POLYMER TRANSLOCATION THROUGH NANOPORE : A MONTE CARLO STUDY

By

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Abstract

In this thesis we investigate polymer translocation through nanopore without external driving force. We used the two dimensional Monte Carlo simulation with Bond Fluctuating method. To prevail over the entropic barrier, we have taken our system consideration that placing polymer in the middle of nanopore. Thus, we studied the static properties of linear polymer like mean square end to end distance $\langle R^2 \rangle$ and mean square radius of gyration $\langle R_g^2 \rangle$ as a function of chain length N. We found that the scaling relations of $\langle R^2 \rangle$ and $R_g^2 \rangle$ with polymer size N,as $\langle R^2 \rangle \sim N^{1.49}$ and $\langle R^2 \rangle \sim N^{1.512}$ which are in agreement with Flory prediction of real polymer chain. We also studied the dynamic properties of linear polymers by investigating diffusion coefficient(D) and escape time (τ) with chain length N, as $D \sim N^{-0.93}$ and $\tau \sim N^{2.512}$ which are in agreement with Rouse model prediction that are $D \sim N^{-1}$ and $\tau \sim N^{1+2\nu}$, where $\nu = \frac{3}{4}$ for 2D . In this work, we have also examine the interplay between the pore size and escape time τ while simulating the translocation process.

Keywords: Monte Carlo method (MC),Bond Flactuation Method (BFM), self avoiding walk (SAW)

Chapter 1

Introduction

1.1 Background of the Study

So far logical advances in natural science have affirmed the idea that physical laws are indeed entirely responsible for how life functions. Another interesting aspect of biological systems is the paramount roles played by several kinds of polymers, which is comprehensive in a huge field, called polymer science. Although many people maybe do not realize it, everyone is familiar with polymers. Polymers are used extensively in the chemical, electronic, optical, pharmaceutical and medical industries as important components of highly functional materials. They are all around as in everyday uses. The usefulness of polymers is due to the many advantages of polymeric materials have compared to metals, e.g., low weight, radiolucency, thermally and electrically insulating, and lower process and maintenance cost. Moreover, at the molecular scale, life is made of biopolymers: DNA, RNA and proteins that are fundamental to biological structure and function [2, 19]. However, these practical application of polymers is affected by their physical properties.

In polymer physics [22, 26], polymers are usually classified by topology *i.e.*, overall connectivity. Linear, branched, and ring polymers are examples of the topological classes in polymer physics. Static properties of polymers are the properties that are characterized by the polymer chain size and shape[5, 26], this means the properties are characterized by the parameters like End-to-End distance($\mathbf{R}$) and Radius of gyration($\mathbf{R}_g$). Where as, the dynamic properties of the polymers are characterized by the parameter like diffusion constant of the molecules (D)[27] as well as the translocation of the polymers through narrow pore.

Polymer translocation is the process by which a polymer chain will pass through a pore to either of the sides of the pore. Translocational transport of polymers through nanopore also plays a crucial role in other numerous biological processes, such as DNA and RNA [2, 10] translocation across nuclear pores, protein transport through membrane channels and virus injections. Moreover, translocation processes might eventually prove useful in various technological applications, such as rapid DNA sequencing, gene therapy, and controlled drug delivery [16]. Thus, in order to determine these properties many simulation methods are employed. The two prominent approaches used to simulate polymers are Molecular Dynamics (MD) and Monte Carlo (MC) methods. These approaches are similar to time and ensemble averaging in statistical mechanics. Monte Carlo simulation method involves generating and accepting or rejecting of possible conformations (states) stochastically [23]. Generally, polymers are studied in the fields such as biophysics, macro-molecular science and polymer sciences which includes polymer physics. Polymer physics deals with the description of the structure and the resulting properties of polymeric materials. The statistical approach of polymer physics is based on an analogy between a polymer and a Brownian motion or some other type of random walk (RW) [22].

To work as an accurate measuring tool the translocation process needs to be controlled and predictable. Hence appropriate nanopores are important[14].T here are two types of pore biological nanopores and solid state nanopores.

Persuaded by this introductory scientific background, we would investigate unbiased translocation of polymer through nanopore.

1.2 Statement of the Problem

Recently, scholars are focused on different polymeric materials due to their technological applications and daily use. The properties of polymers play a crucial role in their applications. Although polymers are important in our daily life. However, static and dynamic properties of polymers are remained with great disputes. Particularly, the properties of linear polymers are still not fully addressed. Even though, a lot of work has been done with simulation of linear polymers focusing mainly on understanding their translocation through nanopore in the absence of external driving force in free space. However, the depth level of theoretical and computer simulations are still in progress. Therefore, this study investigate unbiased translocation of linear polymer through nanopore.

1.3 Research Questions

- What is the scaling exponent of the average-squared radius of gyration of linear polymer with chain length N, $R_g^2 \sim N^{2\nu}$?
- What is the scaling behavior of the mean-squared end-to-end distance of a linear polymer as function of chain length?
- What is the scaling exponent α for the mean translocation time $\tau \sim N^{1+2\nu}$ as a function of chain length N?
- How does the pore size affects the translocation time of linear polymer chains?
- What is the probability distribution of the mean translocation time of a linear chain through a nanopore?
- How does the chain length related with the mean translocation time?
- What is the center of mass diffusivity **D** of the translocating polymer?

1.4 Objectives

1.4.1 General Objective

- To study the translocation of linear polymer chains through nanopore in the absence of a driving force.

1.4.2 Specific Objectives

The specific objectives of this study are:

- To determine the scaling exponent α of the average-squared radius of gyration of linear polymers with chain length.
- To calculate the exponent for the scaling of the mean-squared end-to-end distance of the polymer as a function of the chain length.
- To obtain the scaling behavior ($\tau \sim N^{1+2\nu}$)of the translocation time with chain length.
- To examine the effect of the pore size on the translocation time of the polymers.
- To determine the probability distribution of the mean translocation time of a linear chain through a nanopore.
- To examine the chain length related with the translocation time.
- To calculate the center of mass diffusivity **D** of the translocating polymer

1.5 Significance of the Study

Latterly, polymers have got a grand technological relevance for several applications. For example, as mentioned above, they play a pivotal role in other many biological processes, such as DNA and RNA translocation across nuclear pores, protein transport through membrane channels and virus injections. And also the polymers are useful in several technological applications, such as rapid DNA sequencing, gene medical aid, and controlled drug delivery. Their application depends on their properties. The size and the shape of polymers affect their properties. Based on this fact the result of this study would be the following importance.

- To provide basic knowledge and recommendation to researchers, students and other concerned bodies about unbiased translocation of linear polymer through nanopore.
- To asses the problems and would use as base for further study.

Chapter 2

Litrature Review

In this chapter, we provide a brief review on polymer physics: static and dynamic properties of polymers, starting with basic definition of polymers and polymerization.

2.1 Polymers and Polymerization

Since most materials are consisting of polymers and most of the modern advances in science and technology involve polymers, some have called this the polymer era. In reality, we have always lived in polymer age. The ancient Greeks classified all matters as animal, vegetable, and mineral[5]. All are largely polymeric and are important to life as we know it. Most Chemists, biochemists, and chemical engineers are now involved in some phase of polymer Science.

The word **polymer** is derived from the Greek words **poly** and **meros**, meaning *many* and *parts* respectively[9]. Some Scientists prefer to use the word **macro molecule** or **large molecule**, instead of **polymer**. So, polymers are characterized within the more general concept of macro molecules by the presence of a clear repetitious elements. These reiterative elements are called **monomers**. Although, natural polymers do exist (for example, natural rubber), most polymers are synthesized by

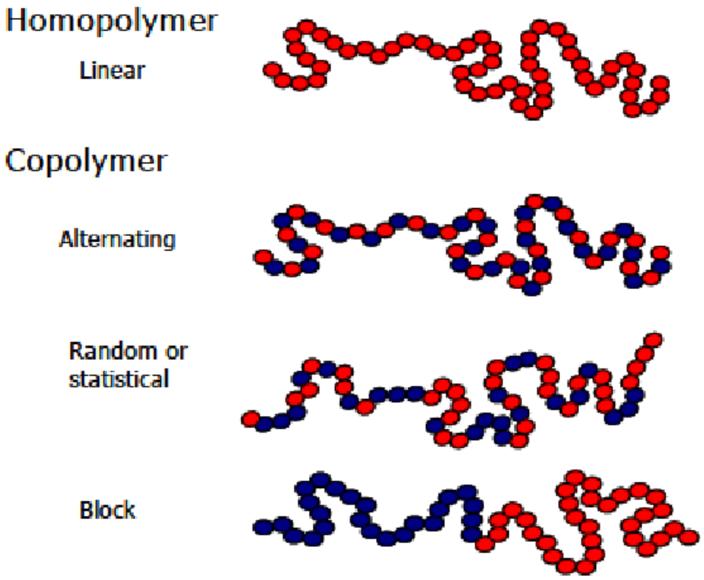

Figure 2.1: Various types of polymer structure[14]

polymerization of monomers from the petrochemical industry. Figure 2.1 illustrates some important types of polymers.

