

12. Pulling a fluctuating, almost stretched-out semiflexible polymer

A “semi-flexible” polymer has a bending energy per unit length of $\frac{1}{2}AK^2$, where K is the local curvature and A the bending modulus. Since A has units of energy times length, this can also be written as $A = k_B T \ell_p$, where ℓ_p is called persistence length (for DNA: $\ell_p \approx 50nm$). We’ll look at a simple case where the polymer only bends within a plane. Just as for our membranes, we can write the energy in Monge parameterization as $E[h(x)] = \frac{1}{2} \int_0^L dx \{A(\Delta h)^2 + F(\nabla h)^2\} = \frac{1}{2} L \sum_q |h_q|^2 (Aq^4 + Fq^2)$, where F is the externally applied (horizontal) pulling force – the equivalent of a lateral tension in a membrane.

1. Using the equipartition theorem in Fourier space, show that

$$\langle |h_q|^2 \rangle = \frac{k_B T}{[L(Aq^4 + Fq^2)]}$$

The Equipartition theorem says that each quadratic term appearing in the Hamiltonian of a system should have average energy $\frac{1}{2}kT$.

Setting the energy of each Fourier term to be $\frac{1}{2}kT$ and solving, I get:

$$\frac{1}{2}kT = \left\langle \frac{1}{2} L |h_q|^2 (Aq^4 + Fq^2) \right\rangle = \frac{1}{2} L (Aq^4 + Fq^2) \langle |h_q|^2 \rangle$$

$$\therefore \langle |h_q|^2 \rangle = \frac{kT}{L(Aq^4 + Fq^2)}$$

2. The total excess length is given by $L_{tot} - L = \Delta L = \frac{1}{2} L \sum_q q^2 \langle |h_q|^2 \rangle$.

Using the replacement $\sum_q \rightarrow \frac{L}{2\pi} \int_{-\infty}^{\infty} dq$, show

$$\tilde{F}_{fluc} = \frac{1}{16} \left(\frac{L_{tot}}{L_{tot} - L} \right)^2 \quad \text{for} \quad \tilde{F}_{fluc} = \frac{F \ell_p}{k_B T} \gg 1$$

First, I will write:

$$L_{tot} - L = \Delta L = \frac{1}{2}L \sum_q q^2 \langle |h_q|^2 \rangle = \frac{LkT}{4\pi} \int_{-\infty}^{\infty} \frac{1}{Aq^2 + F} = \frac{LkT}{4\sqrt{AF}}$$

Above, I have done the integral in Mathematica.

Solving, then, I have:

$$\sqrt{F} = \frac{L}{L_{tot} - L} \frac{kT}{4\sqrt{A}}$$

$$\frac{F\ell_p}{kT} \equiv \tilde{F} = \frac{1}{16} \left(\frac{L}{L_{tot} - L} \right)^2$$

Above, I have made the appropriate substitution of A from the problem statement.

Manipulating this a bit, I have:

$$\tilde{F} = \frac{1}{16} \left(\frac{L}{L_{tot} - L} \right)^2 = \frac{1}{16} \left(\frac{L_{tot} - \Delta L}{L_{tot} - L} \right)^2 = \frac{1}{16} \left(\frac{L_{tot}}{L_{tot} - L} - \frac{\Delta L}{L_{tot} - L} \right)^2 = \frac{1}{16} \left(\frac{L_{tot}}{L_{tot} - L} - 1 \right)^2$$

Finally, if $\tilde{F} \gg 1$, I have:

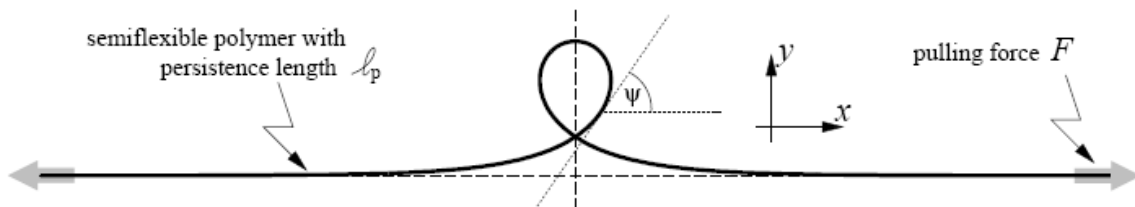
$$\tilde{F} = \frac{1}{16} \left(\frac{L_{tot}}{L_{tot} - L} - 1 \right)^2 \gg 1$$

$$\therefore \frac{L_{tot}}{L_{tot} - L} \gg 1$$

$$\therefore \tilde{F} \approx \frac{1}{16} \left(\frac{L_{tot}}{L_{tot} - L} \right)^2$$

