *lecture notes on polymers and soft condensed matter*, 2006 (http://rsc.anu.edu.au/ sevick/groupwebpages/lectures.html).

[7] R.Dean Astumian, Science, **276**(1997).

[8] H. Risken, *The Fokker-Planck Equation*, 2^{nd} Edition (Springer, 1988).

[9] P.A Forsyth, *An introduction to Computational Finance Without Agonizing Pain*, February 2007 (www.scicom.uwaterloo.ca/paforsyt).

[10] P.Reimann et al, Phys.Rev.Lett. **87**, 1 (2001).

DECLARATION

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

Name: Yigezu Mulugeta

Signature: -----------------------

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

Name: Mulugeta Bekele, PhD

Signature: -----------------------------

Place and date of submission:
Addis Ababa University
Department of Physics
July 2007