2.3. Solutions Set 2

1. A straightforward way to solve the problem is the following. Consider a freely jointed chain consisting of N links of length b. Then $R_{ee} = Nb^2$ as shown in class. Let's put masses in the joints between the links and in the chain ends: $N+1$ masses altogether numbered from $n = 0$ at one end to $n = N$ at the other end. Let's take the position of $n = 0$ mass to be the origin of the coordinates system.

   Note: One may put masses in the centers of the links; for $N \gg 1$ these choices do not matter.

   The radius of gyration of the chain is then defined by:

$$R_g^2 \equiv \frac{1}{N+1}\sum_{n=0}^{N}\left\langle(\mathbf{r_n} - \mathbf{r}_{cm})^2\right\rangle \tag{2.34}$$

   Where

$$\mathbf{r}_{cm} = \frac{1}{N+1}\sum_{m=0}^{N}\mathbf{r}_m \tag{2.35}$$

   Then:

$$\begin{aligned} R_g^2 &\equiv \tfrac{1}{N+1}\textstyle\sum_{n=0}^{N}\langle(\vec{r}_n - \vec{r}_{cm})^2\rangle = \tfrac{1}{N+1}\sum_{n=0}^{N}\langle\vec{r}^{\,2}_n\rangle - 2\left\langle\vec{r}_{cm}\tfrac{1}{N+1}\sum_{n=0}^{N}\vec{r}_n\right\rangle + \langle\vec{r}^{\,2}_{cm}\rangle = \\ &= \tfrac{1}{N+1}\textstyle\sum_{n=0}^{N}\langle\vec{r}^{\,2}_n\rangle - 2\langle\vec{r}_{cm}\cdot\vec{r}_{cm}\rangle + \langle\vec{r}^{\,2}_{cm}\rangle = \tfrac{1}{N+1}\sum_{n=0}^{N}\langle\vec{r}^{\,2}_n\rangle - \langle\vec{r}^{\,2}_{cm}\rangle. \end{aligned} \tag{2.36}$$

   For a freely jointed chain and for our choice of coordinate origin $\langle\vec{r}^{\,2}_n\rangle = nb^2$.

   Next, by definition:

$$\langle r^2_{cm}\rangle = \frac{1}{(N+1)^2}\sum_{n=0}^{N}\sum_{m=0}^{N}\langle\vec{r}_n\vec{r}_m\rangle = \frac{1}{(N+1)^2}\sum_{n=0}^{N}\langle\vec{r}^{\,2}_n\rangle + \frac{2}{(N+1)^2}\sum_{n=0}^{N}\sum_{m=n+1}^{N}\langle\vec{r}_n\vec{r}_m\rangle \tag{2.37}$$

   The first term on the right hand side sums over $m = n$, the second term sums over $m > n$ and a factor 2 accounts for $m < n$. Notice, that for $m > n$: $\langle\vec{r}_n\vec{r}_m\rangle = \langle r^2_n\rangle$. Indeed the part of the chain between n-th and m-th links (let's denote its 'end-to-end' vector $\vec{r}_{nm}$) can rotate freely and is uncorrelated with $\vec{r}_n$: $\langle \vec{r}_n \vec{r}_m \rangle = \langle \vec{r}_n(\vec{r}_n + \vec{r}_{nm}) \rangle = \langle r_n^2 \rangle + \langle \vec{r}_n \vec{r}_{nm} \rangle = \langle r_n^2 \rangle$. Substituting this back into Eq. 2.37, we have:

$$\langle r_{cm}^2 \rangle = \frac{1}{(N+1)^2} \sum_{n=0}^{N} \langle \vec{r}_n^{\,2} \rangle \left(2(N-n)+1\right) \tag{2.38}$$

and then Eq. 2.36 becomes:

$$R_g^2 = \frac{1}{(N+1)^2} \sum_{n=0}^{N} \langle \vec{r}_n^{\,2} \rangle (2n-N) = \frac{b^2}{(N+1)^2} \sum_{n=0}^{N} n(2n-N). \tag{2.39}$$

For those who are not aware of it, the sum of n^2 (and of many other series) can be carried out by representing n^2 as a difference of the consecutive terms of another series: $n^2 = (n+1)^3/3 - n^3/3 - (n+1/3)$. Then in the sum all of the n^3 terms will cancel out, apart from the two at the two ends of the series:

$$\sum_{n=0}^{N} n^2 = \sum_{n=0}^{N} \left(\frac{(n+1)^3}{3} - \frac{n^3}{3} - n - \frac{1}{3} \right) = \frac{(N+1)^3}{3} - \sum_{n=0}^{N} \left(n + \frac{1}{3} \right) = \frac{N(N+1)(2N+1)}{6}. \tag{2.40}$$

