Stat. Mech. of Complex Systems

Project 2
Monte Carlo Calculation of Average Extension of Polymers

The goal of this project is to determine the dependence of the size of a polymer on the number of monomers N it is composed of. We will consider polymers that are linear and unbranched. In addition, we will assume that the polymers are well separated from each other and we can thus neglect the interactions between them. Consequently, the collection of polymers can be described by the physics of a single polymer alone.

Model.- To understand basic properties of polymer chains we will consider models based on a lattice description. Let us assume that the chain follows a regular square (in 2D) or cubic (in 3D) lattice, with points, located at $\{\mathbf{R}_i\}$ with $i = 1, 2...N$, representing polymer monomers and rods connecting them the bonds between such monomers (see Fig. 1). Without loss of generality, we can take the lattice spacing $a = 1$. On this lattice we will consider two different models: a *freely jointed* ideal chain model and an *excluded volume* chain model.

Ideal chain models, even those with short-ranged interactions along the chain, allow the chain to loop back onto itself and segments that are well separated in the chain can overlap. To avoid this unphysical occurrence we require that there is an "excluded volume effect", which in lattice models means that a path on the lattice cannot pass through sites that have been traversed previously. We can thus identify the *freely jointed* ideal chain model to a random walk on a lattice and the *excluded volume* chain to a "self-avoiding" walk on a lattice.

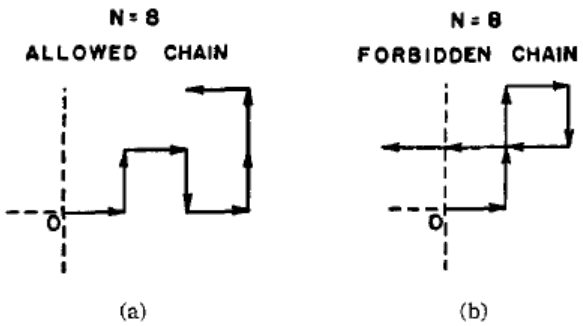

Figure 1: Examples for an allowed chain and a forbidden chain.

Characterization of size of polymer.- An important quantity which is of interest to characterize the size of the polymer chain is the *end-to-end vector* $\mathbf{R}$ which joins one end of the polymer to the other.

$$\mathbf{R} = \mathbf{R}_N - \mathbf{R}_1 = \sum_{n=1}^{N-1} \mathbf{r}_n \,, \tag{1}$$

being $\mathbf{r}_n = \mathbf{R}_{n+1} - \mathbf{R}_n$ the vector of the nth bond. The averaged square root of the square of $\mathbf{R}$ can be used as a measure of the size of the polymer $R_P \sim \sqrt{\langle \mathbf{R}^2 \rangle}$.

Another measure of the size of a polymer is given by its *radius of gyration* R_g. Being $\mathbf{R}_{CM}$ the position of the center of mass of the polymer, its radius of gyration is given by

$$R_g^2 = \frac{1}{N}\sum_{n=1}^{N}\langle(\mathbf{R}_n - \mathbf{R}_{CM})^2\rangle\,. \tag{2}$$

The radius of gyration is a more convenient measure of the size of a bundled polymer since it can be directly obtained from experiments and is a valid measure not only for linear polymers but also for branched polymers.

For both measures, the relevant information is their scaling with the number of monomers N of the polymer. Such scaling is represented through the exponent ν

$$R_P \sim N^{\nu}\,, \qquad R_g \sim N^{\nu}\,, \tag{3}$$

Sampling algorithm of self-avoiding walk model.- In principle the sampling problem seems easy, since in our model every self-avoiding random walk of length N has the same probability of occurrence. We could do a complete sampling of all possible polymers of a given length, and in this way compute the ensemble average exactly. To this end, we could generate all possible free random walks of length N without back-tracking and throw away all intersecting walks. However, this algorithm becomes exceedingly costly very fast: at every step of the free random walk we have 3 possible directions, hence there are 3^N possible free random walks. For example, even for rather short walks with, e.g. $N = 20$, this gives already $3^{20} \approx 3 \times 10^9$ possibilities. It would thus be desirable to sample in the spirit of the Monte Carlo method only a small set of self-avoiding random walks, and use these to estimate the end-to-end distance/radius of gyration.

The Rosenbluth method.- The Rosenbluth method[2] generates M different polymers/self-avoiding random walks independently from each other, by growing every polymer individually. The polymer is grown successively by adding a new subunit at $\mathbf{R}_i$ to the end of the polymer, choosing randomly one of the m_i unoccupied lattice sites adjacent to $\mathbf{R}_{i-1}$. In growing the chain one can encounter the different situations shown in Fig. 2 for the 2D case, with different values of m_i.