Polymerization is the process by which elementary units are covalently bonded together.The entire structure of a polymer is generated during this process. The number of monomers in a polymer is called its **degree of polmerization**, N[1, 22].The **molar mass** M of polymer is equal to its degree of polymerization N times the molar mass M_{mol} of its chemical monomer.

$$M = NM_{mol} \tag{2.1.1}$$

Another important feature controlling the properties of polymeric systems is polymer architecture. Types of polymer architecture include **linear**, **branched**, **cross-linked**, as shown in Figure 2.2

The size and the shape of polymers are closely connected to their properties [22, 26].

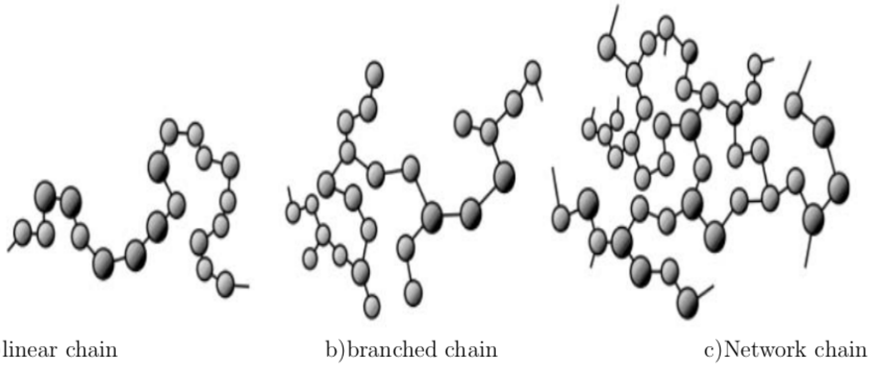

Figure 2.2: Architecture of polymer chain: a linear chain (a), a branched chain (b), and a cross-linked polymer (c). [26]

The shape of polymers is also nearly connected to the size of the various units that comprise the macro-molecule and the various primary and secondary bonding forces that are present within the chain and between chains. We discus the detail in the next sections.

2.2 Static Properties of Polymers

We now discus the properties of ideal chain and real chain polymers.

2.2.1 Ideal Chain

This section are based on the so called freely jointed chain model which is the simplest model to describe a polymer chain. Here, a polymer is regarded as a random walk of finite length and interactions among individual monomers are neglected. Let us start with a freely jointed chain (FJC) model, which consists of massless points connected by bonds with a constant length, l. The bonds are free to rotate. This model is similar to the random walk in two dimension in which the length of a step is l. The two quantities of the random walk, end-to-end vector and radius of gyration, characterizes the most important static properties (*i.e.,* shape and size) of a polymer chain. Here, the bond vector is represented by: $\overrightarrow{r}_n = \overrightarrow{R}_{n+1} - \overrightarrow{R}_n$, where $\overrightarrow{R}_n$ is the position of an n-th monomer, and $|\overrightarrow{r}_n| = l$ for all n.

End-to-end vector : is the sum of all n bond vectors.

$$\overrightarrow{R}_n = \sum_{i=1}^{N} \overrightarrow{r}_i \tag{2.2.1}$$

In this model, the average of end-to-end distances $\langle \overrightarrow{R} \rangle$ can be written as:

$$\langle \overrightarrow{R} \rangle = \langle \sum_{i=1}^{N} \overrightarrow{r}_i \rangle = 0 \tag{2.2.2}$$

and average of squared end-to-end distances is:

$$\begin{aligned} \langle R^2 \rangle = \langle \overrightarrow{R}^2 \rangle &= \langle \left(\sum_{i=1}^{N} \overrightarrow{r}_i \right) \left(\sum_{j=1}^{N} \overrightarrow{r}_j \right) \rangle \\ &= \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \overrightarrow{r}_i . \overrightarrow{r}_j \rangle \\ &= \sum_{i}^{N} \sum_{j}^{N} l^2 \cos\theta_{ij} \\ &= Nl^2 + 2l^2 \sum_{i}^{N} \sum_{i \neq j}^{N} \cos\theta_{ij} \end{aligned} \tag{2.2.3}$$

where θ_{ij} is an angle between two bond vectors, $\overrightarrow{r}_i$ and $\overrightarrow{r}_j$. For freely jointed chain model:

$$\cos\theta_{ij} = \begin{cases} 1, \text{for } i = j \\ 0, \text{otherwise} \end{cases} \tag{2.2.4}$$

Thus equation 2.2.3 becomes:

$$\langle \overrightarrow{R}^2 \rangle = Nl^2 \tag{2.2.5}$$

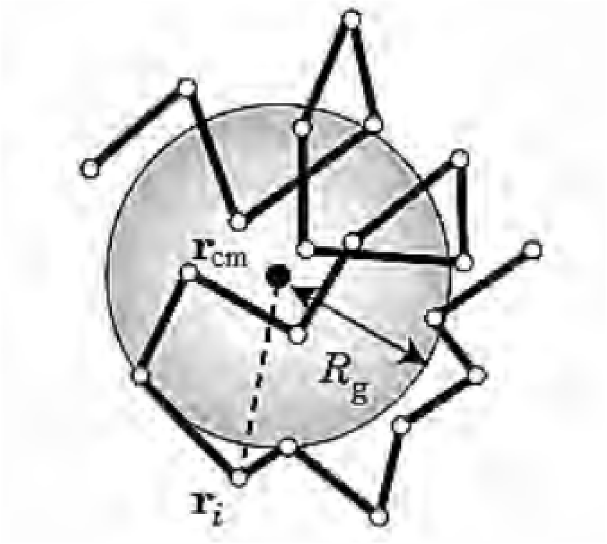

Figure 2.3: Center of mass and the radius of gyration in the bead-stick model. [26]

As it is remarked above,the model is similar to the random walk, i.e. every polymer segment is independent from all others. The end-to-end distance is a well-defined for a linear polymer as mentioned above, but it cannot characterize the size of branched and ring polymers, because they either have too many ends or no ends at all.

Radius of gyration: since, all polymers posses a radius of gyration , it can characterize the size of polymers of any architecture. The square **radius of gyration** is defined as the average square distance between monomers in a given conformation (position vector $\overrightarrow{R}_i$) and the polymer's center of mass (position vector $\overrightarrow{R}_{cm}$)[26]

$$R_g^2 = \frac{1}{N}\sum_{i=1}^{N}\left(\overrightarrow{R}_i - \overrightarrow{R}_{cm}\right)^2 \tag{2.2.6}$$

The position of center of mass of the polymer is the number of average of all monomer position vectors.

$$\overrightarrow{R}_{cm} = \frac{1}{N}\sum_{j=1}^{N}\overrightarrow{R}_j \tag{2.2.7}$$

Substituting equation 2.2.7 into 2.2.6 and rearranging it, gives an expression for the square radius of gyration as a double sum of squares of over all inter-monomer distance :

$$R_g^2 \;=\; \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\overrightarrow{R}_i - \overrightarrow{R}_j\right)^2 \tag{2.2.8}$$

Now we obtain R_g for ideal chains, as a freely joined chain model, whose conformations are given as trajectories of random walkers. The bond vector $(r_i - r_{i-1}\ )$ of the i^{th} bond is then the displacement vector Δr_i of the i^{th} step. The expression of mean square end-to-end distance for a random walk applies to the mean square distance between the i^{th} and j^{th} monomers on the chain just by replacing N with $\mid i-j \mid$. When $\mid i-j \mid$ is large, $r_i - r_j$ of an ideal chain has a Gaussian distribution with variance $\mid i-j \mid l^2$. Which means that

$$\langle (r_i - r_j)^2 \rangle = \mid i-j \mid l^2 \tag{2.2.9}$$

Therefore, the radius of gyration of ideal linear chain polymer is:

$$R_g = \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \mid i-j \mid l^2 = \frac{Nl^2}{6} \tag{2.2.10}$$

