Coulomb Interactions & Polymers

1. *Flory Theory:* The Coulomb energy of a ball of charge Q and dimension R in d spacial dimensions scales as

$$E_c \propto \frac{Q^2}{R^{d-2}}.$$

The proportionality coefficient depends on the exact shape and charge distribution; details that are not relevant to our intended scaling analysis.
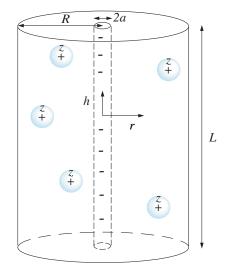
(a) For a charged polymer of length N, estimate the dependence of R on Q and N, by balancing the above Coulomb energy with the entropy associated with confining the polymer to a size R. (Follow the Flory reasoning for self-avoiding polymers.)

(b) For a *polyelectrolyte* in which $Q \propto N$, find the Flory exponent ν_F in the scaling relation $R \propto N^{\nu_F}$. Identify the upper critical dimension d_u above which $\nu = 1/2$ (the Coulomb interaction is *irrelevant*), and the lower critical dimension d_u^F below which $\nu_F = 1$ (the polymer is fully stretched).

(c) Unlike in the case of self-avoiding walks, the Flory estimate is a rather poor description for charged polymers. In fact, it can be shown that the exact value of the swelling exponent for uniformly changed polymers is $\nu = 2/(d-2)$. Identify the correct upper and lower critical dimensions from this formula. Note that a uniformly charged polymer in three dimensions is fully stretched.

(d) A *polyampholyte* is a heteropolymer with charged monomers of both signs. If the charges are randomly and independently chosen to be positive or negative, we expect $\overline{Q^2} \propto N$. What is the Flory estimate of the swelling exponent in this case?

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2. *The Manning Transition:* When ionic polymers (polyelectrolytes) such as DNA are immersed in water, the smaller charged *counter-ions* go into solution, leaving behind an oppositely charged polymer. Because of the electrostatic repulsion of the charges left behind, the polymer is stretched, and shall be modeled as a cylinder of radius a and length L, as depicted in the figure. While thermal fluctuations tend to make the ions wander about in the solvent, electrostatic attractions favor their return and condensation on the polymer. The potential due to a uniform linear charge density is logarithmic, and assuming that the counterions have valence z (chrage ze), their potential energy is given by

$$\mathcal{V} = 2ze^2 n \sum_{i=1}^{N} \ln\left(\frac{r_i}{a}\right).$$

Here, n is the linear density and r_i is the radial coordinate of the ith particle. Note that the Coulomb repulsions between the counter-ions have been left out.

(a) For a cylindrical container of radius R, show that at a temperature T, the canonical partition function Z has the form

$$Z = (\text{constant}) \left[\frac{R^{2(1-\zeta)} - a^{2(1-\zeta)}}{2(1-\zeta)} \right]^N,$$

and give the value of ζ.

(b) Calculate the probability distribution function $p(r)$ for the radial position of a counter-ion, and its first moment $\langle r \rangle$, the average radial position of a counter-ion.

(c) The behavior of the results calculated above in the limit of $R \gg a$ is very different at high and low temperatures. Identify the transition temperature, and characterize the nature of the two phases. In particular, how does $\langle r \rangle$ depend on R and a in each case?

(d) Calculate the pressure exerted by the counter-ions on the wall of the container, in the limit $R \gg a$, at all temperatures.

(e) According to Manning, at low temperatures just enough counterions reattach to the polymer to reduce its charge density such that the value of ζ stays at 1. Along a fully ionized double stranded DNA, unit (negative) charges occur at a separation of $b = 1.7\text{Å}$. Use the Manning reasoning to calculate the fraction of this charge that is neutralized by salt counterions in solutions of either Na Cl or Mg Cl$_2$. (The Bjerrum length in water is $\ell_B = e^2/(\epsilon k_B T) \approx 7\text{Å}$.)

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3. *Packaging DNA in a phage:* After an infected bacterium has duplicated the DNA and coat of an infecting phage, a new phage is assembled with the aid of protein motors. In the case of bacteriophage ϕ29, a 20,000 base pair dsDNA has to be packaged in a capsid, which is a cylinder of radius $r = 42$nm and height $h = 47$nm. Inside the capsid the DNA is arranged like a spool, first winding in a helical shell next to the wall, and then forming successively tighter shells moving inwards. A typical separation between strands in this
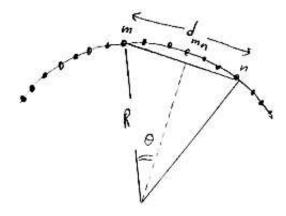
structure is 2.3nm. Single molecule experiments have shown that the work required to pack the DNA in the capsid is approximately $10^5 k_B T$ at room temperature ($T = 300^o$K). In the following, *use order of magnitude estimates* to determine what sets this energy scale.

(a) Estimate the entropy of the DNA in solution, using a persistence length of $\ell_P \approx 50$nm. Can the loss of this entropic free energy account for the work of packaging?

(b) Estimate the energy cost of bending DNA into the helical form found in the capsid. (Express the rigidity parameter κ in terms of the persistence length ℓ_P.) Is bending energy a significant fraction of the overall work of packaging?

(c) Estimate the electrostatic energy of DNA in the capsid: Assume unit charges along the DNA at a spacing of $b \approx 0.17$nm, which interact through a Debye–Hückel potential of screening length $\lambda \approx 1$nm, with charges on nearby strands (separations of around 2nm). Can electrostatic energies account for the work of packaging?