Finally, for R_g we have:

$$R_g^2 = \frac{b^2}{(N+1)^2} \left[\frac{N(N+1)(2N+1)}{3} - \frac{(N+1)N^2}{2} \right] = \frac{Nb^2(N+2)}{6(N+1)} \approx \frac{Nb^2}{6}. \tag{2.41}$$

Comment: A more elegant way of deriving the same relation is by starting with a proof that

$$R_g^2 = \frac{1}{2(N+1)^2} \sum_{n=0}^{N} \sum_{m=0}^{N} \langle (\vec{r}_n - \vec{r}_m)^2 \rangle. \tag{2.42}$$

The proof of it is not complicated (http://cbp.tnw.utwente.nl/PolymeerDictaat/node8.html):

$$\begin{aligned} R_g^2 &\equiv \frac{1}{N+1} \sum_{n=0}^{N} \langle (\vec{r}_n - \vec{r}_{cm})^2 \rangle = \frac{1}{N+1} \sum_{n=0}^{N} \langle \vec{r}_n^{\,2} \rangle - \langle \vec{r}_{cm}^{\,2} \rangle = \\ &= \frac{1}{N+1} \sum_{n=0}^{N} \langle \vec{r}_n^{\,2} \rangle - \frac{1}{(N+1)^2} \sum_{n=0}^{N} \sum_{m=0}^{N} \langle \vec{r}_n \vec{r}_m \rangle = \\ &= \frac{1}{(N+1)^2} \sum_{n=0}^{N} \sum_{m=0}^{N} \langle \vec{r}_n^{\,2} - \vec{r}_n \vec{r}_m \rangle = \frac{1}{2(N+1)^2} \sum_{n=0}^{N} \sum_{m=0}^{N} \langle \vec{r}_n^{\,2} - 2\vec{r}_n \vec{r}_m + \vec{r}_m^{\,2} \rangle = \\ &= \frac{1}{2(N+1)^2} \sum_{n=0}^{N} \sum_{m=0}^{N} \langle (\vec{r}_n - \vec{r}_m)^2 \rangle. \end{aligned} \tag{2.43}$$

I'll let you derive further on from here.

2. First of all a trivial calculation gives for a normally distributed variable x:

$$\langle \exp(iqx)\rangle = \frac{1}{\sqrt{2\pi\langle x^2\rangle}}\int_{-\infty}^{\infty} dx \exp\left(-\frac{x^2}{2\langle x^2\rangle} + iqx\right)$$
$$= \frac{1}{\sqrt{2\pi\langle x^2\rangle}}\int_{-\infty}^{\infty} dx \exp\left[-\frac{1}{2\langle x^2\rangle}\left(x^2 + 2\langle x^2\rangle iqx + (iq\langle x^2\rangle)^2\right) - \frac{q^2\langle x^2\rangle}{2}\right] =$$
$$= \exp\left(-\frac{q^2\langle x^2\rangle}{2}\right)\frac{1}{\sqrt{2\pi\langle x^2\rangle}}\int_{-\infty}^{\infty} dx \exp\left[-\frac{(x - iq\langle x^2\rangle)^2}{2\langle x^2\rangle}\right] = \exp\left(-\frac{q^2\langle x^2\rangle}{2}\right).$$

Then for 3D normally distributed variable r such that $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = \langle r^2\rangle/3$ we have:

$$\langle \exp(i\vec{q}\vec{r})\rangle = \langle \exp(iq_x x + iq_y y + iq_z z)\rangle = \langle \exp(iq_x x)\rangle\langle \exp(iq_y y)\rangle\langle \exp(iq_z z)\rangle =$$
$$= \exp\left(-\frac{q_x^2\langle x^2\rangle + q_y^2\langle y^2\rangle + q_z^2\langle z^2\rangle}{2}\right) = \exp\left(-\frac{(q_x^2 + q_y^2 + q_z^2)\langle r^2\rangle}{6}\right) = \exp\left(-\frac{q^2\langle r^2\rangle}{6}\right) \tag{2.44}$$

