MONTE CARLO SIMULATION OF STATIC AND DYNAMIC PROPERTIES OF RING AND LINEAR POLYMERS IN A CROWDED ENVIRONMENT

By

DEME TESFAYE

A THESIS SUBMITTED TO THE GRADUATE STUDIES OF JIMMA UNIVERSITY IN
PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE IN PHYSICS
(STATISTICAL PHYSICS)

Advisor: Solomon Negash (PhD)

JIMMA, ETHIOPIA
FEBRUARY, 2021

JIMMA UNIVERSITY

DEPARTMENT OF PHYSICS

The undersigned hereby certify that they have read and recommend to the Graduate Studies for acceptance a thesis entitled "**Monte Carlo Simulation of Static and Dynamic Properties of Ring and Linear Polymers in a Crowded Environment**" by **DEME TESFAYE** in partial fulfillment of the requirements for the degree of **Master of Science in Physics(Statistical Physics)**.

Dated: February, 2021

Advisor: _____
Solomon Negash (PhD)

Co-advisor: _____
Solomon Hailemariam (PhD Fellow)

Internal Examiner: _____
Menberu Mengesha (PhD)

External Examiner: _____
Aniley Gesese (PhD)

Chair Person: _____
Menberu Mengesha (PhD)

JIMMA UNIVERSITY

Date: **February, 2021**

Author: **DEME TESFAYE**

Title: **Monte Carlo Simulation of Static and Dynamic Properties of Ring and Linear Polymers in a Crowded Environment**

Department: **Physics**

Degree: **MSc.**   Convocation: **February**   Year: **2021**

Permission is herewith granted to Jimma University to circulate and to have copied for non-commercial purposes, at its discretion, the above title upon the request of individuals or institutions.

_____

Signature of Author

Table of Contents

List of Figures

Abstract

In this paper we investigate Monte Carlo (MC) simulation of static and dynamic properties of linear and ring polymers in the presence of obstacles. To this end we used the bond fluctuation method (BFM) to study the translocation process of a polymer chain of length N in two dimensions. To overcome the entropic barrier, we placed the middle monomers of the two polymers in the middle of the pore which is placed between ordered (cis) and disordered (trans) obstacles. We studied the static properties of the polymers by calculating the average square of radius of gyration of both polymers and mean square end-to-end distance of linear polymer, and we found that the scaling relations of mean square end-to-end distance $\langle R^2 \rangle$ and average square of radius of gyration $\langle R_g^2 \rangle$ as a function of polymer length N are nonuniversal, they strongly depend on the area fraction of crowding agents ϕ. The dynamic properties have also been studied by investigating the translocation of the polymers. Our present work shows that the escape time τ changes with a change of area fraction ϕ. Moreover, the power-law relation of escape time τ as a function of polymer length N, the scaling exponent (α), is nonuniversal. And also, we found that the diffusion of the polymers is subdiffusion in the presence of obstacles. From our simulation study, we also observe that the polymers prefer to translocate towards the disordered obstacles.

Keywords: Linear polymer, ring polymer, Translocation, MC, BFM, Crowded environment

Acknowledgements

First of all, I would like to thank my God, for his follow up and help throughout this work.

Secondly, my heart felt gratitude goes to Dr. Solomon Negash, my advisor, for his valuable suggestions, constant support and constructive comments during this research. His tireless follow up and his consistent support and extreme patience and understanding all my personal problems is never forgettable. I am also grateful to Mr. Solomon Hailemariam (PhD fellow) for his support and encouragement. For me, it was a great pleasure to meet them.

Last but not least, my heart felt gratitude goes to my family, for their constant love and support.

Chapter 1

Introduction

1.1 Background of the Study

Over a long time, the complicated statistics of polymer networks having ring [1,2], star [3,4], and other topologies [5,6] in solution have received a continuous attention due to their practical applications. Although many people probably do not realize it, everyone is familiar with polymers. They are all around us in everyday use, including film packaging, the molded parts of furniture, airplanes, and automobiles, as well as, diverse tools and devices for industry and the medical sciences. The usefulness of polymers is due to the many advantages of polymeric materials have compared to metals, e.g., low weight, corrosion resistance, 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 [7,8]. However, the practical applications of polymers are affected by their physical properties. Mostly, to deal with their physical properties, the particular classes (topologies) of polymers are focused. Ring, the polymers architecture on which we are devoted, form a very interesting class.

A ring polymer is a cyclic polymer network where the two ends are connected. Compared with linear polymers, the physics of polymers, such as static and dynamic properties, in particular translocation process of ring polymers through a nanopore is far more complex due to the change in polymer conformation during translocation.

Static properties of polymers are the properties that are characterized by the polymer chain size and shape. Whereas, the dynamic properties of the polymers are characterized by the parameter like diffusion constant of the molecules (D) as well as the translocation of polymers.

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 [7,9] 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 [10,11], gene therapy, and controlled drug delivery [12].

Although a few work has been done with simulation of this class of polymers focusing mainly on understanding their properties on translocation through nanopore, the deep level theoretical and simulation investigations of static and dynamic properties, in particular the translocation of this class of polymers in crowded environment, are still underway. Many biological environments, both intracellular and extracellular, are densely crowded by large molecules and cells [13,14]. Therefore, it is important to understand how to characterize and quantify transport processes within such crowded systems.

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). So far, in order to determine polymer properties many simulation methods are employed. The two prominent methods used to simulate polymers are Molecular Dynamics (MD) and Monte Carlo (MC) methods. The two approaches are analogous to time and ensemble averaging in statistical mechanics. The core difference between them is, the way of sampling the configuration space available to the system. For MD, new configurations are generated by application of Newtons equations of motion to all atoms simultaneously over a small time step to determine the new atomic positions and velocities. Monte Carlo simulation method involves generating and accepting or rejecting of possible conformations (states) stochastically [15,16].

Motivated by this scientific background, we aimed to investigate Monte Carlo simulation of static and dynamic properties of ring and linear polymers, in a crowded environment.

1.2 Statement of the Problem

In recent years, much attention has been given to different polymeric materials due to their technological applications and daily use. The properties of polymers play a crucial role in their applications. Despite the fact that polymers are important in our daily life and are mostly being used, their static and dynamic properties are remained with great debates. In particular, the physical properties of ring polymers are still not fully addressed. In addition, less attention has been paid to the translocation of polymers in crowded environments. Therefore, this study focused on Monte Carlo

simulation of static and dynamic properties, in particular, on the translocation of ring and linear polymers through nanopore in a disordered medium.

1.3 Research Questions

The following questions have been answered in this study :

• What is the scaling behavior of radius of gyration of both polymers and end-to-end distance of linear polymer, with their respective length N?

• What is the probability distribution of the escape time of both polymers in the presence of obstacles?

• What is the scaling behavior of mean escape time τ with length of ring polymer N, as well as linear polymer?

• What is the effect of crowding on the translocation time of a given polymer?

• How does the pore size affect the translocation time of the polymers?

• What is the effect of the obstacles on the two polymers diffusion?

1.4 Objectives

1.4.1 General Objective

The general objective of this study was to investigate the static and dynamic properties of ring and linear polymers in the presence of obstacles using Monte Carlo simulation.

1.4.2 Specific Objectives

The specific objectives of this study were:

- To describe the scaling behavior of radius of gyration of both polymers, as well as end-to-end distance of linear polymer, with their respective length N.

- To calculate the probability distribution of escape time of both polymers in the presence of obstacles.

- To investigate the scaling behavior of mean escape time τ with length (N) of ring polymer, as well as linear polymer.

- To determine the effect of crowding on the translocation time of a given polymer.

- To examine the effect of the pore size on the translocation time of the polymers.

- To describe the effect of the obstacles on the diffusion of the polymers.

1.5 Significance of the Study

Recently, polymer translocations have got a remarkable technological relevance for various applications. For example, as mentioned above, they play a crucial role in numerous 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 various technological applications, such as rapid DNA sequencing, gene therapy, and controlled drug delivery. Their application depends on their properties. So, the investigated Monte Carlo simulation of their static and dynamic properties in the presence of obstacles, provide basic knowledge and recommendation to researchers, students and other concerned bodies.

Chapter 2

Literature 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. And also, we shall discuss the basic concept of the method used, at the end of the chapter.

2.1   Polymers and Polymerization

Since most materials are polymeric and most of the recent advances in science and technology involve polymers, some have called this the polymer age. The ancient Greeks classified all matters as animal, vegetable, and mineral [17]. 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 or technology.

Polymer physics deals with the description of the structure and resulting properties of polymeric materials. The word **polymer** is derived from the Greek words **poly** and **meros**, meaning *many* and *parts* respectively [19]. Some Scientists prefer to use the word **macromolecule** or **large molecule**, instead of **polymer**. Others name it "giant molecules". So, polymers are characterized within the more general concept
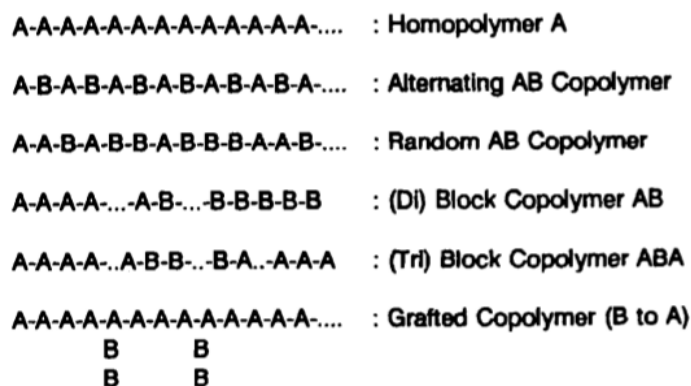
Figure 2.1: Various types of polymer structure [18].

of macromolecules by the presence of a clear repetitive elements. These repetitive elements are called **monomers**. Polymers can be classified based on the numbers of kinds of monomers from which they are built. Figure 2.1 illustrates some important types of polymers.

