1. **Conformational fluctuations of a flexible chain molecule**

Polymers are often caricatured as a collection of idealized beads, linked in sequence by bonds that resist extension. In the simplest such model, the bonds are Hookean springs, giving a free energy:

$$\beta w_0(r^N) = \frac{1}{2\ell^2} \sum_{i=1}^{N} |\mathbf{r}_{i+1} - \mathbf{r}_i|^2 = \frac{1}{2\ell^2} \sum_{i=1}^{N} |\mathbf{b}_i|^2, \tag{1}$$

where $\beta = (k_{\mathrm{B}} T)^{-1}$ and ℓ is a positive constant with units of length. The number of bonds N is imagined to be very large. The three-dimensional vector $\mathbf{r}_i$ denotes the position of bead i, and the bond vector $\mathbf{b}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$ points from bead i to bead $i+1$.

Let

$$Z = \hat{z} \cdot (\mathbf{r}_{N+1} - \mathbf{r}_1) = \hat{z} \cdot \sum_{i=1}^{N} \mathbf{b}_i$$

be the molecule's extension in the z-direction (i.e., along the unit vector $\hat{z}$).

(i) Calculate the probability distribution $p(Z)$ for fluctuations in Z. (Note that $|\mathbf{b}_i|^2 = (b_i^{(z)})^2 + (b_i^{(x)})^2 + (b_i^{(y)})^2$, where $b_i^{(z)}$ is the component of $\mathbf{b}_i$ in the z-direction, etc. These three components are statistically independent fluctuating variables.)

(ii) In some real situations (e.g., in a polymer "melt" – a liquid composed of long chain molecules) the statistics of Z are very well described by the idealized distribution of part (i). The chemical bonds that hold a chain molecule together, however, are almost never well described as Hookean springs. Discuss this paradox, focusing on the question: How can simple statistics of Z emerge from the complicated microscopic interactions governing fluctuations in the conformation of a chain molecule?

(iii) A constant external force f, applied in the z-direction, acts to extend the chain molecule described by Eq. 1, giving a total free energy

$$\beta w = \beta w_0 - \beta f Z.$$

Calculate the canonical partition function $Q(f) \propto \int dr^N \, e^{-\beta w}$ for such a chain. Focus on the f-dependence of $Q(f)$, i.e., discard any constants of proportionality that do not involve f.

(iv) Use your result from part (iii) to calculate the cumulants C_n of the distribution $p(Z)$. (Recall that $C_1 = \langle Z \rangle_0$, $C_2 = \langle (\delta Z)^2 \rangle_0$, etc., where the subscript "0" indicates the absence of an external force.) You should be able to determine C_n for *all* values of n.

(v) Use your result from part (iii) to calculate the average extension $\langle Z \rangle_f$ in the presence of the external force. Your result should depend very simply on f. Would you expect a real chain molecule to respond so simply? Discuss this expectation in physical terms.

(vi) Now imagine that the beads of our idealized polymer are subjected to time-varying forces $\mathbf{f}_i(t)$:

$$\beta w = \beta w_0 - \sum_{i=1}^{N+1} \mathbf{f}_i(t) \cdot \mathbf{r}_i(t).$$

(We will focus on changes in the molecule's internal structure that result from this perturbation, not a drift in its center of mass, $\mathbf{R} = N^{-1} \sum_{i=1}^{N+1} \mathbf{r}_i$. You could imagine that a constraint has been placed on $\mathbf{R}$, or that the $\mathbf{r}_i$ variables refer to displacements away from the center of mass.)

Write equations relating the average time-dependent response $\overline{\Delta r_i}(t)$ to the forces $\mathbf{f}_i(t)$ and the correlation function $\langle \mathbf{r}_i(0)\mathbf{r}_j(t)\rangle_0$.

(vii) If you were asked to estimate $\langle \mathbf{r}_i(0)\mathbf{r}_j(t)\rangle_0$ for a chain molecule in solution, how would you go about it? Describe at least two distinct routes that you think would be productive. One should be primarily (or entirely) analytical, drawing from mathematical calculations you have performed on previous assignments. The other should involve computer simulations like those you have implemented in previous assignments. Both of your routes should address the dynamical influence of the chain's fluctuating environment. You need not do any detailed calculations, just describe in some detail the procedures you would follow.

