EXCLUDED VOLUME EFFECTS ON THE CONFORMATION OF SEMI-FLEXIBLE 2D RING POLYMERS

A Thesis Submited to the Department of Physics in Partial Fulfillment of the
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Table of Contents

List of Figures

Abstract

In this paper we investigate the excluded volume effect on the structural and conformational properties of 2D ring polymer chains using lattice Monte Carlo simulation. In order to take into account chain volume exclusion and crossing of bonds, the bond fluctuation algorithm(BFA) was implemented. Monomer chain flexibility was taken into account by producing chain bending rigidity k_s. Chain properties were studied by varying chain size N and the bending rigidity k_s. We have computed key chains physical quantities such as the radius of gyration R_g and persistence length l_p.

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Acronyms

2D - Two Dimensional

MC - Monte Carlo

MCS - Monte Carlo Simulation

DNA - Deoxyribonucleicacid

RNA - Ribonucleicacid

RW - Random Walk

SAW - Slef-Avoiding Walk

SARW - Self-Avoiding Rrandom Walk

EVE - Excluded Volume Effect

EVI - Excluded Volume Interaction

EV - Excluded Volume

MD - Moleculare Dynamics

SM - Simulation Methode

LM - Lattice Model

BFM - Bond Fluctuation Model

VMD - Visual Molecular Dynamics

F - Actin - Filamenteous Actin

Chapter 1

Introduction

Introduction to biopolymers and polymer physics

Although Polymers have been with us from the beginning of time, many people probably do not realize it, everyone is familiar with polymers. They are all around us in everyday use, our life is made of either naturally occurring or synthetic [1, 2]. Natural polymers form the very basis (building blocks) of life at the molecular scale, life is made of biopolymers, such as DNA, RNA and Proteins that are fundamental to biological structure and function. Life itself may cease with out polymer [3, 4].

The number of monomers in a polymer molecule is called its degree of polymerization N. The large degree of polymerization N, makes it possible the study of polymer behaviors using different simplified models via computer simulations without taking into account the chemical details of the chain and these properties become universal behaviors. Accordingly, the large value of N for a chain and its consequence is larger when 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 [5 - 7].

Generally, polymers are studied in the fields such as biophysics, macro-molecular science and polymer sciences which includes polymer physics [8, 9].

1.1 Real Polymer Chains

Real polymer chain is a polymer molecules which have a physical constraints. In any real polymer chain, two monomers cannot occupy the same space. Even a part of a monomer cannot overlap with a part of the other monomer. These excluded volume effect can affect mostly chain

conformation, due to this reason static properties of polymer chain is also affected. This effect plays a far more important role in polymer solutions [2]. This means that real chains look like self avoiding walks (SAW) rather than random walk (RW), when we compared it with the ideal ones.

1.2 Conformations of polymer chain

The key idea to explore real chains and their influence on properties is that of the conformation of a chain. Conformation is the set of possible shapes a molecule can have by means of rotation about single bonds only and used in reference to the outline or shape of the chain molecule. Polymers typically have a very large number of single bonds around which various conformational states can exist, and a polymer molecule as a whole therefore has a very large number of conformational states [10 - 12].

The conformation that a polymer adopts depends on three characteristics. These are flexibility of the chain, interactions between monomers on the chain, and interactions with surroundings. The inherent flexibility of the chain plays a vital role. Some chains are stiff like a piano wire, while others are quite flexible like a silk thread [1, 7 - 8].

Long flexible macromolecules in nature often appear in the form of closed loops (rings). One can find such polymers inside the living cells of bacteria [13] or sometimes higher eukaryotes [12, 14] where DNA occurs in a ring shape [15]. The ring polymer is an important member of the polymer family. In biopolymer science, there exist circular DNA, cyclic peptides, and cyclic oligosaccharides and polysaccharides [16].

Loop formation is an important feature of chromatin organization [16 - 18], playing a vital role in transcriptional regularization of genes and DNA compactification in the nucleus. On the other hand, many synthetic polymers form circular structures during polymerization and polycondensation. Circular macromolecules play a key role in biology and biotechnology, including DNA replication and maintenance of circular genomes [19], DNA looping [20], plasmid-based DNA vaccines[15, 19] , and biologically active macrocycles as drugs [21].

Even though circular macromolecules have an extremely simple structure similar to linear chains but without ends, there are still call into question our understanding of polymer dynamics [17, 18], diffusion [22, 23], and ordering transitions [24], compared to linear macromolecules. The main reason for the difficulty to describe ring polymers lies in the fixed topological state of each

individual ring and the topological interactions with overlapping molecules. The topology and classification of individual rings in terms of "knots"is a long-standing problem in science ranging from early investigations on the nature of atoms and mathematics to applications in modern science. This is an important point, since for polymers it is known, for instance, that the knot type affects swelling, collapse, and average size of a ring polymer.

Ring polymers are intensely studied in polymer physics, primarily due to their status as a model system for understanding the role of chain topology. Statistics of long flexible polymers in good solvents is known to be characterized by a set of universal properties, independent on details of microscopic chemical structure of macromolecules [25, 26]. Considering polymer rings as building blocks, their size and shape are of eminent importance. Both size and shape strongly depend on two internal biopolymer properties, such as the effective radius of gyration of the polymer chain and the ability to bend. Indeed the shape of polymer rings has been investigated theoretically regarding the influence of the polymer flexibility L/l_p, given by the ratio of total polymer length L and its persistence length l_p [27].

Hence, the aim of above section is to introduce the origin of real polymers, Especially ring polymers and its conformation, which are unknotted.

1.3 Excluded Volume effect

Excluded volume(EV) refers to the idea that one part of a long chain molecule can not occupy space that is already occupied by another part of the same molecule. The interaction among the polymer segments is limited to within a few neighbors along the chain. In reality, however, segments distant along the chain do interact if they come close to each other in space. An obvious interaction is the steric effect. Since the segment has finite volume, other segments cannot come into its own region. This interaction swells the polymer. The coil size of a chain with such an interaction is larger than that of the ideal chain which has no such interaction. Even when there are attractive forces, as long as the repulsive force dominates, the polymer will swell. This effect is called the excluded volume effect.

1.3.1 Flory theory and mean field approach

Flory theory was a key step in the history of critical phenomena, especially in seeing the emergence of power-laws and the role of dimensionality d. He analyzed in detail the concept of equilibrium conformation of real chains by using a mean field approach. The equilibrium size is set by a balance between excluded volume which tends to expand the chain size, and a restoring force due to loss of conformational entropy due to swelling. The energetic contribution due to excluded volume is given by the number of excluded volume interactions within a coil and the cost of each exclusion, k_BT. The number of excluded volume interactions is just the probability of finding a monomer within the excluded volume of another. Then Flory takes that all N monomers are uniformly distributed within the total volume R^3 with no correlation between them. If we assume a mean density of monomers in the coil, $\frac{N}{R^3}$, then, the number of excluded volume interactions per monomer is $\nu\frac{N}{R^3}$ for N monomers in the coil. Flory for the first time, estimated the size of a real polymer by identifying the entropic, $F_{ent}(R,N)$, and energetic contribution, $F_{int}(\vec{R},N)$, to the total free energy $F(\vec{R},N)$:

$$F(\vec{R},N) = F_{ent}(\vec{R},N) + F_{int}(\vec{R},N), \tag{1.3.1}$$

Where, N is the effective number of monomers and $\vec{R}$ is the end-to-end vector.

The entropic contribution to the free energy can be calculated from the probability distribution for end-to-end vector of an ideal polymer which follows a Gaussian statistics,

$$P(\vec{R},N) = \left(\frac{3}{2\pi Nb^2}\right)^{3/2} exp\Big[-\frac{3}{2}\frac{R^2}{Nb^2}\Big]. \tag{1.3.2}$$

resulting in the following entropic contributions to the free energy:

$$S(\vec{R},N) = \kappa_B \; logP(\vec{R},N) = S(0,N) - \frac{3\kappa_B R^2}{2Nb^2}, \tag{1.3.3}$$

Where, κ_B is the Boltzmann constant, T is temperature and $S(0,N) = \frac{3}{2}\kappa_B log\left[\frac{3}{2}\pi N b^2\right]$.