Although natural polymers do exist (e.g natural rubber), most polymers are synthesized by polymerization of monomers from the Petrochemical industry. **Polymerization** is the process by which elementary units (chemical monomers) are covalently bonded together. The entire structure of a polymer is generated during this process. The number of monomers in polymer is called its **degree of polymerization**, N [20,24]. The **molar mass** M of polymer is equal to its degree of polymerization N times the molar mass M_{mol} of its chemical monomer.

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

Consider for example, the general structure of vinyl monomers and polymers, where **R** represents different possible chemical moieties. If the **R** group in Figure 2.2 is
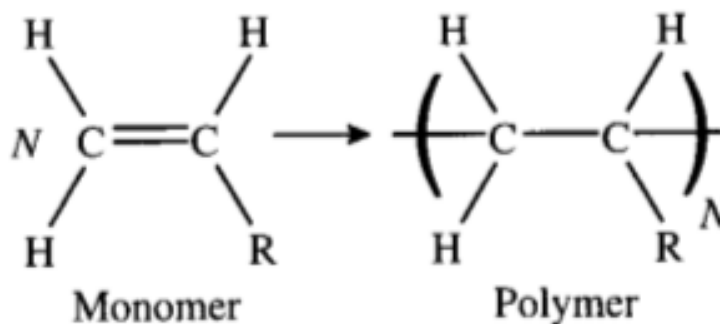
Figure 2.2: Polymerization of vinyl monomers [24].

hydrogen, the polymer is polyethylene. The repeating unit is $-CH_2 - CH_2$ and the polymer is called polyethylene because polymers are traditionally named after the monomers used in their synthesis (in this case ethylene,$-CH_2 - CH_2$ even though polymethylene with repeating unit $-CH_2$ has an identical structure. If the **R** group in Figure 2.2 is chlorine is the polymer is poly(vinyl chloride), with repeating unit $-CH_2 - CHCl$. If the **R** group in Figure 2.2 is a benzene ring, the polymer is Polystyrene. Another important feature controlling the properties of polymeric sys-
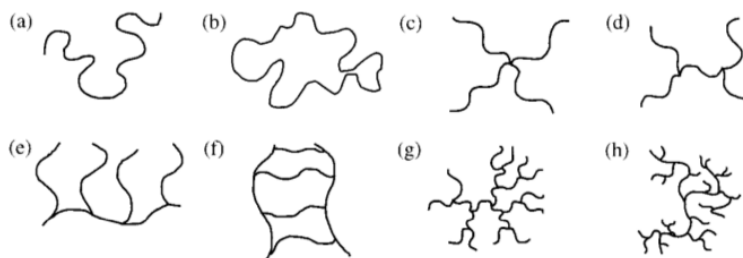
Figure 2.3: Examples of polymer architectures (a) linear, (b) ring, (c) star, (d) H, (e) comb, (f) ladder, (g) dendrimer, (h) randomly branched [24].

tems is polymer architecture. Types of polymer architecture include **linear**, **ring**, **star-branched**, **H-branched**, **comb**, **ladder**,**dendrimer**, or **randomly branched**

as sketched in Figure 2.3 .

Ring polymers are unique by the presence of translational symmetry and having no ends. In bio sciences there exist ciyclic DNA, cyclic peptides and polysacharides. Having no ends, affect their physical properties, like shape, size, flow properties, crystallization, viscosity and some other behaviors of polymers [19]. The size and the shape of polymers are intimately connected to their properties [19,24]. We discus the detail in the next sections.

2.2 Static Properties of Polymers

In this section, we discuss the static properties of polymers. Static properties of polymers are the properties that are characterized by the polymer chain size and shape [17,24]. Therefore, we focus on the parameters End-to-end distance ($\mathbf{R}$) and Radius of gyration ($\mathbf{R}_g$) to study the properties.

2.2.1 Ideal Chain

The most important shortcoming of the concept of an ideal chain is the neglect of long range interaction. Let us start with a very simple model, 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 analogous 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 crucial 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. Look at Figure 2.4.
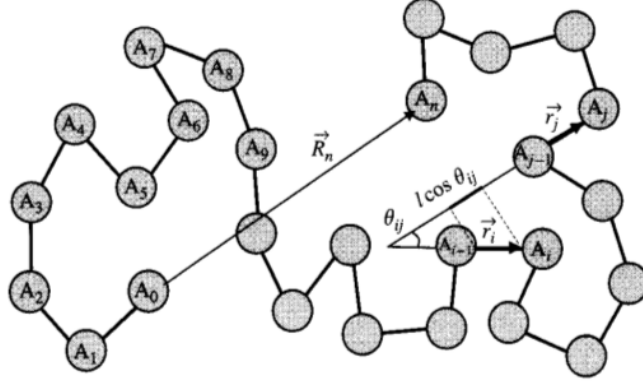
Figure 2.4: Schematic description of the FJC [24].

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

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

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

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

$$\langle R^2 \rangle = \langle \overrightarrow{R}^2 \rangle = \langle \left(\sum_{i=1}^{N} \overrightarrow{r}_i \right) \left(\sum_{j=1}^{N} \overrightarrow{r}_j \right) \rangle \qquad (2.2.3)$$

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

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

Thus equation 2.2.3 becomes:

$$\langle \overrightarrow{R}^2 \rangle = Nl^2 \qquad (2.2.5)$$

As it is mentioned above, the model is analogous to the random walk, i.e. every polymer segment is independent from all others. The end-to-end distance is a well-defined observable 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 of **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 $\overrightarrow{R}_{cm}$) [19], as shown in Figure 2.5.
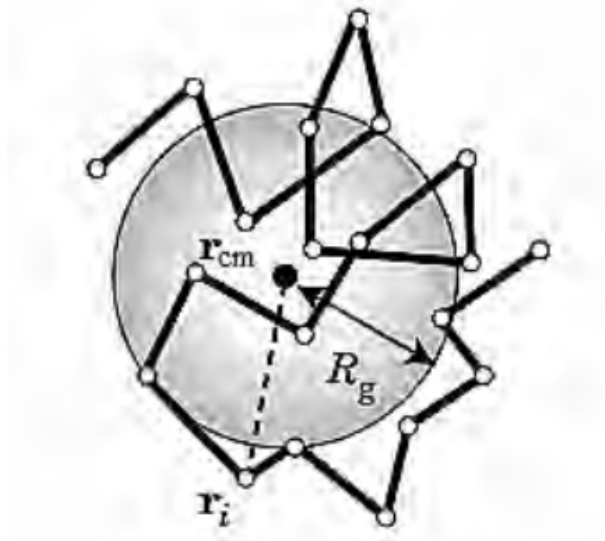
Figure 2.5: Center of mass and the radius of gyration in the bead-stick model [19].

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

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 ith bond is then the displacement vector Δr_i of the ith step. The expression of mean square end-to-end distance for a random walk applies to the mean square distance between the ith and j^{th} monomers on the chain just by replacing N with $|i - j|$. When $|i - j|$ is large, $r_i - r_j$ of an ideal chain has a Gaussian distribution with variance $|i - j| l^2$. Which means that

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

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

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

Comparing this result with equation 2.2.5, we obtain:

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

We can also find a R_g of ring polymer consisting of N segments of length l, assuming Gaussian statistics for any part of the chain and two segments at r and r' separated

by n segments on one side and $N - n$ segments on the other side as [19]:

$$\langle R_{g,ring}^2 \rangle = \frac{1}{2}\langle r - r^{'} \rangle = \frac{1}{12}Nl^2 \tag{2.2.12}$$

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 that are not considered on their ideal models. These constraints affect the static and dynamic properties a polymer chain. In essence, the interactions between monomers of a chain 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 subsequent segment only. Such configurations are known as Self Avoiding Walk (SAW). SAW is a random walk in which points are not revisited. Real polymer chains of excluded volume was analyzed by Flory.

The Flory Calculation of the Flory Exponent (ν)

For N monomers, Flory [26] 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 [27]:

$$F_{rep}\left(N, R\right) = k_B T v_{ex} \frac{N^2}{R^d} \tag{2.2.13}$$

Where k_B is the Boltzmann constant, v_{ex} is the excluded volume, T is the temperature and d is the dimension. And the other contribution to the free energy is an

entropic cost, $F_{entropic}(N, R)$. The entropy loss due to the chain extension [8] can be determined by the probability distribution which is given by:

$$P\left(N, \overrightarrow{R}\right) = \left(\frac{2\pi N l^2}{d}\right)^{\frac{-d}{2}} exp\left(\frac{-d\overrightarrow{R}^2}{2Nl^2}\right) \tag{2.2.14}$$

$$\begin{aligned} S &= k_B ln\left(\left(\frac{2\pi N l^2}{d}\right)^{\frac{-d}{2}} exp\left(\frac{-d\overrightarrow{R}^2}{2Nl^2}\right)\right) \tag{2.2.15}\\ &= k_B \left(\frac{2\pi N l^2}{d}\right)^{\frac{-d}{2}} - \frac{dk_B \overrightarrow{R}^2}{2Nl^2} \tag{2.2.16} \end{aligned}$$

S is the conformational entropy. Hence, the $F_{entropic}(N, R)$ becomes:

$$F_{entropic}(N, R) = -TS\left(N, \overrightarrow{R}\right) = -k_B Tln P\left(N, \overrightarrow{R}\right) \approx \frac{dk_B T\overrightarrow{R^2}}{2l^2 N} \tag{2.2.17}$$

Here, the total free energy of the polymer is the sum of the two energies[18]:

$$F(N, R) = F_{rep}(N, R) + F_{entropic}(N, R) \approx k_B T\left(v_{ex}\frac{N^2}{R^d} + \frac{dR^2}{2l^2 N}\right) \tag{2.2.18}$$

By minimizing equation 2.2.18 with respect to $R(i.e, \frac{\partial F(N,R)}{\partial R} = 0)$, we get the following relation:

$$R \backsim N^{\nu} \tag{2.2.19}$$

where, $\nu = \frac{3}{d+2}$ and d is dimension. These show us, for 2D, $\nu = \frac{3}{4}$ and for 3D, $\nu = \frac{3}{5}$.

