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

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

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

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

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

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

Solution: a) Inserting the definition of $\vec{R}_m$, we have,

$$\begin{aligned}
R_g^2 &= \frac{1}{N}\left\langle \sum_i \left(\vec{R}_i - \vec{R}_m\right)^2 \right\rangle = \frac{1}{N}\left\langle \sum_i \left(\vec{R}_i - \frac{1}{N}\sum_j \vec{R}_j\right)^2 \right\rangle \\
&= \frac{1}{N}\left\langle \sum_i \left(\vec{R}_i - \frac{1}{N}\sum_j \vec{R}_j\right)\cdot\left(\vec{R}_i - \frac{1}{N}\sum_k \vec{R}_k\right) \right\rangle \\
&= \frac{1}{N}\left\langle \sum_i \vec{R}_i^2 \right\rangle - \frac{2}{N^2}\left\langle \sum_i\sum_j \vec{R}_i\cdot\vec{R}_j \right\rangle + \frac{1}{N^3}\left\langle \sum_i\sum_j\sum_k \vec{R}_j\cdot\vec{R}_k \right\rangle \\
&= \frac{1}{N^2}\left\langle \sum_j\sum_i \vec{R}_i^2 \right\rangle - \frac{2}{N^2}\left\langle \sum_i\sum_j \vec{R}_i\cdot\vec{R}_j \right\rangle + \frac{1}{N^2}\left\langle \sum_i\sum_j \vec{R}_i\cdot\vec{R}_j \right\rangle = \frac{1}{N^2}\sum_i\sum_j \left\langle \vec{R}_i^2 - \vec{R}_i\cdot\vec{R}_j \right\rangle .
\end{aligned}$$

In going from the fourth line to the fifth expression we used the fact that $\frac{1}{N}\sum_i 1 = 1$ and relabeled some of the indices.

b) Note that we can rewrite this expression as:

$$\begin{aligned}
R_g^2 &= \frac{1}{N^2}\sum_i\sum_j \left\langle \vec{R}_i^2 - \vec{R}_i\cdot\vec{R}_j \right\rangle = \frac{1}{2}\frac{1}{N^2}\sum_i\sum_j \left\langle \vec{R}_i^2 - \vec{R}_i\cdot\vec{R}_j - \vec{R}_j\cdot\vec{R}_i + \vec{R}_j^2 \right\rangle \\
&= \frac{1}{2}\frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \left\langle \left(\vec{R}_i - \vec{R}_j\right)^2 \right\rangle = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=i}^{N} \left\langle \left(\vec{R}_i - \vec{R}_j\right)^2 \right\rangle .
\end{aligned}$$

c) We follow the general procedure of taking the continuum limit. If N is large, and the discrete segments of polymer is of length l_k, then the sum can be approximated as,

$$\sum_{i=0}^{N} \to \int_0^{Nl_k} \frac{\mathrm{d}s}{l_k}$$

Taking the continuum limit for the expression in (b) then gives us

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

d) This is follows from the behavior of an ideal chaing and applying the same logic we used above to take the continuum limit. Indeed, from SMB (5.3) we have for an ideal chain

$$\langle |\vec{R}|^2 \rangle = \ell_\mathrm{K}^2 N,$$

where N is the number of segments. Considering two points on a chain at positions s_1 and s_2 in the continuum limit, the number of independent Kuhn segments between them is $\left|s_1 - s_2\right| / \ell_\mathrm{K}$ and hence in analogy with () we have for the ideal chain in the continuum limit

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

e) If we move to the coordinate $s_2 \to u = s_1 - s_2$, we have:

$$\int_0^{N\ell_\mathrm{K}} \mathrm{d}s_1 \int_0^{s_1 - N\ell_\mathrm{K}} \mathrm{d}u \frac{|u|}{\ell_\mathrm{K}} = \frac{\ell_\mathrm{K}}{2}\int_0^{Nl_k} \mathrm{d}s_1 \left(s_1 - N\ell_\mathrm{K}\right)^2 = \frac{N^3 l_k^4}{6}.$$

Plugging this result back to the expression for the radius of gyration, we get:

$$R_g^2 = \frac{1}{N^2\ell_{\mathrm{K}}^2}\frac{N^3\ell_{\mathrm{K}}^4}{6} = \frac{N\ell_{\mathrm{K}}^2}{6} = \frac{R_0^2}{6}.$$

□

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.

