# A 2D Monte Carlo Investigation of Static and Dynamic Properties of Ring polymer.

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# Abstract

Monte Carlo simulation technique has been used to investigate the static properties and translocation characteristics of ring polymers in two dimensions. Each chain consists of flexible linkage between monomers forming a closed loop. We consider the unbiased translocation process of the ring where the polymer translocates purely due to thermal fluctuations. The average escape time $\tau$ has been analyzed as a function of chain length $N$. And we found that, the polymer escape time $\tau$ of the ring polymers having a length $N < 100$, also has a scaling behavior $\tau \sim N^{\alpha}$ where $\alpha$ is more closer to $1 + 2\nu$ in which $\nu$ is the Flory exponent of value 3/4 in 2D and 3/5 in 3D. Such scaling is also the scaling behavior of the unbiased long linear chains. We study the static property of the small cyclical polymer chains by calculating the mean-squared radius of gyration $R_g$. Bond fluctuation method (BFM) is implemented to study both characteristics of the particular ring polymers.

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# Chapter 1

# Introduction

Almost everything around us in our daily life is made of either synthetic polymers. Most of these materials are produced by the chemical industry as synthetic polymers or products of living systems as Biopolymers /Natural polymers/ and often used with little or no modifications. At the molecular scale, life is made of Biopolymers: DNA, RNA and Proteins that are fundamental to biological structure and function. Perhaps Mechanics at the Nano-scale can work only with polymers[1, 2].

The word **poly-mer** means **many-parts** and refers to molecules consisting of many structural repeating chemical units known as *Monomers*. The monomers are connected to each other by covalent bonds. Monomers bonded can be of the same type for *homopolymers*, or possibly of a very limited number of different types, for example only two types for a *copolymers*. The fashion of bondage between monomers of a polymer chain can be end-to-end or sometimes in a more complicated ways to form a polymer [3]. The whole structure of a polymer is generated during *polymerization* which is the process by which these chemical units are covalently bonded. The number of monomers in a polymer molecule is its *degree of polymerization* $N$ [4, 5]. For their broad range of properties, which makes both synthetic and natural polymers an essential and ubiquitous role players in everyday life, the study of polymers in different contexts has been and still is intense. 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. Polymer chemistry focuses on the synthesis of polymeric materials and the chemical differences introduced into the material by choice of the different chemical nature of the monomers. However, polymer physics tries to generalize the description of polymer behaviors independently of the individual chemical nature of the different monomers. This task will be accomplished mainly by modeling a generalized polymeric chain in the first place on the basis of Statistical theory and scaling laws. 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). Experimental approaches to polymer physics are also common to determine the chemical, physical and material properties of polymers [5].

## Polymers

Degree of polymerization of polymers vary in wide ranges, a molecule will be a polymer if and only if $N \gg 1$. For instance, synthetic polymers (like polystyrene, polyethylene, etc.) are within ranges of $10^2$ and $10^5$. Whereas, for natural polymers this range can be even wider (example - DNA has around $10^9$ monomers). A polymer chain size ($\sim 10^3 \mathring{A}$) exceeds that of a monomer unit's size ($\sim 1\mathring{A}$) by several magnitude. Their large degree of polymerization, $N$, makes it possible the study of polymer behaviors using different simplified models via computer simulations without taking account the chemical details of the chain and these properties becomes universal behaviors. Accordingly, the large value of $N$ for a chain and its consequence: larger number of possible conformations of the chain, dominate the effect of microscopic details of the polymer on different universal behaviors and makes it suitable for the statistical mechanics description of the physics of the polymer molecule [6, 7].

The entire structure of a polymer is generated during polymerization, from large number of monomers which is referred as the degree of polymerization, N , of the polymer. Consider , for example, the general structure of Vinyl monomers and polymer shown in Fig.1.1 , where **R** represents different possible chemical molecules.

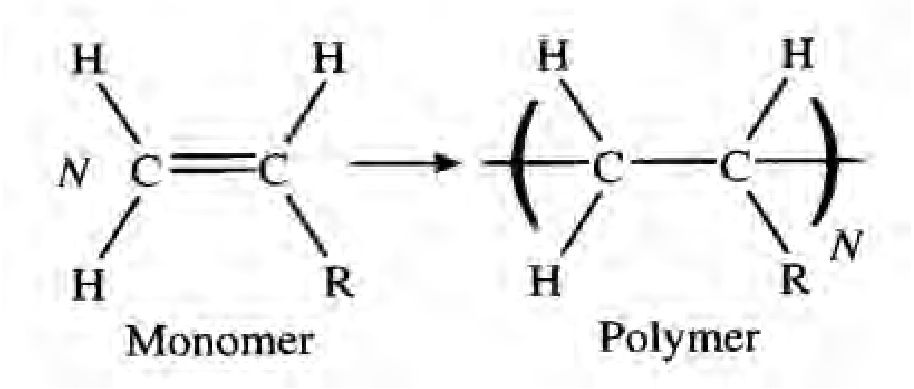

Figure 1.1: Polymerization of Vinyl Monomers.

If the **R** group in fig.1.1 is 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. If the **R** group in Fig.1.1 is chlorine the polymer is poly (Vinyl chloride), with repeating unit $CH_2 - CHCl$, prepared from [polymerization of Vinyl chloride($-CH_2 = CHCl$). If the **R** group in Fig.1.1 is a benzene ring , the polymer is polystyrene.

The chemical identity of monomers is one of the main factors determining the properties of polymeric systems. Another major factor is the polymers microstructure, which is the organization of atoms along the chain that is fixed during the polymerization process.

A polymer chain of a given chemical composition can exist in various *configurations (architectures)* as well as various *conformations* depending on its bonds orientation, location, identities, etc. A polymer of specific configuration will acquire many possible conformations ( shape or form ) in solutions and at a solid state. For instance, if the available bonds at a monomer are two, then the polymerization process can lead to either *(a)* **linear** or *(b)* **ring or cyclic** polymer configurations. When the possible bonds may be also more than two at a monomer then the polymer can acquire *(c)* **star**, *(d)* **H-branched**, *(e)* **Comb**, *(f)* **Ladder**, *(g)* **Dendrimer** or else *(h)* **Randomly branched** configuration [6, 5] as shown on the Figure 1.1 below.

Ring polymer chains are important members of the polymer family. In bio sciences there exist circular DNA, cyclic peptides and polysacharides. Ring formation is also an important feature of chromatin organization, playing a vital role in transcription regularization of genes and DNA compactification in nucleus. Many synthetic polymers also form circular structures during polymerization and poly condensation. Such wide range of physical realizations make them a subject of polymeric studies [1]. Cyclic polymers are distinguished by the presence of translational symmetry and having no ends. They can't "reptate" like linear chains or "retract" as branched polymers. Such absence of branches and end groups affect various polymer properties like shape, size, flow properties, crystallization, viscosity and some other behaviors of polymers. For instance the diffusion mechanism of rings has been suggested theoretically as Amoeba-like motion: they thrust and pull on unentanglement loops [3].

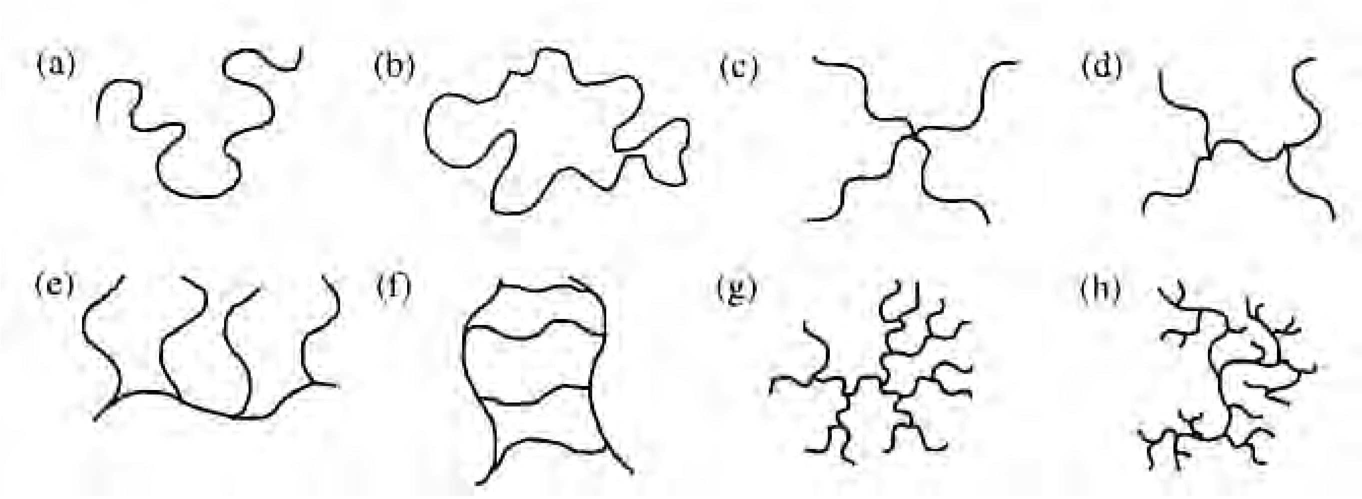

Figure 1.2: Examples of various polymer architectures.

