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

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1 Introduction

One way to think of polymer conformations is to treat conformation the polymer like freely jointed chain where every bond is free to rotate to any angle but the bond distances are fixed (b) and the number of bonds in the chain is fixed (N). We can then think of the polymer conformation as that of a "random walk". What do we mean by that? Imagine you stand in one place, representing the end of the polymer, and take a step of length b in any direction. This corresponds to one bond distance and the position of the second atom in the polymer backbone. Take another step of length b, in any direction. You now stand in the position of the third atom in the polymer backbone. Continue for N steps, however many bonds are in the backbone of the polymer[1]. The FJC model describes polymer as straight, absolutely rigid segments of an equal length connected by free joints, i.e., the angle between neighboring segments can change without energy penalty[2]. The main statistical properties characterizing the chain conformation are:

- End-to-end distance,
- Gyration radius,
- Persistence length[3].

A radius of gyration in general is the distance from the center of mass of a body at which the whole mass could be concentrated without changing its moment of rotational inertia about an axis through the center of mass. For a polymer chain, this is also the root-mean-square distance of the segments of the molecule from its center of mass.[4]

In this practical work, we will concentrate on the end-to-end distance and gyration radius. The main goal is to verify numerically the 4 following theoretical results for $N = 10, 20, 50, 100, 250, 500, 750, 1000$ bonds:

- Mean square end-to-end distance $< Q^2 >= Nb^2$
- Mean square radius of gyration $< R_g^2 >= \frac{Nb^2}{6}$ $(N \to \infty)$
- Singular behavior for $N = 2\Phi(Q) = \frac{Q}{2b^2}$
- Probability distribution end-to-end distance $\Phi(Q) = 4\pi Q^2 \left(\frac{3}{2\pi N b^2}\right)^{3/2} exp\left(-\frac{3Q^2}{2Nb^2}\right)$ for $N = 100$

2 Methods

To start the `script.py` python script discussion first and foremost we must import the necessary libraries and define the essential parameters, for instance N (the number of bonds), T (the number of conformations of the polymer) and b (distance between two monomers). The mentioned code is generating arrays for the gyration radius, end-to-end distance and polymer trajectory using a big `for` loop.

In order to generate a path in `.xyz` format, we proceed with building a random molecule step by step (**Fig. 1**). To start with, we define the monomer 0 at the coordinate $[0,0,0]$. Next, we only change the x coordinate to b, as we can chose the x axis accordingly. Afterwards, we have to define the random angle τ which will be in range $[0;\pi]$ between the b_0 and b_1. We defined it using a random number u in range $[-1;1]$ using equation and the rotation formula for the 2 dimensional case.

$$u = \cos\tau \tag{1}$$

$$\tau = \text{atan2}(\sqrt{1-u^2}, u) \tag{2}$$

To continue with, we use Rodrigue's rotation formula for $\pi - \tau$:

$$\vec{V} = \cos(\pi-\tau)\vec{U} + \sin((\pi-\tau)(\vec{N}\times\vec{U})) + (1-\cos(\pi-\tau))(\vec{U}\vec{N})\vec{N} \tag{3}$$

For the definition of the next monomers not only we have to define the angle τ, but also the angle ϕ. In order to pursue, we defined 2 random numbers in range $[-1;1]$ using the same variable `u`, repeated the same action as in equation (5), and used the Rodrigue's formula also for ϕ.

$$\vec{V} = \cos(\phi)\vec{U} + \sin((\phi)(\vec{N}\times\vec{U})) + (1-\cos(\phi))(\vec{U}\vec{N})\vec{N} \tag{4}$$

At last, all of the generated coordinates are saved in the trajectory file, which we have used to implement the simulation of the molecule using VMD (**Fig. 1**.). Using the same loop we first define the central mass using:

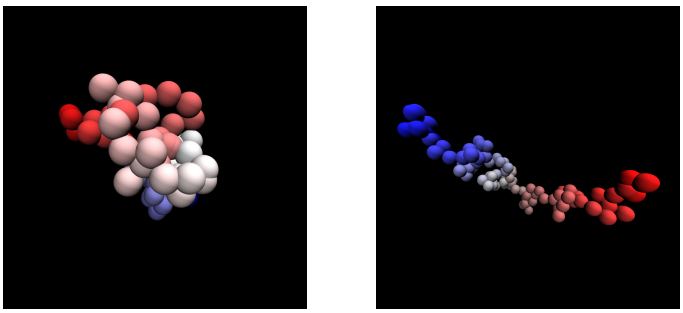

Fig. 1 Two polymer structures generated from FJC model simulations for $T = 500$, $N = 100$ and $b = 3.0$.

