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

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1 Introduction

Polymer physics, crucial for comprehending materials like plastics and DNA, involves studying their behavior at both macroscopic and microscopic levels using statistical mechanics and discrete models. Models such as the freely jointed chain and Worm-Like Chain capture the statistical representation of single chain conformations, accounting for factors like temperature and chain stiffness. This theoretical framework undergoes validation and refinement through diverse research endeavors. For instance, Paul J. Flory's[9] groundbreaking theory in the 1950s explained polymer behavior in solutions by introducing the concept of the excluded volume effect. Monte Carlo simulations have played a pivotal role in exploring polymer thermodynamics and conformations, offering insights into their behavior in different environments. Additionally, advanced techniques like single-molecule experiments[8], including atomic force microscopy[4], have yielded valuable data on individual polymer chains, enriching our understanding and validating theoretical models.

The Freely Jointed Chain (FJC)[2] model is a fundamental tool in polymer physics, offering a simplified yet robust framework for understanding the statistical behavior of polymer chains. With flexible bonds allowing free rotation between monomers, the FJC model finds applications in diverse areas, including studying polymer dynamics in solvents, predicting phase behavior in blends, analyzing rheology and mechanical properties, and exploring structural changes in biopolymers during protein folding.

In this paper, we employed the Freely-Jointed Chain (FJC) model to investigate the statistical properties of the polymeric chain. By fixing the number of conformations (T) and varying the number of monomers from 10 to 1000, we determined the mean square end-to-end distance and mean square radius of gyration, validating the results through theoretical linear fitting. Additionally, for a fixed number of monomers and conformations, we analyzed the probability distribution of end-to-end distance, observing a Lorentzian shape. Singular behavior in the distribution was verified for short 2-monomer chains. In the final part, we explored the structure factor I as a function of wave vector (k) for fixed conformations and monomer numbers, comparing it to the Guinier approximation[6]. This comprehensive approach provides insights into polymer conformational dynamics at different scales.

2 Methods

2.1 Numerical Simulations

In the simulation, The algorithm generates a simulation of a Freely Jointed Chain (FJC) model in three-dimensional space, governed by three key parameters: T, b, and N. The parameter T dictates the number of distinct conformations explored by the chain, b represents the length of the bond connecting consecutive monomers, and N determines the total number of monomers in the chain. The algorithm utilizes a random walk approach, generating sets of random step vectors in three dimensions for each conformation. These steps are normalized to lie on the surface of a unit sphere, ensuring a physically realistic chain. The resulting trajectory of the chain is then stored, and the Cartesian coordinates of each monomer for every conformation are written to a .XYZ file for further analysis and visualization. Figure 1 shows an example of a randomly generated structure:

2.2 Structures simulated

This section shows a sample of visualizations of two randomly generated structures of polymeric chains. These structures were generated using the previously discussed algorithm mentioned in section 2.1. The data files generated(see section 2.4 for a summary) were then visualized using the Visual Molecular Dynamics(VMD) software.

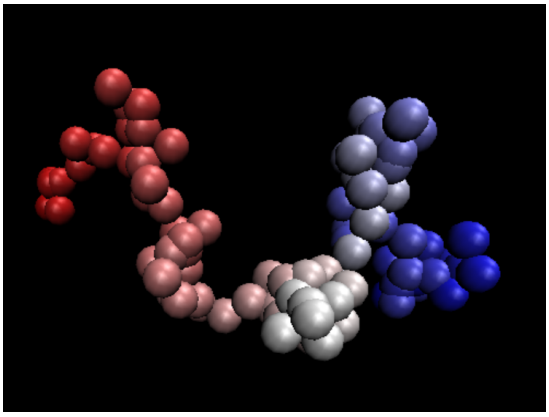

Fig. 1 Polymer structure for T=1000, N=100, b=3.

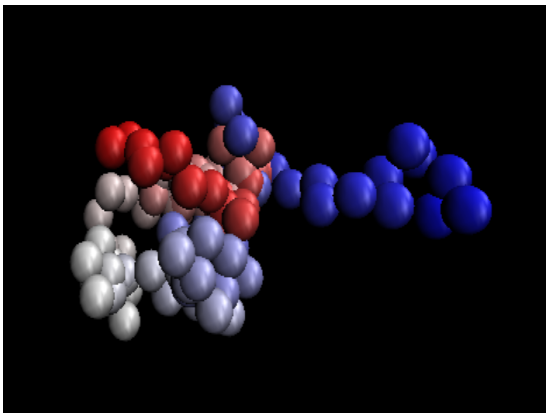

Fig. 2 Polymer structure for T=100000, N=100, b=3.