So far a few works been done with simulation of ring polymers focusing mainly on understanding their properties in melt state and the effect of topological constraints on the ring during a melt. Even, when we see the other aspect of these works about the ring polymers, we can understand two facts. First, the dynamics of ring polymers has been hardly investigated. Second, even those few currently available theoretical and simulation results on ring polymers are full of conflicting views [3, 8].

To this end our work deals with both Static and Dynamic properties of small length ring polymers which are Unconcatenated and Unknotted.

## 1.1 Static Properties of Polymers

We now discus the static properties of ideal polymers like chain size and shape (End-to-End distance and Radius of gyration). Our discussions of 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. In addition, the individual monomers are considered point-like in which the steric effects are not taken into account. Perhaps, for its relative simplicity, it is a useful tool to gain a glimpse of polymer physics.

### 1.1.1 Ideal Chains

The fundamental representation for a polymer molecule is as an ideal chain of monomers with no interaction between non-adjacent monomers. The conformations of such ideal chain is the essential starting point of most models in polymer physics. The version of ideal chain model with no angular constraint on the joints and the monomers is known as freely-jointed chain ($FJC$) model. Such representation of polymer chain can be depicted as a finite length random walk (RW) with the degree of polymerization $N + 1$, number of steps $N$ and distance between the adjacent monomer with the length of the steps of the RW. The total distance traversed during the RW, $L$=$Nb$, is called the *contour length.* But contour length usually does not give that much information about the chain conformation. Therefore, the concepts of random walk give the fundamental frame for the conformations of a chain. 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.

### End-to-end distance $R$

The end-to-end vector, $\vec{R}$ joining one end of the polymer to the other, is the average length that can be thought as an indicator of the extent of spreading out or size of the polymer chain. Consider a linear chain consisting of $N$ bonds of length $b$ with the freely joined chain model and individual monomers with their corresponding position vectors $\vec{r_i}$ ($i$ = *0,1,...,N*). Accordingly the two ends of the $i^{th}$ bond are at $\vec{r}_{i-1}$ and $\vec{r_i}$. Therefore the net displacement which is also the end-to-end vector $\vec{R}$, is defined as

$$\vec{R} = \sum_{i=1}^{N} \vec{r_i} = \vec{r}_N - \vec{r}_o. \tag{1.1.1}$$

$\vec{R}$ doesn't always span the largest dimension of the chain therefore its average length is a good measure of the over all dimension. $\vec{R}$ is also different for each conformations of a chain and its probability of being either $\vec{R}$ or $-\vec{R}$ is equally likely so the ensemble average value $\langle\vec{R}\rangle$ is zero. Therefore its next simplest non-zero average is the mean-square end-to-end distance of the chain, which is given by

$$\langle\vec{R}^2\rangle = \langle\sum_{i=1}^{N} \vec{r_i}.\sum_{j=1}^{N} \vec{r_j}\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N}\langle\vec{r_i}.\vec{r_j}\rangle. \tag{1.1.2}$$

Assuming all bond vectors of equal length, $b$=$|\vec{r_i}|$, the scalar product of the bond vectors will be

$$\vec{r_i}.\vec{r_j} = b^2\cos\theta_{ij}. \tag{1.1.3}$$

Clearly $\langle\cos\theta_{ij}\rangle = 0$ for $i \neq j$, by assuming that there is no correlation between the directions that different bonds take as the configuration of the polymer can be the same as a random walk, and 1 otherwise. Then the mean square end-to-end distance becomes

$$\langle\vec{R}^2\rangle = b^2\sum_{i=1}^{N}\sum_{j=1}^{N}\langle\cos\theta_{ij}\rangle = Nb^2. \tag{1.1.4}$$

This indicates that an ideal polymer chain occupies a roughly spherical region in space with a diameter $\langle R^2\rangle^{\frac{1}{2}}$, proportional to $N^{\frac{1}{2}}$ for the linear chains. For the non-linear chains this quantity is not well defined or not defined at all. For the ring polymer chains the the end-to-end vector is not defined because of the absence of ends on the chain. But all polymer chains of any configuration type has mass which confirm for having radius of gyration which then be the best option to characterize a polymer chain conformation size [5].

**Radius of gyration $R_g$**

Another often used measure of the chain dimension is the root-mean-square distance between the monomers, $R_g^2$, simply radius of gyration. $R_g^2$ is also the second moment around the center of mass of the chain. It can be defined as the mean square of the distance between the beads and the center of mass (Figure 1.2). Roughly, the chain occupies a space of a sphere of radius $R_g$. The center of mass of the chain $\vec{r}_{cm}$ is at

$$\vec{r}_{cm} = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i. \tag{1.1.5}$$

Thus the $R_g^2$ is given by

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} \langle (\vec{r}_i - \vec{r}_{cm})^2 \rangle \tag{1.1.6}$$

Where $\vec{r}_{cm}$ is the position vector of the polymers center of mass where as $\vec{r}_i$ is the position vector of $i^{th}$ monomer. The square radius of gyration averaged over the ensemble of all possible conformations is given by

$$R_g^2 = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle (\vec{r}_i - \vec{r}_j)^2 \rangle. \tag{1.1.7}$$

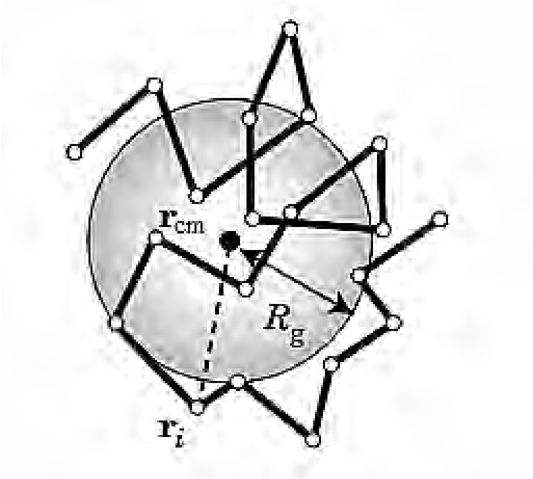

Figure 1.3: Center of mass $r_{cm}$ and the radius of gyration $R_g$ in the bead-stick model.

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 $(\vec{r}_i - \vec{r}_{i-1})$ of the $i^{th}$ bond is then the displacement vector $\Delta r_i$ 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 $|i - j|$. When $|i - j|$ is large, $r_i - r_j$ of an ideal chain has a Gaussian distribution with variance $|i - j|\ b^2$.

Which means that

$$\langle (r_i - r_j)^2 \rangle = |i-j|b^2. \tag{1.1.8}$$

Therefore

$$R_g^2 = \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}|i-j|b^2. \tag{1.1.9}$$

For large N the summation can be replaced by an integration and arrives at

$$R_g^2 = \frac{1}{6}Nb^2. \tag{1.1.10}$$

When we evaluate $R_g$ of a ring polymers, we can think of a ring consisting of N segments of length $b$. Then, we simply consider the ring as chain of monomers in which the monomers are in two segments ending at $r$ and $r'$ having $n$ segments on one of the sides and $N$-$n$ segments on the other side. Thus

$$R_{g,ring}^2 = \frac{1}{2}\langle (r-r')^2 \rangle = \frac{1}{12}Nb^2. \tag{1.1.11}$$

This implies that the ideal ring chains also behave in the same way as the long linear chains considered.

### 1.1.2 Real Polymer Chains

So far we have discussed polymer physics based on ideal model of polymer chains. However, it is obvious that real polymer chains have physical constraints beyond considered on their ideal models. These constraints affect a polymer chain's static and dynamic properties. For example, there are 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 in the next discussions, we try to see such constraints and their effects on the static behaviors of polymer chains. For the sake of simplicity, we will assume the monomers of a chain as spheres.