2.3   Dynamic Properties of Polymer Chains

In this section we discuss the dynamic properties of polymers. In discussing these properties, we focuss on two important parameters, escape time τ and diffusion constant D. And we review translocation of polymers, as it is an other manifestation of dynamic properties. Dynamics of 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 [19]. 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 2.6. The bead will also experience a random or stochastic force $\mathbf{F(t)}$ [34]. Hence, equation of motion is:

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

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

Where the friction constant ξ is given by:

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

η_s is the viscosity of the solvent, $\mathbf{V}$ is the velocity of the motion, $\mathbf{F}$ is the random force and $\mathbf{R}$ is the position of the bead. Furthermore, solving equation 2.3.2 yields:

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

We have to make some assumptions about the stochastic force. In view of its chaotic
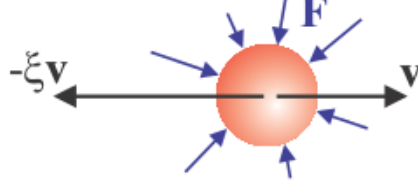
Figure 2.6: A spherical bead moving with velocity $\mathbf{v}$ will experience a friction force of $-\xi\,\mathbf{v}$ opposite to its velocity and random forces $\mathbf{F}$ [34].

character, the following assumptions seem to be appropriate for its average properties:

$$\langle \mathbf{F}(t) \rangle = 0 \tag{2.3.5}$$

$$\langle \mathbf{F}(t).\mathbf{F}(t^{'}) \rangle = C_{v_o}\delta(t - t^{'}) \tag{2.3.6}$$

where C_{v_o} (constant) depend on the initial velocity. Using the equations one can find:

$$\langle \mathbf{v}(t) \rangle_{v_o} = \mathbf{v}_o e^{-\xi t} \tag{2.3.7}$$

$$\langle \mathbf{v}(t).\mathbf{v}(t) \rangle = \mathbf{v}_o^2 e^{-2\xi t} + \frac{C_{v_o}}{2\xi}\left(1 - e^{-2\xi t}\right) \tag{2.3.8}$$

The bead is in thermal equilibrium with the solvent. According to the equipartition theorem, for large t, equation 2.3.8 should be equal to $\frac{3k_B T}{m}$ from which it follows that:

$$\langle \mathbf{F}(t).\mathbf{F}(t^{'}) \rangle = \frac{6k_B T\xi}{m}\delta\left(t - t^{'}\right) \tag{2.3.9}$$

Integrating equation 2.3.4 yields:

$$\mathbf{R}(t) = \mathbf{R}(0) + \frac{v_o}{\xi}\left(1 - e^{-2\xi t}\right) + \int_0^t d\tau \int_0^\tau d\tau^{'} e^{-\xi(2t-\tau^{'})}\mathbf{F}(\tau^{'}) \tag{2.3.10}$$

Hence, the mean square dispalcement is:

$$\langle (\mathbf{R}(t) - \mathbf{R}(0))^2 \rangle_{v_o} = \frac{v_o^2}{\xi^2}\left(1 - e^{-2\xi t}\right)^2 + \frac{3k_B T}{m\xi^2}\left(2\xi t - 3 + 4e^{-2\xi t} - e^{-2\xi t}\right) \tag{2.3.11}$$

For $t \gg 1$ this will be come:

$$\langle(\mathbf{R}(t) - \mathbf{R}(0))^2\rangle = \frac{6k_BT}{m\xi} = \frac{6k_BT}{\zeta} \qquad (2.3.12)$$

Following this, the Rouse model reveals that the mean square displacement $\mathbf{R}^2(t)$ of the molecule's centre of mass(CM) of d-dimension is:

$$\langle\mathbf{R}(t)^2\rangle = 2d\frac{k_BT}{N\zeta}t \qquad (2.3.13)$$

$$\langle\mathbf{R}(t)^2\rangle = 2dDt \qquad (2.3.14)$$

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

$$D = \frac{k_BT}{N\zeta} \qquad (2.3.15)$$

Here after, from equation 2.3.15, it is easy to understand that the Rouse diffusion constant and the number of monomers have inversily relationship:

$$D \sim N^{-1} \qquad (2.3.16)$$

The two important parameters exhibit a distinct scaling dependence on the number of monomers N are:

$$D \sim N^{-1} \qquad (2.3.17)$$

And

$$\tau \sim \frac{R_g^2}{D} \qquad (2.3.18)$$

2.3.2 Polymer Translocation

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 [7,9]. This ubiquitous

phenomenon deals with how electrically charged polymer molecules, such as polynucleotides and proteins, move from one region of space to another in crowded 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 [28], theoretically [30,34], and numerically [6,29].

From statistical physics perspective 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 $al.$ [28] reported that an electric field can drive single stranded DNA and RNA molecules through the -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 order to overcome the entropy near the nano pore and increase the possibility of the translocation.

In the case of unforced polymer translocation, Park and Sung [30] and Muthukumar [33] 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 analysis of diffusion through this entropic barrier yields a scaling prediction of the translocation time $\tau_{tran} \smile N^2$. However, as Chuang et $al.$ [25] noted, this quadratic scaling behavior is at best only marginal for phantom 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* [25]. 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} . 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 addition to this, the studies on polymers [45,46] reported the scaling behaviors of the ring polymers are remarkably similar to long linear polymer chains.

Although a lot of progress has been made in polymers translocation problems, less attention has been paid to the translocation in crowded environments. Our present work dealt with the unbiased translocation of ring and linear polymers through a nanopore in a crowded environment. Without an applied external field, polymer translocation in crowded environments is driven by the concentration difference of crowding agents, as considered in Refs.[37] and [38]. And, when the density of the obstacles at both sides are the same, the translocation is driven by the free energy difference as considered in Ref. [42]. In our case, the same density and sizes of crowding agents are considered, the translocation is due to thermal fluctuation. We shall discuss the detail concept of the method and the model used in the next section.

2.4   Monte Carlo simulation

Monte Carlo method is one of computational methods used to solve scientific problems. It is a way of solving a deterministic problem by a stochastic approach using random numbers.

Monte Carlo methods are nowadays widely used, from the integration of multi-dimensional integrals to solving unfeasible problems in physics, chemistry, medicine, biology, or other sciences. One of the major advantages of MC methods is their systematic improvement with the number of samples N , because the error Δ decreases as follows [16] :

$$\Delta \propto \frac{1}{\sqrt{N}} \tag{2.4.1}$$

MC method is also very popular in statistical physics (MC molecular modeling), when an exact solution to a given problem cannot be found with a deterministic algorithm, and in the context of higher-dimensional integration. In MC method the subsequent configurations of the polymer is generated stochastically (randomly). MC simulation can be used on a lattice or in the continuum. In our study, we used the lattice model to study the properties of self avoiding linear and ring polymers in crowded environment.

About 50 years ago Orr and Montroll [36] proposed the self-avoiding walk (SAW) as a model for a linear polymer in a good solvent, and is still very popular. The SAW is defined on a discrete lattice, often on a square or simple cubic lattice. 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

hard-core monomer-monomer interaction. 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.

Bond-fluctuation method (BFM) was proposed [22] 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 [22,31].

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 [22,23]. 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.

To study the properties of the two polymers, we used the model and the method in the Monte Carlo simulation. To overcome the entropic barrier, we put the middle monomers (the core) tethered mid-way in the pore. We shall discuss the implementation of BFM and the simulation procedure in the next chapter.

Chapter 3

Methodology

3.1 Method

Nowadays, computer simulations are an integral part of contemporary basic and applied scientific research. In engineering and physics, computational, theoretical and experimental explorations are equally important to our daily research and studies of physical systems. Computer simulations not only link analytic, theory and experiment in order to test theories, but can also be used as an exploratory tool in computer experiments under conditions which would be unfeasible, too expensive, or too dangerous for real experiments in the laboratory.

Among the two well known simulation methods, Monte Carlo method (MC) and Molecular dynamics (MD), we have selected to use MC method. 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. Instead, a coarse-grained simulation model on lattice is preferred. Accordingly, our model eliminates microscopic degrees of freedom and represents the polymers by

a simplified structure which retain only the most basic features of the polymers (for example, chain connectivity or bonds and the short-range excluded-volume interactions). Therefore such model is suited to explore general and universal properties of the polymers chains.

We need a way of generating and evaluating for accepting or rejecting the conformations forwarded along each steps (moves). In our simulations, this task is done according to the Bond Fluctuation Method (BFM). The implementation of the method in the lattice model is presented as follows.

3.1.1 Lattice Model with Bond Fluctuation Method

The lattice model simulation of polymers can be done on different lattice geometries. For example our simulation considers square lattice geometry.

BFM has been widely used in recent years to investigate the structure and dynamics of a great variety of polymer systems. The polymers chain will be modeled as a chain of beads or monomers places on a lattice where there is a link (bond) between the end monomers too. To satisfy the SAW condition, each lattice site can only be part of a single monomer. Each monomer on the model occupies 4 vertex 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 $2 \leq b_l \leq \sqrt{13}$, where b_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
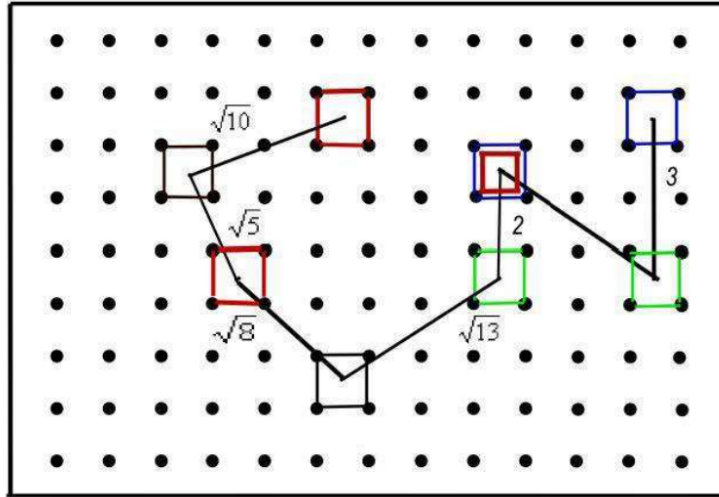
Figure 3.1: The bond length between consecutive monomers in the range $2 \leq b_l \leq \sqrt{13}$ for 2D - BFM.

upper limits $\sqrt{13}$, 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 branched polymers and unknotted ring 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 satisfies both the bond length constraints and the excluded volume interaction, the move is accepted. As it can be seen, Figure 3.1 depicted all the possible positions of a monomer, as the bond length is in the range of $2 \leq b_l \leq \sqrt{13}$ lattice units

The implementation of BFM is as follows :

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.

