Force-Extension Relations for Polymers

1. *Linear polymers:* Using optical tweezers, it is now possible to pull on the two ends of a single molecule. (Actually the tweezers pull on latex balls that are attached to the ends of the polymer; a complication that we shall ignore.) In the presence of the force $\vec{F}$ pulling on the ends of the polymer, there is an additional energy term

$$\delta E = -\vec{F} \cdot \vec{R},$$

where $\vec{R} = \vec{r}_N - \vec{r}_1$ is the end–to–end distance (between the first and $N^{\rm th}$ monomers) of the chain.

(a) For an ideal polymer, the number of configurations with an end–to–end distance of $\vec{R}$ is given by the usual Gaussian formula

$$\Omega_N\left(\vec{R}\right) = \frac{g^N}{\left(2\pi N a^2/3\right)^{3/2}} \exp\left(-\frac{3R^2}{2Na^2}\right).$$

By integrating the Boltzmann weight over all $\vec{R}$, calculate the (Gibbs) partition function $Z(N, F, T)$ at a temperature T. Using this result, obtain the mean extension $R_F = k_B T \partial \ln Z/\partial F$ along the direction of the force $\vec{F}$.

(b) For other cases in which Ω_N does not have a simple form (such as for self-avoiding polymers), it is still possible to obtain the *linear response* of the polymer to small force. To this end, expand the Boltzmann weight $\exp\left(\vec{F} \cdot \vec{R}/k_B T\right)$ to second order in $\vec{F}$, and hence show that

$$R_F = \frac{1}{3k_B T} \left\langle R^2 \right\rangle_0 F + \mathcal{O}(F^3),$$

where $\left\langle R^2 \right\rangle_0$ is the mean end–to–end squared distance of the polymer in the absence of the force.

(c) Dimensional analysis suggests that quite generally the extension–force curve for polymers should have the form

$$\frac{R_F}{\sqrt{\langle R^2 \rangle_0}} = \Phi\left(\frac{F\sqrt{\langle R^2 \rangle_0}}{k_B T}\right).$$

The left hand side is a dimensionless extension; on the right hand side a dimensionless combination involving the force appears as the argument of an unknown function Φ. At large forces F, the polymer becomes stretched such that $R_f \propto N$. For self-avoiding polymers $\sqrt{\langle R^2 \rangle_0} \approx a N^\nu$ with $\nu \approx 0.59$. Use these facts to deduce a non-linear behavior $R_F \propto F^\lambda$ for the extension at large force, and give the value of the exponent λ.

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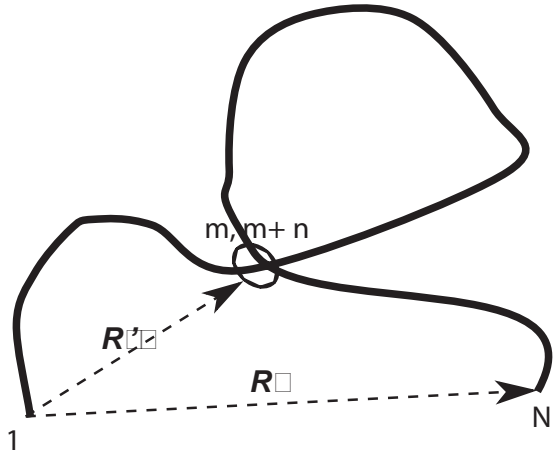
2. *Slip-linked polymer:* Consider a polymer with a slip-link that can slide along it, but that cannot fall off its ends, as depicted in the figure. The slip-link constrains two monomers to be at the same location in space (e.g. monomers m and $m+n$ at $\vec{R}'$, as in the figure).



(a) Assume that the polymer is an ideal random walk, such that the number of configurations of each segment is given by a formula similar to part (a) in problem 1 above. As before, assume that the ends of the polymer are pulled apart by a force $\vec{F}$. Integrate over the position vectors $\vec{R}$ and $\vec{R}'$, to get the partition function, and hence obtain

$$R_F = \frac{a^2}{3k_BT}\left(N - \langle n \rangle_F\right) F,$$

where $\langle n \rangle_F$ is the mean size of the loop. Note that the force is carried by a 'backbone' that excludes the loop. (Quite generally, the manner in which the force is transmitted through a Gaussian polymer network is quite similar to the way that current goes through a resistor network.)

