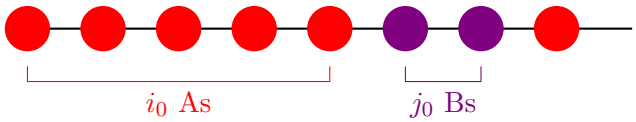
Phase Transitions of Polymers

In this problem, we will exploit a trick to understand the phase transitions of polymers, which, for simplicity, we will take to have two possible states per monomer, which we label as A and B. We can then describe the state of the polymer by a sequence of lengths, $i_0, j_0, i_1, j_1, \ldots$ where i_0 is the length of the first A sequence, j_0 the length of the next B sequence, and so on:



If the chain has N monomers, we of course require

$$N = \sum_k (i_k + j_k).$$

If we assume that the partition function takes the form of[1]

$$Z_N = 2 \sum_{\text{configs}} \prod_m a_{i_m} b_{j_m},$$

with a_n and b_n functions of our choosing, we can actually extract a lot of useful physical information, even if the a_n and b_n have (somewhat) complicated forms. This actually isn't an awful assumption – the most likely place it breaks down is at the ends of the chain, but this is almost always negligible for a long polymer.

We expect that

$$-\frac{k_B T \log Z_N}{N} \to f,$$

a well-defined limit corresponding to free energy per monomer, in the large N limit. So let us begin by defining the function

$$\Gamma(x) = \sum_{N=0}^{\infty} \frac{Z_N}{x^N}.$$

which should be well defined for $f < k_B T x$.

(a) Show that

$$\Gamma(x) \sim \frac{1}{1 - A(x)B(x)}$$

where we have defined

$$A(x) = \sum_{n=0}^{\infty} \frac{a_n}{x^n},$$

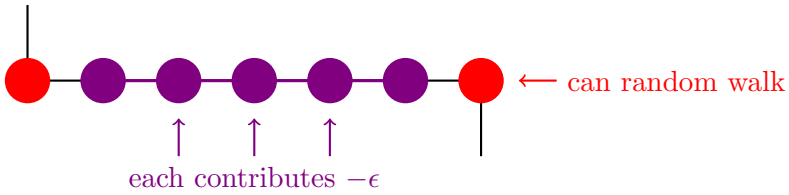
$$B(x) = \sum_{n=0}^{\infty} \frac{b_n}{x^n}.$$

[1] The factor of 2 accounts for the fact that we need to allow for a B to have come first. But by simply "reversing" the chain that is easy to account for – this leads to multiplying by a factor of 2 for all the configurations where a B comes first.

(b) Conclude that the largest x such that $1 = A(x)B(x)$ corresponds to $f/k_{\mathrm{B}}T$.

We now turn to the **helix-coil** transition in proteins: at high temperatures, the protein is in essentially a random state, as the entropy of being in some complicated coil is the dominant component of free energy. At lower temperatures, however, we expect that the protein will tend to form helices, which are stabilized by attractive interactions between the "side groups" on the amino acids, and by hydrogen bonding on the backbone.

Let us denote the coil state with A, and the helix state with B. Let us say that for every amino acid in the helix state surrounded by two other amino acids also in the helix state, we get an energy $-\epsilon$. However, at the ends of the helix state, we do not get this gain in energy. When the chain is in the coiled state, it acts as a random walker in d dimensions. For simplicity, take the random walker to move either forward or backward one step, in every dimension, with equal probability:



(c) Show that $1 = A(x)B(x)$ is equivalent to

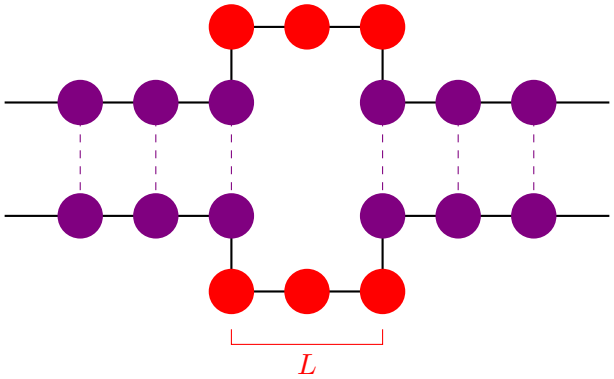
$$(x - \alpha)(x^2 - x - \gamma) = \gamma^2.$$

Find the values of α and γ, which you should show are strictly positive.

(d) Describe the behavior of this model at various T. Show that no phase transitions occur in this model.

Let us now turn to the problem of **DNA melting** using the method introduced above. When DNA "melts" we mean that the double-stranded helix comes apart into two single strands. As before, energetically we favor a double stranded state as there are attractive interactions between the nucleic acids, but entropically we favor having two floppy proteins as opposed to one.

A simple model for this is now proposed, again working in arbitrary dimension d. Let state B correspond to the double stranded state, where the proteins are bound together. State A corresponds to a "bubble": a pair of single stranded states, which form 2 independently moving chains of length L, say, which must meet at the ends:



We assume that it costs an energy ϵ per monomer pair to break the bonds between the nucleic acids, and will treat the double stranded system as one polymer, with states A and B as described above. We

also assume that the polymer is a random walker of the same type described in the previous part. In the single stranded state, of course, the two chains can walk independently, as long as they begin and end together at the ends of the bubble.

(e) Explain why you can pick $b_m = 1$. By estimating the free energy of a loop of length m, show that a_m is of the form

$$a_m = \frac{\beta \alpha^m}{m^{d/2}}.$$

(f) Discuss, as a function of dimensionality, the nature of the melting transition, with increasing T. You'll obviously want to look at the free energy to do this. For what dimensions is it a true phase transition? Is it continuous or discontinuous?