Step 3: Move the selected monomer in the selected direction by one lattice spacing. Call 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.

3.1.2   Simulation Procedure

Since we use a lattice for our simulation purpose, the first thing that we do is preparing the lattice itself. Thus we prepared 2D square simulation box of 400x400 square lattice cells of unit length each, which was wide enough for the simulation of the polymers considered in our work. For the translocation of both polymers through the pore, we need to add a pore between ordered and disordered obstacles with the same density on either sides of the pore. The immobile and fixed size obstacles are first placed on the square lattice with the same area fraction of crowding agents (ϕ) on both the cis and trans sides. On the trans side we placed the disordered obstacles. Whereas, on the cis side we put ordered obstacles. One of our aims is to see the effect on the translocation, when the size of the pore varies. Therefore, to start with, we prepared nanopore of width $W = 6$ lattice unit. The pore is small enough to allow only one monomer or two monomers at minimum separation to pass through it. Then by

putting the center of mass (CM) of polymer at the center of the pore, we try to see how the chain diffuses through time by the bond fluctuation Monte Carlo method explained above. We see how the CM 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 two reasons that excluded volume effects are more apparent and computation times are shorter than three dimensional case.

Our simulation then proceeds as follows. To get the initial configuration of the polymers, we insert linear and nonconcatenated ring polymers symetrically at the center in the simulation box, as shown on the Figure 3.2. We define this configuration
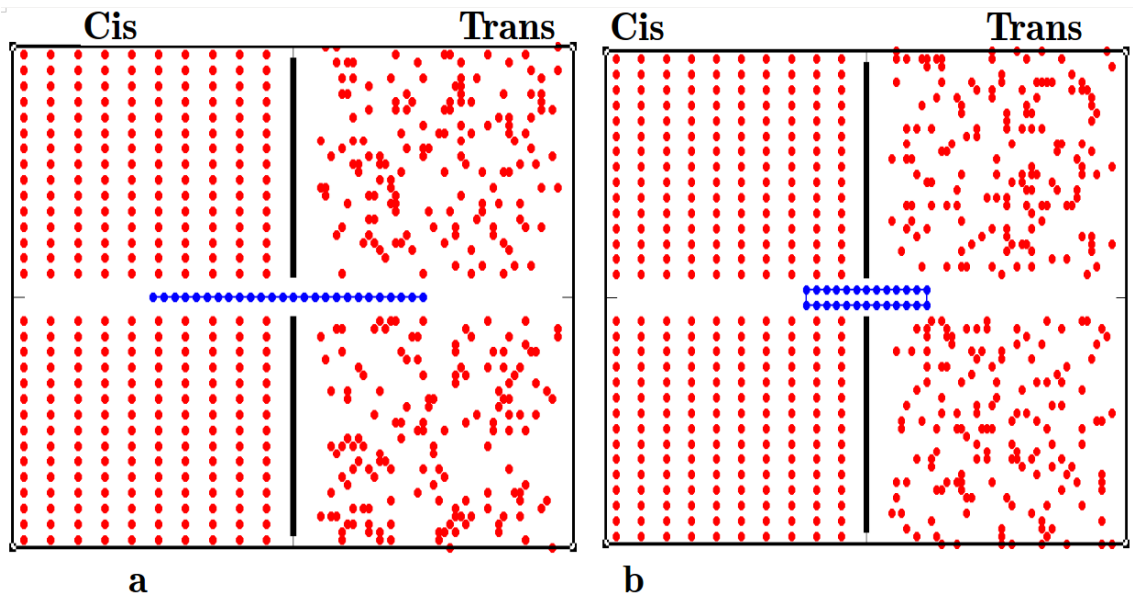

Figure 3.2: Schematic representation of initial conformation of linear (a) and ring (b) polymers of N= 26 each, placed symmetrically in the middle of the pore, in a crowded environment.

assuring any monomer of the ring polymer is connected to two neighbor monomers
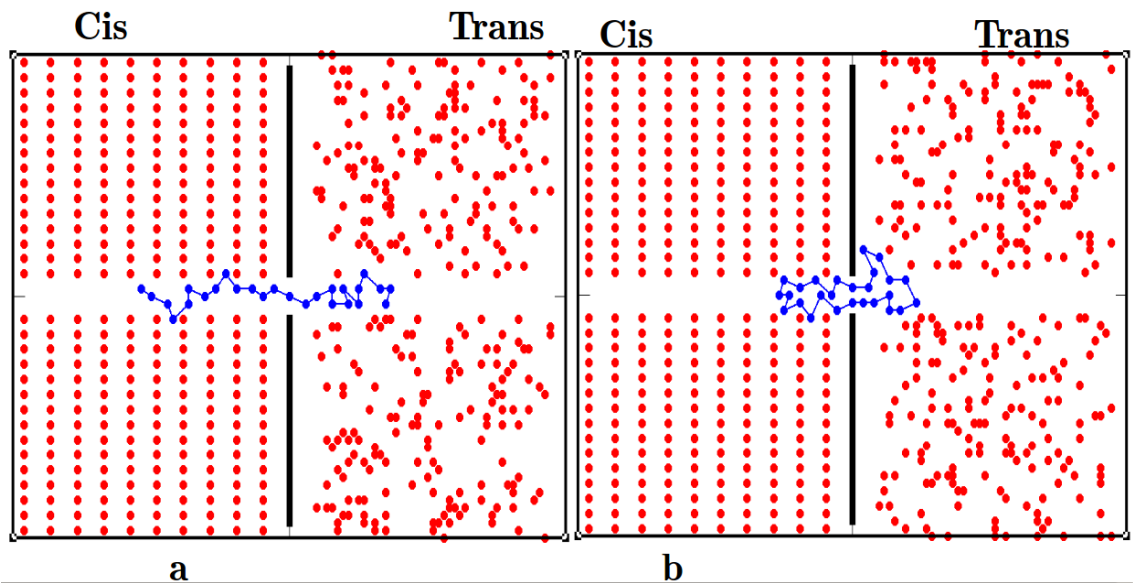
Figure 3.3: Schematic representation of conformation of linear (a) and ring (b) polymers of 26 monomers each, after relaxed for Monte Carlo moves of Nx10^6 in the pore, in a crowded environment.

and there are no ends. And the excluded volume property is introduced by requiring that each lattice site belongs to one square at most. The lengths of the bonds between neighbor monomers are set as BFM on 2D allowed. Starting from the initial polymer configuration many moves are made until the polymer is equilibrated. To generate such an equilibrated configuration, the chain is allowed to relax by attempting local moves. We select monomer randomly and place the middle monomer $((1 + \frac{N}{2})^{th})$ for the linear and the middle monomers (1st and $(1 + \frac{N}{2})^{th}$) for ring in the hole symmetrically to overcome the entropic barrier, 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 uncrossability constraints. In our simulations this relaxation of the ring and linear polymers are executed for longer times than the relaxation time or equilibration time $\tau \sim N^{2.50}$ in two dimension simulations of polymers. To obtain fully

equilibrated conformation 1 x 10^6 Monte Carlo time steps per monomer (MCS) are allotted. After equilibration is finished (Figure 3.3), at $t = 0$, the middle monomers are allowed to move just freely. Thus the simulation ends at a time $t = t' > 0$ when the entire polymer is on either side of the membrane (Figure 3.4). We call
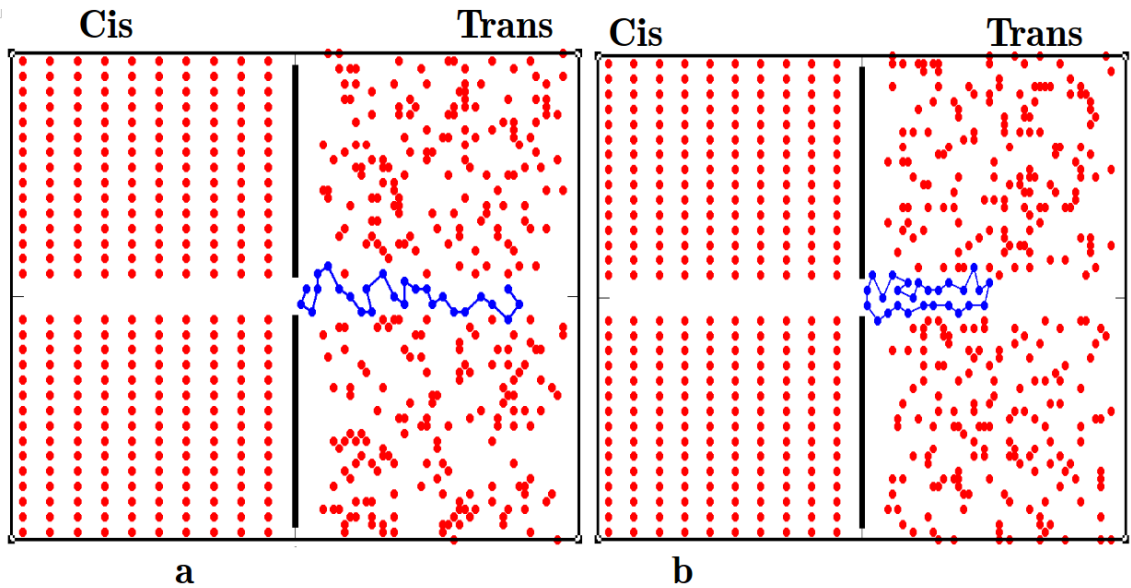
Figure 3.4: Schematic representation of final conformation of linear (a) and ring (b) polymers of 26 monomers each, after escaped from the pore with W =6 lattice unit, in a crowded environment.

this t the escape time (τ). This procedure is repeated for a large number of times for each polymer length N , and take the escape time τ which happened most. We also recorded all these escape time values of all the large number independent times to obtain the probability distribution of the escape time. We used this procedure to investigate the properties of the two types of polymers and compared the results. The results are discussed in the next chapter.