Equating this result with equation 2.2.5,we get:

$$\langle R_g^2 \rangle = \frac{l^2 N}{6} = \frac{\langle R^2 \rangle}{6} \tag{2.2.11}$$

2.2.2 Real Chain And Excluded Volume(EV)

Polymer physics based on ideal model of polymer chains discussed above. However, in real, polymer chains have physical constraints beyond considered on their ideal

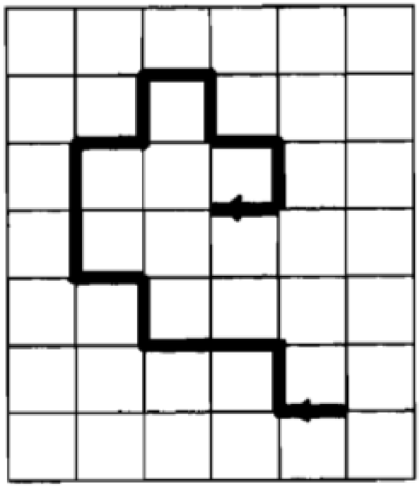

Figure 2.4: Self Avoiding Walk(SAW)

models. These constraints affect the static and dynamic properties a polymer chain. The interactions between monomers of a chain with finite lateral dimensions at the real polymer chains and these interactions can alter the size of the polymer. Therefore, it is important to see such constraints and their effects on the static behaviors of polymer chains.

Real chains have a finite molecular volume and will exclude overlapping configurations. On a lattice this can be implemented by allowing empty sites for each consequent segment only. Such configurations are known as Self Avoiding Walk(SAW). SAW is a random walk in which points are not revisited as shown in Figure 2.4. This intermolecular excluded volume effect leads to an expansion of the chain with respect to the corresponding ideal chain,since the excluded volume effect is proportional to the segment density which is highest at the center of the chain. Real polymer chains of excluded volume was analyzed by Flory.

For N monomers, Flory[8] considered that the monomers are uniformly distributed within the total volume of the chain with neglecting correlation between them and represented the polymer coil a sphere with radius R filled with the polymer segments with mutual repulsive interaction. The repulsive energy is [9]

$$F_{rep}\left(N,R\right)=k_{B}Tv_{ex}\frac{N_{m}^{2}}{R^{d}} \tag{2.2.12}$$

And the other contribution to the free energy is an entropic cost,$F_{entropic}\left(N,R\right)$.The entropy loss due to the chain extension can be determined by the probability distribution which is given by:

$$P\left(N,\overrightarrow{R}\right)=\left(\frac{2\pi Nl^{2}}{d}\right)^{\frac{-d}{2}}exp\left(\frac{-3\overrightarrow{R}^{2}}{2Nl^{2}}\right) \tag{2.2.13}$$

Hence, the $F_{entropic}\left(N,R\right)$ becomes:

$$F_{entropic}\left(N,R\right)=-TS\left(N_{,}\overrightarrow{R}\right)\approx -k_{B}TlnP\left(N,\overrightarrow{R}\right)=\frac{dk_{B}T\overrightarrow{R^{2}}}{2l^{2}N} \tag{2.2.14}$$

Therefore, the total free energy of the polymer is the sum of the two energies

$$F\left(N,R\right)=F_{rep}\left(N,R\right)+F_{entropic}\left(N,R\right)\approx k_{B}T\left(v_{ex}\frac{N^{2}}{R^{d}}+\frac{dR^{2}}{2l^{2}N}\right) \tag{2.2.15}$$

By reducing equation 2.2.15 with respect to $R(i.e.,,\frac{\partial F(N,R)}{\partial R}=0)$, we get the following relation:

$$R\backsim N^{\nu} \tag{2.2.16}$$

Where, $\nu=\frac{3}{d+2}$ and d is dimension.

In general Florys theory for a linear polymer in good solvent is that it yields a universal power-law dependence of polymer size R on the number of monomers N , $i.e$

$$\langle R^{2}\rangle\sim N^{2\nu} \tag{2.2.17}$$

$$\nu = \begin{cases} \frac{1}{2}, & \text{Random walk} \\ \frac{3}{4}, & \text{self-avoiding walk} \\ \frac{1}{3}, & \text{collapsed chain} \end{cases} \tag{2.2.18}$$

2.3 Dynamic Properties of Polymer Chains

Dynamics of linear polymers is modeled by N beads connected by massless, frictionless springs. Such a model is usually called the Rouse model. We discus the detail of the model as follows.

2.3.1 Rouse Model

When a polymer chain moves through a solvent every bead, whether it represents a monomer or a larger part of the chain, will continuously collide with the solvent molecules[26]. Besides a systematic friction force, the bead will experience random forces, resulting in Brownian motion. Consider a spherical bead of radius a and mass m moving in a solvent. Because on average the bead will collide more often on the front side than on the back side, it will experience a systematic force proportional with its velocity, and directed opposite to its velocity as shown in figure 2.5.The bead will also experience a stochastic force $\mathbf{F(t)}$[20]. Hence, equation of motion is:

$$\frac{d\mathbf{R}}{dt} = \mathbf{v} \tag{2.3.1}$$

$$\frac{d\mathbf{v}}{dt} = -\xi V + \mathbf{F} \tag{2.3.2}$$

Where the friction constant ξ is given by:

$$\xi = \frac{\zeta}{m} = \frac{6\pi\eta_s a}{m} \tag{2.3.3}$$

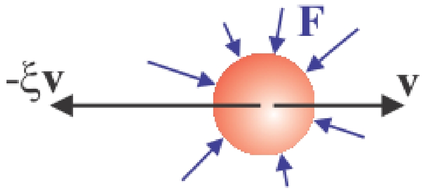

Figure 2.5: A spherical bead moving with velocity v will experience a friction force of $-\xi v$ opposite to its velocity and random forces **F** [20]

where, η_s is the viscosity of the solvent, ζ is friction force , F is stochastic force, and v is velocity. Furthermore, solving equation 2.3.2 gives:

$$\mathbf{v}\left(t\right)=\mathbf{v}_o e^{\xi t}+\int_0^t d\tau e^{-\xi(t-\tau)}\mathbf{F}\left(t\right) \tag{2.3.4}$$

We have to make some assumptions about the stochastic force. In view of its scrambled character, the following assumptions seem to be appropriate for its average properties:

$$\begin{aligned}\langle\mathbf{F}(t)\rangle &= 0 &(2.3.5)\\ \langle\mathbf{F}\left(t\right).\mathbf{F}(t^{'})\rangle &= C_{v_o}\delta(t-t^{'}) &(2.3.6)\end{aligned}$$

where C_{v_o} depend on the initial velocity. Using the equations one can find: The bead is in thermal equilibrium with the solvent and from equipartition theorem, for large t, the mean square displacement is:

$$\langle(\mathbf{R}(t)-\mathbf{R}(0))^2\rangle=\frac{6k_BT}{m\xi}=\frac{6k_BT}{\zeta} \tag{2.3.7}$$

From equation 2.3.7 the Rouse model show that the mean square displacement $\mathbf{R}^2(t)$ of the molecule's center of mass (CM) of d-dimension is given by:

$$\langle \mathbf{R}(t)^2 \rangle = 2d\frac{k_BT}{N\zeta}t \tag{2.3.8}$$

$$\langle \mathbf{R}(t)^2 \rangle = 2dDt \tag{2.3.9}$$

Where D is diffusion constant. Hence,the diffusion constant in this model is:

$$D = \frac{k_BT}{N\zeta} \tag{2.3.10}$$

Here after, from equation 2.3.10, it is easy to understand that the Rouse diffusion constant and the number of monomers have inversely relationship[25]:

$$D \sim N^{-1} \tag{2.3.11}$$

In this study, we consider two key parameters related to the dynamic property of a polymer chain. They are the diffusion constant of the polymer center of mass, D, and the escape time of the polymer chain through a pore, τ . These two parameters shows a distinct scaling dependence on the number of monomers N as

$$D \sim N^{-1} \tag{2.3.12}$$

And

$$\tau \sim \frac{R_g^2}{D} \tag{2.3.13}$$

2.4 Review of Translocation of Polymer

Polymer translocation is one of the most fundamental macromolecular processes in life. For example molecular transport through cell membrane is an essential mechanism in living organisms and it is a translocation process [10, 2]. This ubiquitous phenomenon deals with how electrically charged polymer molecules, such as polynucleotides and proteins, move from one region of space to another in jammed environments. So, beside its biological relevance, the translocation dynamics is also a challenging topic in polymer physics. Accordingly, the polymer translocation has got attention to be studied experimentally[11], theoretically[21], and numerically[11, 24].