13. Pulling on looped polymers: A very different “one loop renormalization”...

We will at first ignore fluctuations. If the polymer is no longer almost flat, its shape (again for two-dimensional bending) can be specified by the angle $\psi(s)$ with respect to the horizontal as a function of arc-length s , as illustrated in the figure below:



The total energy in “angle-arc length” parameterization is

$$E[\psi(s)] = \int ds \left\{ \frac{1}{2} A \dot{\psi}^2 + F(1 - \cos \psi) \right\}. \text{ The first term is the bending energy,}$$

because the curvature K is just $\frac{d\psi}{ds} = \dot{\psi}$; the second term is the tension energy, since $(1 - \cos \psi)ds$ is the excess length relative to the horizontal pulling direction that is multiplied by the force F to get the work done against tension.

1. By setting the variation with respect to $\psi(s)$ to zero, show that the Euler-Lagrange equation of this functional is given by $\ddot{\psi} - \lambda^{-2} \sin \psi = 0$, where

$$\lambda = \sqrt{\frac{A}{F}}. \text{ This, incidentally, is identical to the equation of a planar pendulum!}$$

$$\begin{aligned} \delta E[\psi(s)] &= E[\psi + \delta\psi] - E[\psi(s)] \\ &= \int ds \left\{ \frac{1}{2} A (2\dot{\psi}\delta\dot{\psi} - \delta\dot{\psi}^2) + F(\cos(\psi) - \cos(\psi + \delta\psi)) \right\} = 0 \end{aligned}$$

However, I see that

$$\lim_{\delta\psi \rightarrow 0} \frac{\cos(\psi + \delta\psi) - \cos(\psi)}{\delta\psi} \equiv \frac{d \cos(\psi)}{d\psi} = -\sin \psi$$

Through this I may justify the substitution under a sufficiently small variation,

$$F(\cos(\psi) - \cos(\psi + \delta\psi)) \rightarrow F \sin \psi \delta\psi$$

Further, through integration by parts where I ignore boundary conditions, I may take:

$$\frac{1}{2} A (2\dot{\psi}\delta\dot{\psi}) \rightarrow -A \ddot{\psi} \delta\psi$$

Finally, for sufficiently small variation,

$$\delta\dot{\psi}^2 = O(\delta\psi^2) \approx 0$$

This leaves me with:

$$\delta E[\psi(s)] = \int ds \{-A \ddot{\psi} \delta \psi + F \sin(\psi) \delta \psi\} = 0$$

$$\therefore [-A \ddot{\psi} + F \sin(\psi)] \delta \psi = 0$$

$$\therefore \ddot{\psi} - \lambda^{-2} \sin(\psi) = 0$$

This differential must hold since the variation was always arbitrary and the integral must be zero over all choices of subinterval.

2. Show that $\psi_{loop}(s) = 4 \arctan[\exp\{s/\lambda\}]$ solves this differential equation.

Help: $\sin(4 \arctan x) = \frac{4x(1-x^2)}{(1+x^2)^2}$.

With the caveat that this approach may be contrary to the spirit of this problem, I trust my algebraic manipulation to Mathematica:

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In[2]:= FullSimplify[D[4 ArcTan[Exp[S/lambda]], S] - lambda^-2 Sin[4 ArcTan[Exp[S/lambda]]]]
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Out[2]= 0
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The solution $\psi_{loop}(s)$ corresponds to the loop shown in the picture above. By integrating the identities $\dot{x} = \cos \psi$ and $\dot{y} = \sin \psi$, one can find the following

parametric representation of this loop: $x(s) = s - 2\lambda \tanh\left(\frac{s}{\lambda}\right)$ and $y(s) = \frac{2\lambda}{\cosh\left(\frac{s}{\lambda}\right)}$.