**Excluded Volume Interaction**

Ideal model of polymers takes into account only the short range interaction between monomers close enough to each other along the chain. These interaction don't prevent the possibility that monomers far apart but on the chain from occupying the same region in space or not to loop (cross-over) on to itself. Even in reality no polymer chain can ever intersect itself as assumed by ideal model. So real polymers exist under such physical constraint which is called as *Excluded Volume effect*, EV. If we model the polymer chain as a connected path on a lattice, this excluded volume effect refers to the condition that a path cannot pass through any lattice site that have been traversed previously. Accordingly, the real polymers are like the self avoiding walk (SAW) but the ideal chains are as simple random walk (RW). This excluded volume effect verify the fact that the real polymers have higher average size (swelling) than ideal chain. A detailed analysis of such real polymer chains was carried out by Flory [9] which is briefly discussed below.

### Flory Approach

Analysis of the equilibrium conformations of a polymer in a solution is mainly evaluated using the mean field Flory-type approach. Accordingly, Flory takes the fact that conformations of real polymer chain are decided by the net repulsive energy between monomers and the entropy loss because of the deformations. Therefore, Flory proposes a simple and successful polymer model to capture the balance between these two determining factors mentioned. He has made a rough estimates of both contributions of the total free energy of a conformation as follows.

Consider a polymer of $N$ monomers, swollen to a final size $R$, $R > R_o = \sqrt{N}b$. Then Flory takes that all $N$ monomers are uniformly distributed within the total volume $R^3$ with no correlation between them. The probability of any monomer to be within the excluded volume ($\mathbf{v}$) of another monomer then will be then the product of this $\mathbf{v}$ and number density of monomers in the pervaded volume of the chain, $\frac{N}{R^3}$. The energy cost of being excluded from this volume $\mathbf{v}$, that is the energy due to excluded volume interaction effect, is $K_bT$ per exclusion or per monomer. For all the $N$ monomers of the polymer chain, this interaction energy - $F_{inter}$, is

$$F_{inter} \simeq K_bT\mathbf{v}\frac{N^2}{R^3}. \tag{1.1.12}$$

The second contribution of the total free energy is the energy required to stretch the chain which is the entropic contribution. This entropic contribution of the free energy is then

$$F_{entro} = F_{elastic} \simeq K_bT\frac{R^2}{Nb^2} \tag{1.1.13}$$

Therefore, their sum which becomes the total free energy becomes

$$F \simeq K_bT\left[\mathbf{v}\frac{N^2}{R^3} + \frac{R^2}{Nb^2}\right]. \tag{1.1.14}$$

After minimizing this total free energy of the chain, with respect to $R$ will produce the optimal characteristic equilibrium size $R$ of the real polymer chain. Therefore, this $R$ or sometimes assigned as $R_{Flory}$ will become

$$R(N) = R_{Flory}(N) \simeq bN^{3/5} \tag{1.1.15}$$

Equation 1.1.15 leads to an important result of general scaling relation between number of monomers and the static property $R_g$ of a polymer.

Therefore an important result from Flory's theory for a long linear polymer yields a universal scaling dependence of a polymer end-to-end distance on the number of monomers $N$ as

$$\langle R^2 \rangle = N^{2\nu} \tag{1.1.16}$$

Both $R_g^2$ and the end-to-end distance scales the same way with respect to number of monomers ($N$). The value of the Flory exponent $\nu$ is 3/4 in 2D and 3/5 in 3D. Such connection between $\nu$ and the dimension $d$ in which the polymer resides can be given simply as

$$\nu = \frac{3}{2+d}. \tag{1.1.17}$$

More importantly this equations indicates that, in contrast to ideal polymers where $\nu = 1/2$, the scaling behavior of the polymer size now exhibits a higher Flory exponent of value $\nu = 0.75$ and this value of exponent has a dependence on the dimension of space $d$ in which the polymer resides.

## 1.2 Dynamic Properties of Polymers

### 1.2.1 Polymer Diffusion

Polymer chains are constantly and vigorously moving to change their positions and shapes. Thermal energy causes these motions so that polymer chains can take many different conformations. They are instantly switching from one to another, thereby changing the shape of the polymer chain. Over a long time however the motion is simplified. It is dominated by the translation of the chain as a whole (represented by its *center-of-mass*(CM) diffusion) in the solution for any conformation. Therefore, diffusion of the polymer will be captured by focusing on the diffusion of the center of mass which will be analogous to a single particle diffusion. The diffusion equation of a single particle in one dimension which is

$$\frac{\partial}{\partial t} P(x,t) = D \frac{\partial^2}{\partial x^2} P(x,t). \tag{1.2.1}$$

Where $P(x,t)$ is the probability of the particle being at position $x$ at time $t$. If we solve this differential equation the result is as follows

$$\langle x \rangle = 0. \tag{1.2.2}$$

$$\langle x^2(t) \rangle = 2Dt. \tag{1.2.3}$$

Where $D$ is the diffusion constant. For $d \geq 1$ ($d$ for dimension), we shall have the expression for equation

$$\langle r^2(t) \rangle = 2dDt. \tag{1.2.4}$$

Rearranging equation 1.2.4 we can write the expression for diffusion constant $D$ as

$$D = \frac{\langle r^2(t) \rangle}{2dt}. \tag{1.2.5}$$

Thus this $D$ which is the diffusion constant that expresses the diffusion of a single particle or the center of mass motion. But in actual case it is clear that mean square displacement of the polymer will be quite different than that of a single particle. The Rouse model [10] was developed to describe such dynamics of a polymer molecule in solution. The motion of the polymer was described by the Brownian dynamics of the monomers of the polymer chain. It is a bead-spring model that replaces solvent interactions with a friction force, and simulates the movement of the monomers due to a stochastic force $f_{sto}$. The model considers neither hydrodynamic interactions nor excluded volume effect. The resulting equation of motion is called the Langevin equation and it can be solved using simple mathematics. The Rouse model predicts that the mean-square displacement $\langle r(t)^2 \rangle$ of the polymer center of mass in two dimensions is

$$\langle r_{cm}^2(t) \rangle = 2d \frac{k_B T}{N\zeta} t. \tag{1.2.6}$$

Where $k_B$ is the Boltzmann constant, $T$ for temperature, $\zeta$ is the frictional coefficient of a single monomer and $N$ is the number of monomers. Comparing with equation 1.2.4 and 1.2.6 above the diffusion constant can be written as

$$D = \frac{k_B T}{N\zeta}. \tag{1.2.7}$$

As we can see from equation 1.2.7 the relation between diffusion constant $D$ and the polymer length $N$ is

$$D \sim N^{-1}. \tag{1.2.8}$$

In contrast, Zimm model, which consider the hydrodynamic interaction, suggested that the diffusion of a polymer depends on the dimension and the scaling would be as $D \sim N^{-\nu}$ [6].

In this study, we consider two key quantities 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, $\tau$. These two parameters exhibit a distinct scaling dependence on the number of monomers $N$ as

$$D \sim N^{-1} \tag{1.2.9}$$

and

$$\tau \sim \frac{R_g^2}{D}. \tag{1.2.10}$$

In all case the angular brackets $\langle \rangle$ indicate the averaging over all possible chain conformations.

## 1.3 Translocation of a Polymer

Polymer translocation refers to the process by which a polymer chain will pass through a pore to either of the sides of the pore. This phenomenon has its own biological contexts. For example molecular transport through cell membrane is an essential mechanism in living organisms and it is a translocation process. Most polymer chains are too long while the pores in the membranes are too narrow to allow these molecules to pass through them as a single collapsed unit. In such circumstances, the molecules have to deform themselves in order to squeeze or translocate through the pores [8]. Translocational transport of polymers through nano pore also plays a crucial role in other numerous biological processes, such as DNA and RNA translocation across nuclear pores, protein transport through membrane channels and virus injections. Parallely, the urge to understand the translocation process also stems up from the fact that it has potential technological applications such as in rapid DNA sequencing, gene therapy and controlled drug delivery [3]. In recent times new developments in design and fabrication of nano meter sized pores and etching methods have put translocation at the forefront of single molecule experiments with the hope that translocation may lead to cheaper and faster technology for the analysis of bio molecules. Therefore, polymer translocation has become a subject of intensive experimental [11], numerical [12, 13, 14, 15, 16] and theoretical studies [1, 17].

So far, theoretical, experimental as well as computer simulation studies of such translocation consider the translocation processes to be one among the following three translocation types. First, unbiased translocation where the polymer translocates purely due to thermal fluctuations. Second, field-driven translocation in which translocation is driven by an external field or interactions such as driving mechanisms. The external field may be an external electric field, a chemical potential difference or selective adsorption on one side of the membrane. And the third case, pulled translocation in which the translocation is facilitated by a pulling force at the head of the polymer. Unbiased translocation of polymers is by far the most fiercely debating topic [8].

