

Numerical Simulations of Ideal Chain Model of Polymer using the Freely Jointed Chain (FJC)

Nitesh Khatiwada and Mirza Akbar Ali

Abstract

In this project, we perform numerical simulations of the ideal polymer chain model, namely Freely Jointed Chain (FJC). We verify the mean square end-to-end distance, $\langle Q^2 \rangle$, mean square radius of gyration $\langle R_g^2 \rangle$, the probability distribution of end-to-end distance $P(Q)$, singular behaviour $P(Q)$ for $N = 2$, and structure factor numerically, comparing with the theoretical results. Furthermore, we simulate the extension of the polymer along x -axis by applying force in the same direction, using the Metropolis Monte-Carlo algorithm.

1 Introduction

The physics of polymers involves the study of the physical properties and behaviour of polymeric materials, which are long chains of repeating molecular units called monomers. Polymers are ubiquitous in everyday life and can be found in a wide range of applications, including plastics, fibres, coatings, and adhesives. They are characterized by their large molecular weights, ranging from tens of thousands to millions of atomic mass units.

One key aspect of the physics of polymers is the study of their conformations, or the three-dimensional shapes they can assume. These conformations are governed by the statistical mechanics of the polymer chain, which can be described using various discrete models.¹

One such model is the freely jointed chain model, which assumes that the monomers in the chain are connected by ideal hinges and can rotate freely about these hinges.² This model allows for the calculation of statistical measures such as the radius of gyration, which describes the size of the polymer chain in solution. Another important model is the wormlike chain model, which considers the polymer chain as a continuous, flexible rod. This model is useful for describing the mechanical properties of polymers, such as their stiffness and elasticity.³ It has also been used to study the dynamics of polymer chains in confined geometries, such as in the case of DNA in a cell nucleus.⁴

There have been numerous research studies that have made use of these and other models to investigate the physics of polymers. For example, researchers have used these models to understand the thermodynamic behaviour of polymers in solution,^{5,6} as well as their rheological properties, which describe their response to external forces.⁷ Other studies have focused on the structure and organization of polymers in various environments, such as in the presence of solvent or in the solid state.

1.1 Freely Jointed Chain (FJC) Model

The freely jointed chain (FJC) model is a statistical model that is used to describe the conformational behaviour of polymeric materials, such as polyethylene or rubber. The FJC model assumes that the polymer molecules are flexible chains composed of many small segments/beads, each of which is connected by

a bond that can rotate freely relative to one another, hence the name "freely jointed". The model is based on the idea that the polymer chain can adopt any possible conformation, with a probability that depends on the energy of the conformation. It also assumes that the polymer chain is a random walk, meaning that statistical laws rather than deterministic rules govern the movement of the beads.

The FJC model is typically used to calculate statistical parameters such as the mean square end-to-end distance of the polymer chain, which is a measure of the chain's size and shape. The model can also be used to calculate other quantities, such as the chain's radius of gyration, which is a measure of the chain's compactness, and the persistence length, which is a measure of the chain's stiffness. This prediction can then be compared to experimental measurements of the gyration radius to determine the model's accuracy.

Overall, the study of the physics of polymers is an interdisciplinary field that encompasses a wide range of topics, including statistical mechanics, thermodynamics, and materials science. It is an important research area with numerous practical applications in industries such as pharmaceuticals, electronics, the automotive sector, materials science, and biotechnology.

In this project, we restrict our study to the numerical simulations of the ideal chain model of polymer using FJC model. We calculate and compare the theoretical and simulated values of mean square end-to-end distance, the mean square radius of gyration and structure factors. Then we extend the molecule in a given direction by applying a simulated force \mathbf{F} using the Metropolis Monte-Carlo algorithm.

2 Methods

In the simulation, the monomer units are generated randomly from a uniform distribution inside a unit sphere. We set the bond length $b_{Th} = 3.00^*$ to be equal among N monomer units with no preferred direction. Two such conformations are illustrated in Fig. 1 using Visual Molecular Dynamics (VMD) program.

Suppose \mathbf{Q} be the total end-to-end vector of an ideal chain and \mathbf{r}_i be the vector to the i^{th} monomer unit. Then, in FJC model, the mean square end-to-end distance is calculated as

$$\langle Q^2 \rangle := \sum_{i,j}^N \langle \mathbf{r} \rangle_{ij} = Nb^2 + b^2 \sum_{i \neq j} \langle \cos \theta \rangle_{ij} = Nb^2$$

The end-to-end distance is distributed with the following probability distribution function.

$$P(Q) = 4\pi Q^2 \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp \left(-\frac{3Q^2}{2Nb^2} \right) \quad (1)$$

* All parameters are in arbitrary units for the purpose of the simulation.