The density of monomers within the chain can be expressed as $n(\vec{r}) = \sum_0^N \delta(\vec{r} - \vec{r}_n)$, where $\vec{r}_n$ is the position of the n-th monomer. Then the structure factor:

$$S(q) = \frac{\langle \tilde{n}(\vec{q})\tilde{n}(-\vec{q})\rangle}{N} = \frac{1}{N}\sum_{n=0}^{N}\sum_{m=0}^{N}\langle \exp(i\vec{q}(\vec{r}_n - \vec{r}_m))\rangle = \frac{1}{N}\sum_{n=0}^{N}\sum_{m=0}^{N}\exp(-q^2\langle r_{nm}^2\rangle/6 =$$
$$= \frac{1}{N}\sum_{n=0}^{N}\sum_{m=0}^{N}\exp(-q^2b^2|n-m|/6) \approx \frac{1}{N}\int_0^N dn\int_0^N dm \exp(-q^2b^2|n-m|/6) \tag{2.45}$$

From here on the calculus is identical to the derivation of mean square end-to-end distance for semiflexible polymer, as well as to the diffusion distance by a particle in liquids:

$$S(q) = \frac{2}{N}\int_0^N dn\int_n^N dm \exp(-q^2b^2(m-n)/6) = \frac{2}{N}\int_0^N dn\int_0^{N-n} ds \exp(-q^2b^2 s/6) =$$
$$= \frac{12}{Nq^2b^2}\int_0^N dn(1 - \exp(-q^2b^2(N-n)/6)) = 2N\left(\frac{6}{Nq^2b^2}\right)^2\left[\frac{Nq^2b^2}{6} - 1 + \exp\left(-\frac{Nq^2b^2}{6}\right)\right]. \tag{2.46}$$

Now recalling that for the Gaussian chain $R_g^2 = Nb^2/6$, we get the Debye expression for scattering:

$$S(q) = \frac{2N}{(R_g q)^4}\left[(R_g q)^2 - 1 + \exp(-(R_g q)^2)\right] \tag{2.47}$$

Notice that it essentially depends only on $(R_g q)^2$ and that its behaviour for large q is $\propto q^{-2}$.

3. • How large should be the stiffness $\mathcal{K}$ of the springs, so that $\theta_i \ll 1$ is kept?

   Since the energy of each spring enters the Hamiltonian independently, the equipartition theorem can be applied to each spring individually to obtain characteristic values of θ. As an estimation $\langle \epsilon_i \rangle = \frac{\mathcal{K}\langle \theta_i^2 \rangle}{2} \sim \frac{T}{2}$ would do. To be more precise, one should keep in mind that for each joint there are two independent angles of rotation, say θ_{i1} and θ_{i2}. This matter was discussed in the class for semiflexible chains. For small angles we can write $\theta_i^2 = \theta_{i1}^2 + \theta_{i2}^2$, which is essentially the expression of Pythagoras theorem. Then, the precise calculation would give:

$$\langle \epsilon_i \rangle = \frac{\mathcal{K}\langle \theta_i^2 \rangle}{2} = \frac{\mathcal{K}\langle \theta_{i1}^2 \rangle}{2} + \frac{\mathcal{K}\langle \theta_{i2}^2 \rangle}{2} = \frac{T}{2} + \frac{T}{2} = T. \tag{2.48}$$

   Then,

$$\langle \theta_i^2 \rangle = \frac{2T}{\mathcal{K}}, \tag{2.49}$$

   and the demand $\langle \theta_i^2 \rangle \ll 1$ leads to

$$\mathcal{K} \gg 2T.$$

   • In the case of stiff springs, what is the persistence length, R_0 and Kuhn length of such a chain?

   By stiff we will understand springs which meet the $\mathcal{K} \gg 2T$ condition. The derivation here is very similar to that of freely rotating chain (FRC) model. The main (only?) difference is that θ_i is not a fixed angle, but rather Gaussian distributed one with the characteristic mean square given by Eq. 2.49:

$$\vec{r}_{1N} = \sum_{i=1}^{N} \vec{b}_i,$$

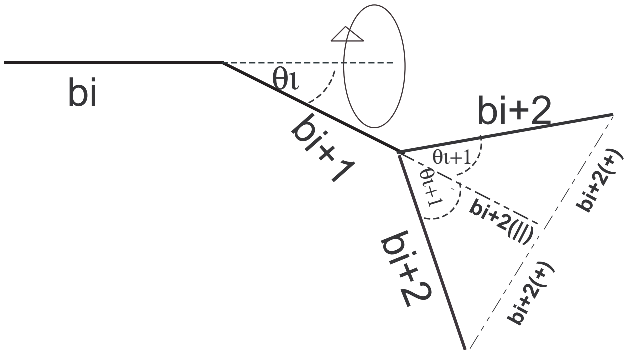
$$R_0^2 = \langle \vec{r}_{1N}^{\,2} \rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} \langle \vec{b}_i \vec{b}_j \rangle = \sum_{i=1}^{N} \langle \vec{b}_i^{\,2} \rangle + 2\sum_{i=1}^{N}\sum_{j=i+1}^{N} \langle \vec{b}_i \vec{b}_j \rangle =$$

$$= Nb^2 + 2\sum_{i=1}^{N}\sum_{k=1}^{N-i} \langle \vec{b}_i \vec{b}_{i+k} \rangle. \tag{2.50}$$