Since the free energy of a polymer is given by $F(\vec{R},N) = U(\vec{R},N) - TS(\vec{R},N)$, the entropic energy due to expansion of a polymer can takes the form:

$$F_{ent}(R,N) \sim k_B T \frac{R^2}{Nb^2}, \tag{1.3.4}$$

and then for a real polymer the energetic contribution to the free energy per unit volume F_{int}/V can be calculated by carrying out a virial expansion in powers of the monomer number density c_n.

$$\frac{F_{int}}{V} = \frac{\kappa_B T}{2}\left[\nu_{exc} c_n^2 + \omega c_n^3 + ...\right] \approx \frac{\kappa_B T}{2}\left[\nu_{exc}\frac{N^2}{R^6} + \omega\frac{N^3}{R^9} + ...\right], \tag{1.3.5}$$

Where, the coefficient of the c_n^2 term is proportional to the excluded volume and the coefficient of the c_n^3 is related to the three body interaction coefficient $\omega \approx b^6$, b is a unit lattice spacing distance between monomers.

In a good solvent, the repulsive nature of the effective monomer-monomer interactions swell the chain. Since under these conditions, the three body interaction term is not important, the equilibrium size of the polymer can be evaluated by just retaining the entropic and the repulsive excluded volume interaction terms. As a result, the repulsion energy is proportional to the excluded volume v_{exc} of each pair of monomers times the number of monomer pairs N^2 per unit of available volume R^3, that is:

$$F_{int}(R,N) \sim \nu_{exc} k_B T \frac{N^2}{R^3}, \tag{1.3.6}$$

Hence, at temperature T the total free energy $F(R,N)$ of the polymer can be written as:

$$F(R,N) = F_o + e_o v_{exc}\frac{N^2}{R^3} + e_1\frac{R^2}{Nb^2}, \tag{1.3.7}$$

Where, e_0 and e_1 are T dependent constants, and F_0 is the remaining part of the free energy. The equilibrium size of an unconstrained polymer would come from a minimization of $F(R,N)$ with respect to R which amounts to equating the two R dependent terms in $Eq.(1.3.7)$.

$$\frac{\partial F(R,N)}{\partial R} = 0, \tag{1.3.8}$$

Which results in

$$R \approx N^{3/5}\nu_{exc}^{1/5} b^{2/5}, \tag{1.3.9}$$

Therefore, Flory theory predicts the scaling for the chain size as:

$$R \sim N^{\nu}, \tag{1.3.10}$$

Where, $\nu = 3/5$ is **Flory exponent** in a three dimensional($3D$) lattice.
The above argument can be generalized to arbitrary dimensions d. The entropy term as given by $Eq.$(1.3.4) is independent of d, but the excluded volume term in $Eq.$(1.3.6) would be replaced by N^2/R^d , R^d being the volume occupied by the polymer. This modifies the free energy as,

$$F(R,N) = F_o + e_o v_{exc}\frac{N^2}{R^d} + e_1\frac{R^2}{Nb^2}, \tag{1.3.11}$$

Minimization of Eq.(1.3.11) then gives,

$$R \sim N^{\nu}, \tag{1.3.12}$$

Equation 1.3.12 leads to an important result of general scaling relation between number of monomers and the static property R_g of a polymer.
Where, the Flory exponent as $\nu = \dfrac{3}{d+2}$. So that the general Flory exponent can be:

$$\begin{aligned} \nu &= \frac{3}{d+2}, \quad for \quad d \leq 4, \\ &= \frac{1}{2}, \qquad for \quad d > 4, \end{aligned}$$

Which agrees with the known exact results like, $\nu = 1$ for $d = 1$, $\nu = \dfrac{3}{4}$ for $d = 2$, $\nu = \dfrac{1}{2}$ for $d > 4$ and is very close to the best estimate $\nu \approx 0.588$ known for $d = 3$ [28, 29].

1.3.2 Mean square Radius of gyration $\langle R_g^2 \rangle$

A more convenient quantity is the radius of gyration $\vec{R}_g$, that measures the dimension of the polymer relative to its center of mass. Since, all objects possess a radius of gyration, it can characterize the size of polymers of any conformation. The square radius of gyration defined as the average square distance between monomers in a given conformation and the polymer's center of mass $\vec{r}_{cm}$ is given by

$$\vec{r}_{cm} = \frac{1}{N}\sum_{i=1}^{N}\vec{r}_i. \tag{1.3.13}$$

The square of the radius of gyration, R_g^2 with Eq.(1.3.13) is given by

$$R_g^2 = \frac{1}{N}\sum_{i=1}^{N}\langle(\vec{r}_i - \vec{r}_{cm})^2\rangle. \tag{1.3.14}$$

where, $\vec{r}_{cm}$ is the position vector of the polymers center of mass and $\vec{r}_i$ is the position vector of i^{th} monomer.

1.4 Bending potential

For modeling a polymer chain with excluded volume interaction(EVI) and chain stiffness, the bending potential $U_{bending}$ is most applicable. Considerable theoretical works and computer simulations have been devoted to scaling properties of polymers. Although excluded volume effects(EVE) and chain stiffness k_S in polymer have already been studied by many previous works, it seems still interesting to characterize the influence of the chain stiffness on the structure and conformation and the scaling laws $\langle R_g^2 \rangle \sim N^{2\nu}$ of excluded volume(EV) chains, especially for semi-flexible chains with bond angle θ. The present work is a study of the scaling properties of such semi-flexible polymer chains with excluded volume effects and stiffness simulated by 2D Monte Carlo simulation.

To model the stiffness of polymer chains, a bending potential $U_{bending}$ is added into the interactions of neighboring beads. The bending potential between two successive bonds is taken as:

$$U_{bending} = k_s(1 + cos\theta). \tag{1.4.1}$$

Where, θ is the bond angle between two successive bond vectors $\vec{r}_i$ and $\vec{r}_{i+1}$. k_s is the bending force constant, which has ranging in our simulations to study the effects of chain stiffness. In the simulations of the first case, bending force constant k_s is set as 0 to model semi-flexible ring polymer chains with only excluded volume effects(EVE) or (no stiffness, $k_s = 0$), but our discussion is concerning for different value of bending force constant k_s.

1.5 Tangent-tangent correlation function

The semi-flexible polymers are modeled as an elastic rod with bending force constant k_s. Representing the polymer by a differential space curve $r(s)$ of length L parametrized by an arc length s, its statistical properties are determined by the elastic energy,

$$H = \frac{k_s}{2} \int_0^L ds(\frac{\partial t(s)}{\partial s})^2. \tag{1.5.1}$$

A central property of the polymer chain is its persistence length l_p , which is the tangent vector correlation length. correlation is a single quantity which describes the degree of relation between variables. The bending force constant must have a relation with the persistence length. To find this relation, calculate the correlation function.

$$\langle t(s).t(s') \rangle = exp(\frac{-|s - s'|}{l_p}). \tag{1.5.2}$$

The persistence length is thus the ratio between bending stiffness k_s and thermal energy k_BT and is therefore a measure of the stiffness of a polymer. The persistence length measured in

units of total polymer length $\frac{L}{l_p}$ [30].

Where, $t(s)$ is the tangent unit vector, s the contour length, and $\langle ... \rangle$ denotes the configurational average. The persistence length is interpreted as a measure of the chains stiffness, is given as

$$l_p = \frac{2}{d-1}\frac{k_s}{k_B T}. \tag{1.5.3}$$

Hence, a large persistence length means directional accordance of averaged tangent chain vectors over large distances on the chains contour. A large persistence length is therefore an indication for stiffness. In contrast, a small persistence length results from low directional tangent vector correlation, which means high flexibility.

Chapter 2

Computational techniques and methods

For deal the properties of polymer, particularly polymer chain conformation in equilibrium, there are many kinds of simulation methods. But, the two most widely used methods and preferably related to this work and Epecially for atomic-level modeling are **Monte Carlo (MC) and molecular dynamics(MD)**.
With Monte Carlo (MC) in each stage, a random move of a molecule is attempted. The random numbers are used to decide whether or not to accept the move, and the decision depends on how favorable the energy change would be. In molecular dynamics (MD) from the molecular positions, the forces acting on each molecule are calculated. These are used to advance the positions and velocities through a small time step [31]. The choice between Monte Carlo and molecular dynamics is largely determined by the phenomenon under investigation. For our problem Monte Marlo Method is most preferable.

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 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). Thus, the simulations are performed with the standard bond-fluctuation model, which is described in the following.

2.1 Bond fluctuation model and simulation method

2.2 Bond fluctuation model

The original Bond Fluctuation Model(BFM) was introduced by Carmesin and Kremer. It was proposed as an alternative to a (single-site) SAW model, which retains the computational efficiency of the lattice without being plagued by severe ergodicity problems [32].
BFM gets its name from the fact that the length of the bond or vector, l, connecting successive beads along a chain, fluctuates over a significant range.