(b) Show that for small force, $\langle n \rangle_F \propto \sqrt{N}$, while for large F, it is reduced to zero (or a small size determined by microscopic considerations). Is the force–extension curve linear in the presence of a slip-link?

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3. *Denaturing RNA by force:* By pulling on the ends of RNA, the hydrogen bonds can be broken to yield a stretched polymer. Let us model the partially denatured state as a sequence of linear segments with no hydrogen bonds and 'blobs' which are hydrogen bonded (opposite to the case of DNA). Assume that the force carrying backbone of the molecule is made up of the linear segments, and that the RNA blobs carry no force (similar

to the loop in problem 2). After integrating over the position vectors, the (Gibbs) partition function of an RNA of length N can be written as

$$Z(N,F) = \sum_{\ell_1,\ell_2,\ell_3,\cdots} P(\ell_1)R(\ell_2)P(\ell_3)\cdots, \qquad \text{with} \qquad \ell_1+\ell_2+\ell_3+\cdots = N.$$

The contributions of linear and blob segments are respectively

$$P(\ell) = g^\ell \exp\left(\frac{F^2a^2\ell}{6k_B^2T^2}\right), \quad \text{and} \quad R(\ell) = f^\ell \frac{A}{\ell^{3/2}}.$$

(a) Exploit the mathematical similarity to the Poland–Scheraga model to evaluate the grand partition function of the model.

(b) Identify the force F_c at which denaturation starts.

(c) Sketch the fraction of denatured sites as a function of force, clearly indicating the nature of the singularity at F_c.

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4. *Pulling RNA:* The server on http://bioinfo.ucsd.edu/rna/ (or its mirror at http://bioserv.mps.ohio-state.edu/rna/) gives force extension curves for RNA based on secondary structure calculations. Use this server to examine force extension curves for: (a) a uniform sequence; (b) an alternating sequence of G and C; (c) an alternating sequence of A and U; (d) an actual RNA sequence. (Choose sequences of roughly the same length.) Comment on the general characteristics of these curves. Does any of them resemble the theoretical result from the previous problem?

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(Optional) 5. *Denaturing DNA by force:* Obtain the phase diagram of DNA pulled by a force $\vec{F}$ by generalizing the Poland–Scheraga model, as follows:

(a) By integrating over the position vectors, show that the (Gibbs) partition function of DNA of length N can be decomposed into products of contributions from double-stranded rods and single stranded bubbles, as

$$Z(N,F) = \sum_{\ell_1,\ell_2,\ell_3,\cdots} R(\ell_1)B(\ell_2)R(\ell_3)\cdots, \qquad \text{with} \qquad \ell_1+\ell_2+\ell_3+\cdots = N.$$

(b) Treat the double stranded segments as rigid rods of fixed length $a\ell$. By integrating over all orientations in three dimensions show that

$$R(\ell) = w^{\ell} \times \frac{\sinh(\beta F a \ell)}{\beta F a \ell},$$

where $w = e^{-\beta\varepsilon}$, and ε is the energy gain of forming the double strand.

(c) Treat the double stranded loop as two random walks of length ℓ connected at the two end points. Integrating over all separations of the two end points show that

$$B(\ell) = \frac{s}{\ell^{3/2}} \left[g^2 \exp\left(\frac{\beta^2 F^2 a^2}{12} \right) \right]^{\ell}.$$

(d) Examine the problem in a (grand canonical) ensemble with variable DNA lengths N, additionally weighted by a factor of z^N. Give the expressions for the (Laplace) transformed $\tilde{B}(z)$ and $\tilde{R}(z)$ in this ensemble in terms of the (Bose) sums $f_m^+(x) = \sum_{\ell=1}^{\infty} x^{\ell}/\ell^m$.

(e) Show that the strands become fully separated at a critical point satisfying $\tilde{R} = \tilde{B}^{-1} = \left(s\zeta_{3/2}\right)^{-1}$, where $\zeta_{3/2} \equiv f_{3/2}^+(1) \approx 2.612$.

(f) For $s = 1$, plot the phase diagram of the model in the coordinates (w/g) and $(\beta F a)$.

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