Chapter 4

Results and Discussion

4.1 Static Properties of Linear and Ring Polymers in a Crowded Environment

4.1.1 End-to-end Distance of Linear Polymer

The end-to-end distance is the average length that can be thought as an indicator of the extent of spreading out or size of the polymer chain. This important static property indicator parameter is dependent on the number of monomers of polymer chains. Ideal polymer models have shown that the power-law scaling relation between these two quantities as $\langle R^2 \rangle \sim N^{\frac{1}{2}}$. But ideal polymers are assumed to have no excluded volume effect between monomers which are not close enough on a polymer chain. Flory, however, showed that the exponent at the scaling relation, should be corrected to a dimension dependent value of $\nu = \frac{3}{2+d}$ using simple and effective approximation on Rouse model of a SAW polymer chain. So, according this theory $\nu = 0.75$ for 2D and $\nu = 0.6$ for 3D. The plots of the mean square end-to-end distance of linear polymer, $\langle R^2 \rangle$ against degree of polymerization N , as represented on Figure 4.1 show the interdependence. However, the plots show the power-law relation

varies with area fraction of the crowding agents (ϕ). In our system we only consider relatively short chain length polymers, due to large amount of computational time needed to simulate long polymers. We saw this, for different values of area fractions of the obstacles, which are $\phi \leq 0.3$ and given by:
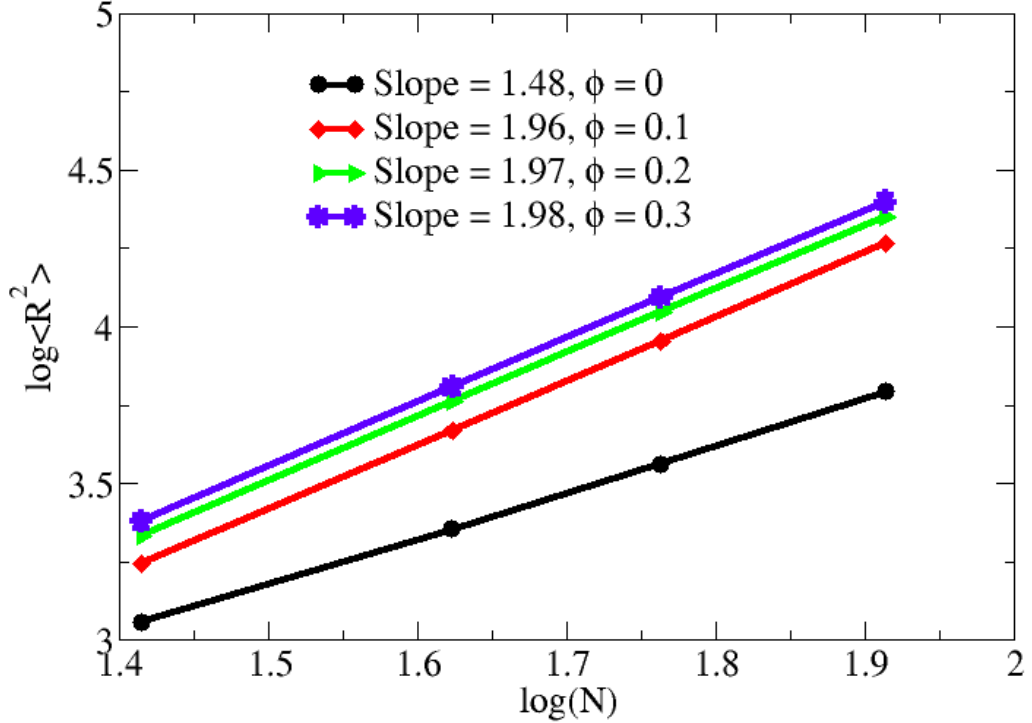
Figure 4.1: The log-log plot of mean square end-to-end distance ($\langle R^2 \rangle$) as a function of linear polymer of length N = 26, 42, 58 and 82, in a crowded environment of area fraction ($\phi = 0.1$, 0.2, and 0.3).

$$\phi = \frac{4N_{crowding}}{A} \tag{4.1.1}$$

where $N_{crowding}$ is number of crowding agents and A is the total lattice points covered by the obstacles and the factor 4 is due to the fact that each obstacles occupies 4 lattice points. The plot indicates that in the absence of obstacles (free environment), the slope is 1.48±0.01, so the value of the slope is very close to 2ν which is in

agreement with the Flory's scaling exponent of end-to-end distance with degree of polymerization, N. If there are no crowding agents at both sides of the membrane, for unbiased translocation of linear polymer of relatively short chains, the scaling relation of mean square end-to-end distance as a function of N is $\langle R^2 \rangle \sim N^{2\nu}$. However, as shown on figure 4.1, in the presence of obstacles, the scaling exponent changes with the concentration of the obstacles. And we observed that the end-to-end distance of the polymer increases, as ϕ increases. As the concentration of the obstacles increases, the bead obstacles close to the monomers, this causes the polymers to stretch [39].

4.1.2 Radius of Gyration of Linear and Ring polymers

The radius of gyration is more convenient quantity that describes both polymers. Like end-to-end distance, it depends on the size of polymers and ideal polymer models have shown that the power-law scaling relation between mean square radius of gyration of the two polymers with their respective chain length as $\langle R_g^2 \rangle \sim N^{\frac{1}{2}}$. In contrast to ideal chains, Flory's theory suggested, $\langle R_g^2 \rangle \sim N^{2\nu}$, where $\nu = 0.75$ for 2D and $\nu = 0.6$ for 3D using his effective approximation on Rouse model of a SAW polymer chain. The plots of mean square radius of gyration versus N, represented in Figure 4.2 show the interdependence of the parameters. It is obvious that the ring polymer obeys the same rule as linear polymer [45,46]. In the absence of obstacles, the slope = 1.49±0.01 for linear polymer and the slope = 1.48±0.01 for ring polymer, which are in agreement with the Flory's scaling exponent ($\langle R_g^2 \rangle \sim N^{2\nu}$). These results show us, the scaling relation of mean square radius of gyration of both polymers as a function of their respective chain length is $\langle R_g^2 \rangle \sim N^{1.5}$. However, one of the features observed in previous studies of polymer conformations in crowded systems
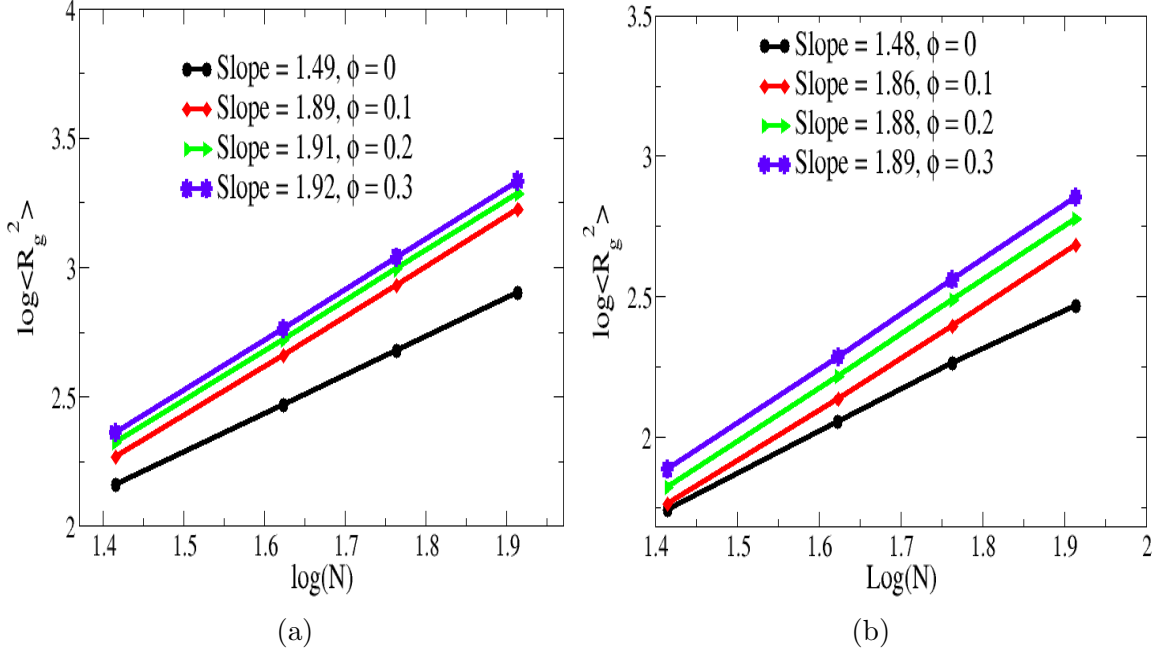
Figure 4.2: The log-log plot of mean square radius of gyration ($\langle R_g^2 \rangle$) as a function of N for linear (a) and ring (b) polymers of length N = 26, 42, 58 and 82, in a crowded environment of area fraction ($\phi = 0.1$, 0.2, and 0.3.)

is the nonmonotonic variation in the polymer size with the obstacle volume fraction [40,44,45]. In the presence of obstacles, Carlos E. and Raymond K. [40] found that for higher ϕ ($\phi > 0.1$), the mean radius of gyration increases and the universal scaling relation of the mean square radius of gyration with chain length ($\langle R_g^2 \rangle \sim N^{2\nu}$) is broken, due to the conformations of the polymers is distorted by the obstacles. Consistent with this, from our simulation results which are represented on Figure 4.2, as ϕ increases, the radius of gyration of the two polymers increases. Therefore, the scaling relation depends on the density of the obstacles. As it can be seen from the figure, the scaling exponents for the two polymers under the same condition, close to one an other. For $\phi = 0.1$, as shown in the graph, the slope for linear polymer is 1.89±0.01 and 1.86±0.01 for ring. And also, for $\phi = 0.2$, the slope for linear polymer is

1.91±0.01 and 1.88±0.01 for ring. Furthermore, from the results, the scaling relation of $\langle R_g^2 \rangle$ of both polymers as a function of their chain size N under the same condition, we found that they obey the same power relation, even in the presence of obstacles.