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 (e.g. a square lattice $2D$). This enlarged monomer size has two important consequences:

1. A priori, many different bond vectors can occur. This multitude is restricted by two conditions.
First, adjacent monomers may not overlap. This limits the bond length $l \geq l_{min} = 2$ (in units of the lattice constant).
Second, the hard-core monomer- monomer interaction should suffice to prevent two bonds from intersecting each other in the course of the simulation.
In $2D$ this only imposes an upper bound on the bond length $l \geq l_{max} = \sqrt{13}$, some smaller bond vectors also have to be excluded.

2. Ergodicity problems are much less severe than for the single-site SAW.
For the BFM a local N-conserving move 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 vectors constraints of the above conditions and the excluded volume interaction, the move is accepted.

2.2.1 Simulation method

The general idea of the analysis is to create a model, which is as similar as possible to the real physical system of interests. Let us see the following procedures.

For modeling a polymer chain with excluded volume and chain stiffness, the bending potential

$U_{bending}$ is most applicable. To model the stiffness of ring polymer chains, a bending potential $U_{bending}$ is added in to the interactions of neighboring beads. The bending potential between two successive bonds is

$$U_{bending} = k_s(1 + cos\theta). \tag{2.2.1}$$

Where, θ is the bond angle between two successive bond vectors, k_s is the bending force constant.

Generally, for all the simulations, we prepare a simple and 2D square simulation box of 10000×10000 square lattice cells of unit length each. In order to obtain the initial configuration, polymer beads are placed in respecting ring polymer form symmetrically 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.
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. A typical simulation then proceeds as follows.

Chain motion is achieved by selecting a monomer randomly and then selecting one of the four lattice directions randomly with equal probability and move the selected monomer in the selected direction by one lattice spacing. Then check, if the trial move violates self avoidance condition(excluded volume and bond length restrictions) and trial move increases the bond length beyond $\sqrt{13}$. If it does, then reject the trial move by placing the monomer in its earlier lattice position. If both requirements, self avoidance and bond length restrictions are met, then take the trial conformation for further processing through Metropolis algorithm and accept the move and update the new lattice conformation.

One of the most important aspects when simulating this system is characterizing equilibration, since, before attempting to perform any measurement, the system should be allowed to reach equilibrium. Characterization of the equilibrium state is a quite delicate task, especially for our system, whose properties fluctuate considerably in time. Thus, equilibration can be performed through the chain diffusion in a reasonable amount of computing time (not significantly larger than the final run to determine properties).

In simulations to model semi-flexible ring polymer with only excluded volume effects(EVE) the bending force constant k_s is set as 0. To model rigid ring polymer with excluded volume effects(EVE), and chain stiffness, the value of bending force constant k_s is set as 15. The resulting configuration are shown in Figure 2.1 and Figure 2.2, respectively.

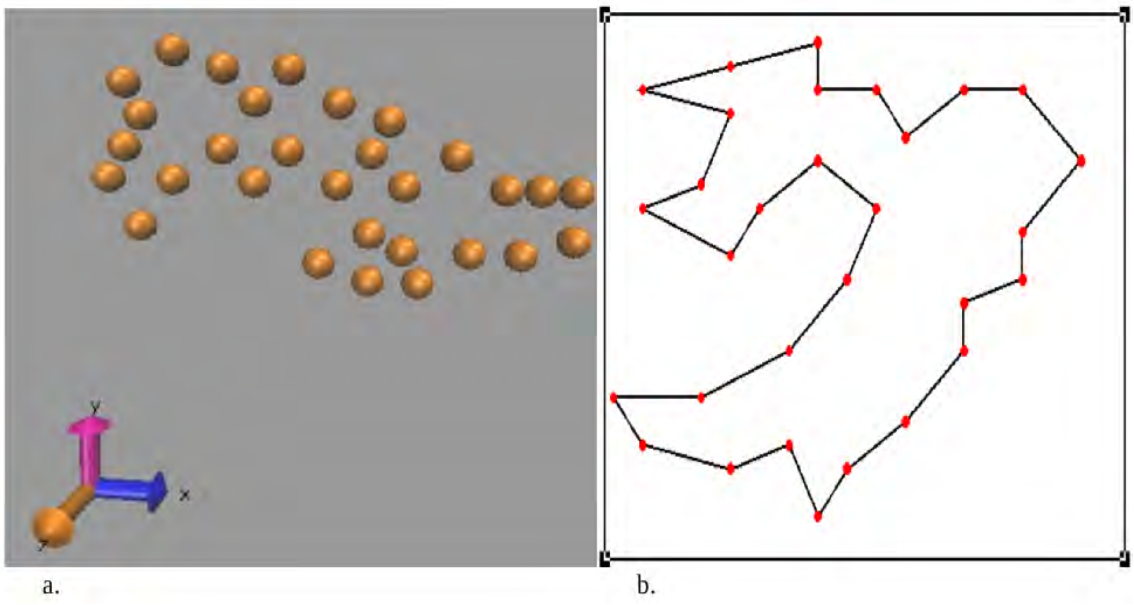

Figure 2.1: **a**.This is snapshot picture taken from the **VMD(Visual Molecular Dynamics)** graphics and **b**. **grace** graphics during the simulation work when the polymer chain size($N = 30$). This is the conformation for **bending force constant**($k_s = 0$) and after relaxation for 10^6 Monte Carlo steps.

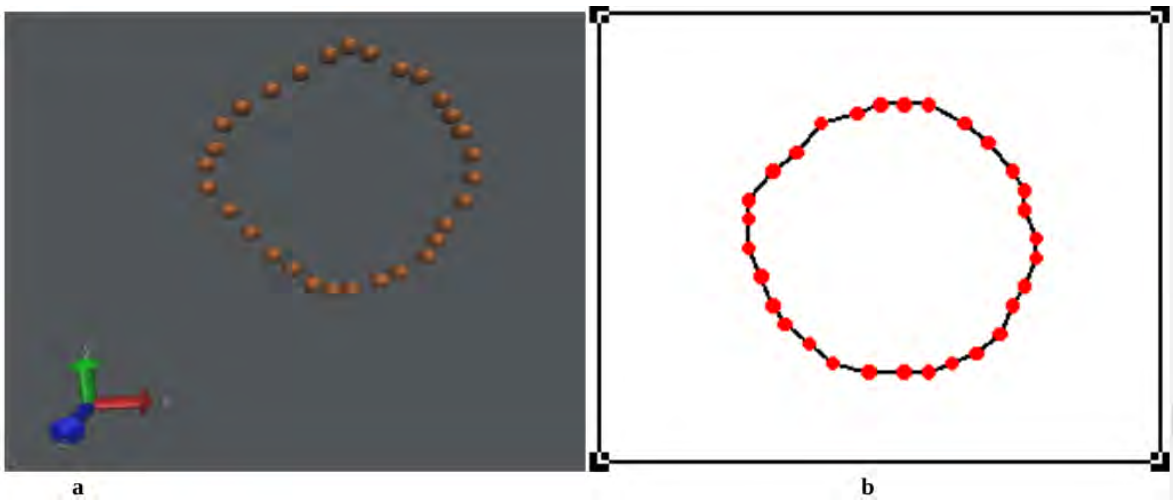

Figure 2.2: **a**.This is snapshot picture taken from the **VMD(Visual Molecular Dynamics)** graphics and **b**. **grace** graphics during the simulation work when the polymer chain size($N = 30$). This is the conformation for **bending force constant**($k_s = 15$) and after relaxation for 10^6 Monte Carlo steps.

Chapter 3

Results and discussion

The results of our study are presented and discussed as, the structural and conformational properties of polymer chains, scaling laws and the persistence length of tangent-tangent correlation were computed results as written briefly below.

3.1 The investigation of the effect of chain stiffness on the structural and conformational properties of semi-flexible ring polymer chain

Polymers are repeating units of atoms that form a chain. As the length of this chain increases, the polymers molecular weight increases. Simple polymers are by definition then, short chain, low number of atoms per molecule structures. Longer chains equal larger molecular weight polymers.

Most polymers become less stiff or high stiff as it depends on their bending potential. The low bending potential of polymer chains are given more freedom to move and the high bending potential of polymer chains are not given more freedom to move. Indeed, excluded volume effect and bending force constant affects polymer conformation and induces conformational transitions as shown in Figure 3.1 concerning on semi-flexible polymer rings. A conformational transition is observed to arise in the semi-flexible regime with bending force constant, non-existing in the stiff regime.

