statistical physics → canonical ensemble ★★

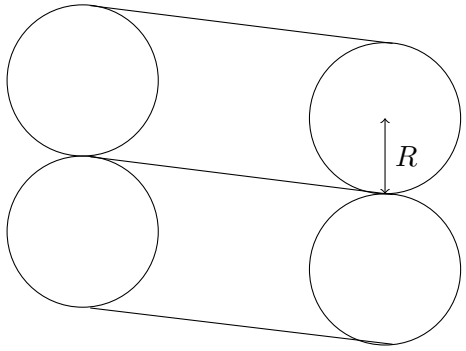
Helix Formation from Entropy

In this problem, we will propose a simple explanation for why flexible polymers can spontaneously form helices. It is known that many biopolymers (such as proteins) can often form helices in their natural configurations. We will propose in this problem that this is due to entropic effects.

To be more precise, consider a very long, flexible polymer of length L and radius R, placed in a solution of hard sphere molecules of radius r, with number n per unit volume, at temperature T. You may assume $L \gg R \gg r$. The presence of the polymer reduces the volume of the container available to the hard sphere molecules. Configurations where the polymer is coiled up reduce the effective volume that the polymer takes up, and we expect this will give these configurations extra free energy. The goal of this problem will be to make this claim a bit more quantitative.

In this problem, you may simplify your life by ignoring O(1) factors – the main goal of this problem is just to get a sense for the physical mechanism involved.

(a) Suppose that this polymer coils up into a helix such that the rods touch each other vertically as they wind around the helix, as follows:



Estimate in terms of R, r and L the difference in the excluded volume around the rod if the rod was straight, to if the rod is in the helix.

(b) From the theory of elastic solids, the energy per unit length it costs to bend the rod into a helix is roughly given by

$$\frac{E}{L} = \frac{c\xi k_B T}{R^2}.$$

Here c is a constant which is about 0.01, and ξ is a constant called the persistence length, which roughly says how floppy the polymer is (small ξ means more floppy). By computing the free energy difference between the straight polymer and helix polymer, determine a condition for whether or not the polymer will spontaneously bend into a helix.

(c) A floppy biopolymer, such as a single stranded protein, may have a very short persistence length of only 3 nm, and have a radius of about 1 nm.[1] Let us assume that the hard sphere molecules are a solution of water molecules of radius 0.25 nm, which crudely has concentration of 1 molecule per nm^3. Using $c \approx 0.01$, explain whether or not the simple model of this problem predicts the protein will form a helix.

[1] By contrast, DNA has a persistence length of about 50 nm.

(d) Do you think that a configuration where the polymer coils up into a solid sphere would be the most favorable, in terms of free energy?