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.* [11] 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 ordered to overcome the entropy near the nano pore and increase the possibility of the translocation.

Inspired by experiments, a number of recent theories [18, 19, 20, 21] have been developed to investigate a polymer translocation. However the case of unbiased translocation of polymers still remains a challenging problem. So our simulation study focuses on the unbiased translocation process of a ring polymer in particular. Among the fundamental quantities defining a translocation process the main one the average time of translocation, $\tau$. $\tau$ 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 mainly 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 $\tau$ as a function of $N$ have been presented. Many have also undertaken an extensive effort to determine $\tau$ as a function of $N$ in a form $\tau \sim N^{\alpha}$ based on high-accuracy numerical simulations to resolve the apparent discrepancy.

Most of these studies use extensive numerical simulations based on the fluctuating bond (FB) and Langevin dynamics (LD) methods with the bead-spring approach [22, 2, 23, 24]. For instance in Refs. [2, 24] the translocation time for long linear polymer chains was found to scale as $\alpha = 2.50 \pm 0.01$ in 2D. This result is in agreement with general scaling expression $\tau \sim N^{1+2\nu}$ where $\nu$ is the Flory exponent ($\nu = 3/4$ for 2D and $\nu = 3/5$ 3D). Standard equilibrium Kramer analysis [25] of diffusion through an entropic barrier for a linear polymer yields $\tau \sim N^2$ for unbiased translocation. However, Chuang *et al.* [16] noted that such quadratic scaling behavior for unbiased translocation cannot be correct for a self avoiding polymers. Therefore, after performing numerical simulations with Rouse dynamics on a 2D lattice model of translocating self avoiding linear polymers, they have come up with a scaling relation $\tau \sim N^{1+2\nu}$ for large $N$ but with a much larger prefactor. Dubbeldam *et al.* [26] have argued that $\alpha = 1 + 2\nu = 1.55$ in 2D. Most recently, Panja *et al.* [27] have argued that $\tau$ scaling to be different than the previous claims and then Numerically find that $\tau \sim N^{(l+2\nu)/(1+\nu)}$, which is 1.43 in 2D. Using the same argument as Storm *et al.* [14], Panja *et al.* [27] further claim that the lower bound for $\tau$ is $N^{2\nu}$, which gives $\alpha = 1.50$ in 2D.

Studies [28, 29] have been also developed on the static and dynamic properties of ring polymers and the scaling relations of some parameters with respect to the number of monomers of the ring chain. They have reported the scaling behaviors of the ring polymers are remarkably similar to long linear polymer chains. But their analysis was limited to degrees of polymerization smaller than the entanglement crossover of linear chains. Our Monte Carlo simulation study result also agrees with these conclusions by predicting the time scaling behavior of the small ring polymers we consider for translocation time $\tau$ as a function of $N$. This scaling usually expressed as a scaling law of the form $\tau = N^{\alpha}$, where the exponent $\alpha$ depends on the Flory exponent $\nu$.

# Chapter 2

# Simulation Method

Computer simulations occupy an important intermediate position between theory and experiments. They can provide a valuable tests of assumptions and predictions of theoretical models as well as attempt to mimic 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) methods. These approaches are analogous to time and ensemble averaging in statistical mechanics.

Here 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 ring polymer by a simplified structure which retain only the most basic features of the ring (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 ring polymer chains.

Monte Carlo simulation method involves generating and accepting or rejecting of possible conformations (states) stochastically. We need a way of generating and evaluation for accepting/rejecting the conformations forwarded along each steps (moves). In our simulations, this task will be done according to the *Bond Fluctuation Method* (BFM). Then the detail of our model and method used is presented as follows.

## 2.1 Lattice Model with Bond Fluctuation Method

### 2.1.1 Lattice Model

It is common and legitimate 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 hard-core monomer-monomer interaction. The lattice model simulation of polymers can be done on different lattice geometries For example our simulation considers square lattice geometry. But such choice of the lattice is somewhat arbitrary and doesn't affect the universal properties because they depend only on its dimension. 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.

### 2.1.2 Bond Fluctuation Method

The bond-fluctuation method (BFM) was proposed [30, 31] as an alternative to a (single-site) SAW model, which retains the computational efficiency of the lattice without being plagued by severe ergodicity problems. 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. 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.

BFM has been widely used in recent years to investigate the structure and dynamics of a great variety of polymer systems. The ring 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 upper limits $\sqrt{13}$ prevents bonds from 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 rings polymers - the objects which this work in devoted to.

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.

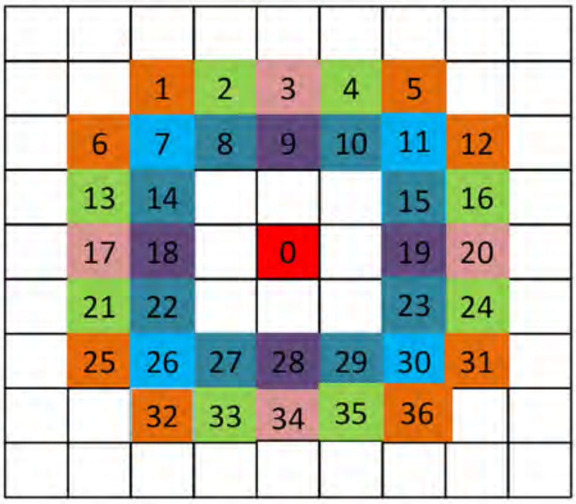

Figure 2.1: This figure shows the restriction of the bond length between consecutive monomers in the range $2 \leq l \leq \sqrt{13}$ for 2D - BFM. Assume a monomer as a bead placed on the square lattice labeled **0** at the center plaquette, then according to BFM the next bead to be connected with this bead, at **0**, can occupy one of the lattices labeled from **1** to **36** which are allowed plaquettes in the bond length ranges set by the BFM.

The implementation of the Bond fluctuation method involves the following particular steps:

1. Start with an initial state of self avoiding conformation of a polymer chain consisting of $N$ monomers.
2. Select a monomer randomly and select one of the four lattice directions randomly with equal probability.
3. Move the selected monomer in the selected direction by one lattice spacing called, this a trial move.
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.
5. If both requirements self avoidance and bond length restrictions are met then accept the move.

It is also possible to include a finite interaction energy between neighboring monomers or consider the energy difference between possible conformations due to an electric field or an adsorbing force to a wall. Then the move is accepted according to the Metropolis criterion. The implementation of Metropolis criteria then will be further included as :

6. Calculate the energy change $\Delta U$ between the new and the old configurations of the system, and if $\Delta U < 0$ the move is accepted, otherwise
7. Generate a random number $r$ such that $0 < r < 1$.
8. If $r < e^{-\Delta U/k_B T}$, accept the move and update the new lattice conformation. After processing this step
9. Go to step 2 above.

The unit of time in this model is defined by Monte Carlo Step (MCS) which will be achieved when on average each monomer has attempted one trial move (i.e $N$ - trial moves or $N$ - MC moves).

## 2.2 Simulation Procedure

Our Computational study of the small $N$ ring polymers implement basically the routines of coarse-grained lattice Monte Carlo simulations via the Bond Fluctuation Method. However, we aimed at investigation different observables of the ring polymer belonging either to its static or dynamic property. We implement specific procedures for these parameters as follows.

Generally, for all the simulations, we prepare a simple and 2D square simulation box of $5000 \times 5000$ square lattice cells of unit length each. We tracked the positions of the monomers of the polymer, by taking snapshots at periodic intervals, to make sure that this lattice space is wide enough to have no effect on any property of the polymer system. In order to obtain the initial configuration, we insert nonconcatenated ring polymer symetrically at the center in the simulation box. we define this configuration assuring any monomer of the ring polymer is connected to two neighbor monomers 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 neighbour monomers are set as permited by BFM on 2D.

A typical simulation then proceeds as follows. Starting from the initial polymer configuration many moves are 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 uncrossability constraints. Throught this equilibration process the $1^{st}$ and $(\frac{N}{2}+1)^{th}$ monomers were anchored not to move. In our simulations this relaxation of the ring polymer is excuted for longer times than the relaxation time or equilibration time $\tau \sim N^{2.50}$ in two dimension simulations of polymers. And we also perform two independent simulations for most sets of parameters investigated and then checked wehther the two results agreed reasonable well. The latter procedure particularly helps us to make sure good stablity of our simulation results and the values were not initial configuration dependent. After equilibration is finished, at $t = 0$, the two middle monomers are allowed to move just like the rest of the monomers of the chain.