3. The excess length $\Delta L_{a,b}$ stored in the loop between $s = a$ and $s = b$ is

$$\Delta L_{a,b} = \int_a^b ds (1 - \cos \psi) = \int_a^b ds (1 - \dot{x}) = \int_a^b (ds - dx) = [b - a] - [x(b) - x(a)].$$

Show that the total excess length is $\Delta L = \Delta L_{-\infty, \infty} = 4\lambda$.

Using the identities above and taking a simple limit, I have:

$$\Delta L_{a,b} = [b - a] - [x(b) - x(a)] = 2\lambda \tanh\left(\frac{b}{\lambda}\right) - 2\lambda \tanh\left(\frac{a}{\lambda}\right)$$

$$\Delta L_{-\infty, \infty} = \lim_{x \rightarrow \infty} \left[2\lambda \tanh\left(\frac{x}{\lambda}\right) - 2\lambda \tanh\left(\frac{-x}{\lambda}\right) \right] = 2\lambda + 2\lambda = 4\lambda$$

4. Since λ depends on the applied force, $L_{tot} - L = \Delta L = 4\lambda$ is a force distance relation. Show that it can be written as:

$$\tilde{F}_{loop} = 16 \left(\frac{\ell_p}{L_{tot} - L} \right)^2 \quad \text{for} \quad \tilde{F}_{loop} = \frac{F \ell_p}{k_B T}.$$

I may manipulate the given expression in light of the identity $A = kT\ell_p$:

$$\begin{aligned}\Delta L &= 4\lambda = 4\sqrt{\frac{A}{F}} \\ \therefore (\Delta L)^2 &= 16\left(\frac{kT\ell_p}{F}\right) \\ \therefore \frac{F\ell_p}{kT} &= 16\left(\frac{\ell_p}{\Delta L}\right)^2 = 16\left(\frac{\ell_p}{L_{tot} - L}\right)^2\end{aligned}$$

And then using the definition of \tilde{F}_{loop} , I get the desired expression:

$$\frac{F\ell_p}{kT} \equiv \tilde{F} = \frac{1}{16}\left(\frac{\ell_p}{L_{tot} - L}\right)^2$$

5. Assume we want to measure the persistence length of a polymer by “pulling against fluctuations” (experiment from problem 12), but we have accidentally attached it to substrate and AFM in such a way that it is bent at its two ends. Evidently, $\tilde{F}_{fluc} = \tilde{F}_{loop} = F$ and we assume $L_{tot} - L = \Delta L$ to be the sum of the two terms from problem 12 part 2 and problem 13 part 4. Show that we again find a force distance behavior such as the result from problem 12 part 2, but with the smaller renormalized

persistence length $\ell_p^* = \frac{\ell_p}{\left(1 + 16\frac{\ell_p}{L_{tot}}\right)^2}$.

First, I write:

$$L_{tot} - L = \Delta L = 4\lambda + \frac{LkT}{4\sqrt{AF}} = 4\sqrt{\frac{A}{F}} + \frac{LkT}{4\sqrt{AF}}$$

Then,

$$\sqrt{F} = \frac{LkT}{4\Delta L\sqrt{A}}\left(16\frac{A}{LkT} + 1\right) = \frac{LkT}{4\Delta L\sqrt{A}}\left(16\frac{\ell_p}{L} + 1\right)$$

Squaring both sides and rearranging some terms, I have:

$$\frac{F\ell_p}{kT} = \frac{1}{16} \left(\frac{L}{\Delta L} \right)^2 \left(16 \frac{\ell_p}{L} + 1 \right)^2$$

$$\therefore \frac{F}{kT} \frac{\ell_p}{\left(16 \frac{\ell_p}{L} + 1 \right)^2} = \frac{F\ell_p^*}{kT} = \frac{1}{16} \left(\frac{L}{\Delta L} \right)^2$$

To get an identity that matches that from problem 12 part 2 exactly, one must make use of $\tilde{F} \gg 1$ so that $L \approx L_{tot}$, just as was shown at the end of problem 12 part 2 above.