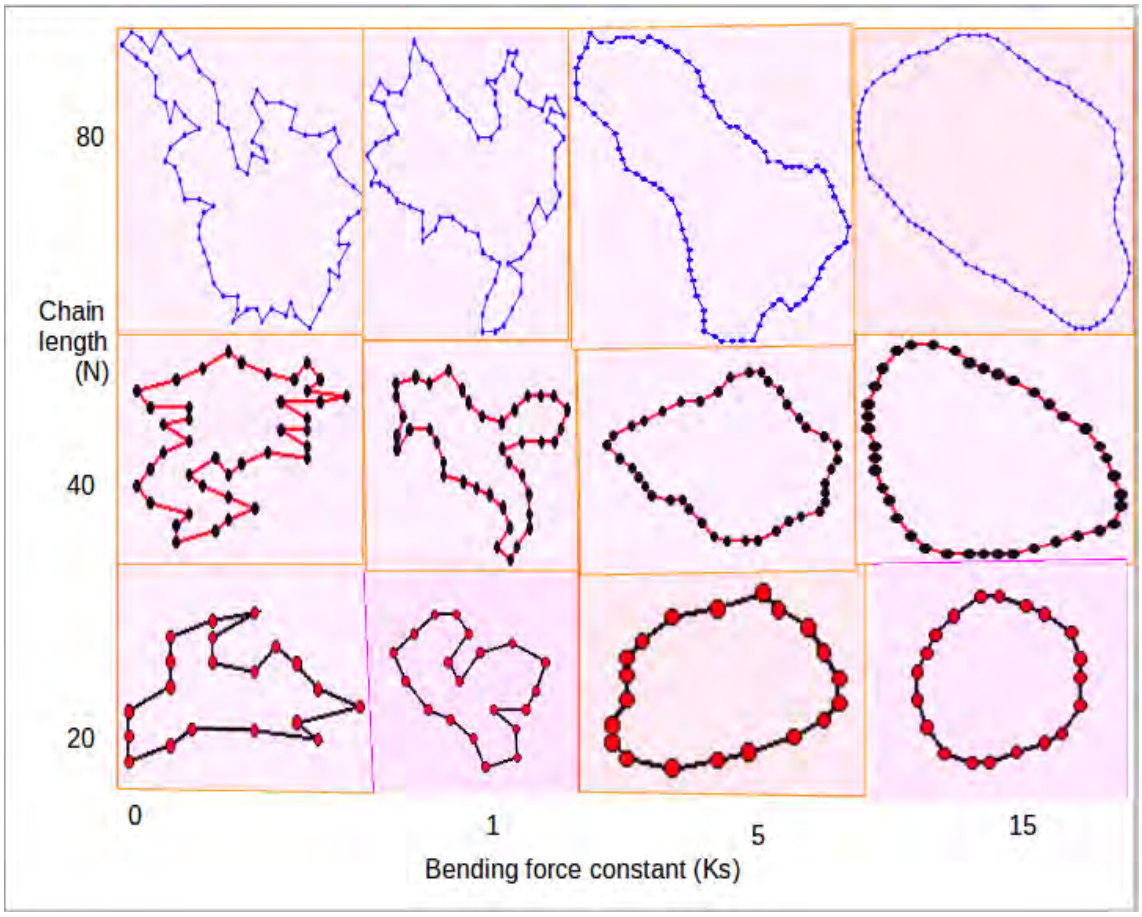

Figure 3.1: Result for different values of chain length N versus different value of bending force constant k_s. It shows that, **the effects of Chain Stiffness on the structural and conformational properties in Monte Carlo simulation** with (chain length $N = 20$, 40, and 80 and bending force constant $k_s = 0$, 1, 5, and 15).

Figure 3.1 shows, the small/short polymer chain is the more rigid it can get than the large/longer polymer chain with in the same bending force constant k_s. Since, the stiff chains are harder to pull it makes flexible. These will tangle up as much, they are strong for a different reason stiff chains can pack together and stick to each other.

3.2 The effect of chain stiffness on statics properties of semi-flexible ring polymer chain

As we have discussed in Eq.1.3.12 the equilibrium properties of a linear polymer, from Florys theory, yields a universal power-law dependence of the number of monomers N on the size of the polymer. In a linear polymer the scaling measures the equilibrium size as $R^2 \sim N^{2\nu}$. Where, the scaling exponent is a dimension dependent value of $\nu = 3/(2+d)$, $= 0.75 = 3/4$ represents for self-avoiding random walk exponent in a two dimensional($2D$) lattice.

This also leads to an important result of general scaling relation between number of monomers and radius of gyration of a polymer. This scaling arguments is defined as $R_g^2 \sim N^{2\nu}$.

The plots of Figure 3.2 the log-log pair of the mean square radius of gyration $\langle R_g^2 \rangle$ of ring polymer for different value of bending force constant k_s and values of the number of monomers N are the simple straight lines, were fitted by linear-law function to lines with slope 2ν. Then the value of the slope for each line becomes 2ν = 1.49, 1.52, 1.72, 1.86, 1.96 for the value of bending force constant k_s = 0, 1, 5, 10, and 15 respectively. Clearly, this implies that the scaling exponent ν assumes a value of 0.745 for the case of bending force constant $k_s = 0$, but for an increasing bending force constant ($0 < k_S \leq 15$) the scaling exponent ν and radius of gyration $\langle R_g^2 \rangle$ of ring polymers are increase.

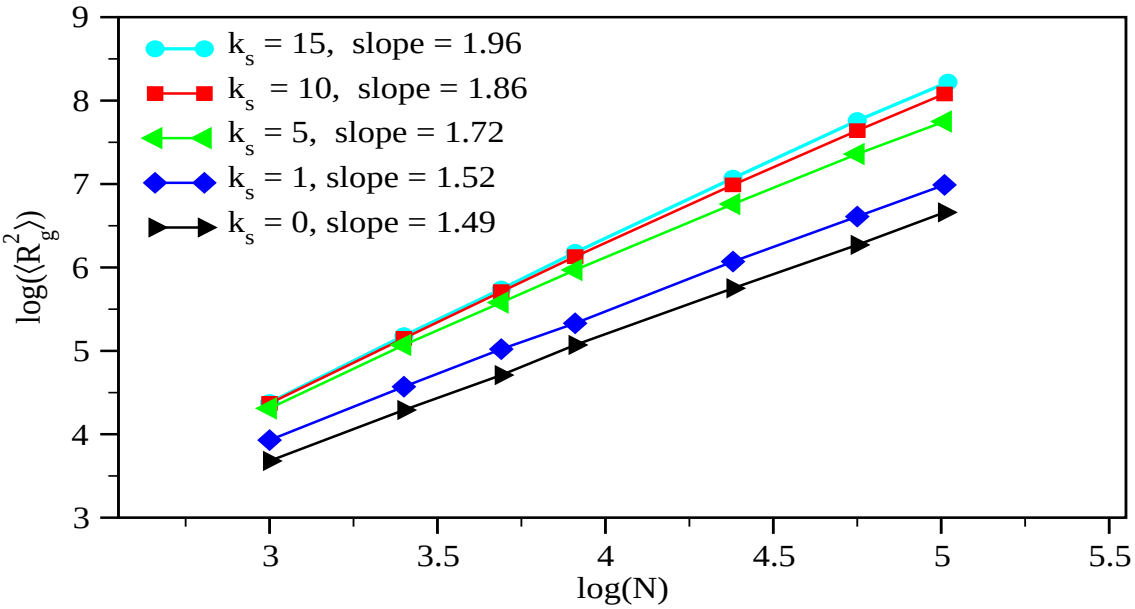

Figure 3.2: Log-log plot of radius of gyration $\langle R_g^2 \rangle$ versus chain length N for self- avoiding walk(with chain length N = 20, 30, 40, 50, 80, 116, 150 and bending force constant k_s = 0, 1, 5, 10, and 15).

For the case of bending force constant $k_s = 0$, result indicates that, for relatively small ring polymer chains considered in our simulations, $20 \leqslant N \leqslant 150$, scaling exponent $\nu \approx 0.75$ is approximately the 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 a scaling power-laws. This leads to conclude that, the radius of gyration R_g of ring polymers are scaling up in the same fashion like a linear chain polymers. But for the case of bending force constant k_s greater than zero the value of the exponents are greater than

from the Flory-theory suggested.