Various dynamical and structural properties are calculated including the mean-squared displacments and diffusion conastant and mean squared radius of gyration. To measure the average size of the ring polymer we implemented the expression for the mean squared radius of gyration which can be defined using the center of mass position and the monomers location. That is according to equation 1.1.6

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle (\vec{r}_i - \vec{r}_{cm})^2 \rangle \tag{2.2.1}$$

where the $\langle\rangle$ refers to the averaging done over the ensemble of the possible conformations. Here we further simplified the $(\vec{r}_i - \vec{r}_{cm})^2$ as $(x_i - x_{cm})^2 + (y_i - y_{cm})^2$ for computational simplicity.. The ensemble average of the squared displacement of the center of mass of the two-dimensional ring polymer is evaluated using $\langle r^2 \rangle = \langle (\vec{r}_{cm}(t) - \vec{r}_{cm}(t = 0))^2 \rangle$ where $\vec{r}_{cm}(t)$ denotes the position vector of the center of mass of the ring polymer at time $t$. Then the diffusion coefficient $D$ is determined from the slope of the $\langle \vec{r}^2(t) \rangle$ at long times as $D = \lim_{t\to\infty} \frac{r^2(t)}{4t}$. We don't put any barrier or pore at any point in the simulation box during evaluation of the above parameters.

For the translocation of the ring polymer through the pore the simulation procedure involves additional task of the wall - pore placment. Therefore, after we prepare square box then a wall, tall enough as the simulation box height, with a nano pore of thickness $L = 3$ and width $W = 7$ lattice constant at its center is placed (built) 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 (Figure 2.2).

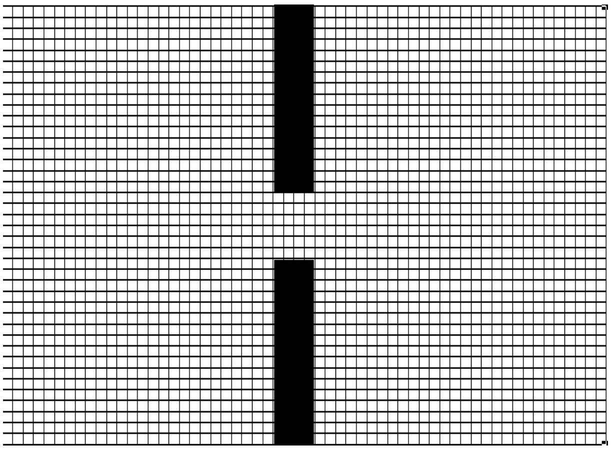

Figure 2.2: Schematic representation of square lattice with size is $5000 \times 5000$ unit square cells and at the middle we put a wall with a nano pore of width $W = 7$ and length $L = 3$ lattice constant.

The wall is constructed from a row of immobile particles arranged in a straight line.Then the ring polymer is initially placed at the middle of the pore with half of the chain in either sides of the dividing wall as shown below (Figure 2.3).

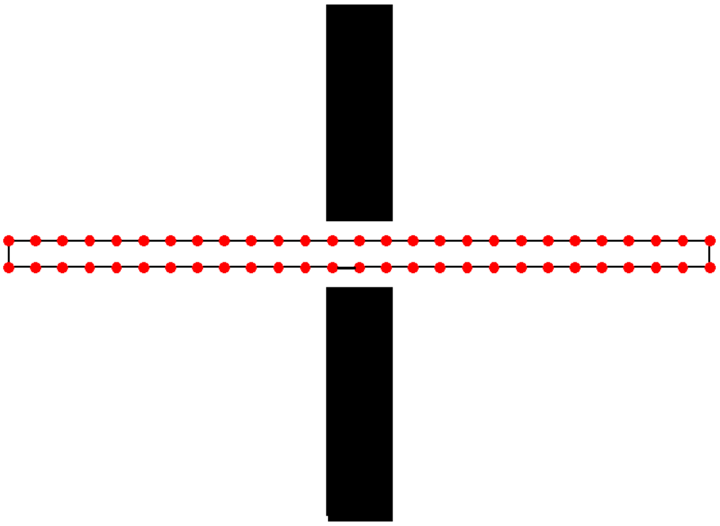

Figure 2.3: This figure shows the initial conformation of a ring polymer of length $N = 54$ placed symmetrically.

This systematic placement is important to over come the effect of the entropic barrier or the wall. The chain is then allowed to relax with local moves while two of its middle monomers (i.e $1^{st}$ and $(\frac{N}{2}+1)^{th}$ monomers) are fixed inside the pore. To obtain fully equilibrated conformation $1 \times 10^6$ Monte Carlo time steps per monomer (MCS) are allotted .

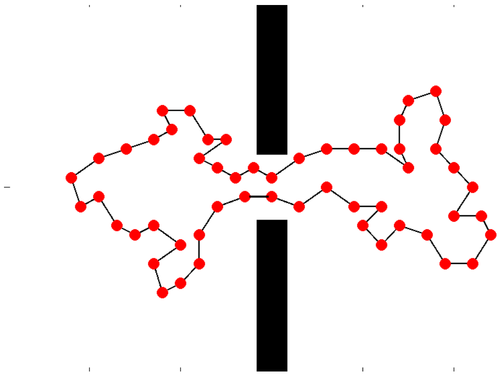

Figure 2.4: Schematic representation of a ring shaped polymer in the process of translocation from the nano pore with length $L = 3$ and width $w = 7$ sites and the polymer size, $N = 54$. This conformation is the most probable conformation after relaxation for $N \times 10^6$ Monte Carlo moves.

After the polymer has relaxed as discussed above, at $t = 0$, the constraint on the two middle monomers is removed and wait till the polymer disengages from the pore escape either to the left or to the right side of the pore as a result of the thermal diffusion (Figure 2.5)

Thus the simulation ends at a time $t = t' > 0$ when the entire polymer is on either side of the wall. We call this $t'$ the escape time $\tau$. This procedure is repeated for a large number of

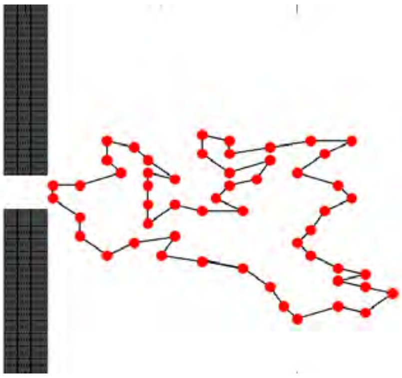

Figure 2.5: Schematic representation of a ring shaped polymer after translocation from the nano pore with length $L = 3$ and width $w = 7$ lattices after relaxing for Monte Carlo moves of $N \times 10^6$ and the polymer size, $N = 54$

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times for each ring polymer of length $N$, and take the escape time which happened most. we also record all these escape time values of all the large number independent times to obtain the probability distribution of the escape time.

# Chapter 3

# Result and Discussion

## 3.1 Static Property of a Ring polymer

### 3.1.1 Radius of Gyration

The mean square radius of gyration of a polymer chain is an indicator of the average conformation size of the polymer. This square radius of gyration are average over the ensemble of allowed chain conformations , but it doesn't mean that the chain always adopt a spherical shape. This important static property indicator parameter is dependent on the number of monomers of polymer chains. The plot of the mean polymer size, $\langle R_g^2 \rangle$ against degree of polymerization $N$, as represented on Figure 3.1 shows this interdependence. Ideal polymer models have shown that the power-law scaling relation between these two quantities as $\langle R_g^2 \rangle \sim N^{\frac{1}{2}}$. But ideal polymers are assumed to have no excluded volume effect between monomers which aren't 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. According to this theory $\nu$ is 0.75 for 2D and 0.6 for 3D.

In our study, this scaling exponent $\nu$ is extracted from the slope of the log-log plot of $\langle R_g^2 \rangle$ with respect to the number of monomers of the ring polymers as described next.

At the plot of figure 3.1 the filled circles, which correspond to the log-log pair of values of the number of monomers $N$ and the mean square radius of gyration of the ring respectively, were fitted to a line with slope $2\nu$. Then the value of the slope becomes $2\nu = 1.5 \pm 0.01$. Clearly, this implies that the scaling exponent $\nu$ assumes a value of $0.75 \pm 0.01$.

The result of our simulations using the above procedures is given at the figure below (Figure 3.1).