From statistical physics view the translocation process of polymers can be seen as a kind of tunneling process over an entropic barrier. This entropic barrier arises because the number of states (conformations) possible or available to the polymer is significantly decreased by the presence of the membrane. In order to overcome such barrier and to speed up the translocation, an external field or interaction is often introduced. For example, in 1996, Kasianowicz *et al*[11]reported that an electric field can drive single stranded DNA and RNA molecules through the α-hemolysin channel of inside diameter $2nm$. In the case of unbiased translocation process some geometrical restriction or systematic placement of the chain is needed in ordered to overcome the entropy near the nanopore and increase the possibility of the translocation.

Elysian by experiments, a number of recent theories[17, 18] have been developed to investigate a polymer translocation. However the case of unbiased translocation of linear polymers still remains a challenging problem. So our simulation study focuses on unbiased translocation of a linear polymer through nanopore.

Among the fundamental parameters defining a translocation process the main one is the average time of translocation, τ. It can also be perceived and referred as the first passage time through the pore or else an escape time from the pore to one of the sides starting from an equilibrated state in which the polymer is threaded halfway through the pore. This quantity will be studied as a function of the number of monomers of the polymer N and is an important measure of the underlying dynamics. The dynamics of such unbiased translocation for linear polymers has been extensively investigated by several independent models both in 2D and 3D. All these studies were aiming at conclusively determining the dynamical scaling exponents. However even recently, various heuristic scaling arguments for τ as a function of N have been presented. Most of these studies use extensive numerical simulations based on the fluctuating bond Method (FBM). In the case of unforced polymer translocation, Sung and Park[14] and Muthukumar[17] considered equilibrium entropy of the polymer as a function of the position of the polymer through the nanopore. The geometric restriction leads to an entropic barrier. Standard Kramer[12] analysis of diffusion through this entropic barrier yields a scaling prediction of the translocation time $\tau_{tran} \backsim N^2$. However, as Chuang *et al*[7]noted, this quadratic scaling behavior is at best only marginal for phantom(illusion) polymers and cannot be correct for a self-avoiding polymer. The reason is that the equilibration time $\tau_{equil} \backsim N^2$ for a phantom polymer and $\tau_{equil} \backsim N^{1+2\nu}$ for a self-avoiding polymer, where ν is the Flory exponent [$\nu = \frac{3}{4}$ and $\frac{3}{5}$ in two-dimensional (2D) and three-dimensional (3D), respectively]. Chuang *et al*[5] performed numerical simulations with Rouse dynamics for a 2D lattice model to study the translocation for both phantom and self-avoiding polymers. They decoupled the translocation dynamics from the diffusion dynamics outside the pore by imposing the artificial restriction that the first monomer, which is initially placed in the pore, is never allowed to cross back out of the pore. We will refer to the translocation time obtained this way as τ_{tran} .

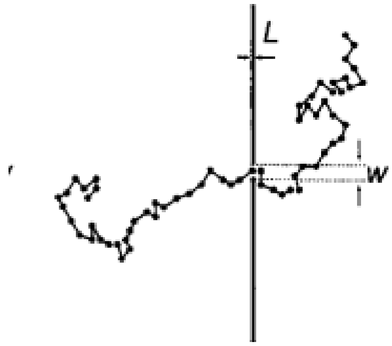

Figure 2.6: The middle of a polymer is initially placed in the center of the pore. The length and width of the pore are L and W, respectively[14]

.

Their results show that for large N, translocation time τ_{tran} scales approximately in the same manner as equilibration time, but with a larger prefactor.

In our study we consider a polymer which is initially placed symmetrically in the middle of the pore as shown in Figure 2.6[15]. In this case, without any external driving force or restriction, the polymer escapes from the hole either to the left or the right side of the pore in an average time defined as the escape time τ . It is clear thatτ_{trans} and τ are different. Namely, the translocation time τ_{trans} includes events where the middle segment reaches the center of the pore but then the first segment returns to the entrance of the pore and the whole translocation process begins all over again. Numerically,τ can be sampled much more efficiently than τ_{tran} , leading to a more accurate determination of the scaling behavior. We will show numerically that $\tau \sim N^{1+2\nu}$, in the same manner as found previously for τ_{tran} . In this study, we investigate polymer translocation through nanopre in the absence of driving force in a 2D lattice model by focusing on τ.

2.5 Review of Bond Fluctuation Method

Bond fluctuation method (BFM) was proposed[3] as an alternative to a (single-site) SAW model, which retains the computational efficiency of the lattice without being plagued by severe ergodicity problems. It is an efficient lattice Monte Carlo (MC) algorithm for coarse-grained polymer chains where each monomer occupies exclusively a certain number of lattice sites on a simple cubic lattice[13]. Also, a coarse-grained simulation model on lattice is preferred [27]. The key idea is to increase the size of a monomer which now occupies, instead of a single site, a whole unit cell of the lattice (for example, a square for the 2D square lattice or a cube for the 3D cubic lattice).

This two dimensional BFM which represent a monomer by a square cell of the lattice allows 36 possible bond vectors and 41 bond angles between two monomers [3, 4]. But the single-site lattice model in two dimension lattice where a monomer is associated with each lattice site instead of the square lattice area permits 3 bond angles. Due to such multitude of different bond lengths and bond angles also the BFM is much closer to continuous space behavior than the single site lattice model. This also makes it clear why the system with BFM escapes situation in which SAW models with monomer at a lattice site freezes in.

Chapter 3

Methods

Computer simulations are intermediate between theory and experiments. They can provide a valuable tests of assumptions and predictions of theoretical models as well as attempt to imitate experimental systems such as polymer solutions, melts and networks etc. There are two main approaches used to simulate polymers: Molecular Dynamics (MD) and Monte Carlo (MC) simulations.

3.1 Monte Carlo Simulation

A method of estimating the value of unknown quantity using the principles of inferential statistics. Here we have selected to use MC simulation. Then we have to make a further decision, whether to do the MC simulation on a lattice or in the continuum. For, long time and large-scale phenomena such as translocation, a realistic and microscopically detailed model would require too much computer time and memory. Accordingly, our model eliminates microscopic degrees of freedom and represents the linear polymer by a simplified structure which retain only the most basic features of the polymer (for example, chain connectivity or bonds and the short-range excluded-volume interactions). Therefore such model is appropriate to explore general and universal properties of the linear polymer chains.

In MC method the subsequent configurations of the polymer is generated randomly. We need a way of generating and evaluation for accepting/rejecting the conformations forwarded along each moves. In our simulations, this task will be done according to the Bond Fluctuation Method (BFM).

3.2 Bond Fluctuation Method

BFM has been widely used in recent years to investigate the structure and dynamics of a great variety of polymer systems. To satisfy the SAW condition, each lattice site can only be part of a single monomer. Each monomer on the model occupies 4 vertexa sites of a square area on the lattice. Then each monomer connected to its nearest neighbor monomer by a predetermined set of bond vectors. Two neighbor monomers on a chain must be within a certain bond distance, which is to vary in the range $2 \leq l \leq \sqrt{13}$[3, 4] , where l is the bond length between two consecutive beads. Although the lengths of the bonds are allowed to fluctuate, they have to belong to the set of lengths 2, $\sqrt{5}$, $\sqrt{8}$, 3, $\sqrt{10}$, $\sqrt{13}$. All spatial distances are measured in units of the lattice spacing constant. The minimum distance 2 guarantees the excluded volume effect and the upper limits $\sqrt{13}$ [3, 4] prevents bonds from cutting and crossing each other. Such restrictions on the bond lengths are topology-preserving, since they prevent the crossing of segments. This feature of the algorithm makes the method very well suitable for simulations of polymers. The BFM allows a local move which consists of selecting a monomer at random and of attempting a displacement by one lattice constant in a randomly chosen lattice direction. If the attempted displacement

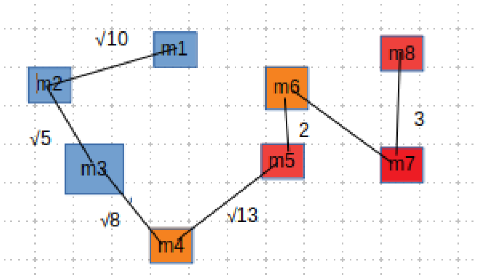

Figure 3.1: The bond length between consecutive monomers in the range $2 \leq l \leq \sqrt{13}$ for 2D BFM.