3.3 The effect of chain stiffness on the value of exponent

The scaling exponent ν is extracted from the slope of the values of mean square radius of gyration $\langle R_g^2 \rangle$ of ring polymers for different value of bending force constant k_s and the number of monomers a power of two-wise of exponent $(N)^{2\nu}$, were fitted by power-law function to lines. From these values, the exponent versus bending force constant k_s were plotted as described Figure 3.3.

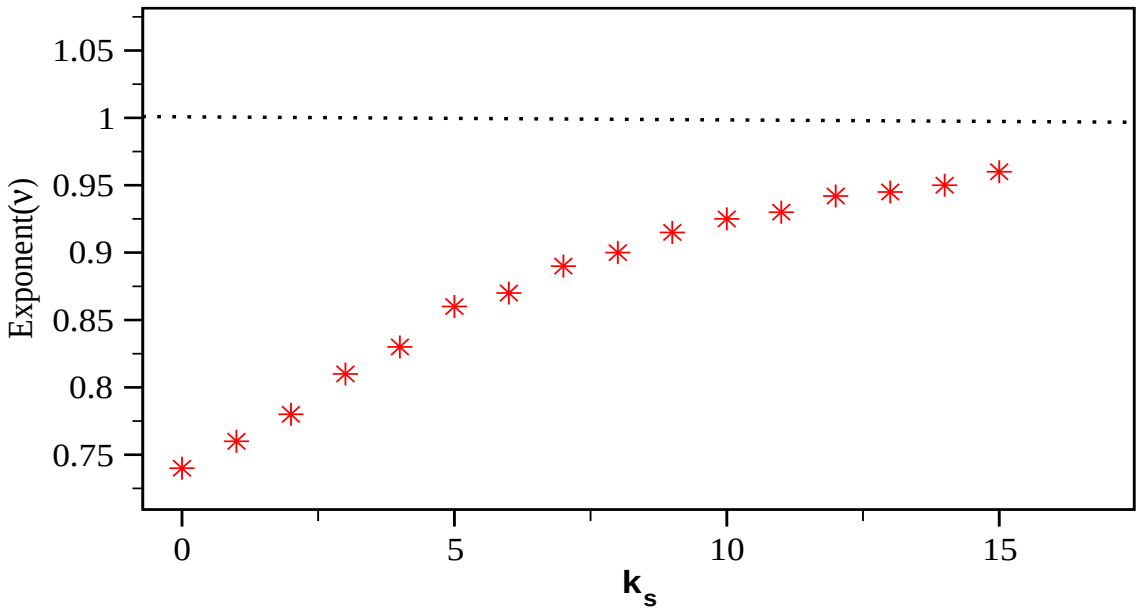

Figure 3.3: The exponent as a function of bending force constant k_s for chain length of (N=20, 30, 40, 50, 80, 116 and 150) and bending force constant ($0 \leq k_S \leq 15$).

The result show that, when the bending force constant k_s is increase and also the exponent ν is slightly increase up to very close to one. This means scaling exponents are in quite satisfactory agreement with those of semi-flexible ring polymer chain becomes and formed circular polymer chain model, indicating that chain stiffness does not influence these scaling properties of the model.

The small rings are quite stiff and can be considered as compact structures with comparable conformation size as the long polymers. Here, the small ring polymers considered here are relatively stiff since EV effect criteria is included during the local moves. Such increase of ν along with stiffness is also evidenced on recent experiment on circular DNA. The experiment showed that ν of a circular DNA changed from 0.75 to 1 as the circular DNA becomes smaller

because a short circular DNA was quite stiff[33].

3.4 The effect of Chain Stiffness on the value of radius of gyration of Semi-flexible ring polymer

The mean square radius of gyration is an indicator of the average conformation size of the polymers. This important static property indicator parameter is dependent on the number of monomers of polymer chains. The plot of the mean square radius of gyration of ring polymers size, $\langle R_g^2 \rangle$ against bending force constant k_s, as represented on Figure 3.4 shows this interdependence.

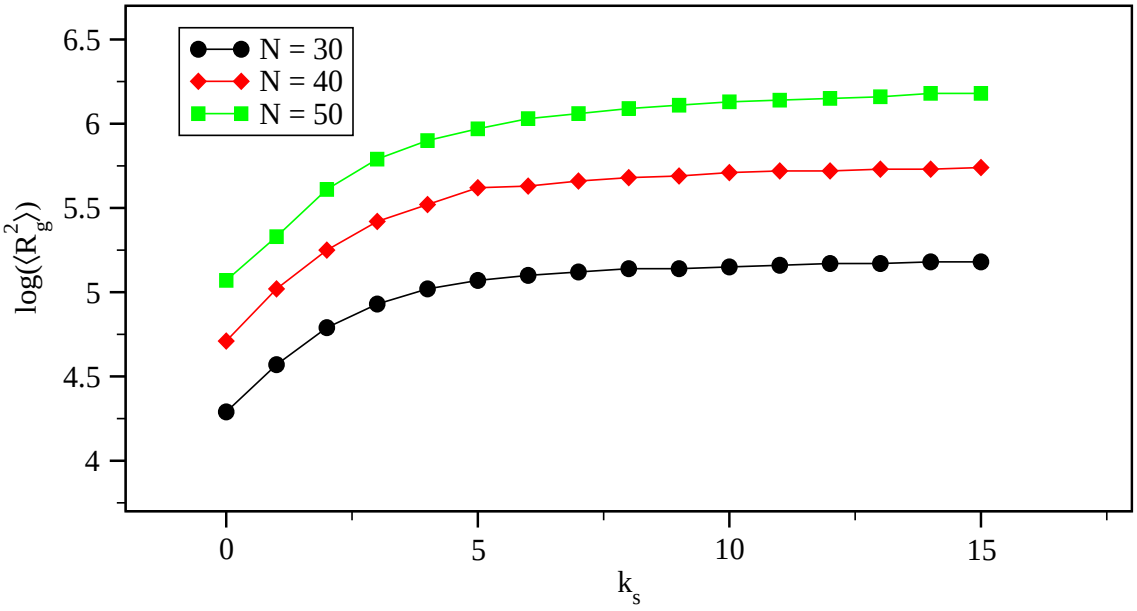

Figure 3.4: The log-mean square radius of gyration $\log(\langle R_g^2 \rangle)$ as a function of different bending force constant (k_s) and the effect of chain stiffness on radius of gyration with the value of chain length ($30 \leqslant N \leqslant 50$) and bending force constant ($0 \leq k_s \leqslant 15$) for the simulation.

The result of Figure 3.4 clearly shows that, the average radius of gyration $\langle R_g^2 \rangle$ for a ring polymer chain of length N increases when the bending force constant k_s increases. The average radius of gyration of ring polymers after some increasing stage it becomes constant as shown each line in the Figure 3.4.

The constant of the average radius of gyration $\langle R_g^2 \rangle$ of ring polymers occurs due to the bending force constant is slightly increases the ring polymer of chains length becomes stiff and rigid, therefore the conformation and the center of mass of ring polymer chains are not much changed. By this reason, the mean square radius of gyration of ring polymer is becomes constant.

3.5 The fluctuation of average radius of gyration with the increasing bending force constant

For each bending force constant k_s the average square distance between monomers in a given conformation and the ring polymers center of mass can be fluctuated by $\frac{\langle R_g^2\rangle}{(\langle R_g\rangle)^2} - 1$. The bending force constant k_s is lower for a given ring polymer chain the fluctuation of radius of gyration is higher. Because average square distance between monomers in a given conformation can be free When the bending force constant k_s increases the ring polymer chains become stiff and rigid also the fluctuation of the value of mean square radius of gyration tends to zero.

$$\frac{\langle R_g^2\rangle}{(\langle R_g\rangle)^2} - 1 \approx 0. \tag{3.5.1}$$

Which is plotted in the following Figure 3.5.