$$\vec{R}_{cm} = \frac{1}{m+1}\sum_{i=1}^{m+1}\vec{R}_i \tag{5}$$

For the next step in the code we change the starting point to the R_{cm} and afterwards calculate the end-to-end distance and the gy-

ration radius using equations (8) and (9).

$$Q = ||\vec{R}_n - \vec{R}_0|| \tag{6}$$

$$R_g = \sqrt{\frac{1}{N+1}\sum_{i=0}^{N}\left\|\vec{R}_i - \vec{R}_{cm}\right\|^2} \tag{7}$$

And finally the generated arrays are saved in the files. Measure of extent of polymer with the presentation of the 2 metrics of interest: In the **Fig. 2** and **Fig. 3** we have plotted the values for the two metrics of interest: gyration radius and the end-to-end distance. We can see that the values have a pretty random

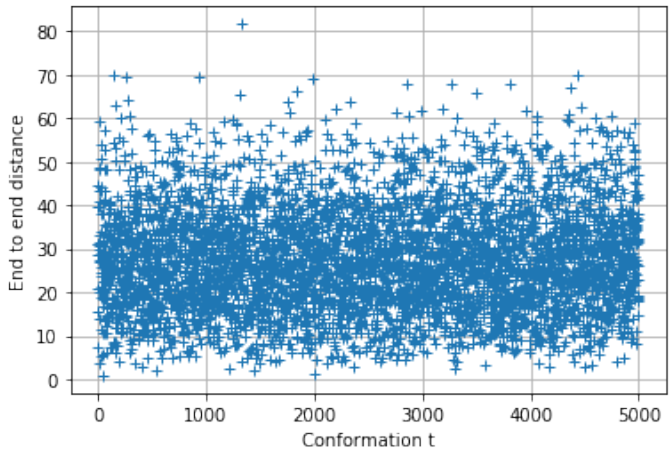

Fig. 2 Gyration radius values for $b = 3$, $T = 5000$ and $N = 100$

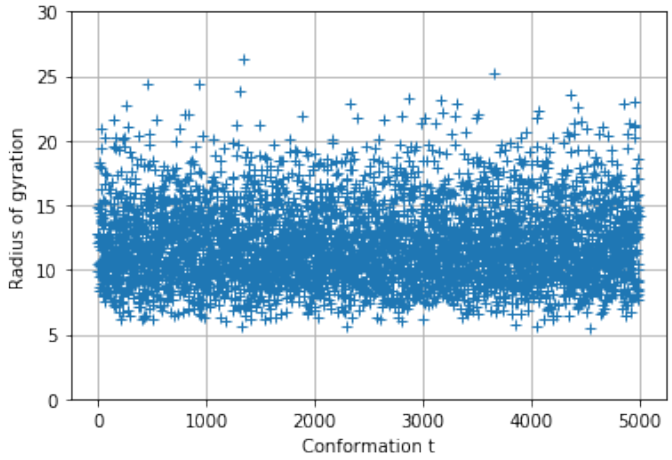

Fig. 3 End-to-end distance values for $b = 3$, $T = 5000$ and $N = 100$

pattern, and hence it is expedient to calculate the mean square of R and Q, and then plot their probability distribution.

3 Results and Discussion

Now our goal is to calculate the mean square value for the end-to-end distance and for the gyration radius, and afterwards to compare them with the analytical value. According to the theory:

$$\sigma_Q^2 = nb^2 \tag{8}$$

$$R_g^2 = \frac{\sigma_Q^2}{6} = \frac{b^2 n}{6} \tag{9}$$

For the simulation we have used $N = 10, 20, 50, 100, 250, 500, 750, 1000$ values. The plots of the results can be seen in **Fig. 4** and **Fig. 5**.

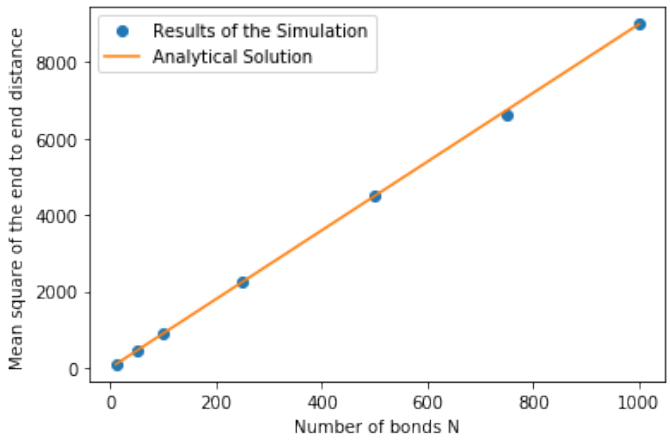

Fig. 4 Comparison of analytical and simulation results for mean squared end-to-end distance

