Lecture 6: Exercise on multiple Markov chains (MMC)

Simulate the absorption of a grafted polymer to an attractive hard wall with a Monte Carlo using the MMC method. The model for the polymer is composed of $N + 1$ monomers in the two-dimensional plane, with coordinates $\vec{r}_i = (x_i, y_i)$ for $0 \leq i \leq N$ (see Fig. 1(a)).

Geometry

- Grafting is imposed by fixing $(x_0, y_0) = (0, 0)$.

- Self-avoidance between any monomers i and j is imposed by requiring $|\vec{r}_i - \vec{r}_j| > c$, with $c = 1$.

- The chain connectivity is achieved by requiring each bond length $\ell_i = |\vec{r}_i - \vec{r}_{i+1}|$ to fluctuate within the interval $[\ell^{\min}, \ell^{\max}]$, with say $\ell^{\min} = c$ and $\ell^{\max} = 1.3c$.

- The hard wall constraint imposes $y_i \geq 0$ for each monomer i.

Thermodynamics

- The attraction between the wall on the monomers derives from an energetic contribution $-\epsilon = -1$ to each monomer with $y_i < h$, say with $h = 1/2$. We may neglect the trivial constant contribution from the grafted monomer $i = 0$. Thus, the total energy of a configuration $\mathcal{C}$ is $E(\mathcal{C}) = -\epsilon n$, where n is the number of monomers in $\mathcal{C}$ with $y_i < h$.

- Each polymer is in a canonical ensemble at its own inverse temperature $\beta \geq 0$ (β's will be different; see the MMC scheme below).

Monte Carlo moves

- Local shifts: choose a displacement $\vec{\delta}$ from a symmetric distribution (e.g., a Gaussian around zero or an appropriate uniform distribution) and try to displace a randomly picked monomer $\vec{r}_i \to \vec{r}_i + \vec{\delta}$. If the geometric constraints are not satisfied, reject the move; otherwise, accept the new configuration $\mathcal{C}'$ according to the Metropolis rule at β.
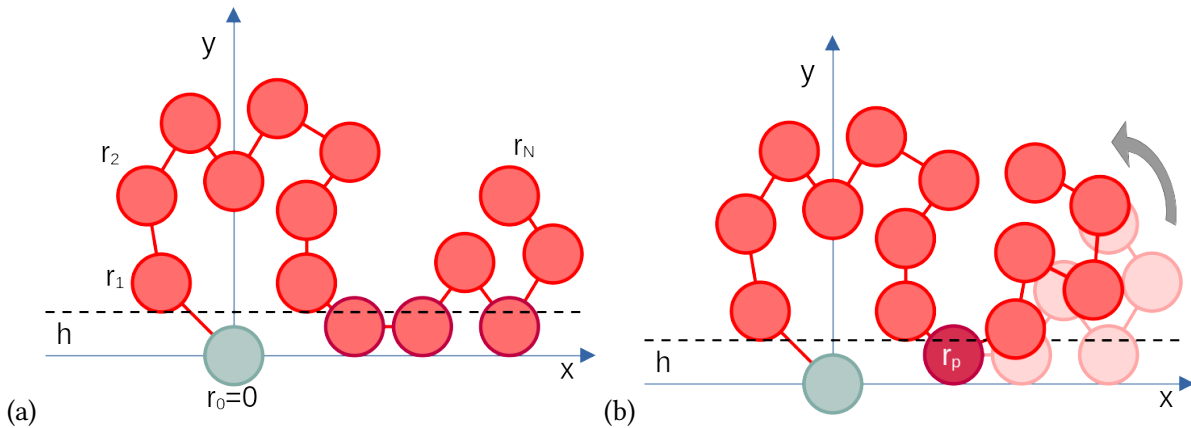

Figure 1: (a) Allowed configuration of the grafted polymer, with $n = 3$ energetic contacts between monomers and wall. (b) Pivot move around $\vec{r}_p$, generating another allowed configuration, reducing contacts to $n = 1$ (thus, accepted with the Metropolis rule with probability lower than 1).