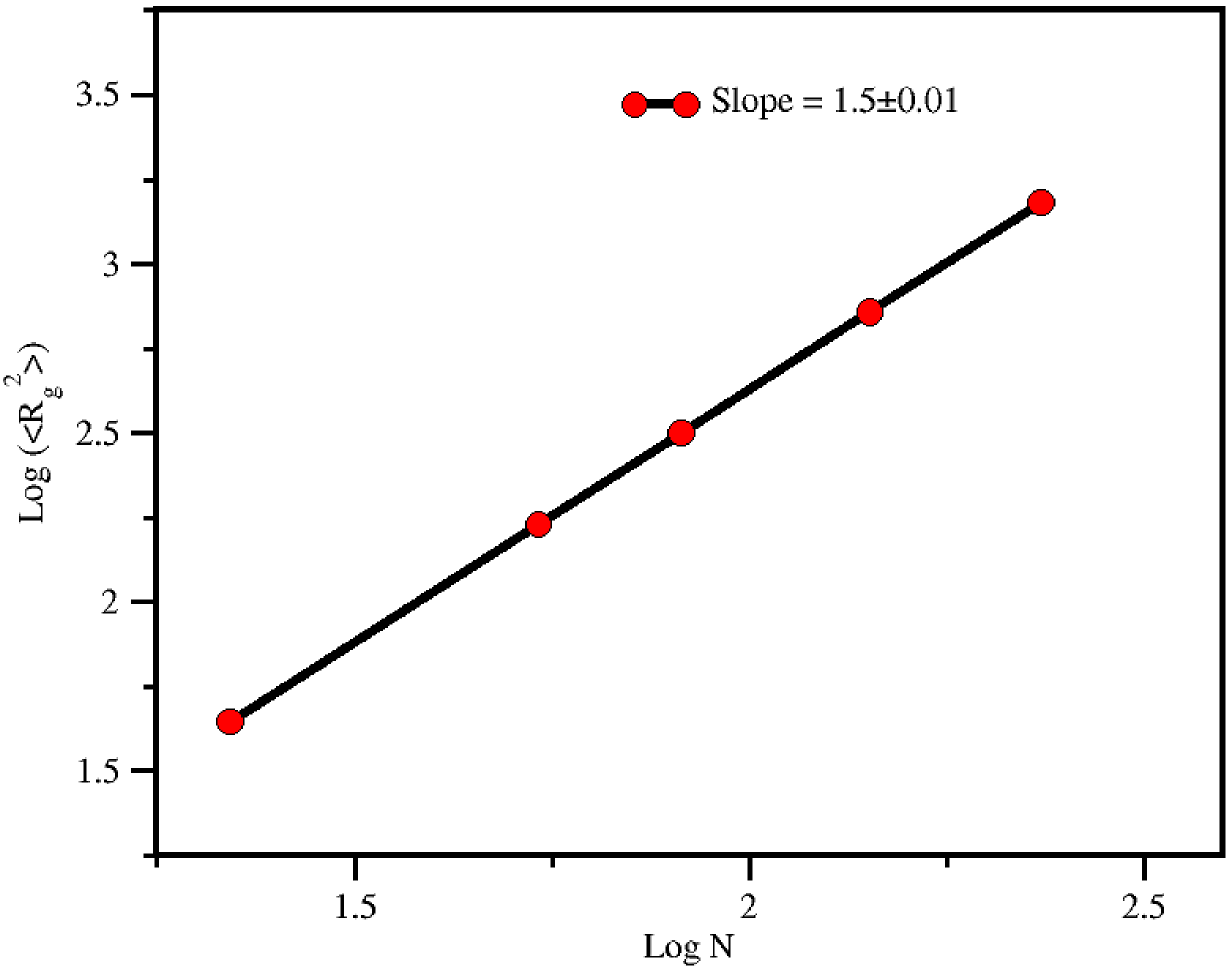

Figure 3.1: Log - Log plot of mean square radius of gyration, $\langle R_g^2 \rangle$, versus ring polymer length, N, for $N = 22, 54, 82, 142$ and 234.

This result indicates that, for relatively small ring polymer chains considered in our simulations, $22 \leq N \leq 234$, scaling exponent $\nu$ is exactly same as the value as the Flory-theory suggested. Therefore the scaling relation between the ring polymer chains mean square radius of gyration with $N$ of the ring polymers could be expressed as $\langle R_g^2 \rangle \sim N^{1.5}$.

This result is the same as the one found for long linear polymers. This is due to the fact that, for the linear polymers as $N \longrightarrow \infty$ the excluded volume interaction between two monomers distant along the chain vanish and the polymer chain tends to contract on to itself to assume a more compact conformation. The small rings are quite stiff collective structure and can be considered as compact structures with comparable conformation size as the long polymers.

The other observation from our simulation is that the Flory exponent increases for rings we have considered than their ideal chain model version. This observation can be evidenced from comparison of the ideal ring polymers described by equation 1.1.11 and our simulation result. This difference is a result of characteristic differences between the ideal and real ring polymers. That is since excluded volume interaction is neglected in ideal models such polymer models are less stiff. However the small ring polymers considered here are relatively stiff since EV effect criteria is included during the local moves. The small rings in our simulations have $\nu > 0.5$. Such increase of $\nu$ along with stiffness is also evidenced on recent experiment on circular DNA. The experiment showed that $\nu$ of a circular DNA changed from 0.75 to 1 as the circular DNA becomes smaller because a short circular DNA was quite stiff [32].

## 3.2 Dynamic Properties of a Ring polymer

### 3.2.1 Ring Polymer Diffusion

As described in the previous sections, we studied dynamic properties of ring polymers by investigating the characteristic of the diffusion motion of the closed loop polymers. Therefore time dependent mean square displacement of the center of mass CM of the chain is $\vec{r}^2(t)$. Which can be calculated as

$$\langle \vec{r}^2(t) \rangle = \langle (\vec{r}_{cm}(t) - \vec{r}_{cm}(0))^2 \rangle \tag{3.2.1}$$

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

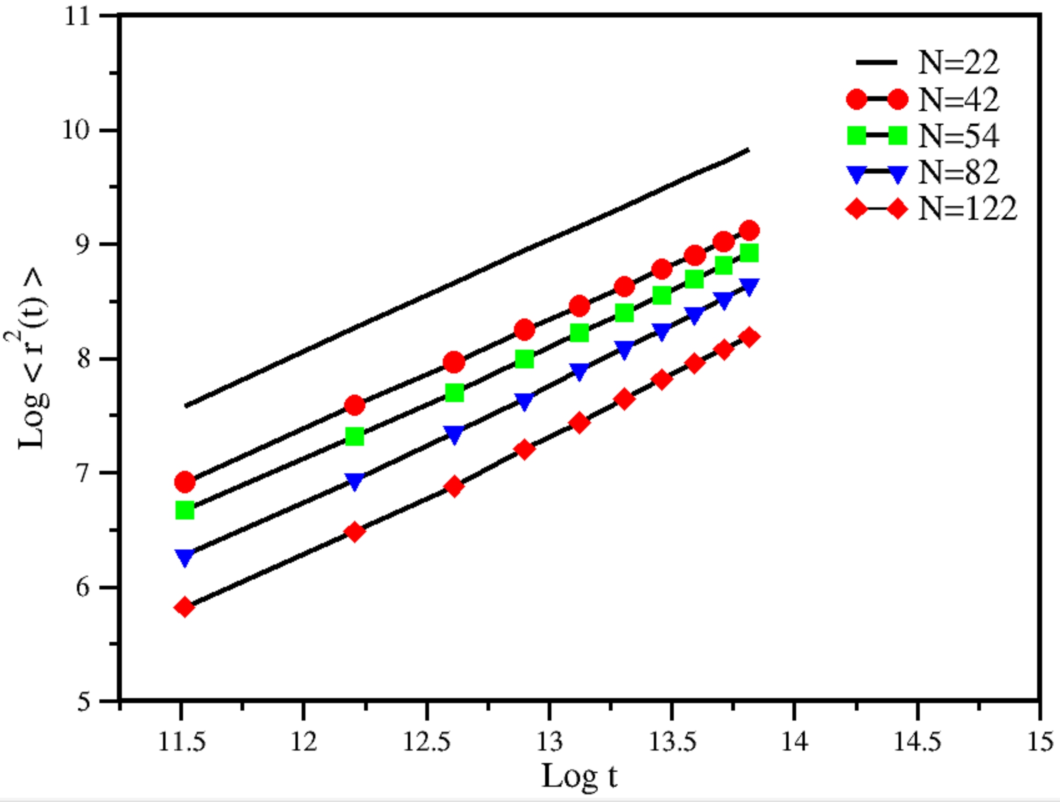

Figure 3.2: Log - Log plot of mean square displacement, $\langle \vec{r}^2(t) \rangle$, versus time, $t$, for different chain length $N = 22, 42, 54, 82$ and 122.