2.3 Theory

In the Freely-Jointed Chain (FJC) model, the statistical parameter denoted as **Q**, represents the vector connecting the two ends of a polymeric chain. The FJC model assumes that the polymeric chain is analogous to a rigid rod an the bonds between the segments are flexible and can rotate freely. The end-to-end vector **Q** in the FJC model is mathematically expressed as the sum of all segments connecting the consecutive monomers.

$$< Q^2 >= \sum_{i,j}^{N} < r_{ij} >= Nb^2 + b^2 \sum_{i \neq j} < cos(\theta_{ij}) >= Nb^2 \quad (1)$$

where:
- **Q** is the end-to-end vector.
- **N** is the number of monomers in the chain.
- $\mathbf{b}_i$ boond length for the monomer i.

Meanwhile, the probability distribution $P(Q)$ for the end-to-end vector Q in the FJC model is derived with the help of statistical tools and thus assumes random and independent orientations of each bond vector in the polymeric chain. It gives the probability of finding the polymeric chain in a particular configuration characterized by Q. In the FJC model, if the chain has N monomers and each segment has a fixed bond length b, the probability distribution of the end-to-end vector Q can be expressed as:

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

Therefore, the most probable value expected $Q_{expected}$ is:

$$< Q^2 >_{expected} = \frac{2}{\sqrt{\pi}} * \frac{2Nb^2}{3} \quad (3)$$

The gyration radius[5] (R_g^2) is a physical quantity that provides information about the spatial extent or size of a polymer chain. It measures how spread out or compact the polymer is in three-dimensional space.

In the context of the FJC model, we calculate the mean square of the radius of gyration which can be expressed as:

$$< R_g^2 >_{expected} = \frac{1}{N} \sum_{i=1}^{N} (R_i - < R_{cm} >)^2 = \frac{Nb^2}{6} \quad (4)$$

The scattering intensity (Structure Factor[7]) $I(k)$ of the FJC model represents the pattern of scattered radiation resulting from the internal structure of a polymer chain. It is often expressed in the context of polymer physics and small-angle scattering. The scattering pattern of a polymer in the FJC model can be related to the form factor of the chain which can be expressed as:

$$I(k) = \sum_{i=0}^{N} \sum_{j=0}^{N} \left\langle \frac{\sin(k \| \overrightarrow{R}_i - \overrightarrow{R}_j \|)}{k \| \overrightarrow{R}_i - \overrightarrow{R}_j \|} \right\rangle \quad (5)$$

In the Freely Jointed Chain (FJC) model context, the Guinier approximation is often applied to analyze small-angle scattering data for polymer chains. The Guinier approximation for the FJC model provides insights into the size of the polymer chain based on the scattering pattern in the small-angle regime.

The approximation of this quantity for the FJC model is expressed as follows:

$$I_{Guinier}(k) = (N+1)^2 \left(1 - \frac{(kR_g)^2}{3} \right) \quad (6)$$

2.3.1 Monte Carlo

Monte Carlo simulations are computational methods used to model physical systems by employing random sampling. For FJC polymer extension, conformations are randomly sampled using Metropolis Monte Carlo simulation[3] based on the Boltzmann distribution. The polymeric chain is stretched at a random monomer with a fixed force vector. The end-to-end vector quantity (Q) is calculated for this new conformation, which further helps to calculate the conformational energy using equation 7. If the energy decreases after the proposed move, we accept it, if not we apply the metropolis condition. This is achieved by generating a random number which is assumed to be the probability of the move, if it is less than the value of metropolis criteria we accept the move, else we reject it. The simulation is done for a certain number of steps, and the simulation itself is repeated multiple times to get the statistical averages.

The theoretical value of the polymer extension is calculated using equation 9, which provides us the insight that the maximum possible extension for the polymeric chain should be given by equation 10.