4.2 Dynamic Properties of Linear and Ring Polymers in a Crowded Environment

4.2.1 Translocation of Linear and Ring Polymers with Effect of Obstacles

In the presence of obstacles, A. Gopinathan and Y. W. Kim [37] and C. Wang *et al.* [38] studied the translocation of polymers without applying external field, which is driven by concentration difference of the obstacles. This means they studied, the translocation of polymers from crowded cis ($\phi_c > 0$) to sparse or uncrowded trans (ϕ_t =0), without applying potential ($\Delta\mu = 0$). However, the unforced translocation of polymer from sparse or uncrowded cis ($\phi_c = 0$) to crowded trans ($\phi_t > 0$) is difficult. And, very recently, Qu-Cheng Gao *et al.* [42] studied the translocation of linear and ring polymers in crowded environment of the same density of obstacles at both cis and trans sides, without applying electric potential, wich is driven by the free energy difference.

   As we mentioned, in our simulation set up, we considered a crowded environment of the same concentrations ($\phi_c = \phi_t$) and sizes of obstacles at both sides of the membrane, and we studied the unforced translocation of linear and ring polymers in the crowded environment, which is solely due to thermal fluctuation. In all simulations, we considered pure excluded volume obstacles and polymers (no polymer-obstacle interaction). The results are discussed as follows.

Probability Distribution of Escape Time for Linear and Ring Polymers Translocation

As important information about the translocation process can be obtained from the probability distribution of escape times, we have calculated the probability distribution $(P_N(\tau))$ of escape time τ for the two polymers translocating through the pore in the presence of obstacles. Figure 4.3 (a) and Figure 4.3 (b) show the probability distribution of escape time of linear and ring polymers translocation in a crowded environment for $\phi = 0.1$ respectively, for length of N = 26, 42, 58, and 82. As we can
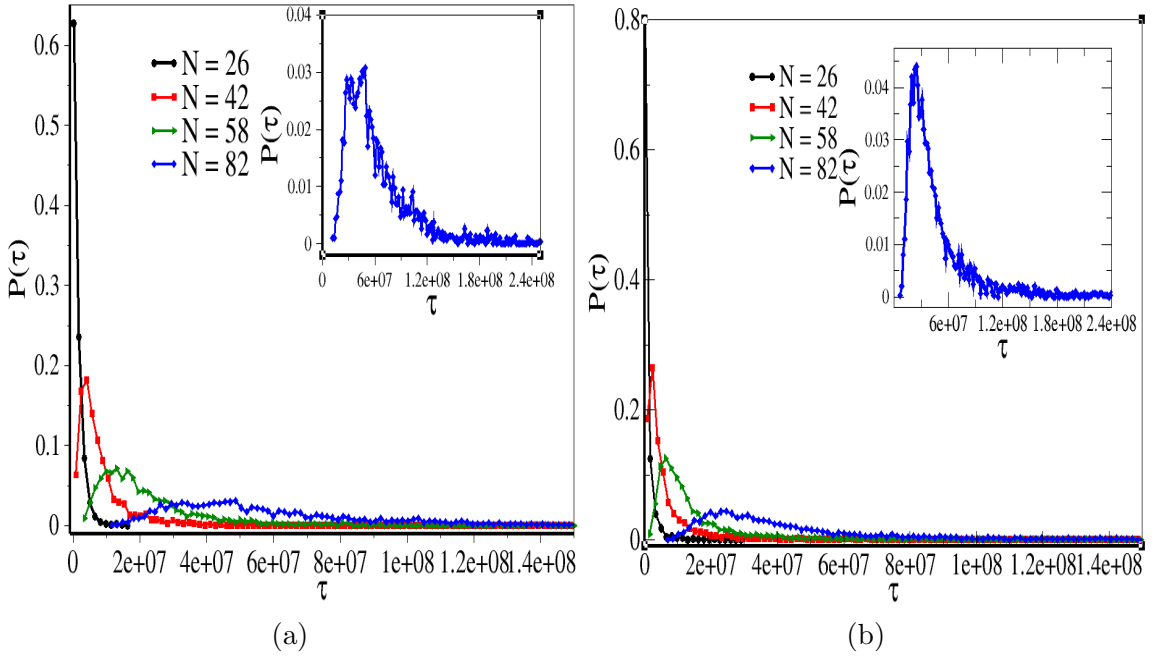

Figure 4.3: The probability distribution $(P_N(\tau))$ of escape time τ for linear (a) and ring (b)polymers translocation of length N = 26, 42, 58 and 82, in a crowded environment of area fraction $\phi = 0.1$, obtained from 3000 runs each.

see from the plots, Figure 4.3, our simulations reveal that the relatively small polymers of both polymers escape in shorter time than those of long polymers considered in our work. Moreover, we found that the ring polymer is faster to translocate than the same chain size (N) of linear polymer under the same condition. Most of the monomers of ring polymers located near the pore, as they are two linear polymers

connected end to end. This means, the size of ring polymers ($\langle R_g^2 \rangle$) is less than that of linear polymers of the same chain size, so that less entropic barrier affects the translocation of ring polymer [8]. This make them faster to transloacte. And also, as shown on the figure, our simulation results show that the histogram of the escape time is a long tailed distribution, as the probability distribution function decays for large values of escape times.
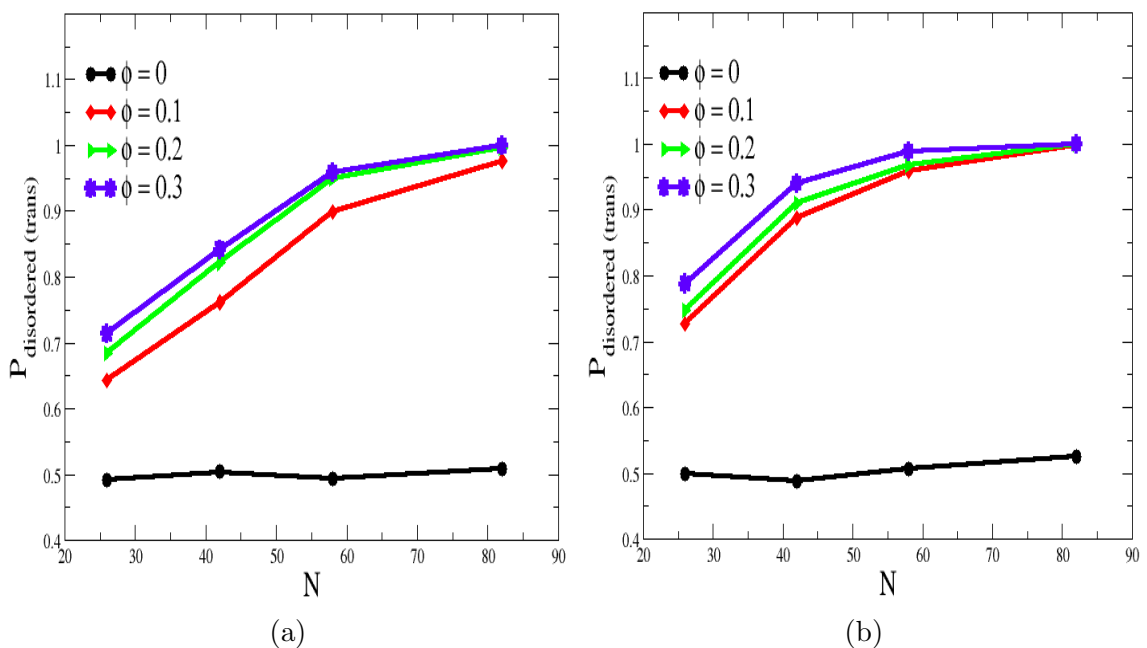

Figure 4.4: The plot of the probability to translocate towards disordered obstacles as a function of N of the linear (a) and ring (b) polymers, for different area fraction of crowding agents.

As there is no external force that pushes the polymers to either of the sides, the polymers escape to the side they prefer. From our simulations, we found that the two polymers prefer to translocate to the disordered side (trans). As the density of the crowding agent increases, the probability to translocate to trans increases. As it can be seen, from our simulation set up (Figure 3.1), the disordered obstacles are put randomly, so that they densely placed at some area by leaving free some places. To clarify this we plotted the graph of the probability to translocate to trans (disordered)

as a function of the chain length N of the polymers, as shown on Figure 4.4. And, in agreement with Qu-Cheng Gao *et al.* [42] we observe that the probability of the ring polymer to translocate to trans is greater than that of the linear polymer.