- Pivot (Fig. 1(b)): choose a monomer p at random in the range $0 \leq p \leq N - 1$ and rotate the monomers with $i > p$ as a rigid body with respect to $\vec{r}_p$ of an angle θ drawn randomly from an interval $[-\theta^*, \theta^*]$. Again, after checking if the geometry is fine, accept the move to $\mathcal{C}'$ according to the Metropolis rule. Note that the difference in energy $E(\mathcal{C}') - E(\mathcal{C})$ depends only on the changes for $i > p$.

MMC

- Choose a reasonable set of K inverse temperatures $\{\beta_k\}$, in python or C language indexed from $k = 0$ to $k = K - 1$: at larger β's, the polymer should be mostly absorbed; at small β it should float freely; at a critical β_C, it should display the largest fluctuations in energy and other geometrical indicators.

- We do not want to copy configurations in a swap because it takes $2 \times N \times 2$ operations. It is convenient to track which configuration belongs to a given β_k using an array of indices I. Initially $I = (I_0 = 0, I_1 = 1, ..., I_{K-1} = K - 1)$. Then, each time there is a swap at $k, k + 1$, only indices swap:

$$(I_0, I_1, ..., I_k = A, I_{k+1} = B, ..., I_{K-1}) \to (I_0, I_1, ..., I_k = B, I_{k+1} = A, ..., I_{K-1})$$

  In this scheme, the moves at β_k act on its current configuration, stored at position I_k. This is the first index in a multidimensional matrix (the second is the monomer index i, where its (x_i, y_i) are found). In summary, at β_k, we have $r(I_k, i, 0)$ for the x_i of the configuration and $r(I_k, i, 1)$ for y_i.

- As a typical recipe, for every β_k, a block of moves contains one attempted pivot and N attempted local shifts. Furthermore, one swap between configurations at neighboring β_k and β_{k+1} (with randomly picked $k \in [0, K - 2]$) should be attempted at the end of the K blocks. This recipe is by no means rigid; it is just an example.
  Between samplings, B blocks of moves should be performed to decorrelate data sufficiently.

- To monitor the state of the system, evaluate:

  - The average energy $U(\beta) = \langle E \rangle_\beta$ and its variance $VU(\beta) = \langle E^2 \rangle_\beta - \langle E \rangle_\beta^2$.
  - The mean squared end-to-end distance $R_e^2(\beta) = \langle |\vec{r}_N|^2 \rangle_\beta$, its variance $VR_e^2(\beta)$.
  - The mean height of the end, $Y_e(\beta) = \langle y_N \rangle_\beta$, and its variance $VY_e(\beta)$.

Questions

1. Show the energy histograms for all β_k in the same plot. Is there a good overlap between histograms of neighboring β_k's? What was the logic for settling down to a final list of β's after your initial attempts?

2. Plot the listed quantities as a function of β for a given N or many N's. Do the plots meet your expectations? Is there any signature of the critical temperature?

3. What did you find an *appropriate* distribution for the random displacements in the local shifts?

4. Why do we use a symmetric interval $[-\theta^*, \theta^*]$ in the pivot move? Should θ^* depend on β?

5. Given the same B blocks of moves at all β_k, how does the autocorrelation in data vary with β?

Lecture 7: Gillespie algorithm

Implement the Gillespie algorithm to simulate the Brusselator model, whose transition rates for a state $\mathcal{C} = (X, Y)$ are

$$w_1 = a\Omega \qquad \text{for} \quad (X, Y) \to (X + 1, Y) \tag{1a}$$

$$w_2 = X \qquad \text{for} \quad (X, Y) \to (X - 1, Y) \tag{1b}$$

$$w_3 = \frac{1}{\Omega^2} X(X - 1)Y \qquad \text{for} \quad (X, Y) \to (X + 1, Y - 1) \tag{1c}$$

$$w_4 = bX \qquad \text{for} \quad (X, Y) \to (X - 1, Y + 1) \tag{1d}$$

Run some simulations using $a = 2, b = 5$ and for different volume sizes: $\Omega = 10^2, 10^3, 10^4$. What can one note by varying Ω?