Exercise sheet #11

Problem 1. In this problem we calculate the radius of gyration R_g of the ideal chain model for a case in which all the monomers have the same mass.

a) Let $\vec{R}_i$ denote the positions of the points joining the vectors $\vec{\ell}_i$ of the ideal chain model. In terms of the mean position $\vec{R}_m$ is

$$\vec{R}_\mathrm{m} = \frac{1}{N}\sum_{i=1}^{N}\vec{R}_i,$$

and the radius of gyration is defined as the mean square distance from the center of mass,

$$R_\mathrm{g}^2 = \frac{1}{N}\sum_{i=1}^{N}\left\langle\left(\vec{R}_i - \vec{R}_\mathrm{m}\right)^2\right\rangle.$$

Show that you can write the expression for R_g as

$$R_\mathrm{g}^2 = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle\left(\vec{R}_i^2 - \vec{R}_i\cdot\vec{R}_j\right)\right\rangle.$$

b) Rewrite the above expression for the mean radius of gyration in the form

$$R_\mathrm{g}^2 = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=i}^{N}\left\langle\left(\vec{R}_i - \vec{R}_j\right)^2\right\rangle.$$

c) Since we are interested in the large- N limit, we can switch to continuum coordinates s_1 and s_2 along the chain, which vary between zero and $N\ell_\mathrm{K}$. Show that this allows us to write the expression for R_g in b as

$$R_\mathrm{g}^2 = \frac{1}{N^2\ell_\mathrm{K}^2}\int_0^{N\ell_\mathrm{K}}\mathrm{d}s_1\int_{s_1}^{N\ell_\mathrm{K}}\mathrm{d}s_2\left\langle\left(\vec{R}(s_1) - \vec{R}(s_2)\right)^2\right\rangle$$

d) Argue that for the ideal chain model, one can write

$$\left\langle\left(\vec{R}(s_1) - \vec{R}(s_2)\right)^2\right\rangle = \frac{s_1 - s_2}{\ell_\mathrm{K}}\ell_\mathrm{K}^2.$$

e) Using the results in (d) and (c), perform the s-integrals by going to the difference variable $s_1 - s_2$ to show that

$$R_\mathrm{g}^2 = \frac{N\ell_\mathrm{K}^2}{6} = \frac{R_0^2}{6}$$

Problem 2. In this problem, we'll make an attempt at estimating the force-extension relation of the worm-like chain model using scaling arguments. At relatively large forces, we expect the individual segments of our chain to 'more or less' line up with the direction of the force; the 'more or less' here is of course colloquial, but also accurately represents the fact that we still have a distribution of alignments. We can now introduce a unit of length ξ in between the large total chain length L and the small size b of a single segment as we'd have in a freely-jointed chain. At very short length scales, the polymer is simply straight; at our new intermediate length scales, the polymer is still relatively straight (as it resists bending) but not necessarily aligned with the external force. Therefore, this segment consists of a number of correlated links, which (following Marantan and Mahadevan), we'll call 'clinks'. Clinks are deformed through thermal fluctuations (of magnitude $k_{\mathrm{B}}T$), and resist bending because of the bending energy. Their resulting shape is an arc-like structure, deforming a distance h away from a straight line, reducing the end-to-end distance of that straight line from ξ to $\xi - \Delta$, see figure below.

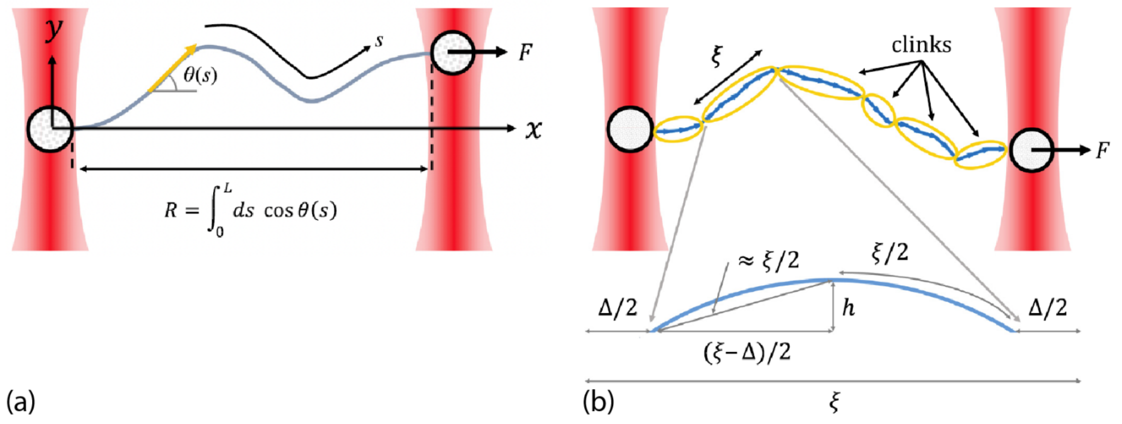

Figure 4.3: Force-extension experiment of a polymer. (a) The positions of the ends of the polymer are constrained by two beads; the distance between the beads is given by equation (4.29). (b) 'clinks' as used in the scaling approach of problem 8. Figure from Marantan and Mahadevan, Am. J. Phys. 2018.

a) If we approximate the shape of the clink as a circular arc, find its curvature in terms of h and ξ, in the approximation where both Δ and h are significantly smaller than ξ.

b) Calculate the bending energy of a clink, making use of appropriate approximations. You should get that the bending energy scales with $K_{\mathrm{eff}}\, h^2/\xi^3$.

c) By comparing the bending energy in equilibrium with the thermal energy $k_{\mathrm{B}}T$, estimate $\langle h^2 \rangle$, and from that estimate, show that the end-to-end shrinkage of the clink is approximately given by $\Delta \sim \xi^2/\xi_{\mathrm{p}}$ (where, as before, $\xi_{\mathrm{p}} = K_{\mathrm{eff}}\,/k_{\mathrm{B}}T$).

d) The work done by the external force is now proportional to $F\Delta$. Argue why.

e) Show that thermal fluctuations at equilibrium then lead to a typical clink size $\xi \sim \sqrt{\xi_{\mathrm{p}}/f}$, where $f = F/k_{\mathrm{B}}T$.

f) On average, clinks will align with the applied external force. Given that there are L/ξ clinks in a chain of length L, which each have shrunk by an amount Δ, show that the average end-to-end distance will scale with the applied force as

$$\langle R \rangle \sim L\left(1 - \frac{1}{\sqrt{f\xi_{\mathrm{p}}}}\right).$$

(The actual relation has an extra factor $\frac{1}{4}$ in front of the second term, which we cannot get from a scaling argument. Even so, not bad for a calculation that requires nothing more complicated than Pythagoras' theorem!).