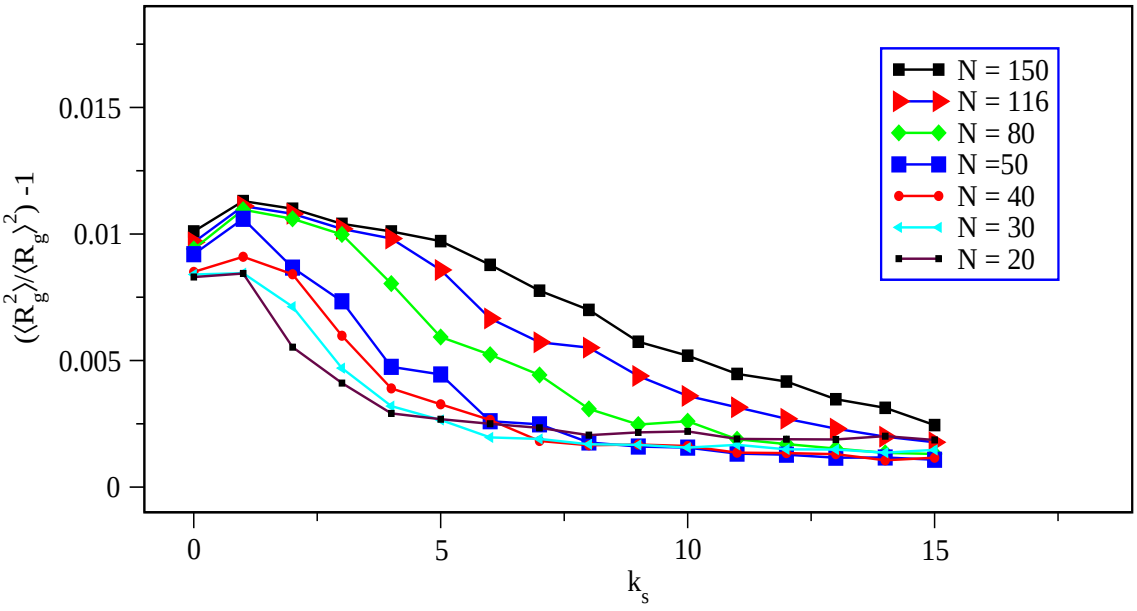

Figure 3.5: Shows that, the fluctuation of radius of gyration $\frac{\langle R_g^2\rangle}{(\langle R_g\rangle)^2} - 1$ with different chain length as a function of different bending force constant ($0 \leq k_S \leq 15$) with the chain length (N=20, 30, 40, 50, 80, 116 and 150).

As we see from Figure 3.5, the fluctuation of average radius of gyration after some decreasing stage it becomes constant. The constant of average radius of gyration occurs due to the bending force constant is increases the ring polymer of chain length becomes stiff and rigid, therefore the conformation of ring polymer chain is not much changed, the ring polymer chain length is not changed, the center of mass of ring polymer chain is not much changed and the reason the fluctuation of average radius of gyration is becomes constant.

3.6 The effect of chain stiffness on tangent-tangent correlation of semi-flexible ring polymer

The following results are performed for tangent-tangent correlation of semi-flexible ring polymer chain for different number of monomer N and bending force constant k_s. By setting the different value of bending force constant between $0 \leqslant k_s \leqslant 10$, we have found that the tangent correlation of ring polymer chain. The bending force constant have a relation with the persistence length. To find this relation we need to calculate the correlation function as:

$$\langle t(s).t(s')\rangle = exp(\frac{-|s-s'|}{l_p}). \tag{3.6.1}$$

3.6.1 The effect of chain stiffness on tangent-tangent correlation for number of monomer(N = 40)

Chain stiffness strongly affects the tangent correlation and thus the persistence length. To examine impact of chain stiffness on tangent correlation of ring polymer and persistence length l_p, the value of tangent correlations versus $|s-s'|/L$ were drawn in Figure 3.6.

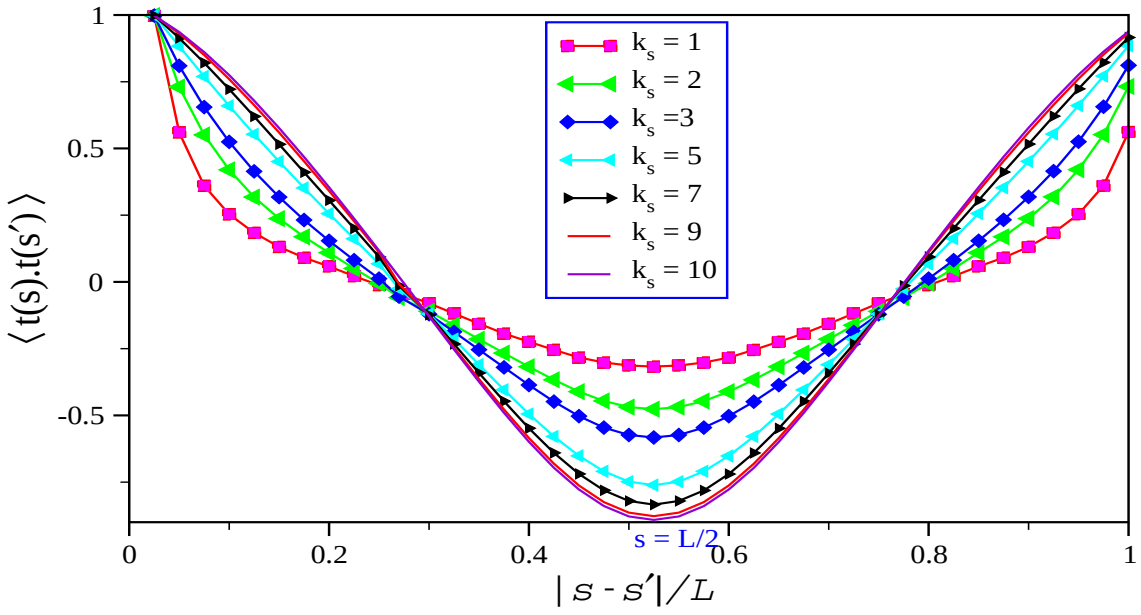

Figure 3.6: Mean tangent-tangent correlation $\langle t(s).t(s')\rangle$ along the polymer backbone $s \in [0, L]$, semi-flexible ring polymer over bending force constant $(1 \leqslant k_s \leqslant 10)$ and N = 40.

The result shows, with the increase of bending force constant k_s the steepness of curves monotonically decreases, but that the decline rate of steepness of curves also decreases. When k_s is over 7, all curves almost coincide (simulations with $k_s = 9$, 10 were performed). The steepness of curve reflects the decay rate of tangent correlation. The bigger the steepness, the more rapidly tangent correlation decay. This can explain the fact that the bigger k_s is, the farther the correlation

pass along through the chain. The saturation effect observed for $k_s > 7$ indicates that the fluctuations of the bond angle become very small for these stiffness values.

The short ring polymer restricts the available conformational space, thus increasing the directional correlation. The negative directional correlation is a relationship between two variables in which one variable increases as the other decreases, and vice versa. As shown the statistics of Figure 3.6, a perfect negative correlation of ring polymer is represented by the value -1, while a 0 indicates no correlation and +1 indicates a perfect positive correlation of ring polymer. In order to respect the circular topology, the correlation function must become more negative on distances $s = L/2$. In summary, the short polymer appears effectively stiffer.

3.6.2 The effect of chain stiffness on tangent-tangent correlation for number of monomer(N = 100)

The tangent-tangent correlation of ring polymer exhibits an oscillatory character and the negative directional correlation decreased. The oscillatory behavior of the tangent-tangent correlation function becomes more pronounced with increasing the bending force constant k_s and ring polymer chain rigidity.

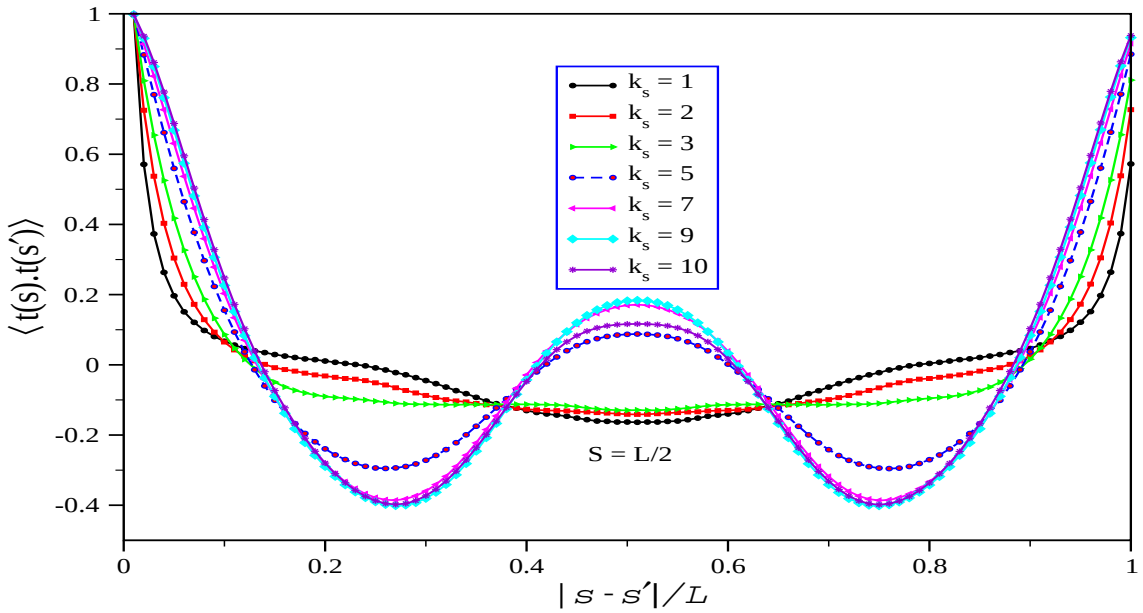

Figure 3.7: Mean tangent-tangent correlation $\langle t(s).t(s')\rangle$ along the polymer backbone $s \in [0, L]$, semi-flexible ring polymer over bending force constant $(1 \leqslant k_s \leqslant 10)$ and N = 100.

