Homework 9

Confining a Self-Avoiding Polymer in a Space with Low Dimensionality[1]

In this exercise, we will provide an example of Flory approach in polymers by studying how the confinement of a chain affects its conformational properties. Let us consider a self-avoiding polymer made of N bonds of length b, and let R and b^3 be the average end-to-end distance and the excluded volume, respectively.

1. Show that within the Flory theory[2] $R \sim bN^{3/5}$.
2. Imagine to take two long layers and to put them parallel to each other at a distance b. If we fill the space between the two layers with the chain, we intuitively expect its conformation to be perturbed because of confinement. Find the new value R_{2D} of the end-to-end distance. Is it larger or lower than the "unperturbed" value?
3. Now imagine to confine our polymer in a tube of diameter b. What is the new value R_{1D} of the end-to-end distance? How is this value with respect to the previous case and the unperturbed chain?

Confining a Polymer in a Space with Low Dimensionality (Scaling Approach)[3]

In this exercise, we will provide an example of scaling approach in polymers by studying how the confinement of a chain affects its conformational properties. The system under study is a generalization of previous one, where we were able to find the exponents of a self-avoiding walk in various dimensions by constructing a Flory free-energy.
Let us consider a polymer made of N bonds of length b, and let R be its average end-to-end distance.

1. Imagine to take two long layers and to put them parallel to each other at a distance h, with $b < h < R$. If we fill the space between the two layers with the chain, we intuitively expect its conformation to be perturbed because of confinement. Find the new value of the end-to-end distance R' for an ideal ($R \sim bN^{1/2}$) and a self-avoiding ($R \sim bN^{3/5}$) chain. Is it larger or lower than the unperturbed value?
2. Now imagine to confine our polymer in a tube of diameter h. What are the new values of R'? How are those values with respect to the previous case and the unperturbed chain?

[1] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.

[2] Actually, such an exponent is but an approximation of the real one (which is roughly 0.588 according to simulations), thus showing how results from Flory theory are not to be blindly trusted. It is nonetheless true that this is a simple theory which gives a "flavor" of the physics behind the system, and its results turn often out to be not so far from the real ones.

[3] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.

Hint: you can assume that up to length scale h the polymer follows its unperturbed statistics. Remember that in the case of a self-avoiding chain embedded in a two-dimensional space, the exponent changes from 3/5 to 3/4. What is the exponent when the embedding space is one-dimensional?

Scaling Theory of a Chain under Tension[4]

In this exercise, we will derive by a scaling approach some formulas for the behavior of a chain under the action of an external pulling force f. The basic idea relies on the fact that the long wavelength modes "feel" the stretching more than the low ones, since in order to reach a given end-to-end distance the chain tries to minimize the entropy penalty to pay. In other words, one can assume at a first approximation that there exists a certain length scale ξ such that the unperturbed chain statistics are preserved at all the lower length scales, while the chain is almost perfectly stretched at larger length scales. In this way, one can describe the chain as made of n "blobs" of size ξ, each made of g monomers, such that the section of the chain within a single blob is described by the usual formula $\xi \sim bg^{\nu}$ (e.g. $\nu = 1/2$ for an ideal chain), while on the other end the overall end-to-end distance can be simply given by $R \sim n\xi$. The size ξ can be found by properly comparing the stretching work and the thermal energy, which at this scale are expected to be roughly equal.
Within this framework, show that

1. In the case of an ideal chain ($\nu = 1/2$) one has that an entropic version of Hooke's law holds:

$$f_{1/2} \sim \frac{k_B T}{bN^{\frac{1}{2}}} \frac{R}{bN^{\frac{1}{2}}} \tag{1}$$

2. In the case of a self-avoiding chain ($\nu = 3/5$) a nonlinear version of the previous formula is found:

$$f_{3/5} \sim \frac{k_B T}{bN^{\frac{3}{5}}} \left(\frac{R}{bN^{\frac{3}{5}}} \right)^{\frac{3}{2}} \tag{2}$$

   Is it easier to stretch an ideal chain or a self-avoiding one?

3. In the general case with arbitrary ν, one has

$$f_{\nu} \sim \frac{k_B T}{bN^{\nu}} \left(\frac{R}{bN^{\nu}} \right)^{\frac{\nu}{1-\nu}} \tag{3}$$

How are the corresponding formulas for the free-energy?

[4] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.