satisfies both the bond length constraints and the excluded volume interaction, the move is accepted. From Figure 3.1 all the possible positions of a monomer that could be bonded with the monomer positioned at 0. As the bond length is in the range of $2 \leq l \leq \sqrt{13}$ lattice units, lattices with the same color represent equal bond lengths. Bond fluctuation model is a lattice model for simulating polymer systems. It is useful for obtaining static and dynamic properties of polymers. It is common and lawful to consider simple models which capture the essential physics of the problem. For instance, they ought to yield the same universal properties as the real system. Such model for macro molecular configurations is the self-avoiding walk (SAW) on a lattice known commonly as Lattice model. Each site on the lattice which is occupied by the walk will correspond to a monomer, and the bond length equals the lattice constant which connects two subsequent steps of the walk and the bond angles are restricted by the lattice geometry and by the repulsive hardcore monomer-monomer interaction. The lattice model simulation of polymers can be done on different lattice geometries. For example our simulation considers square and hexagonal lattice geometry. The generation of SAW conformations of a given polymer configuration on a given lattice would be done by specific algorithms from different methods. One particularly popular lattice model simulation method is the bond fluctuation method (BFM). It is used to give an algorithm that allows for an analysis of dynamic properties in all dimensions and which is more ergodic.

Implementation of Bond Fluctuation model:

Step 1: Start with an initial state of self avoiding conformation of a polymer chain consisting of N monomers.

Step 2: Select a monomer randomly and select one of the four lattice directions randomly with equal probability, for a 2D square lattice.

Step 3: Move the selected monomer in the selected direction by one lattice spacing called, this a trial move.

Step 4: Check if the trial move violates self avoidance and bond length constraints. if it does, then reject the trial move by returning the monomer to its earlier lattice position and go to step 2.

Step 5: If both requirements self avoidance and bond length restrictions are met then accept the move.

Step 6: Go to the second step. N elementary moves define one MC time step.

3.3 Simulation procedure

For all our simulations, we set up a 2D square simulation box of 800 X 800 square cells of unit length each us shown in Figure 3.2.This lattice space is wide enough to have no effect on any property of the polymer system. Since we use a lattice for our simulation purpose, the first thing that we do is preparing the lattice itself. Then by putting the center of mass of polymer at the center of the lattice, we try to see how the chain diffuses through time by the bond fluctuation Monte Carlo method explained above. We see how the center of mass of the polymer diffuses from the initial position for different times, and we compute the diffusion constant D.

To study the effect of self-avoidance on translocation in the coiled state, higher dimensional simulations ($d > 1$) are necessary. Two dimensional polymers are ideally suited to this purpose for dual reasons that excluded volume effects are more apparent, while computation times are shorter than three dimensional case.

A typical simulation then proceeds as follows. Starting from the initial polymer configuration many moves are to be made until the polymer is equilibrated. To generate such an equilibrated configuration, the chain will be allowed to relax by attempting local moves. We select monomer randomly and then attempt a trial move of by one lattice unit and it is accepted if it does not violate the excluded volume, chain connectivity and chain constraints. Thought this equilibration process the middle of the polymer is anchored not to move. In our simulations this relaxation of the polymer will be executed for longer times than the relaxation time or equilibration time $\tau \sim N^{2.5}$ in two dimension simulations of polymers. And we will also perform two independent simulations for most sets of parameters investigated and then check whether the two results agreed reasonable well. The latter procedure particularly helps us to make sure good stability of our simulation results and the values are not initial configuration dependent.

For unbiased translocation of the linear polymer through the pore the simulation procedure involves additional task of the wall pore placement. Therefore, after we prepare square box then a wall, tall enough as the simulation box height, with a

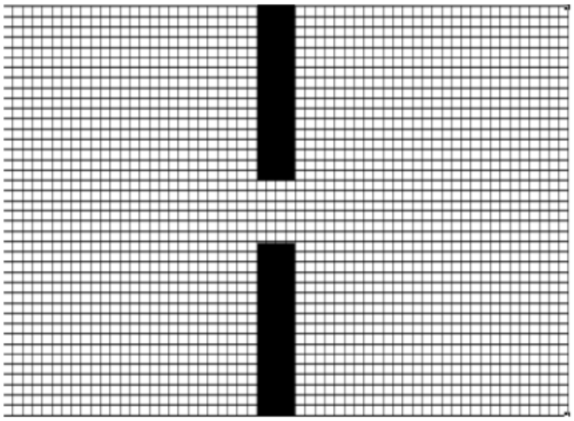

Figure 3.2: Schematic representation of square lattice with size 800x800 unit square cells and at the middle we put a wall with a nanopore of width W= 6 and length L=2

nanopore of length $L = 2$ and width $W = 6$ lattice constant at its center is placed at the middle of the this lattice plane. The pore is small enough to allow only one monomer or two monomers at minimum separation to pass through it. The linear polymer is initially placed at the middle of the pore with half of the chain in either sides of the wall[14] as shown in Figure 3.3 This deliberate position is critical to over come the impact of the entropic boundary or wall. The chain is then permitted to relax with neighborhood moves while one of its center monomer is fixed inside the pore. To get completely equilibrated adaptation us shown in Figure 3.4 with 1 x10^6 Monte Carlo time steps per monomer (MCS) are allocated . After equilibration is finished, at $t = 0$, the middle monomer is allowed to move just like the rest of the monomers of the chain as shown in Figure 3.5

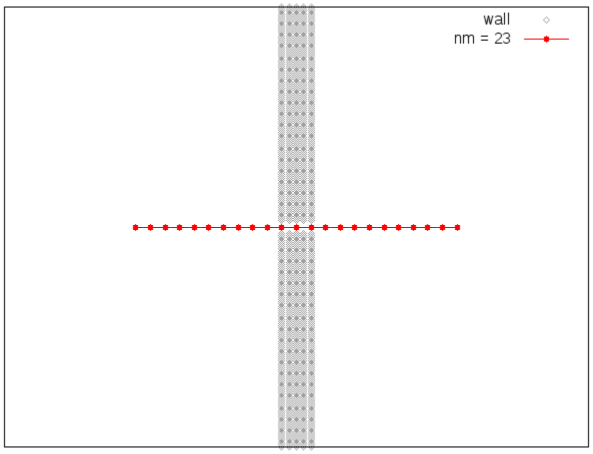

Figure 3.3: The initial conformation of a linear polymer of length N = 23 placed symmetrically.

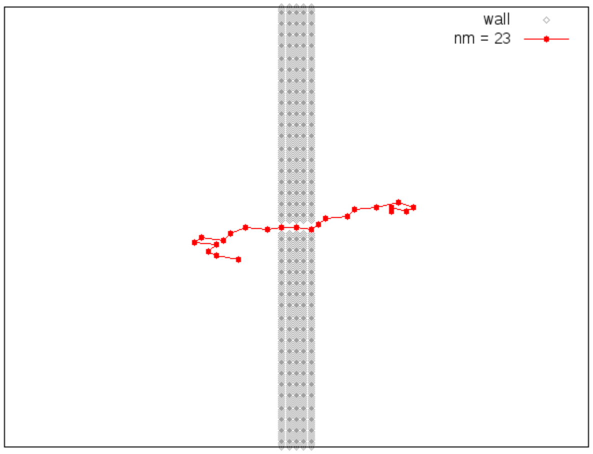

Figure 3.4: Schematic representation of a linear polymer during the time spent translocation from the nano pore with length L = 2 and width w = 6 sites and the polymer size, N = 23. This confarmation is the most likely adaptation after relaxation for $N * 10^6$ Monte Carlo moves.