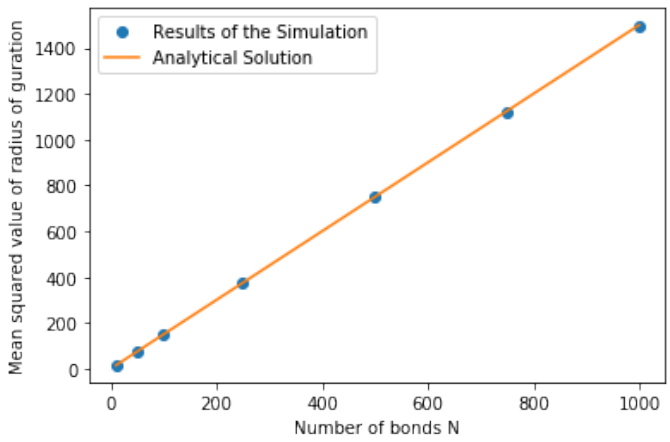

Fig. 5 Comparison of analytical and simulation results for mean squared gyration radius

Next, we calculate the probability distribution for end-to-end distance. Firstly we start with the singular behaviour in the particular case of $N = 2$. For the analytical results we have used the following formula and compared with the analytical results (**Fig. 6**). As we can see, the dependence of Q is linear, which is also visible in the graph.

$$\Phi(Q) = \frac{Q}{2b^2} \tag{10}$$

Afterwards we have calculated the probability distribution using the general formula for probability distribution for $N = 100$ case. As we can see the result is a Gaussian function, and the analytical

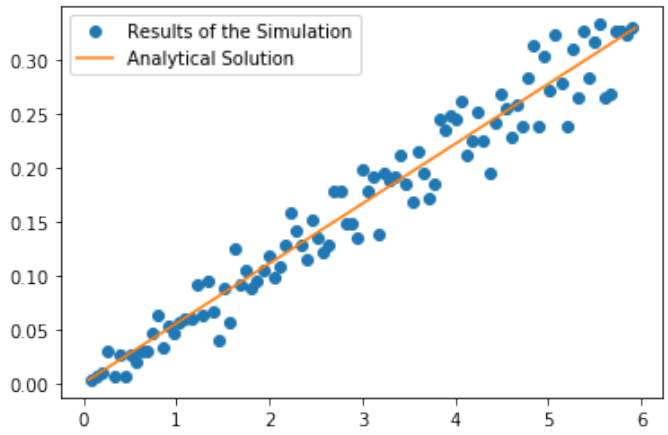

Fig. 6 Probability distribution for $N = 2$

solution is a good interpolation of the results of the simulation.

$$\Phi(Q) = 4\pi Q^2 \left(\frac{3}{2\pi N b^2}\right)^{3/2} exp\left(-\frac{3Q^2}{2Nb^2}\right) \tag{11}$$

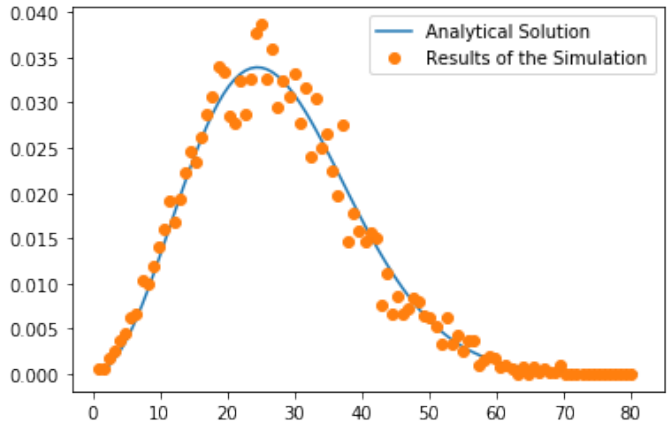

Fig. 7 Probability distribution for $N = 100$

4 Conclusion

As we can view from the graphs, the results of the simulation correspond to the analytical results with a rather good precision. Although on the other hand some slight changes are visible, the inaccuracies can be justified with the inaccuracy of the computer. To conclude with, the free joint model is still very handy while solving various problems where the N is very large and quantum effects can be ignored.

5 References

Notes and references

1 Introduction to Polymers, 3rd Edition, 2011, by Robert J. Young and Peter A. Lovell, page 253

2 Improved Approximations for Some Polymer Extension Models, Rafayel Petrosyan, arXiv:1606.02519

3 The theory of polymer dynamics, M. Doi and S. F. Edwards, Oxford Science Publications

4 The Elements of Polymer Science and Engineering, Alfred Rudin and Phillip Choi (Section 3.2.6 Radius of Gyration from Light-Scattering Data)