The Relation of Translocation Time with Chain Length of the Polymers

The scaling relationship between translocation time and polymer size N is an important concept in polymer physics. We take the most probable values of the escape
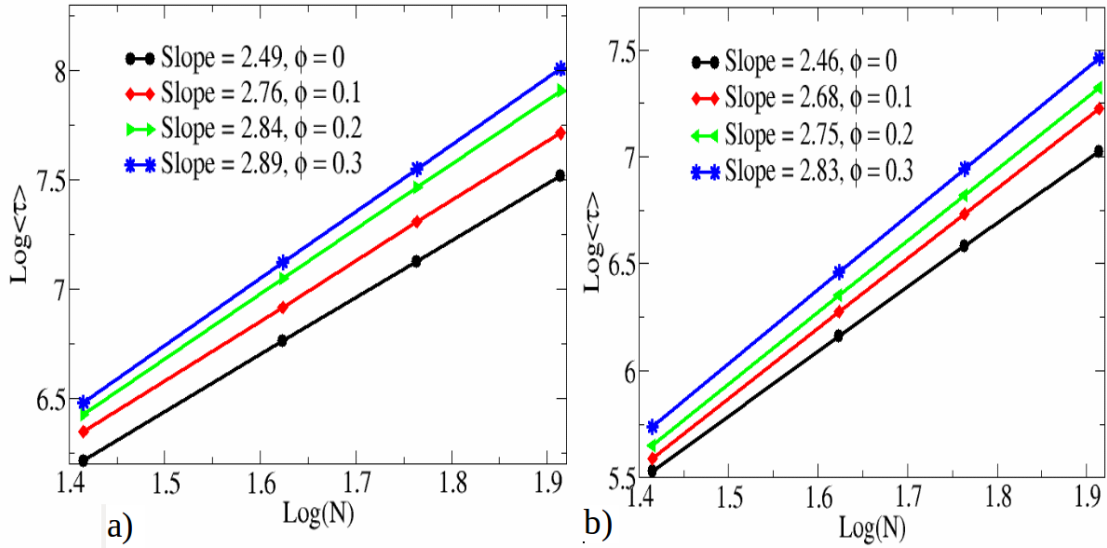

Figure 4.5: The log-log plots of escape time τ as a function of chain length N of linear (a) and ring (b) polymers, for different area fraction of crowding agents ϕ =0.1, 0.2, and 0.3.

time of both polymers and plot against the sizes N of the polymers in a log-log scales as shown on Figure 4.5. The dependence of the escape time of small linear and ring polymers, like those considered in this study, with their size N is a power law. The slope of the log-log graph represents the exponent α of N on the scaling relation. Therefore, the scaling relation is $\tau \sim N^{\alpha}$. The results of our simulations showed us, α= 2.49±0.01, for linear and α = 2.46±0.01, for ring polymer, for unbiased translocation of the polymers in the absence of obstacles. These results are agreed with Rouse model prediction, which is $\alpha = 1 + 2\nu = 2.5$.

Nevertheless, the presence of obstacles shows different. In the presence of obstacles, A. Gopinathan and Y. W. Kim [37] found that the translocation time decreases, as ϕ_c increases. Inconsistent with this, W. P. Cao *et al.* [38] for both unforced ($\Delta\mu = 0$) and forced ($\Delta\mu > 0$), they found that the dependence of τ on ϕ_c is nonmonotonic. And again, Chen Y. and Kaifu L., in the presence of driving force, they found that the escape time τ decreases, as ϕ increases, and they observed that the scaling relation of τ and chain length N, α is nonuniversal. Different from these, Qu-Cheng Gao *et al.* [42], in their study of the translocation of linear and ring polymers in crowded environment without applying electric potential, they found that the presence of obstacles does not change the translocation time. For our case, our simulations results, enabled us to find that the scaling relation varies with the density of the crowding agents, as it can be seen from the Figure 4.5. And the increment of escape time with ϕ is due to the entropic barrier rises, when the concentration of the obstacles increases.

Effect of pore size on the translocation of the polymers

The translocation of polymers also depends on the size of the pores. Qu-Cheng Gao *et al.* [42] found the relation of translocation time and size of the pore is nonmonotonic. It depends on the radius of gyration which is used as a balance in their study. To see the effect of the size of the pores, we added Figure 4.6. As shown on the figure, we simulated, the translocation of the two polymers, through the pores of W = 6, 8 and 10. From our simulation results, we observed that the translocation time decreases, as the size of the pore increases. This means, when the size of the aperture increases, its tendency to resist the move of the monomers decreases.
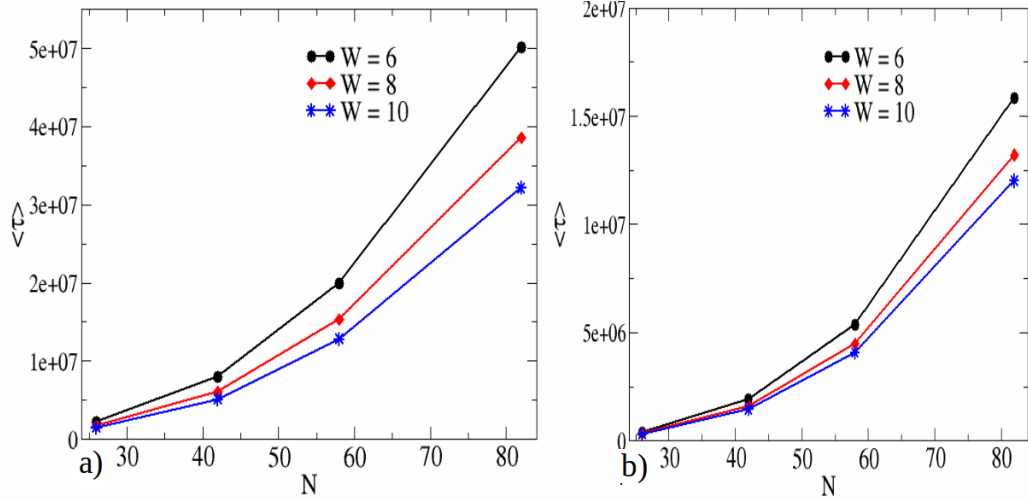
Figure 4.6: The plot of escape time τ as a function of chain length N of linear (a) and ring (b) polymers, for different sizes of pores in a crowded environment of $\phi = 0.1$.

4.2.2 Diffussion of Linear and Ring Polymers with Effect of Obstacles

As explained in chapter two, we monitored the diffusion of the center of mass of the polymers chain by using dynamic Monte Carlo method to study the dynamical properties of both polymers. We studied these properties of the polymers by investigating the characteristic of the diffusion motion of the linear and closed loop polymers. The time dependent mean square displacement of the center of mass CM of the chain is $\langle \overrightarrow{r}^2(t) \rangle$ and is given by:

$$\langle \overrightarrow{r}^2(t) \rangle = \langle (\overrightarrow{r}_{cm}(t) - \overrightarrow{r}_{cm}(t = 0))^2 \rangle \qquad (4.2.1)$$

$\langle \overrightarrow{r}^2(t) \rangle$ describes the diffusion of the over all system. From Rouse model the following equation is expected:

$$\langle \overrightarrow{r}^2(t) \rangle \sim t \qquad (4.2.2)$$

and

$$D \sim N^{-1} \qquad (4.2.3)$$

Therefore, in the absence of obstacles, W. P. Cao et al. [38] and Adam J. *et al.* [43]
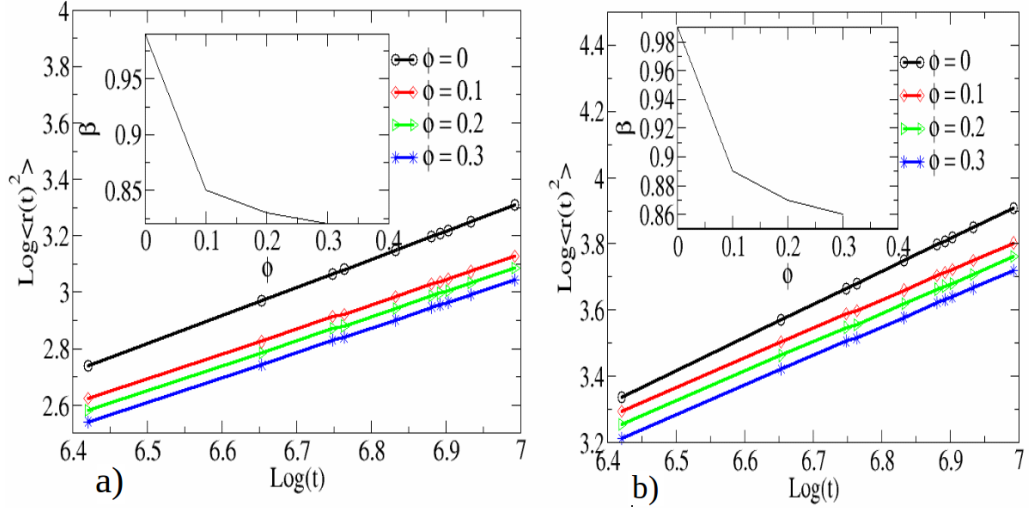
Figure 4.7: The log-log plot of mean square displacement ($\langle \vec{r}(t)^2 \rangle$) as a function of time (t) for linear (a) and ring polymers of length N = 26, in a crowded environment of area fraction (ϕ = 0.1, 0.2, and 0.3).

found that $< r(t)^2 > \sim t^\beta$, $\beta = 1$, means the diffusion is normal diffusion, and in the presence of obstacles the diffusion changes to subdiffussion ($\beta < 1$). In agreement with this, as it can be seen from the Figure 4.7, we observed that the diffusion is Fickian diffusion (normal diffusion, means $\beta = 1$) for the absence of obstacles, and subdiffusion ($\beta < 1$) for the presence of obstacles. The value of β is extracted from the log-log plot of the mean square displacement versus time. Also, from the Figure 4.7, we could observe that mean square displacement of both polymers of size N = 26 in the absence of obstacles is larger than mean square displacement of the same size in the presence of obstacles. In addition to this, we also found that the mean square displacement of ring polymer is greater than that of the same size of linear polymer, under the same condition.

The diffusion coefficient of polymers D is defined as equation 4.2.4 in the absence of obstacles. The slope of the respective mean square displacements to the time t yields the diffusion coefficient D corresponding to each chain length N implied by:

$$4D = \lim_{t \to \infty} \frac{\langle \vec{r}^2(t) \rangle}{t} \tag{4.2.4}$$
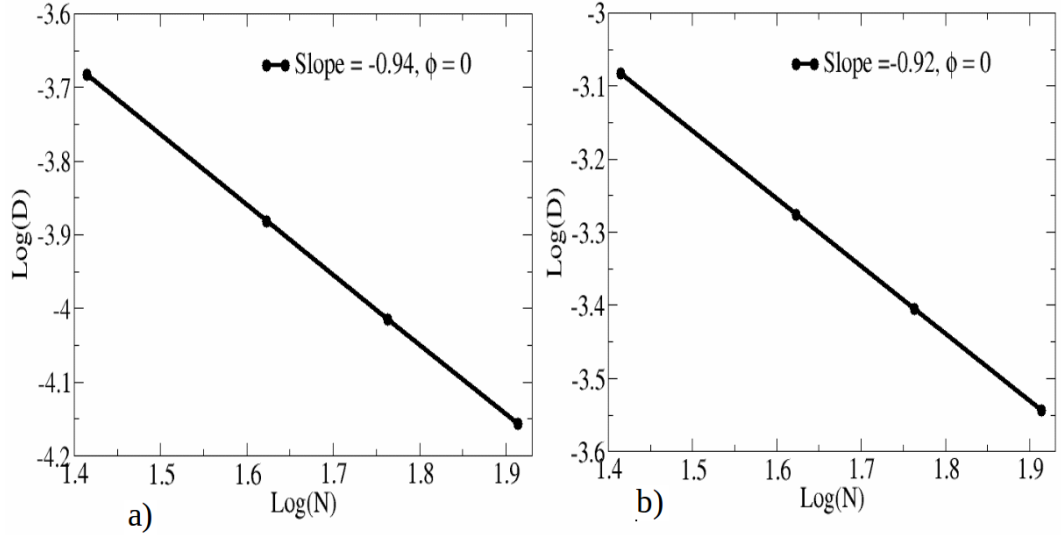
Figure 4.8: The log-log plot of diffusion constant (D) as a function of chain length N for linear (a) and ring polymers of length N = 26, 42, 58 and 82, in the absence of obstacles ($\phi = 0$).