Figure 3.2 represents the mean square displacement of each rings as a function of simulation time $t$ for different number of monomers in the range $22 \leq N \leq 122$. The mean-square displacement is proportional to $t$ and are all linear to the time $t$. At long times, $\langle \vec{r}^2(t) \rangle \sim t$ is recovered because eventually the monomer diffuses with the diffusion coefficient of the whole chain. The straight lines for log-log graph of mean square displacement the time are in regime of simple diffusion.

Moreover, average mean square displacement of relatively small rings is higher than those of long polymers. But the diffusion mechanism of the ring polymers can't be identified from their mean square displacement versus time graphs. Rather other techniques which can show how each monomer displaces during the diffusion could help better. However different studies made so far suggested that these chains neither reptate like linear polymers except for some large $N$ in a very confined environments nor retract as the branched ones, rather they use Amoebic kind of diffusion or a kind of new reptation mode of motion.

The slope or ratio of the respective mean square displacements to the time $t$ produces the diffusion coefficient $D$ corresponding to each chain length $N$ implied by

$$4D = \lim_{t \to \infty} \frac{r^2(t)}{t} \tag{3.2.2}$$

The variation of these values for each rings and theories then will lead us to test the dependence of the diffusion coefficient on the degree of polymerization $N$ of rings. Therefore the double logarithmic plot of the diffusion constant against $N$ for the small rings indicates the existence of the inter dependence of the diffusion constant of small rings and their degree of polymerization. Our simulations result for this relationship can be put as a power-law scaling expression which is $D \sim N^{-0.90}$ with the Flory exponent $\nu = -0.90 \pm 0.01$. However this result is not same as the one forwarded by Zimm ($\nu$ is equal to $-0.75$). It is closer to the Rouse model scaling relationship of the form $D \sim N^{-1}$. Zimm model considered the strong hydrodynamic interaction between the monomers in the polymer chain and also between monomers and the solvent within the pervaded volume of the chain. However our simulations don't include these effects and therefore leads to slower diffusion as the Rouse model.

We can also understand that this scaling approximation of our simulation to be reasonable combining the approximation given at Equation 1.2.10 and the result obtained for similar scaling between the relaxation time $\tau_{relax}$ as

$$D \sim \frac{\langle R_g^2 \rangle}{\tau} \sim \frac{N^{2\nu}}{N^{2\nu+1}} \tag{3.2.3}$$

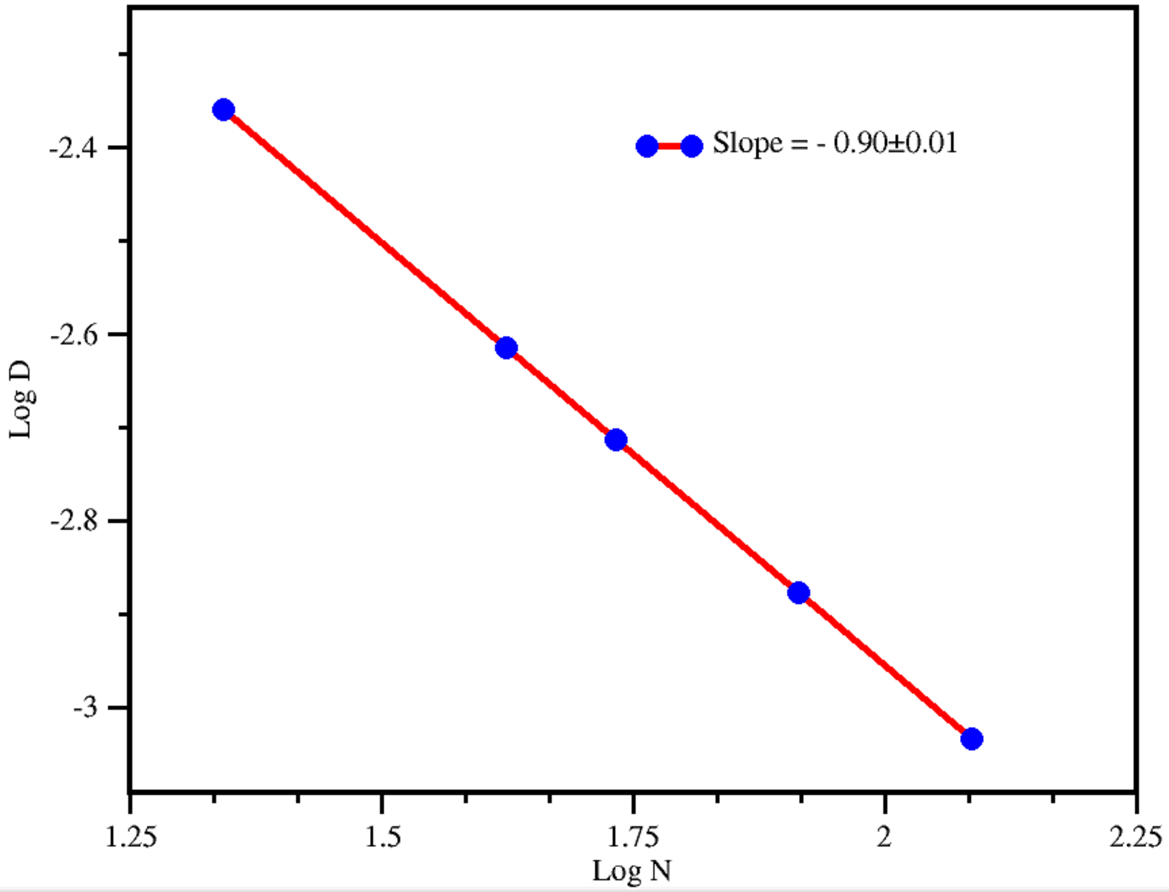

Figure 3.3: Log - Log plot of diffusion coefficient, $D$, versus chain length, $N$, for self-avoiding polymers of four different chain lengths $N = 22, 42, 54, 82$ and 122.

### 3.2.2 Translocation of a Ring Polymer

#### Probability Distribution Function (PDF) for ring polymer translocation

The other important manifestation of dynamic properties of ring polymers is the translocation phenomena of ring polymers through tiny pores. In our simulations, we numerically measure the probability distribution $P(\tau)$ of the translocation time $\tau$ for different chain sizes. The most probable translocation time is given by the maximum of $P(\tau)$. We computed the probability distribution of the escape time $\tau$ for $N = 22, 42, 54$ and 82 through a fixed pore size of thickness 3 lattice units and width of 7 lattice units.