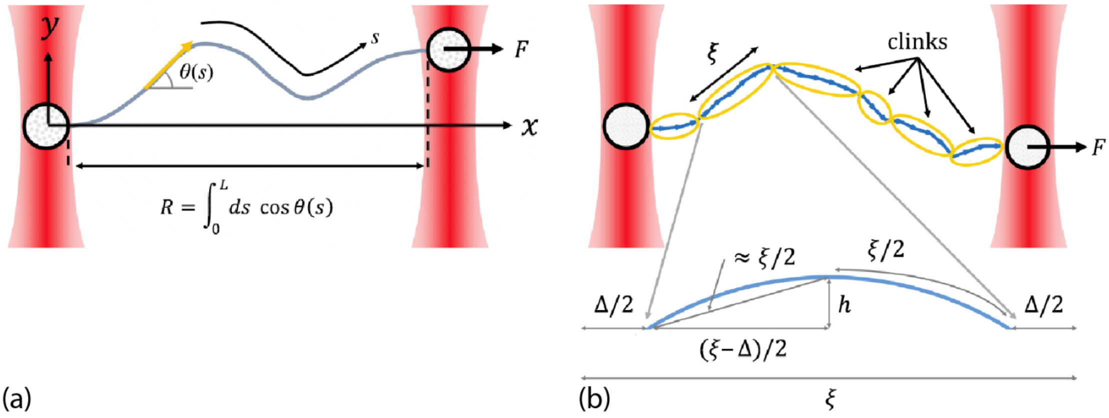

Figure 4.3: Force-extension experiment of a polymer. (a) The positions of the ends of the polymer are constrained by two beads; the distance between the beads is given by equation (4.29). (b) 'clinks' as used in the scaling approach of problem 8. Figure from Marantan and Mahadevan, Am. J. Phys. 2018.

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 $K_{\text{eff}}\, h^2/\xi^3$.

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, $\xi_{\mathrm{p}} = K_{\text{eff}}\,/k_{\mathrm{B}}T$).

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!).

Solution: a) We need to find the radius of the circular arc. Defining the opening angle of (half of) the arc as α, this radius is given by $\rho = \frac{1}{2}(\xi-\Delta)/\sin(\alpha)$. The angle also relates the base and height of the triangle in the arc, through $\tan(\alpha) = h/\frac{1}{2}(\xi-\Delta)$. Now if both h and Δ are much smaller than ξ, we have $\tan(\alpha)\approx\sin(\alpha)$ and $\xi-\Delta\approx\xi$, so we get

$$\rho = \frac{\frac{1}{2}(\xi-\Delta)}{\sin(\alpha)} \approx \frac{\left(\frac{1}{2}(\xi-\Delta)\right)^2}{h} \approx \frac{1}{4}\frac{\xi^2}{h},$$

and for the curvature we find $\kappa = \rho^{-1} \approx 4h/\xi^2$.

b) The bending energy is simply the integral of the square of the curvature:

$$E_{\text{bend}} = \frac{1}{2}K_{\text{eff}}\int_0^{\xi}\kappa(s)^2\,\mathrm{d}s = \frac{1}{2}K_{\text{eff}}\,\xi\left(\frac{4h}{\xi^2}\right)^2 = 2K_{\text{eff}}\,\frac{h^2}{\xi^3}.$$

c) We have

$$\langle E_{\text{bend}}\rangle = 2K_{\text{eff}}\frac{\langle h^2\rangle}{\xi^3} \approx k_{\mathrm{B}}T \quad\Rightarrow\quad \langle h^2\rangle \approx \frac{k_{\mathrm{B}}T\xi^3}{2K_{\text{eff}}} = \frac{\xi^3}{2\xi_{\mathrm{p}}}.$$

To get Δ, we use the approximation that in the triangle in figure 4.3(b), the hypothenuse is roughly $\xi/2$, and thus

$$\frac{1}{4}\xi^2 = h^2 + \frac{1}{4}(\xi-\Delta)^2 \approx h^2 + \frac{1}{4}\xi^2 - \frac{1}{2}\xi\Delta,$$

so

$$\Delta \approx \frac{2\langle h^2\rangle}{\xi} = \frac{\xi^2}{\xi_{\mathrm{p}}}.$$

d) The work done per clink to convert the current configuration to a completely straight one is the work necessary to stretch each clink by an additional amount Δ, i.e., $F\Delta$.

e) We simply equate the work to the thermal energy:

$$k_{\mathrm{B}}T = F\Delta \approx F\frac{\xi^2}{\xi_{\mathrm{p}}} \quad\Rightarrow\quad \xi \approx \sqrt{\frac{k_{\mathrm{B}}T\xi_{\mathrm{p}}}{F}} = \sqrt{\frac{\xi_{\mathrm{p}}}{f}}.$$

f) We have

$$\langle R\rangle = L - \frac{L}{\xi}\Delta = L\left(1-\frac{1}{\xi}\frac{\xi^2}{\xi_{\mathrm{p}}}\right) = L\left(1-\frac{\xi}{\xi_{\mathrm{p}}}\right) \approx L\left(1-\frac{1}{\sqrt{f\xi_{\mathrm{p}}}}\right).$$

□