As we seen in Figure 3.7, the symmetry of the correlation function situated at half the distance along the polymer backbone $s = L/2$ arises due to the topology of a ring. The negative

directional correlations do not reach down to $\langle t(L/2)t(s')\rangle = -1$ due to fluctuations. With increasing flexibility the ring topology locally loses influence of the bending force constant k_s, thus the correlation function gradually approaches a symmetric exponential decay.

3.6.3 The effect of chain stiffness on tangent-tangent correlation for number of monomer(N = 200)

In this part also the tangent-tangent correlation of ring polymer exhibits the increased number of an oscillatory character and the negative directional correlation much decreases we compared with Figure 3.6 and Figure 3.7. The degree of polymerization $N = 40 < 100 < 200$. So, when the bending force constant increase between $(1 \leqslant k_s \leqslant 10)$, those type of polymer chain becomes stiff and stiff, but small polymer chain more stiffer than from larger one.

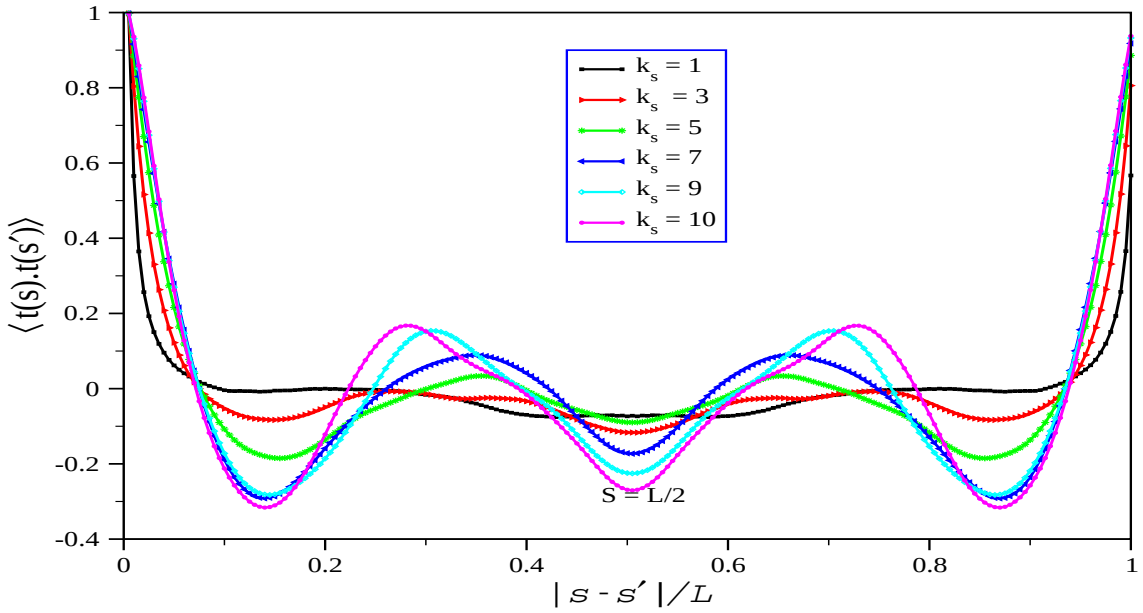

Figure 3.8: Mean tangent-tangent correlation $\langle t(s).t(s')\rangle$ along the polymer backbone $s \in [0, L]$, semi-flexible ring polymer over bending force constant $(1 \leqslant k_s \leqslant 10)$ and N = 200.

As we observe from Figure 3.8, rather than respecting the circular topology and negative directional correlation on distances, it is pushed to respect the number of oscillation and fluctuation due to degree of polymerization N and bending force constant k_s. The correlation function does not become more negative. In summary, the long polymer appears effectively flexible.

3.6.4 The interdependence of persistence length on chain stiffness

It should be clear that, the persistence length l_p is actually a measure of flexibility of ring polymer, because the relative orientations of sections of the ring polymer chain separated by more than this length are certainly random, whereas sections of the ring polymer chain that are somewhat closer together have non-random relative orientations. Slightly more sophisticated considerations lead to the flexible ring polymer chains have low persistence lengths and rigid ring polymer chains have high persistence lengths l_p.

Chain stiffness strongly affects the persistence length l_p. To examine impact of chain stiffness on persistence length, tangent correlations versus $|s - s'|/L$ were drawn in Fig 3.6, 3.7 and 3.8. The persistence length l_p was extracted by fitting the tangent correlation function with the non-linear curve fitting-law of function. The result is plotted as Figure 3.9.

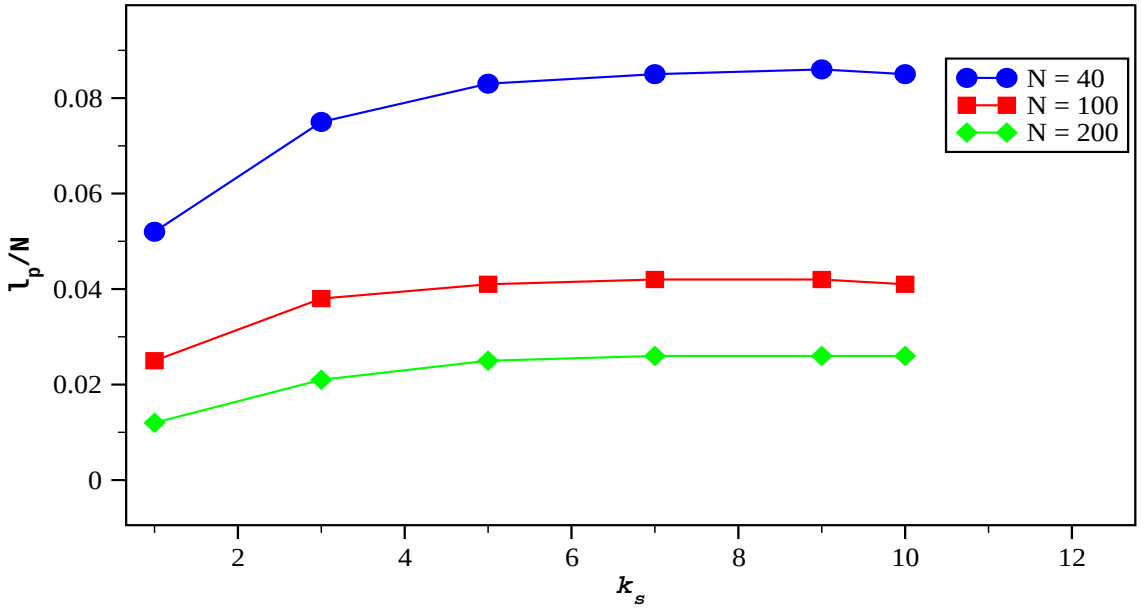

Figure 3.9: The scaled persistence length l_p/N as a function of bending force constant k_s for different value of number of monomers N.

The result shows that, when the bending force constant k_s increases and also scaled persistence length l_p/N increase but, it can increase until the ring polymer chains are stiff, after stiffed the scaled persistence length is constant. Its scaled persistence length l_p/N of monomer number of $40 > 100 > 200$, because short/small ring polymer chains are stiffer than long/large ring polymer chains.