2. **Compression of a stiff filament**

This problem also concerns a fluctuating filament, but in a very different regime of flexibility. Whereas in the previous problem different bond vectors were taken to be independent, here we will consider the chain to be very stiff, with only modest deviations from straightness.

We will work in two dimensions, so that a configuration can be specified by a scalar function $\theta(s)$ describing the filament's orientation at a distance s along its contour. Specifically, $\theta(s)$ is the angle between the local tangent vector at s and the unit vector $\hat{z}$ along the z-axis, as sketched below.
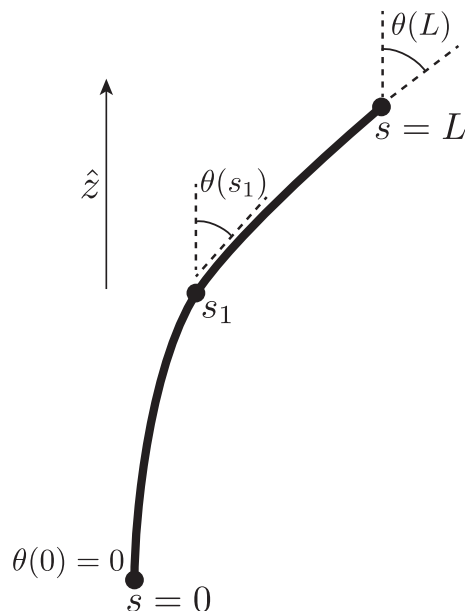
(The configurations we have in mind are not nearly as bent as the one shown, which is exaggerated for clarity of illustration.) We will fix the orientation at one end of the filament ($s = 0$) to be parallel to $\hat{z}$, i.e., $\theta(0) = 0$. The other end ($s = L$, where L is the total contour length) is unconstrained.

For small deviations from a perfectly straight configuration, the bending energy can be written

$$U_0[\theta(s)] = \frac{1}{2}\alpha \int_0^L ds \left|\frac{d\theta}{ds}\right|^2,$$

where α is a positive constant that sets the stiffness of the filament.

The questions below concern the response to a compressive force f along the z-axis. The total energy in the presence of this force is

$$U = U_0 + fZ, \qquad \text{where} \qquad Z = \int_0^L ds \, \cos\theta(s) \approx L - \int_0^L ds \left[\frac{1}{2}\theta^2(s) - \frac{1}{4!}\theta^4(s)\right].$$

Assume that θ is small throughout these questions (unless they explicitly state otherwise), justifying use of the fourth-order polynomial approximation for Z.

(i) For simplicity, restrict your attention to filament configurations described by

$$\theta(s) = \kappa s, \tag{2}$$

where κ is an s-independent parameter determining the filament's shape. For this case, write U as a function of the shape parameter κ.

(ii) Sketch $U(\kappa)$ as a function of κ, for several values of f. Choose force values that demonstrate the progression in the shape of $U(\kappa)$ as f increases.

(iii) The filament shape with the highest equilibrium probability is the one that minimizes U. What value(s) κ^* correspond(s) to this minimum?

(iv) You should find that the optimal shape parameter κ^* is particularly sensitive to variations in force near a special value f_c. Identify this critical force in terms of α and L.

(v) You should also find that, for forces near f_c, the optimal shape parameter κ^* scales in a simple way with the deviation $f - f_c$ away from the critical force. Determine this scaling relation, $|\kappa^*| \sim (f - f_c)^\zeta$, by identifying the exponent ζ.

(vi) Plot κ^* as a function of force f. Is this function analytic, or is it singular in some way?

(vii) Given that $\theta(s) = \kappa s$ is a good approximation for stiff chains of finite length, sketch your expectation for $\langle Z \rangle_f$, the average value of Z in the presence of force, as a function of f. Make separate plots for the cases of zero temperature and nonzero temperature. Describe in words how these results differ, and why.

(viii) Is the filament's response to force a true phase transition? Discuss your reasoning, giving specific attention to the role of temperature.

(ix) Phase transitions at nonzero temperature often require a limit of large system size. Describe your expectations for filament compression in the limit $L \to \infty$ of an infinitely long filament. (The small-deflection approximations invoked above are not appropriate in this limit. Why?). Your results for the ideal chain molecule of problem 1 should be pertinent to this discussion.