PH419: Physics of Biological Systems
Assignment 5
Equilibirium Models and Polymers

1. **Polymerization processes**

   Many cellular processes involve polymerization, where a bunch of monomers bind together to form a polymer. Examples include transcription, translation, construction of the cytoskeleton, etc. Here we consider a simple model of polymerization where each monomer is added to the growing chain with the same equilibrium binding constant K.

   This situation is described by the following set of chemical equations:

$$X_1 + X_1 \overset{K}{\rightleftharpoons} X_2$$

$$X_1 + X_2 \overset{K}{\rightleftharpoons} X_3$$

$$\vdots$$

$$X_1 + X_{n-1} \overset{K}{\rightleftharpoons} X_n$$

$$\vdots$$

   The symbol X_n denotes a polymer n monomers in size. In equilibrium, there will be polymers of all different sizes.

   (a) Find an expression for the probability that a polymer is n monomers in length in terms of K and $x = [X_1]$, the concentration of free monomers. Use this result to get an expression for the average polymer size $\langle n \rangle$.

   (b) Show that the average polymer size can be written as

$$\langle n \rangle = \frac{d \ln Q}{dKx},$$

   where $Q = 1 + Kx + (Kx)^2 + (Kx)^3 + ...$ is the binding polynomial.

   (c) Plot $\langle n \rangle$ as a function of Kx. How does $\langle n \rangle$ behave as $Kx \to 1$ from below?

2. **Carbon monoxide and hemoglobin**

   Carbon monoxide is a deadly gas that binds hemoglobin roughly 240 times as tightly as oxygen does (this means that CO has 1/240 the dissociation constant of O_2 , or $240K_{CO} = K_{O_2}$, where $K_{O_2} = 26mmHg$).

   (a) Using a lattice model, calculate the probability that haemoglobin will be saturated with oxygen, and the probability that haemoglobin will be saturated with carbon monoxide. For simplicity, ignore haemoglobin states with partial occupancy.

   (b) In experiments, Hemoglobin binding to carbon monoxide has a Hill coefficient of 1.4 and hemoglobin binding to oxygen has a Hill coefficient of 3.0. Modify the formula derived above in light of these experimental Hill coefficients. Estimate the numerical probabilities for oxygen saturation and carbon monoxide saturation when the partial pressure of CO is $2mmHg$. Assume that atmospheric oxygen constitutes roughly 21% of air (1atm = 760 mmHg).

   (c) Plot the probability of O_2 binding to hemoglobin as a function of the partial pressure of CO assuming the oxygen partial pressure remains constant.

   (d) Show that CO and O 2 will have an equal probability of binding when the condition

   $$\left(\frac{[O_2]}{K_{O_2}}\right)^{n_{O_2}} \left(\frac{K_{CO}}{[CO]}\right)^{n_{CO}} = 1$$

   is satisfied and work out the partial pressure of CO at which this occurs.

3. **Radius of gyration**

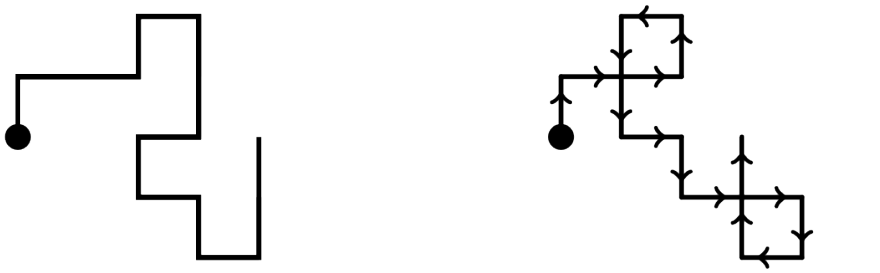
   Prove the relation between the contour length and the radius of gyration of a Freely Jointed Chain (FJC) polymer given by

   $$< R_G^2 >= \frac{Na^2}{6}$$

   where a is the Kuhn length of the polymer.

4. **Self-avoiding chains**

   One of the most important modifications to the Random Walk (RW) polymer is the concept of a Self Avoiding Walk (SAW) polymer, where the chain cannot cross itself. Thus for a Self Avoiding Walk, each step is independent of the previous steps (exactly as in the RW), with the only additional constraint being that two segments cannot cross each other. While the properties of a SAW polymer cannot be calculated analytically, we can do a simple scaling analysis to understand the key properties.



(a) A self-avoiding walk (b) A simple random walk

Figure 1:

(a) Consider a SAW in one dimension. Using simple physical arguments, calculate how the size of the polymer R scales with the number of Kuhn segments N.

(b) Now consider a SAW in any general d dimension. The free energy consists of two components, F_{el}, the elastic contribution due to the entropic nature of the polymer (same as in RW polymer), and F_{rep}, the repulsive component due to the self avoiding nature. For a polymer of N segments and a typical size R, the internal concentration of monomers is

$$c_{int} \sim \frac{N}{R^d}$$

The repulsive contribution to the Free energy can be then estimated as

$$F_{rep} = \int c_{int}^2 dV$$

where c_{int}^2 denotes the probability of two monomers coming into contact. Estimate F_{rep} as a function of R and N.

(c) Now use the random walk result for F_{el} to compute the total free energy,

$$F = F_{el} + F_{rep}$$

(d) Minimize the above free energy with respect to R to obtain the scaling of the polymer size R with the number of segments N. You may ignore all numerical coefficients. Does that answer satisfy the one dimensional result obtained in (i)?

(e) Simulate a SAW polymer on a 2D square lattice with $N = 64, 128, 256, 512$. Plot the average end-to-end distance $R \equiv \sqrt{< R^2 >}$ vs the number of segments N. Fit the curve to a functional form $R \sim N^\nu$ and estimate the scaling exponent ν. How does the simulation result compare with the scaling answer obtained previously?

(f) In what dimension does the SAW polymer reduce to the RW polymer? Can you physically explain the result?