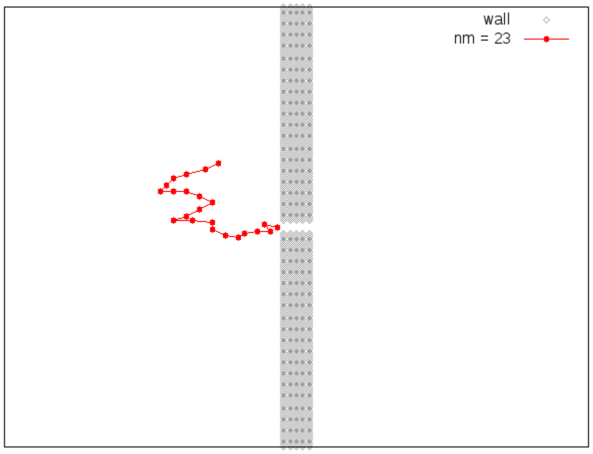

Figure 3.5: Schematic representation of a polymer of length N = 23 after translocated through a pore of length L=2 and width W=6

Chapter 4

Results and Discussion

In our study here We tried to discussed our methods, data we used as well as the results of our study in detail as such we categorized it into two sections such as static properties of a linear polymer chains and Dynamic properties of a linear polymer chains translocating through a nanopore with the bond fluctuating model combined with the single-segment Monte Carlo moves.

4.1 The static properties of a linear polymer chains

Mean squared end to end distance of a linear polymer as a function of the chain length.

The mean square end to end distance of a polymer chain is a measure of the average conformation of the polymer. The mean square end to end distance is static property of polymer chain depend on the number of monomers of polymer chains. The plot of the mean square end-to-end distance $\langle R^2 \rangle$ as a function of polymer chain length N depicted in Figure 4.1 which describe the mutual dependence of the parameters. In ideal polymer models the two parameters have the power-law scaling relation $\langle R^2 \rangle \sim N^{\frac{1}{2}}$. In ideal polymer models no excluded volume effect between monomers. In contrast, the scaling relation of mean square end to end distance as the function of N is $\langle R^2 \rangle \sim N^{2\nu}$ in real polymer chains. However, Flory theory suggested that the exponent at the scaling relation is dimension dependent given by $\nu = \frac{3}{2+d}$ with approximation on Rouse Model of a SAW of polymer chains.

In our study, the scaling exponent is calculated from the slope of the log-log plot of $\langle R^2 \rangle$ as a function of the number of monomers of polymer as shown in Figure 4.1. The log-log plot of $\langle R^2 \rangle$ versus N have a slope of 1.487 ± 0.01 which is in agreement with Flory prediction of the scaling exponent in two dimension. We observed that the mean squared end-to-end distance of linear polymer with chain length N have close to the scaling power of $\langle R^2 \rangle \sim N^{2\nu}$,where ν is Flory exponent $\nu = \frac{3}{4}$ for 2D and $\nu = \frac{3}{5}$ for 3D.

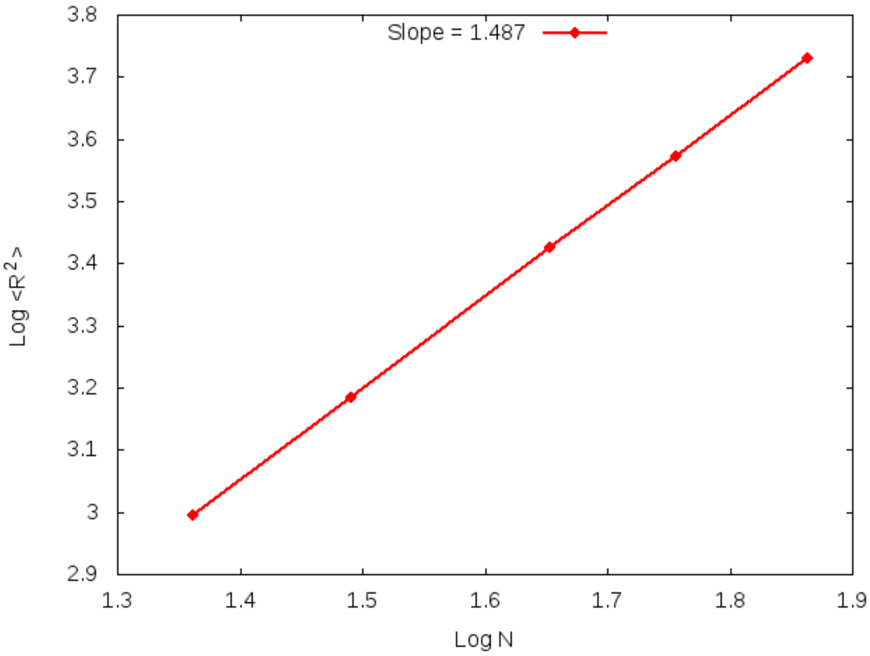

Figure 4.1: Log-log plot of mean square end to end distance $\langle R^2 \rangle$ as a function of polymer chain length N for N = 23, 31, 45, 57,73

Mean-squared radius of gyration of linear polymers with chain length

An alternative representation of the size of a polymer coil often used as the root mean square of the radius of gyration defined as the average distance of a chain element from the center of gravity of the chain. The plot of the mean square radius of gyration $\langle R_g^2 \rangle$ against polymer chain length N is represented in Figure 4.2. In ideal polymer models the two quantities have the power-law scaling relation $\langle R_g^2 \rangle \sim N^{\frac{1}{2}}$. Ideal polymer models have no excluded volume effect between monomers. On the contrary, the scaling relation of mean squared radius of gyration as the function of N is $\langle R_g^2 \rangle \sim N^{2\nu}$ in real polymer chains However, Flory showed that the exponent at the scaling relation is dimensional dependent $\nu = \frac{3}{2+d}$.

In our study, the scaling exponent is extracted from the slope of the log-log plot of $\langle R_g^2 \rangle$ with respect to the number of monomers of a linear polymers as shown in Figure 4.2. The log-log plot of $\langle R_g^2 \rangle$ versus N have a slope of 1.512 ± 0.01 which is in agreement with Flory exponent. We examined the scaling exponent of the average squared radius of gyration of linear polymer with chain length N is approach to 2ν, where ν is Flory exponent.

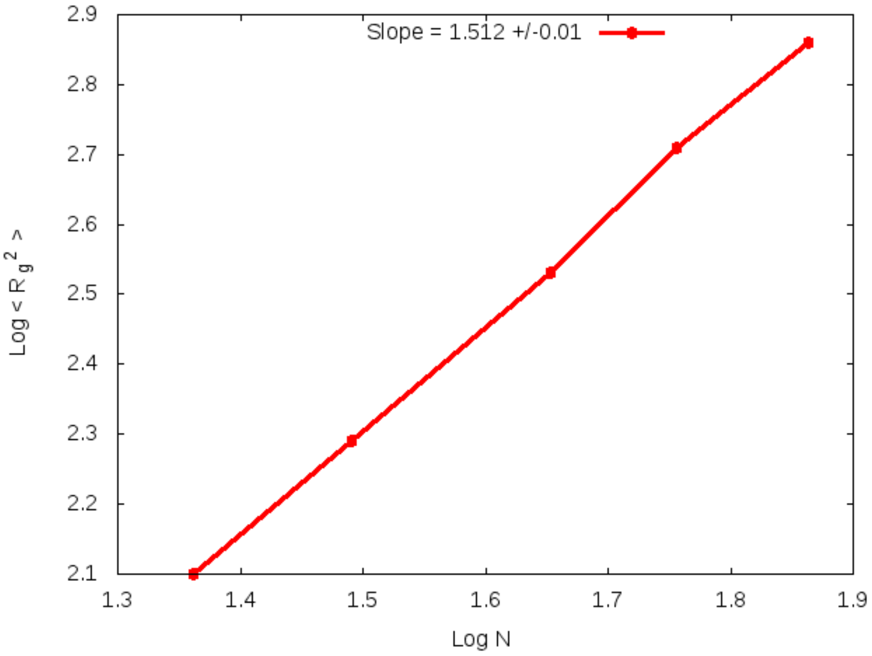

Figure 4.2: Log-log plot of mean square radius of gyration $\langle R_g^2 \rangle$ versus polymer chain length N, for N =23, 31, 45,57,73

4.2 Dynamic Properties of a linear polymer

Diffusion of linear polymer

As delineated in chapter two, we considered specific properties of a linear polymer by investigating the feature of the diffusion of linear polymers. Subsequently, time dependent mean square displacement of the center of mass CM of the chain is $\langle \mathbf{r}^2(t) \rangle$. Which can be determined as

$$\langle \mathbf{r}(t)^2 \rangle = \langle (r_{cm}(t) - r_{cm}(0))^2 \rangle \tag{4.2.1}$$

$\langle \mathbf{r}^2(t) \rangle$ can be representative for the motion of linear polymer chain.

