

## Solutions to problem set 4

### Problem 2

#### Electrostatics for folded RNAs and proteins.

- a) Size estimate for 100 aa (amino acid) protein or 100 nt (nucleotide) RNA. The density  $\rho = 1.35 \text{ g/ml}$  ( $= 1350 \text{ kg/m}^3$ ) is given.

$$\rho = \frac{M}{V} \Rightarrow V = \frac{M}{\rho} = \frac{4}{3}\pi R^3 \quad (1)$$

assuming a sphere in the last step. Solving for the radius and plugging in numbers:

$$\Rightarrow R = \left( \frac{3}{4\pi} \frac{M}{\rho} \right)^{1/3} \quad (2)$$

$$\Rightarrow R_{\text{Protein}} = \left( \frac{3}{4\pi} \frac{100 \cdot 110 \text{ Da} \cdot 1.66 \cdot 10^{-27} \text{ kg/Da}}{1350 \text{ kg/m}^3} \right)^{1/3} \approx 1.5 \text{ nm} \quad (3)$$

$$\Rightarrow R_{\text{RNA}} = \left( \frac{3}{4\pi} \frac{100 \cdot 330 \text{ Da} \cdot 1.66 \cdot 10^{-27} \text{ kg/Da}}{1350 \text{ kg/m}^3} \right)^{1/3} \approx 2.1 \text{ nm} \quad (4)$$

- b) For the RNA, every residue has  $-1e$  charge, the total charge is  $Q_{\text{RNA}} = -100e$ .  
 For the protein, out of 20 amino acids 5 are charged, of which 2 are negatively charged (glutamic acid and aspartic acid) and 3 positively charged (arginine, lysine, and histidine). Therefore,  $Q_{\text{Protein}} = +\frac{3}{20}100e - \frac{2}{20}100e = +5e$ .
- c) Now we assume that the charges calculated in part b) are uniformly distributed over the spheres with radii computed in part a) (this, btw, is not a great assumption for proteins, since for folded proteins charged residues tend to be on the outside, exposed to the solvent). The electrostatic energy of a uniformly charged sphere is

$$E_{\text{elec}} = \frac{1}{4\pi\epsilon\epsilon_0} \frac{3Q^2}{5R} \quad (5)$$

The  $3/5$  comes from integrating the “charging contributions” over the entire sphere (see e.g. [http://www.feynmanlectures.caltech.edu/II\\_08.html](http://www.feynmanlectures.caltech.edu/II_08.html)); for an order-of-magnitude estimate leaving out the  $3/5$  is fine, too.

**In vacuum.** With  $\epsilon \approx 1$ , we find

$$E_{\text{elec,RNA}} = \frac{1}{4\pi \cdot 8.85 \cdot 10^{-12} \text{ C}^2/(\text{N m}^2)} \frac{3}{5} \frac{(-100 \cdot 1.6 \cdot 10^{-19} \text{ C})^2}{2.1 \cdot 10^{-9} \text{ m}} \approx 6.6 \cdot 10^{-16} \text{ J} \approx 1.6 \cdot 10^5 k_B T \quad (6)$$

Similarly, we find

$$E_{\text{elec,Protein}} = \frac{1}{4\pi \cdot 8.85 \cdot 10^{-12} \text{ C}^2/(\text{N m}^2)} \frac{3}{5} \frac{(+5 \cdot 1.6 \cdot 10^{-19} \text{ C})^2}{1.5 \cdot 10^{-9} \text{ m}} \approx 2.3 \cdot 10^{-18} \text{ J} \approx 560 k_B T \quad (7)$$

**In water.** With  $\epsilon \approx 80$ , we find

$$E_{elec, \text{RNA}} \approx 2000 k_B T \quad (8)$$

$$E_{elec, \text{Protein}} \approx 7 k_B T \quad (9)$$

### Problem 3

#### Debye-Hückel: Charged sphere in ionic solution.

- a) Choose a spherical coordinate system. Due to symmetry, the angles do not matter and we can consider the problem as an effective 1D problem in the radial coordinate. Following steps identical to the ones carried out in class for the infinite plane, we have that the bulk concentration far from the sphere is  $c_+ = c_- = c_\infty$ . At finite distance  $r$ , the concentrations for the positive and negative species are given by (for generality, we include the valency  $z$ , which is simply equal to one in our case):

$$c_+ = c_\infty \exp(-ze\phi(r)/k_B T) \quad (10)$$

$$c_- = c_\infty \exp(+ze\phi(r)/k_B T) \quad (11)$$

Taking into account the mobile charges, the Poisson equation then reads (where  $\rho(r)$  is the charge density):

$$\nabla^2 \phi(r) = -\frac{\rho(r)}{\epsilon \epsilon_0} = \frac{z e c_\infty}{\epsilon \epsilon_0} (\exp(ze\phi(r)/k_B T) - \exp(-ze\phi(r)/k_B T)) \quad (12)$$

This is the Poisson-Boltzmann equation for a simply 1:1 ionic solution. Now we linearize the exponential, an approximation known as the Debye-Hückel limit:

$$\nabla^2 \phi(r) = \frac{2z^2 e^2 c_\infty}{\epsilon \epsilon_0 k_B T} \phi(r) = \frac{1}{\lambda_D^2} \phi(r) \quad (13)$$

In the last step, we have introduced the Debye length  $\lambda_D$ . We now need to write the Laplace operator for the radial coordinate to get the differential equation for  $\phi(r)$ :

$$\nabla^2 \phi(r) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi(r)}{\partial r} \right) = \frac{1}{\lambda_D^2} \phi(r) \quad (14)$$

- b) To show that the *Ansatz*  $\phi(r) = \frac{C_1}{r} \exp(-r/\lambda_D) + \frac{C_2}{r} \exp(r/\lambda_D)$  solves the differential equation 5, we can simply plug it in and show that, after applying the chain and product rules, it satisfies the equation. Far away from the sphere the potential is zero, by convention, and therefore the exponentially growing part of the solution has to be zero, i.e. the constant  $C_2$  has to be zero, leaving the  $C_1$  term as the relevant solution.

The key observation here is that for an ionic solution, the potential of a sphere does not simply fall as  $\propto 1/r$  (as it would in vacuum or air), but that there is an additional exponential cut-off with a characteristic length scale given by  $\lambda_D$ .

- c) Debye length  $\lambda_D$  for 100 mM monovalent salt  $\approx 9.6 \text{ \AA}$ ; Debye length at 1.0 M salt  $\approx 3 \text{ \AA}$ . There are even online calculators (see e.g. <http://www.surfchem.info/calculate/Debye/>). Note that the Debye length is on the same order as molecular dimensions (e.g. the DNA radius), which means that in ionic solutions, electrostatic interactions are strongly reduced over rather short distances.