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

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1 Introduction

- General introduction about physics of polymer. Discrete models. Examples

- Theory of FJC model.

- Presentation of measure of extent (metrics). Relationship with experimental measurement.

- Goal of the practical work

Polymer physics deals with complex substances through a simple approach. Understanding the properties of polymers from a molecular point of view is key to unveil their complexity.

Given an ensemble of polymers, we can use tools from statistics to derive some properties that apply to the ensemble at any given instant. To do so we model each polymer as a (continuous or discrete) ideal chain of monomers along with some constraints. Some examples of these models include the Freely Jointed Chain, the Freely Rotating Chain, the wormlike chain, the hindered rotating chain, the rotational isometric state model, among others[5].

The first, most straightforward (yet illustrating) approach is the Freely Jointed Chain model. The FJC is a chain consisting of N links, each of length b and able to point in any direction independently of each other (thus the simplicity).

2 Methods

- Numerical simulations: Parameters + Brief description of the algorithm

- Examples of structures generated

- Time series + mean square and distributions statistical tools (theory) + Monte-Carlo

- Summary of data produced (ex: Table)

The first script analyzes the simulation data of a $3D$ FJC polymer for different chain lenghts N. The parameters are the bond length b, the N values we wish to test for, and the number of configurations T we wish to analyze. An XYZ file containing T polymer configurations is read, and for every configuration the end-to-end distance Q and the radius of gyration R_g is computed. Finally both quantities are squared and averaged over all configurations yielding $\langle Q^2 \rangle$ and $\langle R_g^2 \rangle$. This algorithm is looped over for every N.

The second script is built over the first one. The only extra parameter needed are the number of bins for the histogram. After computing the end-to-end distance Q, the algorithm builds a histogram out of these values, treating them as samples from a probability distribution. The histogram is then normalized so that it can be directly compared to the gaussian distribution.

The third simulation focuses on computing the structure factor for a polymer of `N = 100` and `b = 3`. An array k is introduced, spanning values from 0 to 1 (in our case, sampling every 0.01 steps). One of the files containing the simulated polymers is held in memory. Then, we use the formula

$$I(k) = \sum_{i=0}^{N} \sum_{j=0}^{N} \left\langle \frac{\sin(k|\mathbf{R}_i - \mathbf{R}_j|)}{k|\mathbf{R}_i - \mathbf{R}_j|} \right\rangle \tag{1}$$

where $\mathbf{R}_i, \mathbf{R}_i$ are coordinates of the monomers in 3D space obtained from the simulated polymer.

Then, the Guinier approximation is computed on the same k array to compare them side by side.

2.1 Polimer Extension

A considerable ammount of attention has been driven toward the physical manipulation of polymers that are not large to be on termodynamic equilibrium, the extension of a polymer by the stretching of a canteliver is a recurrent example[?] in this regard, an expression for the force - extension relationship has been found by[?] .

$$|\vec{Q} \cdot \vec{u}_x| = Nb \left[\coth \alpha - \frac{1}{\alpha} \right]; \alpha = \frac{Fb}{K_B T} \tag{2}$$

In order to test this analytical formula with experimental data, a simulation was performed, where one polymer of 100 monomers was exposed to a range of constant forces from 0 to 10 pN. The polymer is modeled as a chain of fixed-length bonds, and its configuration is updated by randomly perturbing individual bond orientations.

Each trial move changes the end-to-end vector and the associated potential energy due to the applied force. The acceptance of these moves follows a Boltzmann-like (Metropolis) criterion, which ensures that configurations are sampled according to thermal equilibrium at temperature T T. This energy-based acceptance allows the algorithm to capture thermal fluctuations and generate physically meaningful polymer conformations under force. For the details of the algorithm look to Algorithm 1.