   The problem thus is again reduced to calculating the correlations in the directions of links separated by k other links along the chain contour. For $k = 1$:

$$\langle \vec{b}_i \vec{b}_{i+1} \rangle = b^2 \langle \cos\theta_i \rangle \approx b^2 \left(1 - \frac{\langle \theta_i^2 \rangle}{2}\right) = b^2 \left(1 - \frac{T}{\mathcal{K}}\right)$$

In order to treat $k = 2$, we split $\vec{b}_{i+2}$ into components parallel and normal to $\vec{b}_{i+1}$ (see figure). Then



$$\langle \vec{b}_i \vec{b}_{i+2} \rangle = \langle \vec{b}_i \vec{b}_{i+2,\parallel} \rangle + \underbrace{\langle \vec{b}_i \vec{b}_{i+2,\perp} \rangle}_{=0} = \langle \vec{b}_i \vec{b}_{i+1} \cos\theta_{i+1} \rangle = b^2 \langle \cos\theta_i \cos\theta_{i+1} \rangle =$$
$$= b^2 \langle \cos\theta_i \rangle \langle \cos\theta_{i+1} \rangle = b^2 \langle \cos\theta \rangle^2,$$

where the independence of θ_i and θ_{i+1} angles was taken into account. Similarly one can show that for arbitrary k:

$$\langle \vec{b}_i \vec{b}_{i+k} \rangle = b^2 \langle \cos\theta \rangle^k. \tag{2.51}$$

Substituting the last relation into Eq. 2.50 and assuming $N \gg 1$, we have:

$$R_0^2 = Nb^2 + 2b^2 \sum_{i=1}^{N} \sum_{k=1}^{N-i} \langle \cos\theta \rangle^k \approx Nb^2 + 2b^2 \sum_{i=1}^{N} \sum_{k=1}^{\infty} \langle \cos\theta \rangle^k =$$
$$= Nb^2 + Nb^2 \frac{\langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle} = Nb^2 \frac{1 + \langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle} \approx \frac{2\mathcal{K}}{T} Nb^2, \tag{2.52}$$

where $\langle \cos\theta \rangle \approx 1 - \dfrac{T}{\mathcal{K}}$ was used.

Since the Kuhn length is defined as $l_K = R_0^2/L$ where $L = Nb$ is the length of the polymer, we have

$$l_K = b \frac{1 + \langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle} \approx \frac{2\mathcal{K}b}{T} \tag{2.53}$$

The Eq. 2.51 can be written as

$$\langle \vec{b}_i \vec{b}_{i+k} \rangle = b^2 \exp\left(-\frac{s}{l_p} \right), \tag{2.54}$$

where $s = kb$ is the contour length between the links and

$$l_p = \frac{b}{|\ln\langle \cos\theta \rangle|} \approx \frac{\mathcal{K}b}{T} = \frac{l_K}{2} \tag{2.55}$$

is the persistence length of the chain.

- Show that the continuous limit of such a chain is the worm like chain (WLC). What is the relation between the parameters of the chain N, b,K and the respective parameters of the worm-like chain.

  The Hamiltonian for WLC is

$$\mathcal{H}_{WLC} = \frac{\kappa}{2}\int_0^L ds \left(\frac{d\vec{t}}{ds}\right)^2 \tag{2.56}$$

  where $\vec{t}$ is the tangent vector to the chain contour.

  For our spring-link discrete chain $\vec{t_i} = \vec{b}_i/b$ plays the role of such tangent vector. The Hamiltonian for discrete chain is

$$\mathcal{H}_{discr} = \frac{\mathcal{K}}{2}\sum_{i=1}^{N}\theta_i^2, \tag{2.57}$$

  where from geometry it is clear that $2\sin(\theta_i/2) = |\vec{t}_{i+1} - \vec{t_i}| = |\Delta\vec{t_i}|$. For stiff springs (and when going to continuous limit, i.e. having very small segments, the corresponding springs will always be stiff): $2\sin(\theta_i/2) \approx \theta_i$ and therefore $\theta_i^2 \approx \Delta\vec{t}_i^2$. Then the Hamiltonian for the discrete chain can be written as:

$$\mathcal{H}_{discr} = \frac{\mathcal{K}b}{2}\sum_{i=1}^{N} b\left(\frac{\Delta\vec{t_i}}{b}\right)^2 = \frac{\mathcal{K}b}{2}\sum_{i=1}^{N}\Delta s_i\left(\frac{\Delta\vec{t_i}}{\Delta s_i}\right)^2, \tag{2.58}$$

  where $\Delta s_i \equiv b$. Taking limit $\Delta s_i \to 0, N \to \infty$ while keeping $N\Delta s_i = L$ we will arrive at the integral expression for WLC. $\mathcal{K}b$ has a meaning of the rigidity of a unit length of a polymer and should tend to constant κ as the chain becomes continuous.

  Comment: Notice that the expressions for l_p and l_K for the discrete chain with stiff springs transform smoothly into those for WLC. Notice also that the dependence of the correlations between tangent vectors $\langle t(\vec{s_0})t(s_0 \vec{+} s)\rangle = \exp\left(-\frac{s}{l_p}\right)$ was proven here for the discrete chain. Since WLC is the limiting case of the discrete chain, we can expect that this relation will be correct for WLC as well. In any case, an alternative proof for WLC was given in the class. .

4. We do Flory-type estimation for DNA. Let a polymer be comprised of N Kuhn segments of length b and excluded volume v each. Before collisions enter into play, the

polymer is ideal so its end-to-end distance is $R_0^2 = Nb^2$. R_0 is a bit like a coil diameter (or we could take R_g to be the radius). Then the coil volume can be estimated as $\pi R_0^3/6 = \pi N^{3/2}b^3/6$ and the fraction of its volume occupied by monomers is respectively $6Nv/\pi N^{3/2}b^3 = 6v/\pi N^{1/2}b^3$. The probability of any monomer to collide with some other monomer is equal to this occupancy fraction. Then the number of collisions within the coil is estimated as $N_{col} = 3Nv/\pi N^{1/2}b^3 = 3N^{1/2}v/\pi b^3$ (cut in half because the collisions are pairwise). We are looking for the polymer length N' for which $N_{col} = 1$: $N' = (\pi b^3/3v)^2 \sim (b^3/v)^2$. For a flexible chain we expect $v \sim b^3$ and therefore $N' = 1$, i.e. collisions set in right after the Kuhn length is exceeded. For semiflexible polymer such as DNA, however, the Kuhn segments are cylinder like with a length b and diameter d. Their excluded volume was calculated in the previous set of problems and found to be: $v = (\pi/2)db^2$. Then:

$$N' = \left(\frac{2b}{\pi d}\right)^2 . \tag{2.59}$$

Since $b/d \sim 25$ is a larger parameter and is yet squared, $N' \approx 250$ is a large number. Recall that N' is a number of Kuhn segments and each Kuhn segment is 100 nm, so excluded volume interactions appear in coils over ~ 25 μm or about 90,000 base pairs.

5. • We will first try to see that in the current case the derivatives over s can be replaced with derivatives over x.

$$dx = ds \cos\phi,$$

where ϕ is the angle between the local tangent to the polymer contour and X-axis. Let's estimate ϕ. Assume thermal fluctuations bend polymer into a circular arc of radius R covering an angle $\alpha = L/R$. If axis X passes through the ends of such arc then at maximum $\phi = \alpha/2 = L/(2R)$. We expect the typical radius R of the arc to be found from:

$$H = \frac{\kappa}{2}\frac{L}{R^2} \approx \frac{T}{2}. \tag{2.60}$$

Then

$$\phi \sim \sqrt{\frac{TL}{4\kappa}} = \sqrt{\frac{L}{4L_p}}$$

$$\cos\phi \approx 1 - \frac{\phi^2}{2} \approx 1 - \frac{L}{8L_p} = 1 - O\left(\frac{L}{L_p}\right)$$

Thus to L/L_p order we can neglect the differences between dx and ds for $L \ll L_p$. Note that similar relation can be obtained by considering the difference between R_{ee} and L.

Furthermore, we can decompose $\vec{r}$ into components parallel to X axis and perpendicular to it: $\vec{r} = x\hat{x} + \vec{r}_\perp$.

Then

$$\frac{\partial^2 \vec{r}}{\partial s^2} \approx \frac{\partial^2 \vec{r}}{\partial x^2} = \frac{\partial^2 \vec{r}_\perp}{\partial x^2}$$

- We will decompose displacements along the contour into Fourier modes and show that the Hamiltonian simplifies into a sum of separate contributions from each mode. We will find the mean square amplitude of each mode from equipartition and then sum them up to find the mean-square displacement of a monomer.