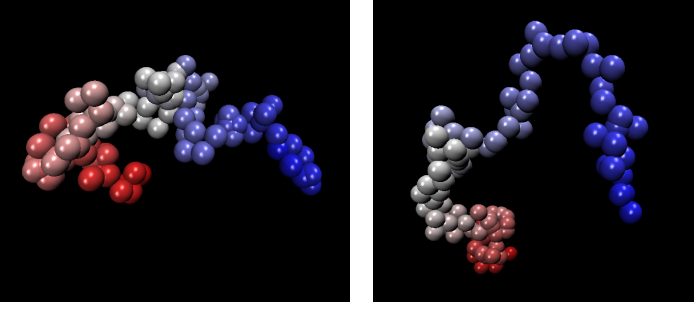


Fig. 1 Two polymer structures generated using Visual Molecular Dynamics (VMD) program for $N = 100$ and $b = 3.00$

Then the most probable value $\langle Q \rangle_{Th}$ can be derived as

$$\langle Q \rangle_{Th} = \frac{2}{\sqrt{\pi}} \cdot \frac{2Nb^2}{3} \quad (2)$$

The mean square of the radius of gyration for $N \rightarrow \infty$ is calculated as

$$\langle R_g^2 \rangle_{Th}^2 := \frac{1}{N+1} \sum_{i=1}^{N+1} (\langle R \rangle_i^2 - \langle R \rangle_{CM}^2) = \frac{Nb^2}{6}$$

where R_{CM} denotes the centre of mass of the conformation. The structure factor of a polymer is measured from Small Angle X-Ray Scattering (SAXS) experiment. The intensity as a function of the scattering vector k is given as

$$I(k) = \sum_{i=0}^N \sum_{j=0}^N \left\langle \frac{\sin(k||\mathbf{R}_i - \mathbf{R}_j||)}{k||\mathbf{R}_i - \mathbf{R}_j||} \right\rangle \quad (3)$$

This result can also be approximated for small k values, known as Guinier approximation:

$$I_{Guinier}(k) = (N+1)^2 \left[1 - \frac{(kR_g)^2}{3} \right] \quad (4)$$

Furthermore, we simulated the extension of the polymer in the x direction by application of force \mathbf{F} along x -axis. The move is accepted if the new conformation has lower energy than the previous conformation. The energy of the conformation is calculated as

$$E = -\mathbf{F} \cdot \mathbf{Q}$$

If not accepted, the move can again be accepted or rejected based on the Metropolis Monte-Carlo algorithm, where the function is chosen to be a Boltzmann distribution.

$$\mathcal{P} = e^{-E/k_B T}$$

where E is the energy of the new conformation, k_B and T are the Boltzmann constant and temperature, respectively. The theoretical value for the extension of the polymer is given as

$$|\mathbf{Q} \cdot \mathbf{u}_x| = Nb \left[\coth(\alpha) - \frac{1}{\alpha} \right], \alpha = \frac{\mathbf{F} \cdot \mathbf{b}}{k_B T} \quad (5)$$

Henceforth, the maximum possible extension is

$$\max Q_x = L = Nb$$

where L is the contour length of the polymer.

3 Results and Discussion

The plot of mean square end-to-end distance $\langle Q^2 \rangle$ from the simulation for different N shows a linear characteristic, as shown in the Fig. 2.

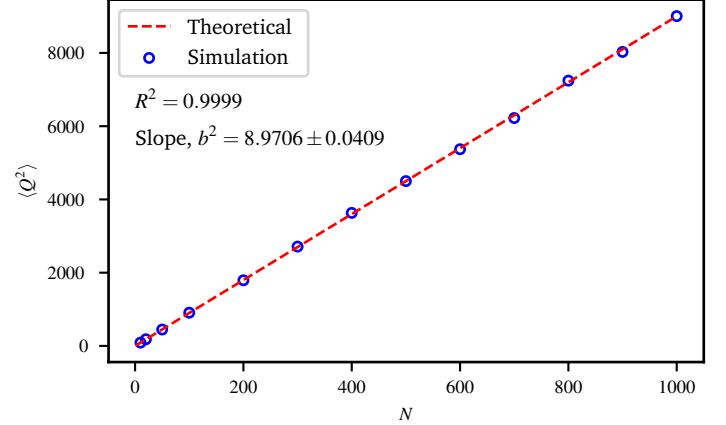


Fig. 2 Comparison of mean square end-to-end distance $\langle Q^2 \rangle$ between simulated data points and the theoretical calculations for 10^3 conformations. The uncertainty in the slope Δm is calculated from the coefficient of determination R^2 using