Algorithm 1 Monte Carlo Polymer Extension Under Force

1: Initialize N bond vectors uniformly on the unit sphere, scaled by bond length b
2: Compute monomer positions and end-to-end vector $\mathbf{Q}$
3: Set external force $\mathbf{F} = (F_x, 0, 0)$ and energy $U = -\mathbf{F} \cdot \mathbf{Q}$
4: **for** step $= 1$ to n_{steps} **do**
5:     Randomly select bond index i
6:     Propose new bond direction $\hat{u}$ and bond $\mathbf{b}'_i = b\hat{u}$
7:     Compute proposed $\mathbf{Q}'$ and U'
8:     $\Delta U \leftarrow U' - U$
9:     **if** $\Delta U < 0$ **or** rand $< e^{-\Delta U/k_B T}$ **then**
10:        Accept move: update bonds, $\mathbf{Q} \leftarrow \mathbf{Q}'$, $U \leftarrow U'$
11:        Recompute monomer positions
12:    **end if**
13:    Store $\mathbf{Q}$ and U
14:    **if** step mod $n_{\text{skip}} = 0$ **then**
15:        Save polymer configuration to file
16:    **end if**
17: **end for**
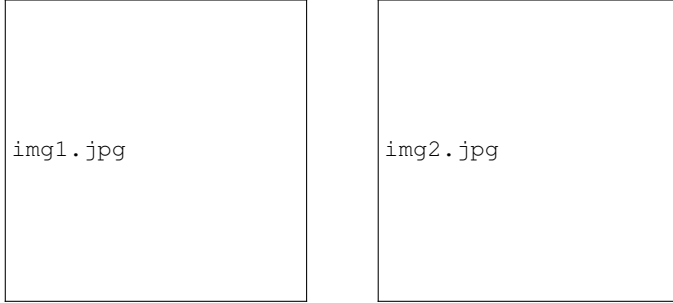18: Combine saved frames into a trajectory file

Fig. 3 Probability distribution

Fig. 4 Structure factor (simulated)

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

Fig. 5 Structure factor comparison (simulation and Guinier approximation)

3 Results and Discussion

- Description of the numerical results (Parts 1 to 4)

- Comparison with theoretical results (qualitatively and quantitatively)
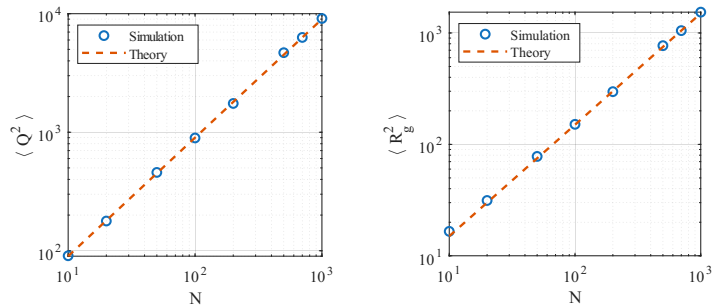
- Discussion