  OK, now to work:

$$\vec{r}_\perp = \sum_{k=1}^{\infty} \vec{r}_{\perp k} \sin\left(\frac{\pi k x}{L}\right)$$

$$H = \frac{1}{2}\kappa \int_0^L dx \left(\frac{\partial^2 \vec{r}_\perp}{\partial x^2}\right)^2 =$$

$$= \frac{1}{2}\kappa \sum_{k=1}^{\infty}\sum_{n=1}^{\infty} \left(\frac{\pi k}{L}\right)^2 \left(\frac{\pi n}{L}\right)^2 \vec{r}_{\perp k}\vec{r}^{\,*}_{\perp n} \int_0^L dx \sin\left(\frac{\pi k x}{L}\right) \sin\left(\frac{\pi n x}{L}\right) =$$

$$= \frac{1}{2}\kappa \sum_{k=1}^{\infty}\sum_{n=1}^{\infty} \left(\frac{\pi k}{L}\right)^2 \left(\frac{\pi n}{L}\right)^2 \vec{r}_{\perp k}\vec{r}^{\,*}_{\perp n} \frac{L}{2}\delta_{k,n} =$$

$$= \frac{\pi^4 \kappa}{4L^3} \sum_{k=1}^{\infty} k^4 |\vec{r}_{\perp k}|^2$$

There are two independent polarizations "Y" and "Z" to each $\vec{r}_{\perp k}$. Then according to the Equipartition Theorem each term in the sum gives $2\frac{T}{2}$ on average:

$$\frac{\pi^4 \kappa}{4L^3} k^4 \langle |\vec{r}_{\perp k}|^2 \rangle = T$$

$$\langle |\vec{r}_{\perp k}|^2 \rangle = \frac{4TL^3}{\pi^4 \kappa k^4} = \frac{4L^3}{\pi^4 L_p k^4}.$$

Now let's get back to monomer displacements:

$$\langle \vec{r}_\perp^{\,2}(x)\rangle = \sum_{k=1}^{\infty}\sum_{n=1}^{\infty}\langle \vec{r}_{\perp k}\vec{r}_{\perp n}\rangle \sin\left(\frac{\pi k x}{L}\right)\sin\left(\frac{\pi n x}{L}\right) =$$

$$= \sum_{k=1}^{\infty}\sum_{n=1}^{\infty}\langle |\vec{r}_{\perp k}|^2\rangle \delta_{k,n}\sin\left(\frac{\pi k x}{L}\right)\sin\left(\frac{\pi n x}{L}\right) = \sum_{k=1}^{\infty}\langle |\vec{r}_{\perp k}|^2\rangle \sin^2\left(\frac{\pi k x}{L}\right) =$$

$$= \frac{4L^3}{\pi^4 L_p}\sum_{k=1}^{\infty}\frac{\sin^2\left(\frac{\pi k x}{L}\right)}{k^4}$$

For the position in the middle $x = L/2$, the $\sin^2$ - functions will give 1-s for odd values of k and 0-s for even values:

$$\langle \vec{r}_\perp^{\,2}\rangle_{|x=L/2} = \frac{4L^3}{\pi^4 L_p}\sum_{k=1,3,5,\ldots}^{\infty}\frac{1}{k^4} = \frac{4L^3}{\pi^4 L_p}\left[\sum_{k=1}^{\infty}\frac{1}{k^4} - \sum_{k=2,4,6,\ldots}^{\infty}\frac{1}{k^4}\right] =$$

$$= \frac{4L^3}{\pi^4 L_p}\frac{15}{16}\sum_{k=1}^{\infty}\frac{1}{k^4} = \frac{4L^3}{\pi^4 L_p}\frac{15}{16}\zeta(4) = \frac{4L^3}{\pi^4 L_p}\frac{15}{16}\frac{\pi^4}{90} = \frac{1}{24}\frac{L^3}{L_p},$$

where we made use of Riemann Zeta function $\zeta(n) = \sum_{k=1}^{\infty}\frac{1}{k^n}$ and its value at $n = 4 : \zeta(n) = \pi^4/90$.

Notice, that as a matter of *estimating* the fluctuations, we could use ϕ defined in the previous question:

$$\langle \vec{r}_\perp^{\,2}\rangle \sim \left(\frac{L}{2}\sin\phi\right)^2 \sim \frac{L^3}{16L_p},$$

which as estimations go is pretty good.