Mean square displacement is the standard term that linearly goes with time. Some monomer has moved over a very large distances undergone a large number of collisions then mean square displacement is proportional to time and the proportionality constant is 4D where D, being the diffusion constant. Figure 4.3 depicted a measure for progress of translocation for chain length N = 23, 31, 45, 57, 73 over time t.

$$\langle \mathbf{r}^2(t) \rangle \sim t \tag{4.2.2}$$

$$D = \frac{1}{4} \lim_{t \to \infty} \frac{\langle r(t)^2 \rangle}{t} \tag{4.2.3}$$

The proportion of respective mean square displacement to the time t that creates diffusion coefficient D relating to each chain length N described by equation 4.2.3. Figure 4.4 elaborates the interdependence of diffusion constant and their degree of polymerization. Park et.al assumed the chain diffusion coefficient(D) to be inverse

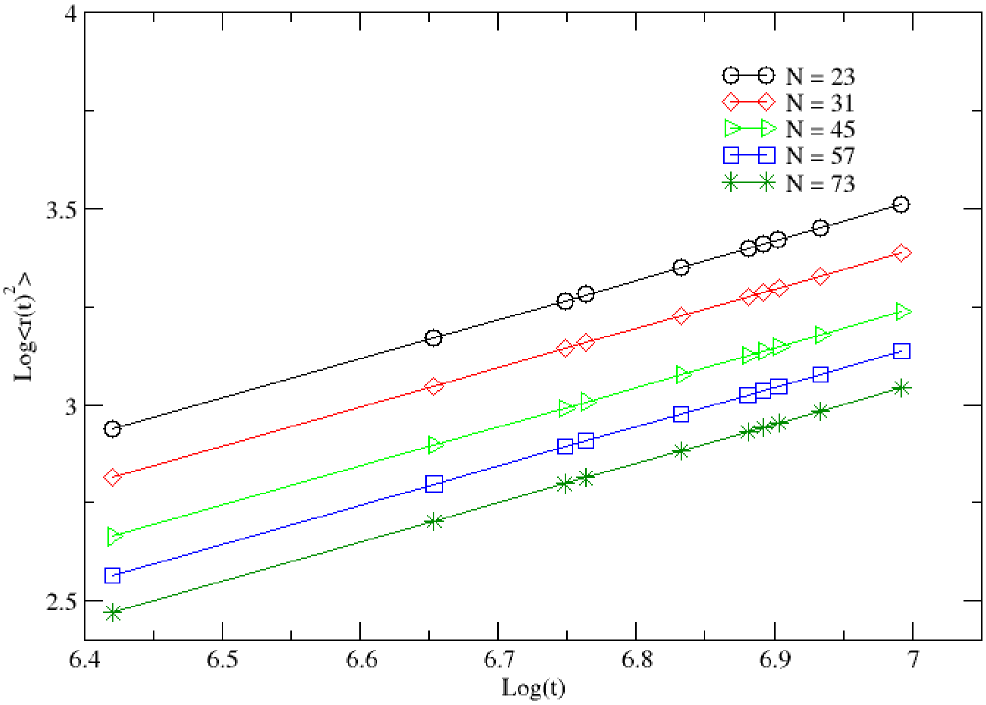

Figure 4.3: Log-log plot of mean square displacement $\langle r^2(t) \rangle$ versus time t, for N =23, 31, 45,57,73

relation to chain length N[25]. Our simulation result shows $D \sim N^{-0.93\pm0.01}$ in agreement with Rouse model scaling relationship of the form $D \sim N^{-1}$ with the theoretical Flory exponent $\nu = -1$

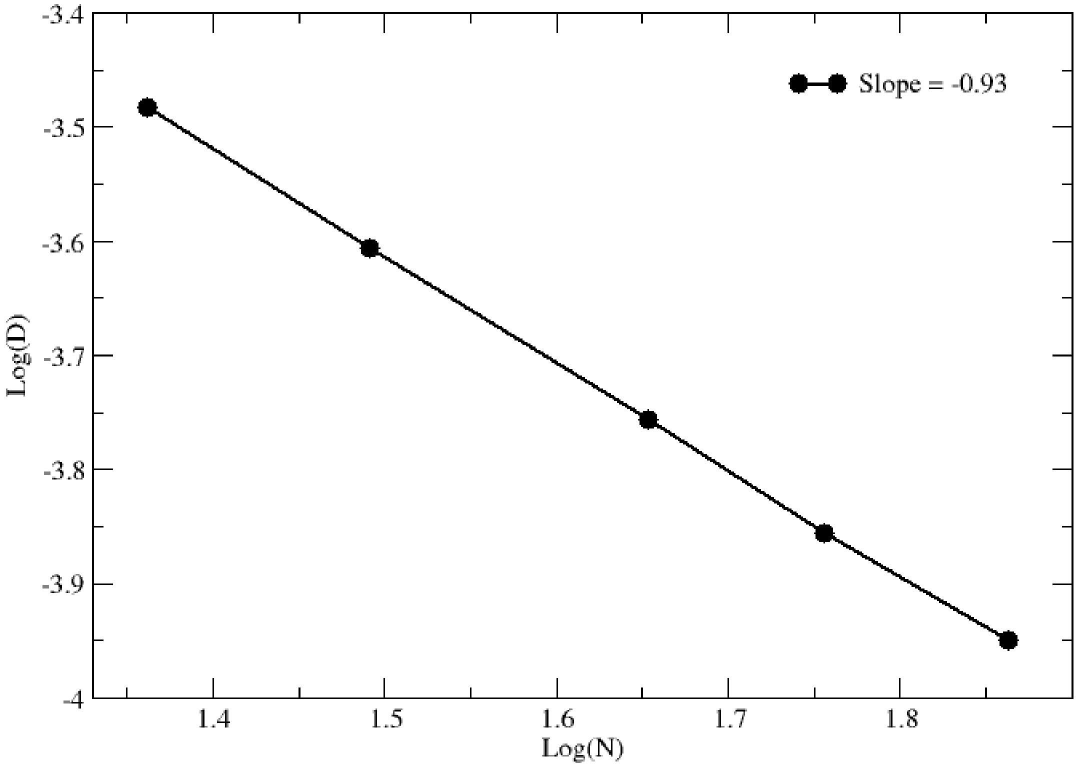

Figure 4.4: Log-log plot of diffusion coefficient D versus polymer chain length N, for N =23, 31, 45,57,73

Translocation of a linear Polymer

The probability distribution of the mean translocation time of a linear chain through a nanopore.

We have studied the translocation of a self-avoiding polymer through nanopore in two dimensions. We attempted to see the dispersion of the escape times of a polymer through a pore. As can be seen,from the table 4.1 the probabilty to translocate either of the sides are almost equal.

Table 4.1: The probability to translocate either of the sides

No	polymer chain length	Iteration	Left	%	right	%	
1	23	1000	521	52.1	479	47.9	
2	31	1000	488	48.8	512	51.2	
3	45	1000	480	48	520	52	
4	57	1000	471	47.1	529	52.9	
5	73	1000	508	50.8	492	49.2	

The most probable translocation time is given by the maximum of P(τ). We computed the probability distribution of the escape time τ for N = 23, 31, 45 and 57 we took randomly through a fixed pore size of length 2 lattice units and width of 6 lattice units. Figure 4.5 we exhibit that the plots of the escape time is a long tailed distribution in agreement with [6] as the probability distribution function decays for large values of escape times.