3.6.5 The Comparison between persistence length of different ring polymer chain for increasing bending force constant

The scaling persistence length l_p/N and different degree of polymerization N for different bending force constant k_s is described in the Figure 3.10.

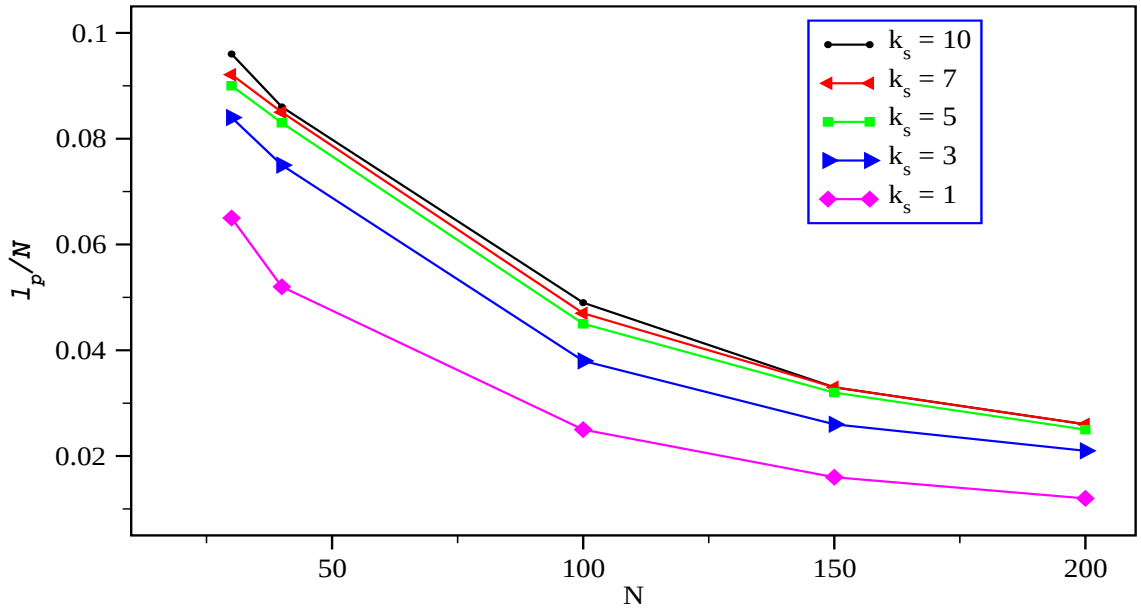

Figure 3.10: The scaling persistence length l_p/N as a function of chain length ($N = 30, 40, 100, 150, 200$) for a given bending force constant.

The result in Fig 3.10 shows that, the size of ring polymer chain N increases but, the scaled persistence length l_p/N slightly decreases from small ring polymer chain of high scaled persistence length to large ring polymer chain of low scaled persistence length. Because the small ring polymer chain is stiffer than that of larger ring polymer chain with in the same bending force constant.

3.6.6 The flexibility for polymer chain (N = 40)

One of the most basic characteristics of macromolecules is the flexibility L/l_p of the polymer chains. Any long macromolecule is flexible, but different polymers have different mechanisms of flexibility L/l_p. As shown in the following figure, $\langle R_g^2 \rangle$ normalized with the radius of gyration of a rigid circle, namely $\langle R_g^2 \rangle / R_c^2$, is plotted versus the flexibility parameter L/l_p for the considered ring polymer chain models.

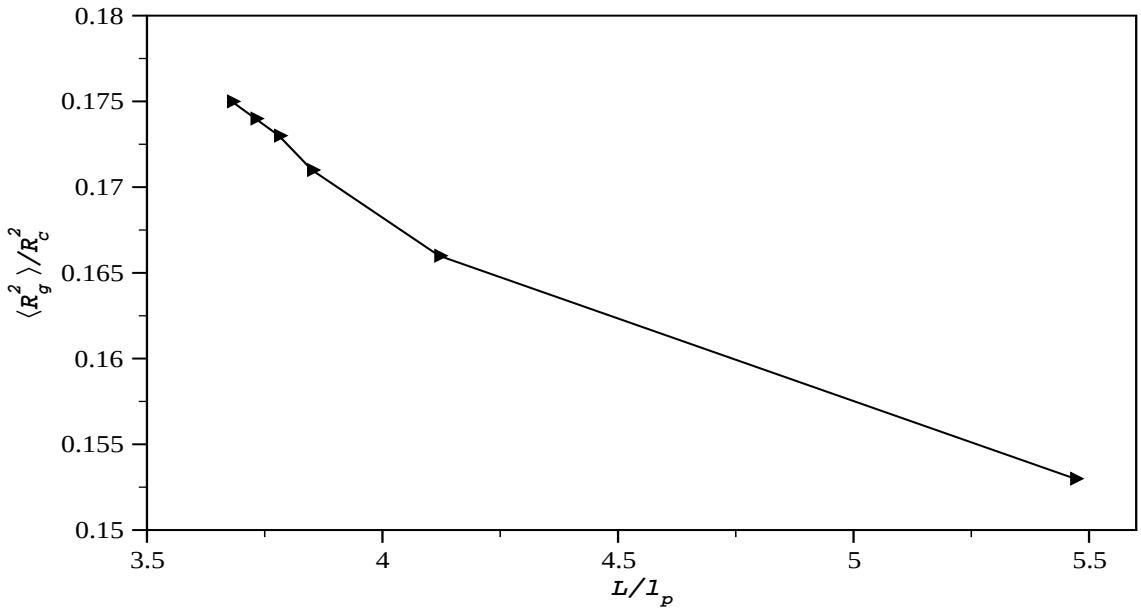

Figure 3.11: Squared radius of gyration $\langle R_g^2 \rangle(N)$ compared to the size of the corresponding rigid ring R_c^2 or $(L/2\pi)^2$ and L/l_p.

The linear decay shows that, stiff regime extends up to high flexibilities. This effect can be accounted for an effective stiffening due to the topology of a ring polymer chain. For polymers with different bending force constant the squared radius of gyration follows the result for the stiff limit up to even higher flexibilities of approximately L/l_p indicating a further effective stiffening due to the polymer size, i.e., as a result of chain stiffness and excluded volume. Similarly, this effective stiffening also affects the overall size of the polymer as measured by the squared radius of gyration $\langle R_g^2 \rangle$. This is in agreement with the observation of enhanced correlations in the tangent-tangent correlation.

Figure 3.11 is in agreement for semi-flexible ring polymer chains, providing solid evidence that a description of DNA as a semi-flexible polymer with persistence length l_p and gives a faithful description of DNA conformations.

Chapter 4

Summary and conclusion

In this work, we have analyzed the impact of excluded volume effect and chain stiffness on the structural and conformational properties of semi-flexible ring polymer chain using **2D** lattice Monte Carlo simulations by taking in to account chain size N and bending rigidity k_s. From the comparison of the models, we determined two core effects.

First, in the semi-flexible regime Florys swelling is recovered. We have examined this, using the bending force constant k_s as tune and setting between $0 \leqslant k_s \leqslant 15$. It could be affected the conformation of our model and its statics properties(R_g^2 and ν) of this model. For the value of bending force constant $k_s = 0$, results reproduced well the scaling behavior predicted by Flory theory in good solvents, but for bending force constant $k_s > 0$ exponents are greater than from Flory suggested exponent. The scaling exponents in scaling laws which we examined reflect global properties. When the bending force constant k_s increase the value of $\langle R_g^2 \rangle$ increase up to a certain point and after that point it becomes slightly constant.That means, fluctuation would be tends to zero. The model respected circular topology of polymer and the conformation of the model and its center of mass of this model could not be much changed. For this sequential event the exponent changed from $\nu \approx 0.75$ to $\nu \approx 1$.

Second, in tangent-tangent correlation, the coincide effect for large k_s indicates that the fluctuations of the bond angle become very small for these stiffness values. The persistence length l_p increase, when the bending force constant k_s is increase, i.e. the persistence length of number monomer, $\mathrm{N} = 40 > 100 > 200$ in the same bending force constant k_s. For long polymer chain the scaled persistence length l_p/N is tends to zero when we compared to with the shorter one. Showing these, all properties should enable a new understanding of the structural and conformational statistics of biopolymers such as DNA and F-actin. A basis on which biopolymer assemblies can be designed to develop new nano-materials.

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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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Signature:– – – – – – – – – – –

Place and time of submission: Addis Ababa University, June 2017

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

Name: Dr.Tatek Yergou

Signature:– – – – – – – – – ––