6. Semiflexible polymer is more or less aligned along the tube and hits the tube walls due to undulations only (see Fig.1). We'll label the distances between the consecutive points of collision L_e, the entanglement length. Consider three points of collision. From geometry the characteristic curvature radius is determined from:

$$(R - D)^2 + L_e^2 = R^2$$
$$R = \frac{L_e^2 + D^2}{2D} \approx \frac{L_e^2}{2D}$$

These bends cost energy, thus the system sets L_e in such a way that the characteristic energy of such bend is about thermal energy k_BT:

$$k_BT \sim \frac{\kappa}{2}\int_0^{L_e} ds\left(\frac{\partial \vec{t}}{\partial s}\right)^2 \approx \frac{\kappa}{2}\left(\frac{1}{R}\right)^2 L_e \approx \frac{2\kappa D^2}{L_e^3}$$

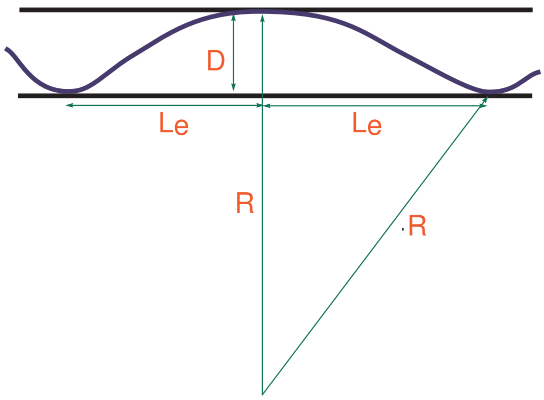


FIG. 4: Semiflexible polymer in a tube of diameter D. We assume $D \ll l_p$, and thus $D \ll R$, where R is the typical curvature radius of a polymer.

Then

$$L_e \approx \left(\frac{2\kappa D^2}{k_B T}\right)^{1/3} = (2l_p D^2)^{1/3} \qquad (2.61)$$

Notice, that not surprisingly the relation between D, L_e and l_p is that same (up to a numeric coefficient) as between $\langle \vec{r}_\perp^{\,2} \rangle$, L and l_p respectively in the previous problem. We could use that result for a more precise calculation.

The free energy increase is about $k_B T$ per collision and there are about L/L_e collisions between the polymer and the tube. Thus:

$$\Delta F \approx k_B T \frac{L}{L_e} \approx k_B T \frac{L}{(2l_p D^2)^{1/3}}$$

7. • Low forces limit: we expect the behavior similar to that of ideal chain under tension. Let's check it. Expand Marko-Siggia expression in $x/L \ll 1$:

$$\frac{f l_p}{k_B T} \approx \frac{x}{L} + \frac{1}{4}\left(1 + 2\frac{x}{L}\right) - \frac{1}{4} = \frac{3x}{2L}$$
$$f = \frac{3k_B T}{2l_p L} x = \frac{3k_B T}{R_0^2} x,$$

as expected.

• High forces limit: the polymer is almost fully extended along axis x, extension is approaching total length L. Small parameter is $1 - x/l \ll 1$. Then Marko-Siggia expression gives:

$$\frac{fl_p}{k_BT} \approx \frac{1}{4\left(1-\frac{x}{L}\right)^2}$$

Let's try to explain this. Take the result of the previous question: semiflexible polymer in a tube. That one was also extended along x axis and its free energy we evaluated already. That one was confined to a tube of diameter D. However, if we know what was its extension x we will know the free energy of a polymer as a function of its extension (large forces limit of course).

In the first approximation its extension is of course L, but we need to go beyond that. Let's denote L_{arc} as the arc length at the scale of entanglement length. Then $L_e \approx \sqrt{L_{arc}^2 - D^2} \approx L_{arc}(1 - \frac{D^2}{2L_{arc}^2})$.

The overall projected length, which here is denoted as x is

$$x = \frac{L}{L_{arc}} L_e \approx L\left(1 - \frac{D^2}{2L_{arc}^2}\right) \approx L\left(1 - \frac{D^2}{2L_e^2}\right)$$
$$\approx L\left(1 - \frac{D^2}{(2L_pD^2)^{2/3}}\right) \approx L\left(1 - \left(\frac{D}{L_p}\right)^{2/3}\right),$$

where we used the result from previous question for L_e and we dropped the numeric coefficients.