After calculating the mean square displacement as a function of time for each size of both ploymers, we obtained the diffusion coefficient D using the definition. To see the dependence of the diffusion coefficient and chain length of the polymers, we plotted the log-log plot of diffusion coefficient D as a function of N, as shown on Figure 4.8. The log-log plot of the diffusion constant against N of small linear and ring polymers indicates the interdependence of the two parameters. In free environment, our simulations result for this relationship can be put as a power-law scaling expression which are $D \sim N^{-0.94\pm0.01}$ for linear and $D \sim N^{-0.92\pm0.01}$, and are closer to the Rouse model scaling relationship of the form $D \sim N^{-1}$. As we can see from the figure, the diffusion coefficient of relatively smaller polymer is greater than those of longer polymers considered in our study. And also, comparing the two polymers, Figure 4.8 (a) for linear and Figure 4.8 (b) for ring polymers, the diffusion coefficient of ring polymer is greater than diffusion coefficient of the same size of linear polymer.

Chapter 5

Conclusion

In our computational study, we presented and tested a Monte Carlo algorithm for both static and dynamical simulations of linear and ring polymers in a crowded environment. To be physically realistic, we implement a fluctuating bond length between adjacent polymer's monomer molecules to capture a realistic dynamics for both polymers structures.

We presented polymer diffusion and polymer translocation through a nanoscopic pore in a crowded environment having the same area fraction ϕ of crowding agents at both sides. Our numerical results show that end-to-end distance of linear polymer and radius of gyration of both polymers strongly depend on the polymer length N and ϕ. Moreover, we investigated that the scaling relation of $\langle R^2 \rangle$ and $\langle R_g^2 \rangle$ with polymer length N varies with ϕ. We also found that the translocations prefer to the disordered side (trans) and comparatively, the ring polymer is faster to translocate. From our simulations, also the escape times τ of the two polymers for different ϕ are obtained. And we found that τ increases as ϕ increases, therefore the scaling relation of τ with polymer length N, α, is nonuniversal.

Bibliography

[1] K. Haydukivska and V. Blavatska, J. Phys.: Condens. Matter 1,4629 (2014).

[2] Johannes Reiter. Monte carlo simulations of linear and cyclic chains on cubic and quadratic lattices. Macromolecules, 23(16):3811-3816, 1990.

[3] Tohru Gemma, Akira Hatano, and Tomonari Dotera. Monte carlo simulations of the morphology of abc star polymers using the diagonal bond method. Macromolecules, 35(8):3225-3237, 2002.

[4] Gary S Grest, Kurt Kremer, and TA Witten. Structure of many arm star polymers: a molecular dynamics simulation. Macromolecules, 20(6):1376-1383, 1987.

[5] Kaifu Luo, Santtu TT Ollila, Ilkka Huopaniemi, and Ala-Nissila et al. Dynamical scaling exponents for polymer translocation through a nanopore. Physical Review E, 78(5):050901, 2008.

[6] Arnold J Storm, Cornelis Storm, and Chen et al. Fast dna translocation through a solid-state nanopore. Nano letters, 5(7):1193-1197, 2005.

[7] Daniel Branton, David W Deamer, Andre Marziali, Hagan Bayley, and Benner et al. The potential and challenges of nanopore sequencing. In Nanoscience and technology: A collection of reviews from Nature Journals, pages 261-268. World Scientific, 2010.

[8] Murugappan Muthukumar. Mechanism of DNA transport through pores. Annu. Rev. Biophys. Biomol. Struct., 36:435-450, 2007.

[9] Peter Hinterdorfer and Antoine Van Oijen. Handbook of single-molecule biophysics. Springer Science Business Media, 2009.

[10] J. Han, S. W. Turner, and H. G. Craighead, Phys. Rev. Lett. 83, 1688-1999.

[11] S. W. P. Turner, M. Calodi, and H. G. Craighead, Phys. Rev. Lett. 88, 128103 2002.

[12] Amit Meller. Dynamics of polynucleotide transport through nanometre-scale pores. Journal of physics: condensed matter, 15(17):R581, 2003.

[13] M.Weiss, M. Elsner, F. Kartberg, and T. Nilsson, Biophys. J. 87, 3518 (2004).

[14] R. J. Ellis, Trends Biochem. Sci. 26, 597-604 (2001).

[15] Harvey Gould, Jan Tobochnik, and Wolfgang Christian. An introduction to computer simulation methods, volume 1. Addison-Wesley New York, 1988.

[16] Martin Oliver Steinhauser. Computer simulation in physics and engineering. Walter de Gruyter, 2012.

[17] Charles E Carraher Jr. Introduction to polymer chemistry. CRC press, 2017.

[18] Menno A Van Dijk and Andr e Wakker. Concepts in polymer thermodynamics, volume 2. CRC Press, 1998.

[19] Iwao Teraoka. Polymer solutions: an introduction to physical properties. John Wiley Sons, 2002.

[20] D.I Bower. Morphology and motion. An Introduction to Polymer Physics,(Cambridge University Press, Cambridge, 2002), pages 133-137, 2002.

[21] S. Brown and J. Szamel. J. chem. phys. 109(14,6192), 1998.

[22] I. Carmesin and Kurt Kremer. The bond fluctuation method: a new effective algorithm for the dynamics of polymers in all spatial dimensions. Macromolecules, 21(9):2819 2823, 1988.

[23] I. Carmesin and Kurt Kremer. Static and dynamic properties of two-dimensional polymer melts. Journal de Physique, 51(10):915-932, 1990.

[24] Michael Rubinstein, Ralph H Colby, et al. Polymer physics, volume 23. Oxford university press New York, 2003.

[25] Jeffrey Chuang, Yacov Kantor, and Mehran Kardar. Anomalous dynamics of translocation. Physical Review E, 65(1):011802, 2001.

[26] Paul J Flory and M Volkenstein. Statistical mechanics of chain molecules. Biopolymers: Original Research on Biomolecules, 8(5):699-700, 1969.

[27] AY Grosberg and AR Khokhlov. Statistical physics of macromolecules (aip, woodbury, ny). 1994.

[28] John J Kasianowicz and Brandin et al. Characterization of individual polynucleotide molecules using a membrane channel. Proceedings of the National Academy of Sciences, 93(24):13770-13773, 1996.

[29] A. Bhattacharya, Poly. Sci. 5, 3 (2013).

[30] P. J. Park and W. Sung, J. Chem. Phys. 108, 3013 (1998).

[31] Kurt Kremer and Kurt Binder. Monte carlo simulation of lattice models for macro- molecules. Computer Physics Reports, 7(6):259-310, 1988.

[32] Kaifu Luo, Tapio Ala-Nissila, and See-Chen Ying. Polymer translocation through a nanopore: A two-dimensional monte carlo study. The Journal of chemical physics, 124(3):034714, 2006.

[33] M Muthukumar. Polymer escape through a nanopore. The Journal of chemical physics, 118(11):5174-5184, 2003

[34] Johan T Padding. Theory of polymer dynamics. https://www. scribd. com/document/181367522/THEORYOF-POLYMER-DYNAMICS-Paddings, 2005.

[35] Debabrata Panja and Gerard T Barkema. Simulations of two-dimensional unbiased polymer translocation using the bond fluctuation model. The Journal of chemical physics, 132(1):014902, 2010.

[36] W. J. C. Orr Trans. Faraday Soc. 43 (1947);. E. W. Montroll, markoff chains and excluded volume effects in polymer chains, j. chem. phys. (18,734), 1950.

[37] A. Gopinathan and Y. W. Kim, Phys. Rev. Lett. 99, 228106 (2007).

[38] W. P. Cao, L. Z. Sun, C. Wang, and M. B. Luo, J. Chem. Phys. 135, 174901 (2011).

[39] J. H. Huang, Z. F. Mao, and C. J. Qian, Polymer 47, 2928 (2006). physic, Vol. 389(1927), PP. (457-484).

[40] Carlos Echeverria and Raymond Kapral, J. Chem. Phys. 132, 104902 (2010)

[41] Chen, Yuhao, and Kaifu Luo. The Journal of Chemical Physics 138.20 (2013): 204903.

[42] Qu-Cheng Gao, Zhuo-Yi Li, Yi-Wei Xu, Chen Guo and Ji-Xuan Hou. Modern Physics Letters B 33.26 (2019): 1950318.

[43] Adam J. Ellery, Matthew J. Simpson, Scott W. McCue, and Ruth E. Baker, J. Chem. Phys. 140, 054108 (2014).

[44] V. Yamakov and A. Milchev, Phys. Rev. E 55, 1704 1997.

[45] A. Bhattacharya, J. Phys.: Condens. Matter 16, S5203 2004.

[46] H. W. de Haan and G. W. Slater, Phys. Rev. E 87 (2013) 042604.

[47] H. W. de Haan and G. W. Slater, Phys. Rev. E 90 (2014) 020601.

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.

Name: **Deme Tesfaye**

Signature:− − − − − − − − − − − −−

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:− − − − − − − − −