These quantities provide insights into the extension behavior of the polymer chain under the applied force. Below are the equations used in the simulation:

Energy Conformation:

$$V = -F.Q \quad (7)$$

Boltzmann distribution:

$$\rho = exp\left(\frac{-V}{K_B T} \right) \quad (8)$$

Theoretical value for extension of polymer:

$$|Q.u_x| = Nb\left(coth(\alpha) - \frac{1}{\alpha} \right); \alpha = \frac{F.b}{K_B T} \quad (9)$$

Maximum possible extension:

$$max(Q_x) = L = Nb \quad (10)$$

2.4 Summary of Data Generated

.xyz file	N	T	b
File1.xyz	100	10	3
File2.xyz	100	100	3
File3.xyz	100	1000	3
File4.xyz	100	10000	3
File5.xyz	100	100000	3
File6.xyz	10	10000	3
File7.xyz	20	10000	3
File8.xyz	50	10000	3
File9.xyz	200	10000	3
File10.xyz	500	10000	3
File11.xyz	800	10000	3
File12.xyz	1000	10000	3
File13.xyz	2	100000	3

Table 1 Table of data for different values of parameters T and N, with fixed b

3 Results and Discussion

3.1 Average Q^2 behaviour

One of the statistical tools employed in analyzing the Freely Jointed chain (FJC) model involves studying the behavior of Q^2 as a function of the number of monomers (N). In our investigation, Q^2 values were computed across a range of monomer counts, specifically from $N = 10$ to $N = 1000$, while maintaining a fixed number of conformations ($T = 100000$). The observed Q^2 behavior was subjected to linear fitting, and the resulting plot exhibited a distinct linear trend, aligning with theoretical expectations (see Figure 2).

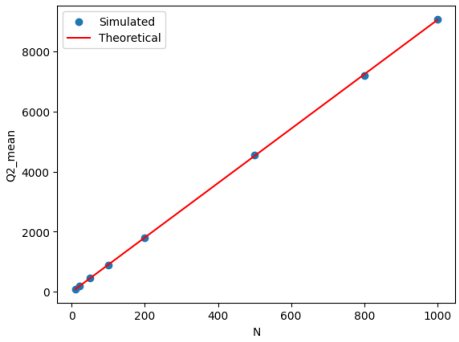

Fig. 3 Behaviour of average value of Q^2 as a function of N

Notably, the slope of the Q^2 behavior was determined to be 9.0537, remarkably close to the anticipated behavior of b^2 where $b = 3$. Additionally, the intercept of the behavior approached the value -5.6035, closely approximating the expected ideal value of zero. This analysis confirms its adherence to theoretical predictions especially that the score of the linearly predicted model was 0.9999 confirming the linearity of the quantity of interest.

3.2 Average R_g^2 behaviour

In a similar fashion to what we did in section 3.1, the study of R_g^2 also shows the linear behavior as a function of the quantity N, varied from N=10 to N=1000 while fixing T at 10000, as shown in Figure 3:

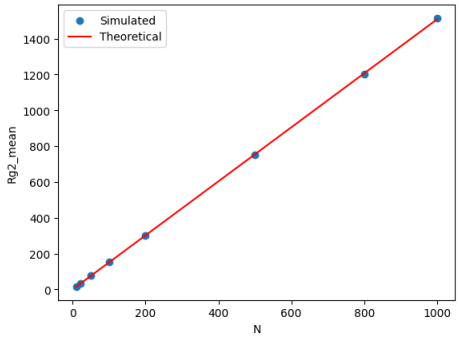

Fig. 4 shows the behavior of Average value of $Rg^2 as a function of N$

We note that the slope of the behavior of R_g^2 is 1.5072 which is very close to the theoretical value $\frac{b^2}{6}$. Meanwhile, the intercept approached the value of 0.2668, also close to the expected ideal value of 0. It is worth mentioning that the score of the linearly predicted model was 0.9999 confirming the linearity of the quantity of interest.

3.3 Probability distribution as a function of end-to-end distance

Exploring the probability distribution as a function of the end-to-end distance is a pivotal aspect of FJC model analysis. This investigation is bifurcated into two cases.

The first case focuses on a long chain configuration where the number of monomers (N) is set to 100 and $T = 100000$. The Q^2 values are computed following the methodology outlined in Section 3.1, and the probability distribution is subsequently derived based on the theoretical equation presented in Section 2. The results are graphically depicted in Figure 4, showcasing the calculated Q^2 values. Additionally, Figure 5 visually represents the histogram of the probability distribution for the aforementioned end-to-end distance, providing a visual insight into the statistical characteristics of the FJC model.

