Polymer Sizes

A polymer is a chain-like molecule with many repeated units, called monomers. On very large length scales, characterized by a length scale called the **persistence length** L_p, a polymer begins to act like a floppy chain. Crudely speaking, you can think of a polymer with length $L \gg L_\mathrm{p}$ as a random walker which takes steps of length L_p. Work in a d dimensional space, with d arbitrary.

(a) Using the random walker model, estimate the distance $R(L)$ between the endpoints of the polymer.

An alternative model would be a "sphere packing" model: assume that the polymer is made up of many repeated units which are spheres of radius L_p, each of which thus takes up a volume of approximately L_p^d.

(b) If the polymer was able to perfectly pack these spheres into a spatial volume with minimal surface area, we would find $R(L) \sim L^\nu$. What is ν?

This is all great, except for a fatal flaw: we did not take into account the geometric obstruction that the random walk cannot return to the same place twice! This problem introduces you to Flory's model, which is a very simple prediction for the size of a large self-avoiding polymer.

We want to describe the free energy $F(R)$ of a polymer chain of length L at temperature T, if it has persistence length L_p, as a function of the size R of the polymer. The free energy $F = E - TS$ has two terms, one corresponding to energies and one to entropies. We need to take into account both.

(c) Using the random walker model above, estimate the entropy for large L and R.

The second contribution is an energy. Following Flory, we make the following simple argument:

$$E = C\frac{L}{L_\mathrm{p}}k_\mathrm{B}T \times \left(\frac{L_\mathrm{p}}{R}\right)^d$$

Here $C > 0$ is a dimensionless constant. The first term just corresponds to the fact that the energy should depend linearly on the length, and have the right dimensions. The second term corresponds to the fact that the energy of the chain should be repulsive, and depend on, roughly speaking, the concentration of monomers.

(d) Find the size $R(L)$ of the polymer by minimizing $F(R)$, and show that

$$R(L) = \left(\frac{3}{dC}\frac{L}{L_\mathrm{p}}\right)^\nu L_\mathrm{p}.$$

where

$$\nu = \frac{3}{d+2}.$$

(e) The previous answer breaks down for $d > d_\mathrm{c}$. Find d_c and justify your answer.