$$\left| \frac{\Delta m}{m} \right| = \sqrt{\frac{1}{N-2} \cdot \frac{1-R^2}{R^2}}$$

where m denotes the slope. The same applies in all figures.

The slope b^2 from the linear regression yields the value of the bond length, $b = 2.995 \pm 0.007$, which agrees to the theoretical value b_{Th} .

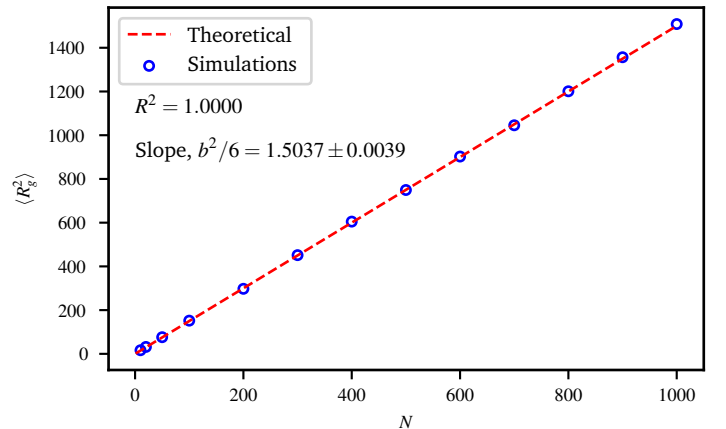


Fig. 3 Comparison of mean square radius of gyration $\langle R_g^2 \rangle$ between simulated data points and the theoretical calculations for 10^3 conformations.

Similarly, from the slope $b^2/6$ of the linear fit of the simulated data points for the mean square radius of gyration, the bond length b is calculated to be 2.994 ± 0.004 , which is also in agreement within the range of the theoretical value b_{Th} .

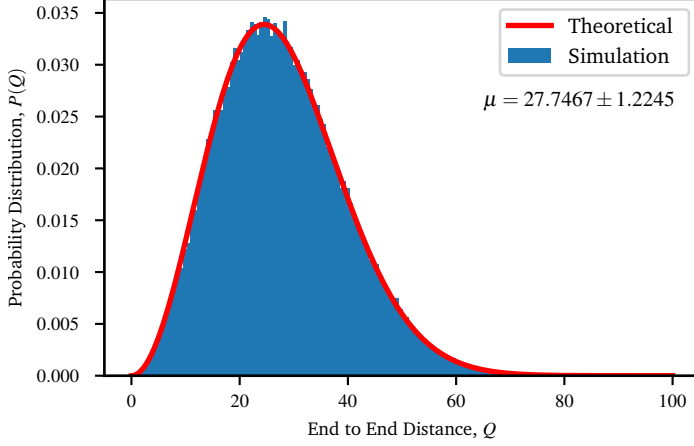


Fig. 4 Comparison of probability distribution of end-to-end distance $P(Q)$ between simulated data points and the theoretical calculations for 10^4 conformations and $N = 100$

The histogram plot, as shown in the Fig. 4, of the probability distribution of the end-to-end distance for $N = 100$ follows a Gaussian-shaped curve, given by the equation 1. The agreement is limited only to a large number of conformations. From visual inspection, we can agree that the simulated results ($T = 10^4$ conformations) are in good agreement with the theory. The experimental most probable value μ agrees to the theoretical most probable value $\langle Q \rangle_{Th}$, equation 2, for $N = 100$. This agreement helps us to calculate the value of the bond length from the simulation in the limiting case $N = 2$. The probability distribution of end-to-end distance for the singular behaviour $N = 2$ reduces to

