

Solutions to problem set 4

Problem 1

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):

$$c_+ = c_\infty \exp(-ze\phi(r)/k_B T) \quad (1)$$

$$c_- = c_\infty \exp(+ze\phi(r)/k_B T) \quad (2)$$

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

$$\nabla^2 \phi(r) = -\frac{\rho(r)}{\epsilon \epsilon_0} = \frac{z e c_\infty}{\epsilon \epsilon_0} (\exp(ze\phi(r)/k_B T) - \exp(-ze\phi(r)/k_B T)) \quad (3)$$

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:

$$\nabla^2 \phi(r) = \frac{2z^2 e^2 c_\infty}{\epsilon \epsilon_0 k_B T} \phi(r) = \frac{1}{\lambda_D^2} \phi(r) \quad (4)$$

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

$$\nabla^2 \phi(r) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi(r)}{\partial r} \right) = \frac{1}{\lambda_D^2} \phi(r) \quad (5)$$

- 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 λ_D .

- c) Debye length λ_D for 150 mM monovalent salt $\approx 7.8 \text{ \AA}$; Debye length at 1.5 M salt $\approx 2.5 \text{ \AA}$. See the separate matlab code for the calculation. This means that in ionic solutions, electrostatic interactions are strongly reduced over rather short distances.

Problem 2

Estimates of molecular forces.

- a) C-C bond:

$$E = 348 \text{ kJ/mol} = 348 \text{ kJ/mol} \cdot 1000 \text{ J/kJ} / (6 \cdot 10^{23} / \text{mol}) = 5.8 \cdot 10^{-19} \text{ J}$$

$$F = E / \Delta x = 5.8 \cdot 10^{-19} \text{ J} / (10^{-10} \text{ m}) = 5.8 \cdot 10^{-9} \text{ N} = 5.8 \text{ nN}$$

N-N bond:

$$E = 2.8 \cdot 10^{-19} \text{ J}$$

$$F = 2.8 \text{ nN}$$

i.e. the rupture forces for covalent bond are in the nN range. For more information, see Michel Crandbois, Martin Beyer, Matthias Hauke Clausen-Schaumann, Hermann E. Gaub, *How Strong Is a Covalent Bond?*, *Science* (1999)

- b) Non-covalent bonds in biological systems have to be stronger than $E = 4 \text{ pN}\cdot\text{nm} = 10^{-21} \text{ J}$ and have to withstand forces larger than $\approx 4 \text{ pN}\cdot\text{nm}/1 \text{ nm} = 4 \text{ pN}$, otherwise thermal fluctuations would constantly break them. At the same time, they are considerably weaker than covalent bonds with energies in the range of $E \approx 10^{-19} \text{ J}$ and forces $\approx 1 \text{ nN}$. Therefore, typical rupture forces for non-covalent bonds are 10-100 pN and typical energies $10\text{-}100 \text{ pN}\cdot\text{nm} \approx 2\text{-}20$ times $k_B T$.

Problem 3

3D Gaussian chain. Use the updated/corrected formula for $P(\vec{R}; N)$:

$$P(\vec{R}; N) = \left(\frac{3}{2\pi \cdot Nb^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2 \cdot Nb^2} \right) \quad (6)$$

- a) We want to find the maximum of the squared end-to-end distance and then take the square root to find the maximum of the end-to-end distance distribution. To find the maximum of $P(\vec{R}; N)R^2$ set it equal to zero and solve for R_{max} :

$$\frac{\partial}{\partial R} P(\vec{R}; N)R^2 = 0 \quad (7)$$

$$0 = 2R \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2 \cdot Nb^2} \right) - R^2 \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2 \cdot Nb^2} \right) \frac{3 \cdot 2R}{2Nb^2} \quad (8)$$

$$0 = 2R - R^3 \frac{3}{Nb^2} \quad (9)$$

$$R_{max} = \sqrt{\frac{2}{3} Nb^2} \quad (10)$$

- b) Boltzmann relation: $S(\vec{R}) = k_B \ln(P(\vec{R}; N))$. Now we want to go from the unperturbed end-to-end length $\sqrt{Nb^2}$ to a new value $\sqrt{R^2}$. The change in entropy is

$$\Delta S = S(R^2) - S(Nb^2) = k_B \left(\frac{3}{2} - \frac{3}{2} \frac{R^2}{Nb^2} \right) = \frac{3}{2} k_B \left(1 - \frac{R^2}{Nb^2} \right) \quad (11)$$

- c) The Gaussian chain has only entropy as a contribution to its free energy. Thus $\Delta G = -T\Delta S$. In addition, we have that the force is given by $F = -\partial\Delta G/\partial R$, therefore we find

$$F = \frac{3k_B T}{Nb^2} R \quad (12)$$

- d) The spring constant is simply the pre-factor in front of the R in the last equation, i.e. $\frac{3k_B T}{Nb^2}$. This agrees with the result that we obtained in the lecture from looking at the low force limit of the FJC force-extension relationship.