Now we can express the free energy obtained in the previous question through x:

$$\Delta F \approx k_BT\frac{L}{(2l_pD^2)^{1/3}} \sim k_BT\frac{L}{l_p(D/l_p)^{2/3}} \approx k_BT\frac{L^2}{l_p(L-x)}$$

Our claim now is that we can disregard the tube: if we bring the polymer to the extension x by any means we will have to pay ΔF in free energy. If we do that by applying force along the direction x, then we can find the needed force by taking derivative of ΔF:

$$f = \frac{\partial \Delta F}{\partial x} \approx \frac{L^2}{l_p(L-x)^2} = \frac{k_BT}{l_p(1-x/L)^2},$$

which up to a coefficient corresponds to the limit of high forces in Marko-Siggia equation.

8. •

$$L = \int_0^{L_\parallel} dx \sqrt{1 + \left(\frac{\partial \vec{r}_\perp(x)}{\partial x}\right)^2} \approx \int_0^{L_\parallel} dx \left(1 + \frac{1}{2}\left(\frac{\partial \vec{r}_\perp(x)}{\partial x}\right)^2\right) =$$

$$= L_\parallel + \frac{1}{2}\int_0^{L_\parallel} dx \left(\frac{\partial \vec{r}_\perp(x)}{\partial x}\right)^2,$$

$$L_\parallel = L - \frac{1}{2}\int_0^{L_\parallel} dx \left(\frac{\partial \vec{r}_\perp(x)}{\partial x}\right)^2 \approx L - \frac{1}{2}\int_0^{L} dx \left(\frac{\partial \vec{r}_\perp(x)}{\partial x}\right)^2,$$

where we assumed small fluctuations perpendicular to x axis, thus in zero-th approximation $L = L_\parallel$. Put attention that $\vec{r}_\perp(x)$ has two components (polarizations): y and z.

- Hamiltonian for chain under force is just a Hamiltonian of relaxed semiflexible chain minus $fL_\parallel$ term. We use the expression for $L_\parallel$ from previous item and disregard fL: we are interested in the reaction of the polymer to external force f and L is not a reaction this is just a constant polymer contour length.

- Use expansion:

$$\vec{r}_\perp(x) = \frac{1}{\sqrt{L}}\sum_q \vec{h}_q e^{iqx},$$

where

$$q = \frac{2\pi n}{L},\ n = \pm 1, \pm 2, \pm 3, \ldots$$

$$\int_0^L e^{i(q-q')x} dx = L\delta_{qq'}$$

Substitute it into the Hamiltonian:

$$H = \frac{1}{2L}\int_0^L dx \sum_{q,q'} \vec{h}_q \vec{h}^*_{q'} (\kappa q^2 q'^2 + fqq') e^{i(q-q')x} = \frac{1}{2}\sum_q |\vec{h}_q|^2 (\kappa q^4 + fq^2)$$

Use equipartition to find the average amplitude of the modes:

$$\langle |\vec{h}_q|^2 \rangle = \frac{2k_B T}{\kappa q^4 + fq^2},$$

where factor 2 stems from two polarizations.

- We express $\langle L_\parallel \rangle$ in terms of Fourier modes and substitute the previous result for mode amplitudes:

$$\langle L_{\parallel}\rangle \approx L - \frac{1}{2}\int_0^L dx \left\langle \left(\frac{\partial \vec{r}_{\perp}(x)}{\partial x}\right)\left(\frac{\partial \vec{r}^{\,*}_{\perp}(x)}{\partial x}\right)\right\rangle = L - \frac{1}{2}\sum_q q^2\langle|\vec{h}_q|^2\rangle =$$

$$= L - \frac{1}{2}\sum_q q^2 \frac{2k_BT}{\kappa q^4 + fq^2} = \left[\Delta q = \frac{2\pi}{L}\right] = L - \frac{1}{2}\sum_q \frac{2k_BT}{\kappa q^2 + f}\left(\frac{L\Delta q}{2\pi}\right) \approx$$

$$\approx L - \frac{L}{2\pi l_p}\int_{-\infty}^{+\infty}\frac{dq}{q^2 + f/(k_BTl_p)} = L - \frac{L}{2\pi l_p}\sqrt{\frac{k_BTl_p}{f}}\left[\arctan\left(q\sqrt{\frac{k_BTl_p}{f}}\right)\right]_{-\infty}^{+\infty} =$$

$$= L\left(1 - \frac{1}{2}\sqrt{\frac{k_BT}{fl_p}}\right)$$

Or rewriting in a way similar to Marko-Siggia expression:

$$\frac{fl_p}{k_BT} \approx \frac{1}{4\left(1 - \frac{\langle L_{\parallel}\rangle}{L}\right)^2}$$