$$P(Q) = \frac{Q}{2b}$$

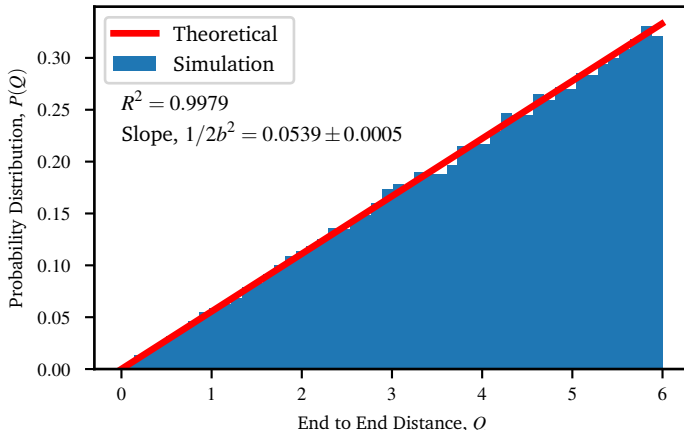


Fig. 5 Comparison of the probability distribution of end-to-end distance $P(Q)$ for $N = 2$ (singular behaviour) between simulated data points and the theoretical calculations for 10^4 conformations.

The linear fit on the data gives the bond length value $b = 3.046 \pm 0.014$, agreeing to the theoretical result b_{Th} .

The intensity of the scattering $I(k)$, defined in equation 3, from the simulation is compared to the Guinier approximation, equation 4.

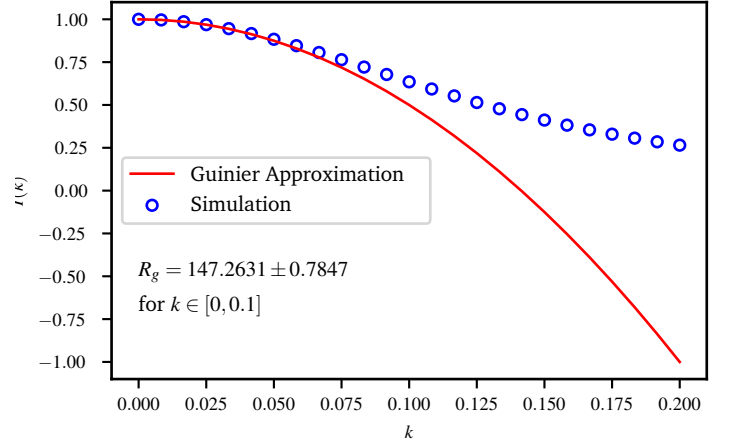


Fig. 6 Comparison of intensity of scattering $I(k)$ between simulated data points and the Guinier approximation for 10^3 conformations and $N = 100$. The R_g value is deduced from the linear regression as a function of k^2 .

The agreement to the Guinier approximation is limited to $k < 0.1$, as seen in the Fig. 6. Solving linear regression as a function of k^2 , gives the value of the radius of gyration, R_g , which is close to the theoretical result for $N = 100$ and $b_{Th} = 3.00$.

Furthermore, we continued with the simulation where the polymer is extended along the x . For $N = 100$ and $\mathbf{F} = (10, 0, 0)^T$, where T denotes the transpose, the end-to-end distance of the extended polymer along the x -axis is presented in the Fig. 7.

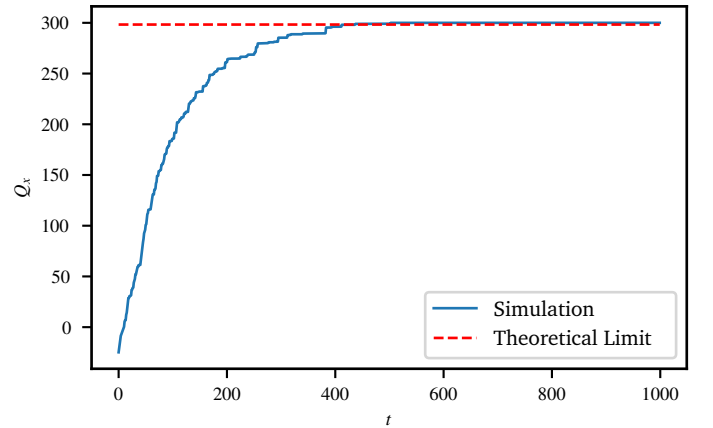


Fig. 7 End-to-end distance along the x axis for different conformations t while simulating the extension of the polymer with application of force $F = 10$ a.u. along the x axis. $N = 100$

The maximum extension from the experiment $\max Q_x$ agrees to the theoretical limit. This concludes that the form factor of the simulated polymer is very close to 1, or equivalently, the simulated polymer behaves like a freely jointed chain model.