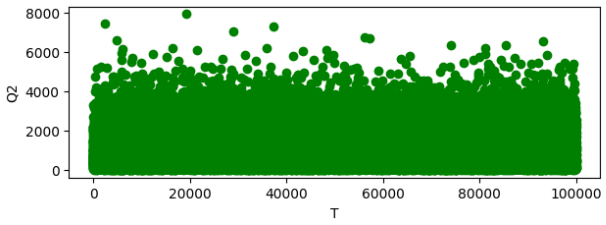

Fig. 5 Q^2 calculated as a function of increasing number of conformations

Figure 5 shows that the histogram obtained from the probability distribution is fit by the Lorentzian envelope according to the theoretical equation() in section 2. The most probable value for Q is calculated to be 23.4479 which is close to the theoretical value,

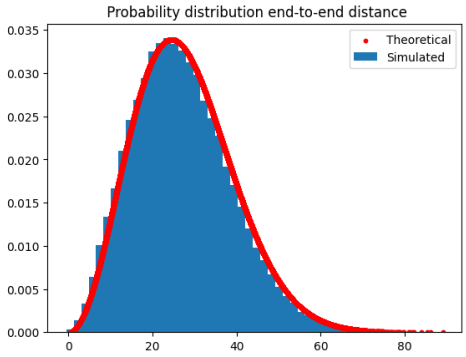

Fig. 6 Behavior of Probability distribution as a function of Q, for N = 100

26.0197 calculated from the equation (3).

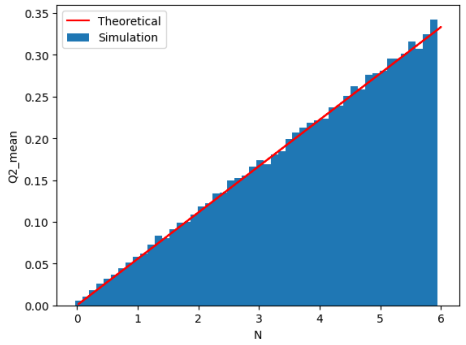

Fig. 7 Behavior of Probability distribution as a function of Q, for short chain with N = 2

On the other hand, the second case is the study of a short-chain configuration with the number of monomers(N) set to 2 while keeping the other parameters the same as in the first case. The histogram of this distribution is shown in figure 7.

From Figure 7, we can see that for such short polymeric chains, the probability distribution follows a linear trend according to the mathematical equation presented in Section 2.

3.4 Structure Factor

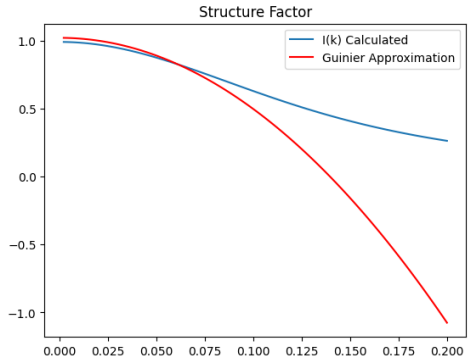

Fig. 8 Behaviour of the structure factor of polymer in comparision with the Guinier approximation

Our results show that, at small angles the structure factor shows a high agreement with the Guinier approximation. Meanwhile, the difference becomes significant as the length of scattering vector increases.

In theory, The Guinier approximation is a simplified mathematical expression used to analyze small-angle scattering data, particularly when the scattering object is relatively large and exhibits a relatively homogeneous structure. It assumes that the scattering object can be approximated by a sphere, and for small angles, the intensity of scattering can be linearly related to the wave vector q. The structure factor, on the other hand, describes the spatial correlations in the arrangement of scatterers within the sample. For small angle values, the correlation between segments in a polymer chain or scatterers in a system remains relatively high over short distances. As a result, in this regime of small angles, the spatial correlations captured by the structure factor align with the assumptions made in the Guinier approximation, leading to an agreement between the two in describing scattering behavior.

This makes the Guinier approximation valid for its usage in advanced techniques such as Small-Angle X-ray Scattering[1] (SAXS) or small-angle neutron Scattering[1] (SANS) to study polymer structures in detail.

3.5 Monte Carlo Simulation

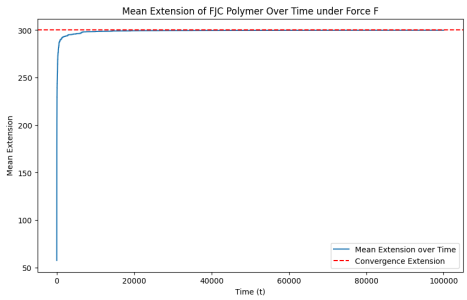

Fig. 9 Behavior of the Mean extension of the polymer as a function of the time t.