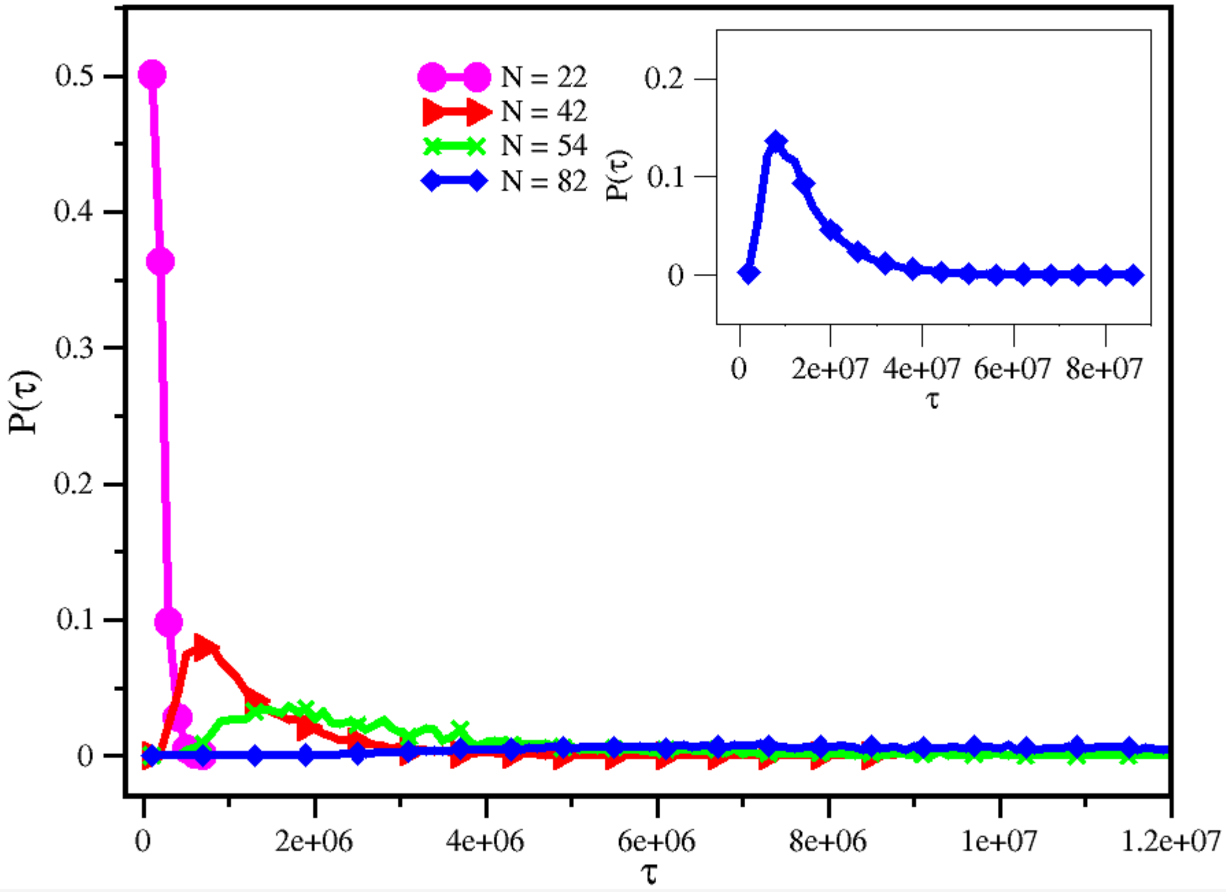

Figure 3.4: Probability distribution P($\tau$) of escape time $\tau$ for $N = 22, 42, 54$ and 82 which is obtained from 100,000 times for each size.

As we can see from the plots of Figure 3.4 the smaller ring polymers will escape from the pore relatively sooner as compared to rings that are larger. Most escape times are large simulation times as compared to the Rouse relaxation time of the chain. Extreme situations, such as extreme geometry and restarting the translocation process to an opposite side, can cause these large escape times.

The polymer with a polymerization degree $N$ can be assumed to leave the pore to either sides most likely around the most probable translocation time. These most probable times for each ring sizes are useful to calculate the scaling relation between escape time and the degree of polymerization. Our simulations describe that the probability decays for long value of escape times and thus the distribution of the escape times is a fat-tailed distribution in relative to normal distribution.

### Translocation time as function of the chain length

The scaling relationship between translocation time and polymer size $N$ is an important concept in polymer physics. It estimate the characteristic of escape time for ranges of $N$ and the vise versa. We take the most probable values of the escape time of each rings and plot against the sizes $N$ of the rings in a log-log scales as shown at Figure 3.5.

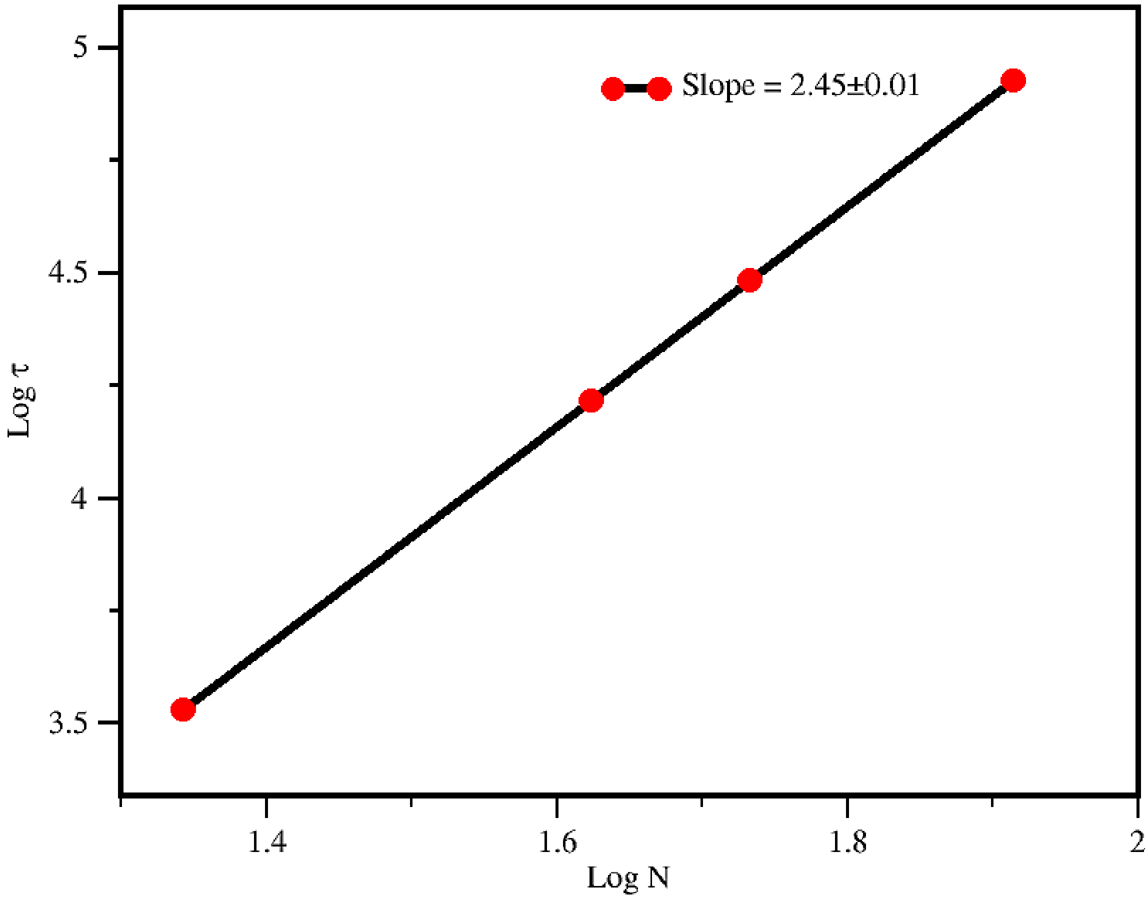

Figure 3.5: Log - Log plot of escape time, $\tau$, as a function of polymer chain length, N, for $N = 22, 42, 54$ and 82.

The dependence of the escape time $\tau$ of small 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 $\alpha$ of $N$ on the scaling relation. Therefore the scaling relation is $\tau \sim N^{\alpha}$. The results of our simulations implied $\alpha$ to be $\alpha = 2.45 \pm 0.01$. This result of $\alpha$ is closer to the same result for long linear polymer which is $\alpha = 2.5 \pm 0.01$. This scaling relation is also consistent with the Rouse model predictions for linear chains. This equivalence is due to the conformations According to earlier theories, equilibration time also scales similarly as the escape time. Most of the monomers of a long linear polymer are distributed around the pore since it becomes more wrinkled. The ring polymers can be also considered as two linear polymers connected end to end and because of their small $N$ most of the monomers will be located near the pore. These conditions make the local moves during translocation at the pore to have comparable probability and as a result equivalent escape times.

# Chapter 4

# Conclusion

In our computational study, we presented and tested a Monte Carlo algorithm for both static and dynamical simulations of ring polymers. To be physically realistic, we implement a fluctuating bond length between adjacent polymer's monomer molecules to capture a realistic dynamics for ring polymer structures. We presented polymer diffusion and polymer translocation through a nanoscopic pore in the absence of any external driving force or simply as unbiased translocation. We addressed the translocation problem numerically. Our numerical results show that accurate estimates for the scaling exponents of the static behavior of a polymer chain, particularly the average squared radius of gyration as a function of the polymer length $N$ is obtained. We were able to see the dependency of radius of gyration on $N$. In particular, the scaling property of this parameter for ring polymer of considered lengths in our study, is same as to that of the linear chains.

We have also studied the dynamical behaviors of a polymer chain. We calculated the self diffusion constant and the escape time of a ring polymer chain. polymer diffusion plays a major role in the translocation process. In the translocation process we investigated the most probable escape time and the probability distribution of these escape times for different polymer lengths. The presence of the wall produces an entropic barrier between the opposite sides of the pore. Therefore, unlike other translocation kinds, we tried to overcome this entropic barrier by initially placing the central monomers of the ring polymer at the center of the pore or at a symmetric position. This symmetry condition trigger the translocation process of the polymer to either the left or to the right to be equally likely. It was then shown that the translocation time of a polymer chain depends on the chain length $N$. We observe that the ring polymers' escape time scales more or less like the long linear chains with exponent of $\nu = 2.45 \pm 0.01$.

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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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