

## Problem set 4 (Hand in by May 20)

### Problem 1

**Debye-Hückel: Charged sphere in ionic solution.** In class, we discussed the interaction of an infinite charged plane with an ionic solution. While an infinite plane can be a good model for a cell membrane, the more important and useful result is the solution for a charged sphere in solution. In this problem, you will derive the electrostatic potential for a charged sphere (with radius  $R$  and total charge  $Q$ ) in ionic solution in the Poisson-Boltzmann limit. For simplicity, you can assume that there is a simple monovalent salt (i.e. one species of charge +1 and one ionic species of charge -1) with a bulk concentration of  $c_\infty$ . In addition, you can assume that the sphere is only weakly charged, such that the exponential function of the Boltzmann factor can be simplified according to  $\exp(\pm x) \approx 1 \pm x$ .

- a) Derive a differential equation for the electrostatic potential  $\phi$  as a function of the radial distance from the sphere. You can essentially follow the derivation used in class. However, for the spherical problem, it is best to use a spherical coordinate system. Hint: The relevant differential operator in spherical coordinates reads

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\phi}{dr} \right) \quad (1)$$

- b) Show that the solutions are of the form  $\phi(r) = \frac{C_1}{r} \exp(-r/\lambda_D)$  where  $C_1$  is a constant and  $\lambda_D$  is the Debye length  $\lambda_D = \sqrt{(\epsilon\epsilon_0 k_B T)/(2e^2 c_\infty)}$ . Hint: You can use an *Ansatz* of the form  $\phi(r) = \frac{C_1}{r} \exp(-r/\lambda_D) + \frac{C_2}{r} \exp(r/\lambda_D)$ . Show that this solves the differential equation. What happens to the  $C_2$  term? As an extra credit exercise: What is the constant  $C_1$  in terms of the parameters of the problem?
- c) What is the value of the Debye length  $\lambda_D$  for 150 mM monovalent salt (an approximately physiological salt concentration)? For 1.5 M salt?

### Problem 2

**Estimates of molecular forces.** In this problem, we will carry out some very simple estimates of the forces required to break interactions in biomolecular systems. A simple estimate of the force  $F$  required to break a certain interaction can be obtained by considering the characteristic energy  $E$  and the typical length scale  $\Delta x$  over which it acts:  $E = F \cdot \Delta x$ .

- a) Estimate the forces required to break covalent bonds. A C-C bond has a binding energy of 348 kJ/mol; a N-N bond has an energy of 170 kJ/mol. You can assume that the bonds break over a characteristic distance of  $\approx 1 \text{ \AA}$ .
- b) Biological interactions are often mediated by non-covalent bonds. Non-covalent interactions tend to be weaker and longer ranged than covalent bonds. Obtain a rough estimate of the energies and rupture forces of non-covalent interactions, by assuming that they act over distances of  $\approx 1 \text{ nm}$  and taking into account that they are much weaker than covalent interactions but still stronger than forces due to thermal fluctuations. Hint: the thermal energy at room temperature is  $k_B T \approx 4 \text{ pN}\cdot\text{nm}$ .

### Problem 3

**3D Gaussian chain.** The end-to-end vectors of an ideal chain in 3D are Gaussian distributed.

$$P(N, \vec{R}) = \left( \frac{3}{2\pi \cdot Nb^2} \right)^{2/3} \exp \left( -\frac{3\vec{R}}{2 \cdot Nb^2} \right) \quad (2)$$

The mean is  $\langle \vec{R} \rangle = 0$  and the variance is  $\langle \vec{R}^2 \rangle = Nb^2$ . The square root of the mean squared radius is interpreted as the “unperturbed end-to-end distance”.

- a) Calculate the exact maximum of the end-to-end distance distribution function.
- b) Use the Boltzmann relation (i.e. the connection between entropy and probability) to calculate the free energy change if an ideal chain is perturbed from an unperturbed end-to-end distance to an arbitrary end-to-end distance  $R$ .
- c) Calculate the force associated with the conformational change in b).
- d) What is the effective “spring constant” of an ideal chain?