In our simulation methodology, we introduced a scaling factor of 0.01, associating it with a given force. This factor dictates the change in the position of the monomer, ensuring that the new position is a result of the addition of the old position with the scale factor that is multiplied by the force. Subsequently, to preserve the bond length condition (b=3), the bond length of the newly generated polymer configuration is normalized.

Following this, we compute the potential energy of the newly formed conformation. The Metropolis Monte Carlo condition is then applied to determine whether to accept or reject the proposed move due to the new conformation. This iterative process persists over a designated time interval, with each time unit representing the acceptance of one move. The simulation continues until the polymer reaches its fully stretched state. To enhance computational efficiency, we repeat this algorithm ten times and then extract the mean extension from these iterations, which will later be plotted as a function of time as seen in Fig.9.

In Fig.9, our Monte Carlo simulation of the Freely Jointed Chain polymer extension is subjected to a constant force of 10 units. Initially, as time progressed from 0 to 700 units (representing a change in the mean extension), a remarkably sharp increase was observed, swiftly reaching approximately 290 angstroms. The high and sudden extension signifies the rapid unfolding and stretching of the polymer chain under the applied force, which is what we expect as the probability of having an accepted move by the Metropolis Monte Carlo condition is very high at the beginning. However, beyond this point, the rate of extension slowed notably, with less significant extension. As time further advanced towards 100,000 units, the extension further progressed, albeit at a much slower pace. The mean extension trend appears to asymptotically converge to the theoretical maximum extension limit of $N*b$=300 angstroms around t ~18,000, with the simulation attaining a steady state of convergence with the theoretical limit with further increase in t.

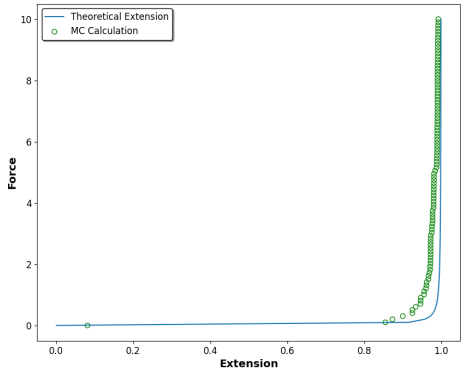

Fig. 10 Behavior of the Mean extension of the polymer as a function of the time t.

As the further step, the applied force was varied ranging from [0,10] a.u. and the Metropolis simulation employed previously was run for for each value. In a particular moment in time i.e, after a certain number of extensions, the polymers were examined to find the impact of varying force on the mean extension ratio of the polymer. The mean extension ratio is computed by dividing the current extension of the polymer by its maximal possible extension.

From the graph obtained, we can see a compelling alignment between the simulation results and theoretical expectations. Notably, as the force gradually increases to 10 units, the data consistently tends to converge toward an extension ratio of 1.0. This convergence suggests that, at higher force magnitudes, the polymer undergoes complete stretching. Consequently, our simulation results are not only consistent with theoretical predictions but also demonstrate a compelling trend toward the polymer reaching its fully stretched state.

4 Conclusion

This paper delves into the realm of polymeric physics through the lens of the Free-Jointed Chain (FJC) Model framework and showcases the importance of various statistical tools devised to study the polymer in detail. The results shown impeccably align with the approximations posited by the FJC model, thus proving it to be one of the robust models to gain insights into polymeric structures.

In section 2, the paper emphasizes the numerical algorithm used for the simulation of the randomly generated polymeric chain and resultant structures visualized using the Visual Molecular Dynamics(VMD) software. The section also discusses the essential theory and statistical tools crucial for comprehending the FJC model. In section 3, the paper presents the calculations and results obtained for various statistical quantities and establishes their conformity with theoretical expectations. Notably, our exploration extends to the application of the Metropolis Monte Carlo simulation to get a glimpse of the behavior of the polymeric chain subjected to a constant force in one dimension.

All these calculations were undertaken for the data generated by random sampling for varying numbers of monomers and number of conformations of the polymer, which is shown in Table 1. The computational work undertaken here has been conducted using Python programming language and with the help of numerical packages Numpy and, Scipy for efficient data fitting. This study not only enhances our understanding of polymeric physics but also underscores the efficacy of the FJC model in capturing the nuances of polymer behavior.

Notes and references

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