For different forces, the simulation is repeated and compared to the theoretical result, equation 5. The plot of F_x and the ratio of extension, where extension equals 1 means that the polymer has reached the theoretical limit given by the equation 5, is presented.

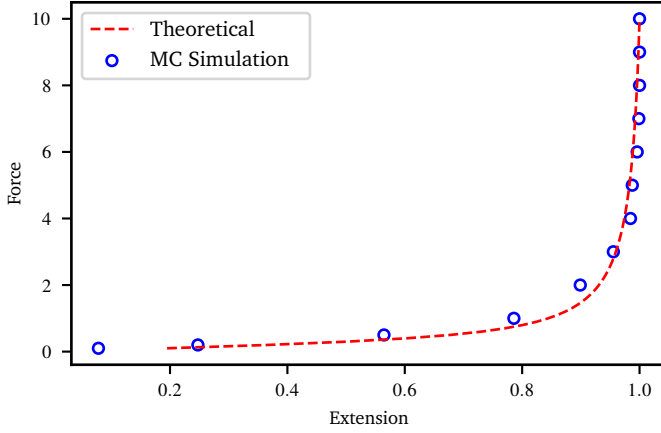


Fig. 8 Comparison of the extension for different forces between Monte-Carlo simulation and the theoretical model.

The agreement with the theoretical model is visible in the plot. The interesting observation is that this method can be useful to deduce the persistence length of the polymer from a comparison of the theoretical maximum value of extension to the contour length L of the polymer. In our case, the persistence length is equivalent to the bond length.

4 Conclusion

We consider the FJC model discarding self-avoiding random walk, no interaction between bonds or monomers of the polymer, without rigidity constraint, and bond length is a fixed among all monomer units, making it an ideal polymer. By fixing the polymer's bond length, we characterized various properties of the polymer, including end to end distance and its most probable value, the radius of gyration for any number of monomers $N \geq 2$. The structure factor of the polymer is then calculated using the Guinier approximation for the parameters calculated from the FJC model.

We find the linear characteristics of mean square end-to-end distance and mean square radius of gyration for different N to be in agreement with theoretical values. We find that for large values of N , the probability distribution of end-to-end distance for possible conformations follows the Gaussian-shaped curve. The most probable value of end-to-end distance also agrees with the theoretical prediction. Similarly, we can deduce the radius of gyration of the polymer from the intensity as a function of the scattering vector k (which depends on the incident and scattered beam wavevectors) for $k \in [0, 0.1]$. This results also agrees to the theoretical prediction.

Since the FJC model assumes a flexible polymer, we can stretch it to the maximum possible length. Though all configurations of a flexible polymer have the same energy, it still requires one to exert a force to stretch it in a particular direction. The length of the fully

extended polymer turned out to be Nb in the FJC model, which is not realistic since we have not considered bond stretching due to applied force. It is safe to conclude that an extended polymer will always have a length larger than the proposed theoretical value in an actual experiment. In conclusion, FJC model still provides a general framework for comparing other types of polymers as well.

Notes and references

- 1 Nobuhiro Gō and Harold A Scheraga. On the use of classical statistical mechanics in the treatment of polymer chain conformation. *Macromolecules*, 9(4):535–542, 1976.
- 2 Pierre-Gilles De Gennes. *Introduction to polymer dynamics*. CUP Archive, 1990.
- 3 Joshua N. Milstein and Jens-Christian Meiners. *Worm-Like Chain (WLC) Model*, pages 2757–2760. Springer Berlin Heidelberg, Berlin, Heidelberg, 2013.
- 4 J Langowski. Polymer chain models of dna and chromatin. *The European Physical Journal E*, 19(3):241–249, 2006.
- 5 Isaac C Sanchez and Robert H Lacombe. Statistical thermodynamics of polymer solutions. *Macromolecules*, 11(6):1145–1156, 1978.
- 6 Costas Panayiotou. Thermodynamic characterization of polymers. *Polymer*, 136:47–61, 2018.
- 7 Oluranti Sadiku-Agboola, Emmanuel Rotimi Sadiku, Adesola Taoreed Adegbola, Olusesan Frank Biotidara, et al. Rheological properties of polymers: structure and morphology of molten polymer blends. *Materials Sciences and Applications*, 2(01):30, 2011.