For each polymer k grown we record the positions of all monomers $\mathbf{R}_i^{(k)}$. In addition, we record the statistical weight of the polymer

$$w_k^{(N)} = \prod_{i=1}^{N} m_{k,i} \tag{4}$$

where $m_{k,i}$ is the number of unoccupied lattice sites encountered in the growing process. The averaged end-to-end distance or radius of gyration can be calculated by the weighted average

$$R_P^2 = \frac{\sum_k^M w_k^{(N)}(\mathbf{R}_N^{(k)} - \mathbf{R}_1^{(k)})^2}{\sum_k^M w_k^{(N)}}\,, \qquad R_g^2 = \frac{\sum_k^M w_k^{(N)}\left[\frac{1}{N}\sum_{n=1}^{N}(\mathbf{R}_n^{(k)} - \mathbf{R}_{CM})^2\right]}{\sum_k^M w_k^{(N)}}\,. \tag{5}$$

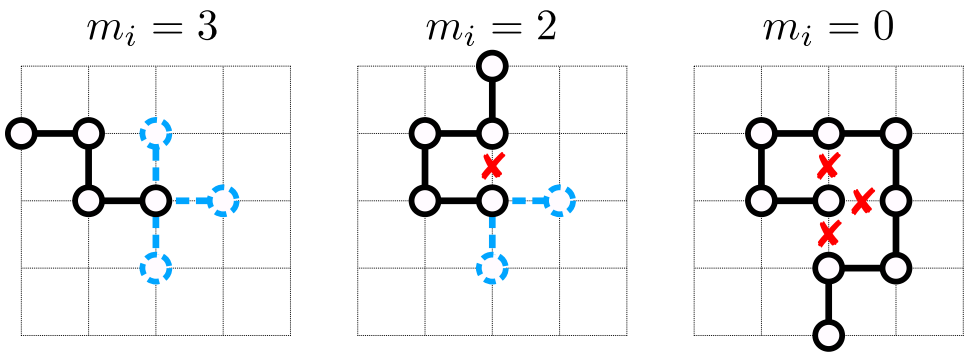

Figure 2: Different situations in polymer growing. The one on the right with $m_i = 0$ corresponds to a terminating chain.

EXERCISE:

A. Ideal polymer.

1. Implement a growing algorithm of an ideal polymer as a random walk process on (i) a square lattice (2D); (ii) a cubic lattice (3D). You can assume, without loss of generality, that the first monomer is at $(0, 0, 0)$ and the second is at $(1, 0, 0)$.

   (a) Calculate the dependence of R_P^2 and R_g^2 on the number of monomers for $N < N_{max} = 100$. Plot your results.

   (b) Extract the exponent ν defined in Eq. 3.

   Do your calculations considering a number of at least $M = 1000$ independent realizations of your polymers.

B. Excluded volume polymer.

1. Implement a growing algorithm of an excluded volume polymer as a self-avoiding walk process on: (i) a square lattice (2D); (ii) a cubic lattice (3D). Procedure: starting from $(0, 0, 0)$, each new link/monomer of the chain is chosen randomly and with equal probability among all the available possibilities (excluding nodes of the lattice where there is already a link/monomer.)

2. Implement the Rosenbluth method to properly sample excluded volume polymers.

   (a) Calculate the dependence of R_P^2 and R_g^2 on the number of monomers for $N < N_{max} = 100$. Do the averages: (i) using bare averages over the polymers generated; (ii) using the Rosenbluth sampling method.

   (b) Represent R_P^2 and R_g^2 vs N for the two averaging methods. Show your results on a log-log plot.

(c) Extract the exponent ν defined in Eq. 3.

Do your calculations considering a number of at least $M = 1000$ independent realizations of your polymers.

Note that:

- When generating M polymers of length N we also generate M polymers of all lengths $< N$. Hence, if we keep track of the weights at every growth step, we can compute from one simulation the complete length dependence of the end-to-end distance or the radius of gyration (up to length N).
- When a polymer gets stuck (for $i < N$ the chain gets terminated), you will end up with less than M polymers beyond a certain length, which needs to be considered in doing the averages.

References

[1] W. Krauth, *Statistical Mechanics: Algorithms and Computations*, Oxford university press, 2006.

[2] Rosenbluth, M. N., Rosenbluth, A. W. *M*onte Carlo calculation of the average extension of molecular chains. The Journal of Chemical Physics, **23**, 356-359 (1955).