Coulomb Interactions

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 polymers, 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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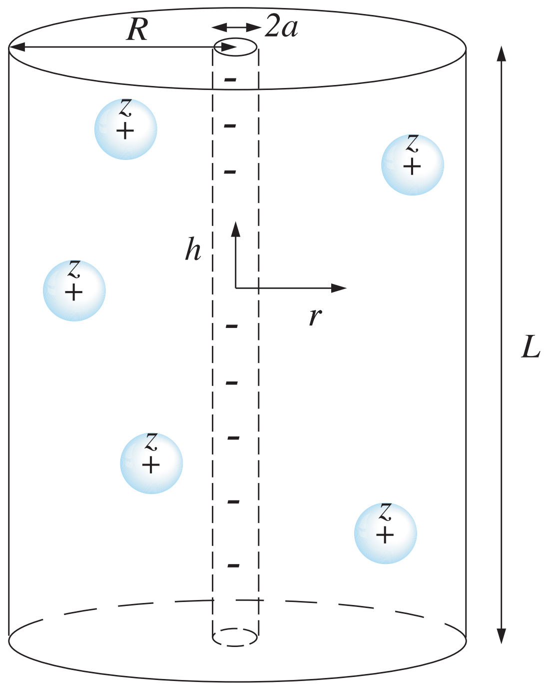
2. *The Manning Transition:* When ionic polymers (polyelectrolytes) such as DNA are immersed in water, the smaller charged *counter-ions* go into solution, leaving behind an oppositely charged polymer. Because of the electrostatic repulsion of the charges left behind, the polymer is stretched, and shall be modeled as a cylinder of radius a, 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

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

Here, n is the linear density and r_i is the radial coordinate of the i^{th} 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 $b = 1.7\AA$. 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 $\ell_B = e^2/(\epsilon k_B T) \approx 7\AA$.)

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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 $\phi 29$, 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 membrane:* Consider a flat membrane of uniform charge density σ, immersed (on both sides) in a neutralizing background of counterions of charge ze.

(a) Write down the self-consistent (Poisson–Boltzmann) equation linking the electrostatic potential ϕ, and the counterion charge density ρ.

(b) Give the solution to the above equation, and plot the electric field as a function of the separation from the membrane.

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

(Optional) (d) 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 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 calculation presented in lectures for a polymer.)

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