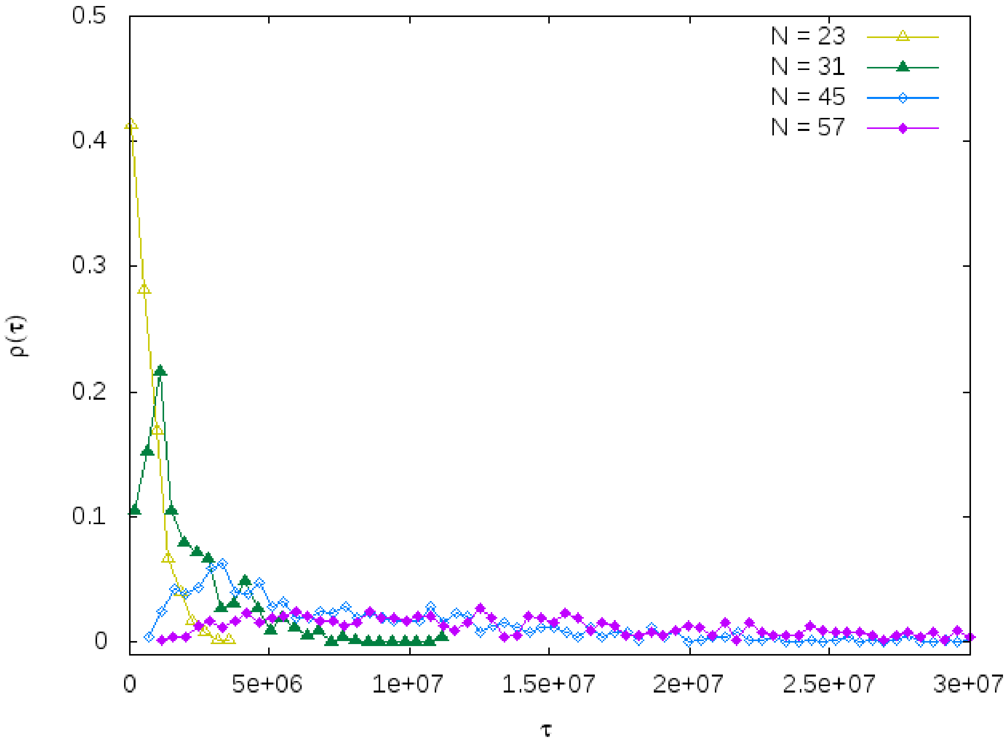

Figure 4.5: Probability distribution P(τ) of escape time τ for a linear polymer chain N, for N =23,31, 45, 57 obtained from 1000 runs each

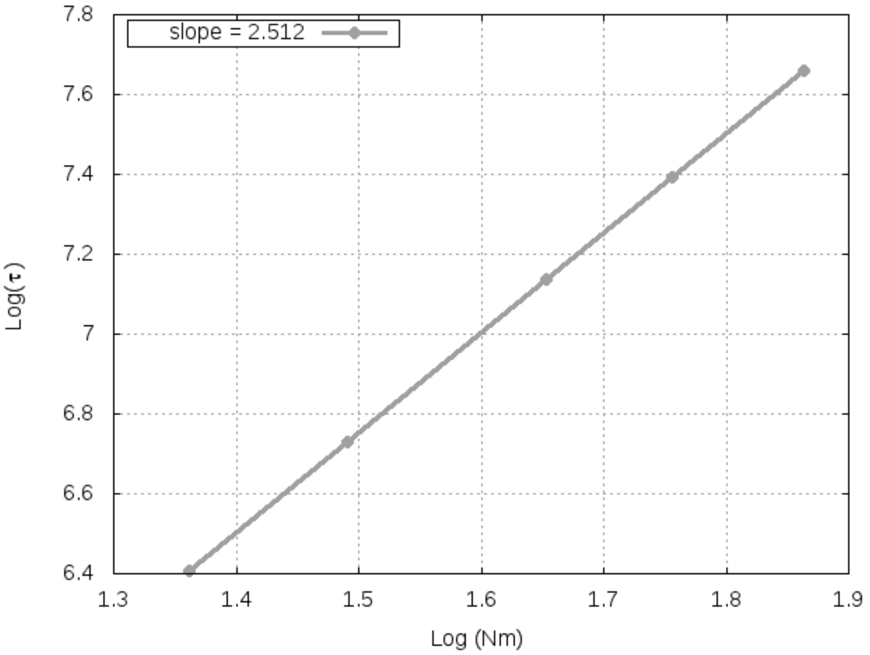

Figure 4.6: Log - Log plot of escape time, τ , as a function of polymer chain length, for N =23,31,45,57,73

The translocation time as function a linear polymer chain length

The scaling relationship between translocation time and polymer chain N is significant concept in polymer science. It estimates the properties of escape time for ranges of N and the vise versa. We take the most likely estimations of the escape time of each linear and plot against the sizes N of the linear in a log-log scales as appeared in Figure 4.6. The slope of log-log plot of escape time τ versus polymer chain N shown in Figure 4.6 that shows $\tau \sim N^{\alpha}$ where $\alpha = 1 + 2\nu$ and from our simulation $\alpha = 2.512 \pm 0.01$ that in agreement with $\tau \sim N^{1+2\nu}$,where $1 + 2\nu = 2.5$ in two dimensional self avoiding walk.

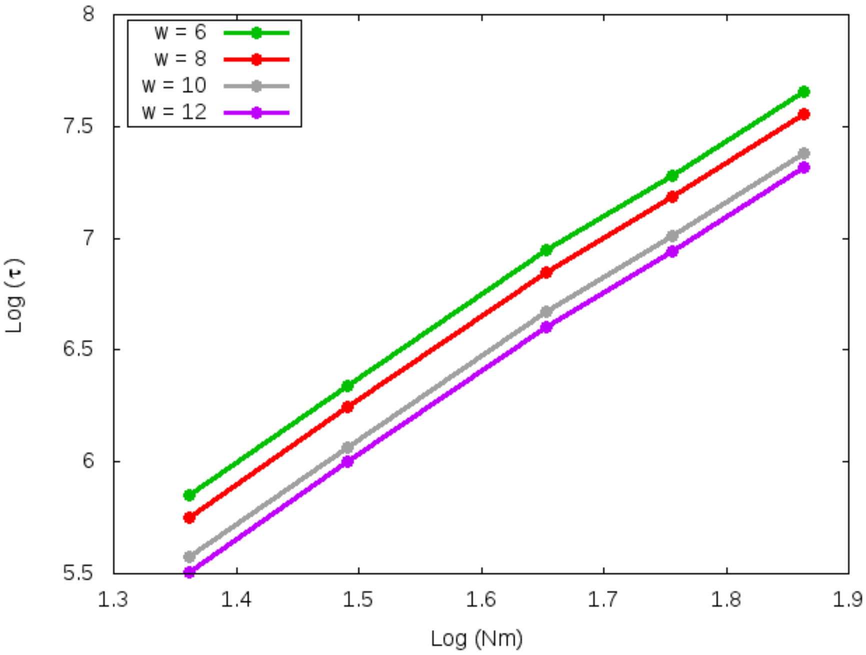

Figure 4.7: Plot of average escape time, τ , versus the chain length for a linear polymer translocation through width w = 6, 8,10,12

The effect of the pore size on the translocation time of linear polymers

In this subsection we examine the average escape time as a function of polymer chain N = 23,31,45,57 and 73 for various pore widths. Figure 4.7 below elaborate the translocation of a polymer chain through pore widths having value, W = 6, 8, 10, 12 . As can be seen,from the plot 4.7 when the width of the pore increase the time required for a similar size of a polymer chain to escape from the pore is less as it can get to numerous places inside the pore. In this manner, we observed an inverse relation between the average escape time and the pore width. Our simulation result shows as the pore's width increase the escape time of linear polymers chain length decrease.

Chapter 5

Conclusion

In our study of polymer translocation, we have employed computational method on a Monte Carlo calculation for both static and dynamical simulation of linear polymers. We executed a fluctuating bond length between adjoining polymer's monomer molecules to realize dynamics for linear polymer architectures. We introduced polymer diffusion and polymer translocation through a nanopore without any outside potential that might enhance translocations.

Our simulation results are in a good agreement with the scaling exponent of the static behavior of a polymer chain. In we found that the average squared end to end distance $\langle R^2 \rangle$ and squared radius of gyration $\langle R_g^2 \rangle$ as a function of polymer length N are obtained. We clearly observed the dependency of mean square end to end distance and mean square radius of gyration on N . We have investigated the mean square end to end distance $\langle R^2 \rangle = 1.49 \pm 0.01$ and mean square radius of gyration $\langle R_g^2 \rangle = 1.521 \pm 0.01$ that made in agreement with Flory prediction of the scaling exponent in two dimension.

We have contemplated the dynamic properties of a polymer chain to determine diffusion constant and the escape time of a linear polymer chain. Polymer diffusion plays a significant function in the translocation process. We explored translocation process was the most plausible get away time and the likelihood distribution of these escape times for polymer chains. We have examined that the probabilty to translocate either of the sides are almost equal . The theoretical mean time translocation investigated by Flory was 2.5. As such our work had shown a good agreement valued 2.512±0.01 in 2D SAW. We conclude that in this our work pore size and escape time τ have inverse relation in unbiased polymer translocation.

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Declaration

This thesis is my original work, has not been presented for a degree in any other University and that all the sources of material used for the thesis have been dully acknowledged.

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Place and time of submission: Jimma University, January, 2021

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

Name: **Solomon Negash (Ph.D.)**

Signature:− − − − − − − − − −