Here are a couple of articles on the packaging of DNA in a phage: *P. K. Purohit, M. M. Inamdar, P. D. Grayson, T. M. Squires, J. Kondev, and R. Phillips,* Forces during Bacteriophage DNA Packaging and Ejection- *Biophys. J., February1, 2005; 88(2): 851 - 866. (http://www.biophysj.org/cgi/reprint/88/2/851)*; and S. Tzlil, J. T. Kindt, W. M. Gelbart, and A. Ben-Shaul, Forces and Pressures in DNA Packaging and Release from Viral Capsids- *Biophys. J., March1,2003; 84(3): 1616 - 1627. (http://www.biophysj.org/cgi/reprint/84/3/1616).*
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4. *Charged membranes:* In class, we solved the Poisson–Boltzmann for a flat membrane of uniform charge density σ, with a neutralizing background of counterions of charge e.

(a) Extend the solution to counterions of charge ze, and compute their density at a distance y from the membrane.

(b) There is an overall constant of proportionality that can be fixed by examining the electric field at the charged surface. Plot the electric field as a function of y.

(c) Check the overall neutrality of the system by integrating over the density of counterions.

(d) Calculate the self-consistent potential and charge density between two uniformly charged plates. (Each plate has uniform charge density σ, the neutralizing counterions have charge ze, and the plates are separated by L.)

(Optional) (e) Solve the Poisson–Bolzmann equation around a cylinder of radius a and charge density $n = e/b$. (Hint: By changing variables to $x = \ln(r/a)$ and $\psi = \beta ze\phi - 2x$, you should be able to reduce the two dimensional problem to the already solved one dimensional case.) Can you make connections to the results in problem 2 on Manning condensation?
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5. *Bending a charged polymer:* As indicated in the figure below, bending a polymer reduces the distances between its monomers.

(a) For two monomers which are at a distance $d_{mn} = b|m - n|$ when the polymer is straight, compute the change $\delta d_{mn}(R)$, when the polymer is bend into a circle of radius $R \gg d_{mn}$.

3

(b) Assume that unit charges at each monomer interact through the Debye potential

$$V(d) = k_B T \ell_B \frac{e^{-d/\lambda}}{d},$$

where ℓ_B and λ and the Bjerrum and screening lengths, respectively. Compute the change in this pairwise energy if the distance is changed from d to $d + \delta d$.

(c) Show that bending increases the energy of the charged polymer by an amount proportional to L/R^2, where $L = Nb$ is the total length of the polymer.

(d) The overall bending modulus for a charged polymer can be written as $\kappa = \kappa_b + \kappa_e$, where κ_b is the cost of deforming the backbone, while κ_e comes from the additional electrostatic energy. Compute κ_e using the model explored in the previous parts.

(e) Is electrostatic energy a significant component of the cost of bending a double stranded DNA? (For DNA in water, $b \approx .17$nm, $\ell_B \approx .7$nm, $\lambda \approx 1$nm, and $\ell_P \approx 50$nm. What about single-stranded DNA or RNA?)

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6. *Bending a charged membrane:* Consider a membrane with a uniform charge density σ immersed in a solution with salt ions. Assuming that the charges interact through a Debye–Hückel potential with screening length λ, estimate the electrostatic contribution to the bending rigidity κ? (Follow the steps in the previous problem for a polymer.)

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7. *Force/extension of 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^{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

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

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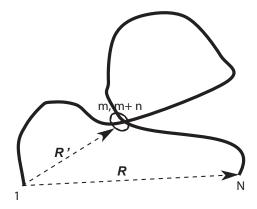
$$\frac{R_F}{\sqrt{\left\langle R^2 \right\rangle_0}} = \Phi \left(\frac{F\sqrt{\left\langle R^2 \right\rangle_0}}{k_B T} \right).$$

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 $\sqrt{\left\langle R^2 \right\rangle_0} \approx aN^\nu$ 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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8. *Force/extension of 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

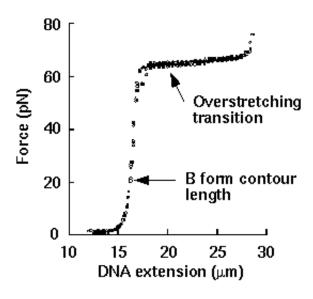$$R_F = \frac{a^2}{3k_B T} \left(N - \langle n \rangle_F \right) F,$$

5

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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9. *Over-stretching DNA:* In standard (B–from) DNA the basepairs stack in spiral fashion at separation of 3.4Å. As indicated in the following figure [from S. B. Smith, Y. Cui, C. Busta-mante, Science **271**, 795 (1996), and *http://alice.berkeley.edu/~ steve/DNAstr.html*], pulling on DNA with optical tweezers causes it to greatly stretch at forces of around 65±5pN.

(a) One interpretation is that this represents a transition to a new structure of over-stretched DNA, in which the separation of bases has increased to 5.8Å. As a very simple model of this putative state consider DNA as a one dimensional chain in which each unit can either be in the regular form of size 3.4Å, or in the stretched form of size 5.8Å. Assume that an energy U is required to change the regular form to the stretched form. For this part of the problem ignore the three dimensional orientations of each segment, and assume that the state of each element is independent of its neighbors. Calculate the length $L(F,T)$ for this model when pulled by a force F at a temperature T.

(b) Compare the result from part (a) to the experimental figure, and thus estimate the parameter U from the data in the above model from experiments. Is the width of the transition region in F consistent with the assumptions of the model.

(c) Now consider a more realistic model in which neighboring elements tend to be in the same state. Would this lead to a sharpening or widening of the transition region in F?

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Suggested reading: Chapter 7 of *Biological Physics* by Philip Nelson.