4 Conclusion

- General conclusion about FJC model

- Summary of the main results

- Perspectives

5 References

1 Masao Doi and Samuel F. Edwards. *The Theory of Polymer Dynamics*. Oxford University Press, Oxford, 1986.
2 Nicholas J. Giordano. *Computational Physics*. Prentice Hall, Upper Saddle River, NJ, 2006.
3 Rubin H. Landau, Manuel J. Páez, and Cristian C. Bordeianu. *Computational Physics: Problem Solving with Python*. Wiley-VCH, Weinheim, 2015.
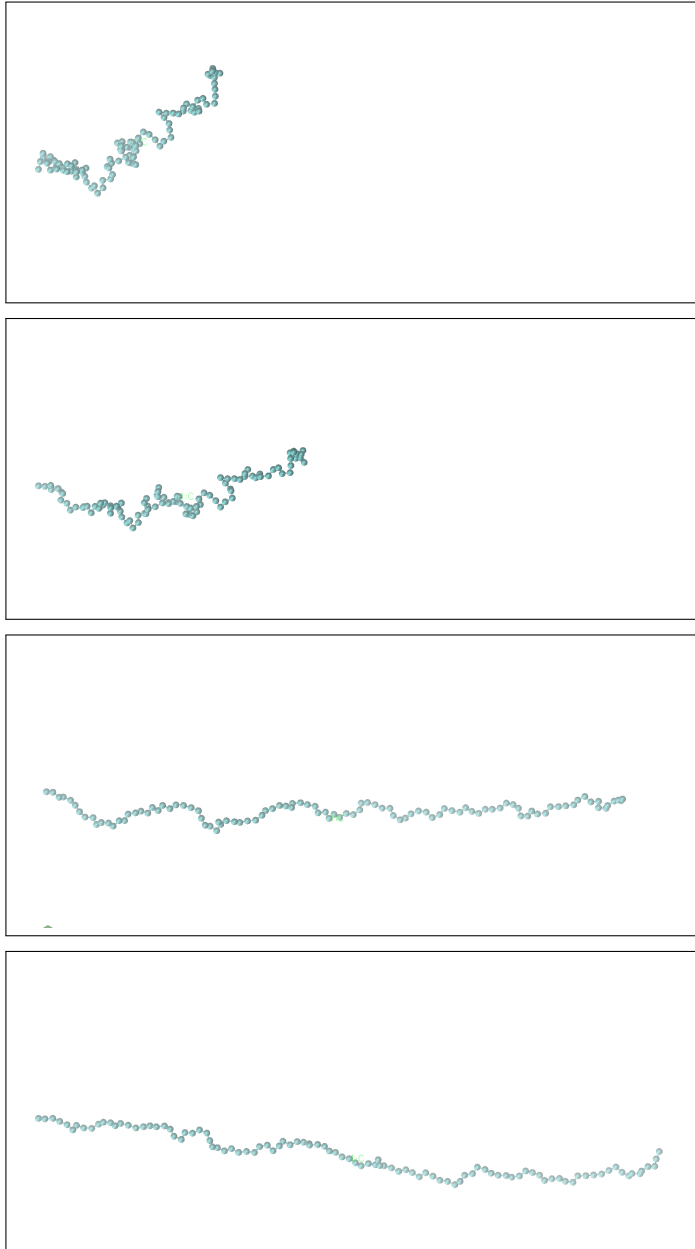
Fig. 2 $\langle Q^2 \rangle$ (left) and $\langle R_g^2 \rangle$ (right)

Fig. 7 Extension evolution of the polymer, sturating to the theoretical value

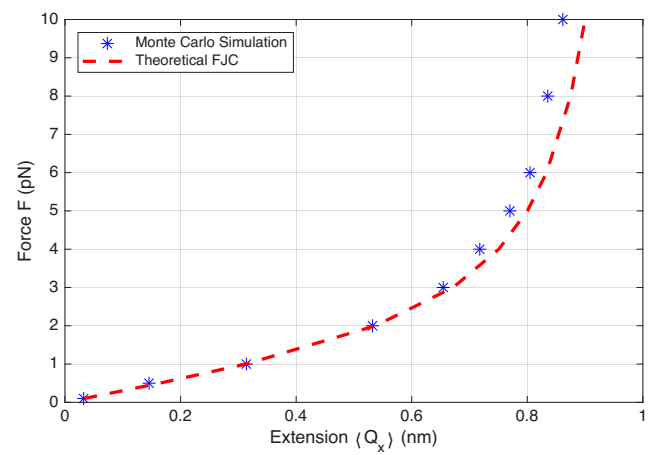**Fig. 6** Extension of the polymer using Monte-Carlo simulation

Fig. 8 Extension - Force curve

4 Fabio Manca, Stefano Giordano, P. L. Palla, Fabrizio Cleri, and Luciano Colombo. Monte carlo simulations of single polymer force-extension relations. In *Journal of Physics: Conference Series*, volume 383, page 012016. IOP Publishing, 2012.

5 Michael Rubinstein and Ralph H. Colby. *Polymer Physics*. Oxford University Press, Oxford, 2003.