Homework Week 4:
Exercises 8-12

Material to study for the part about ions:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 3: paragraphs: 3.1 – 3.8
Lecture notes on Debye-Huckel theory

List of constants:
Boltzmann constant: $k = 1.38 \times 10^{-23}\ m^2\,kg\,s^{-2}\,K^{-1}$
Avogadro number: $N_A = 6.022 \times 10^{23}\ mol^{-1}$
Radius of a Na^+ ion: 0.095 nm
Radius of a Cl^- ion: 0.181 nm
Radius of a water molecule: 0.14 nm
The dielectric permittivity of free space: $\varepsilon_0 = 8.85 \times 10^{-12}\ C^2\,J^{-1}\,m^{-1}$
Dielectric constant of vacuum: $\varepsilon = 1$
Dielectric constant of oil: $\varepsilon = 2$
Dielectric constant of water: $\varepsilon = 80$ (298 K)
Elementary charge: $e = 1.6 \times 10^{-19}$ C

Ionic interaction

8.
Here, we want to first examine the properties of Coulombic interactions for a pair of ions, and then apply it to the formation of an ionic crystal.
a. Given a Na^+ and a Cl^- ion that form an ionic contact pair in vacuum, show that the pair potential at the smallest possible separation has a value of ~ 200 kT.
b. At what distance will the thermal energy be sufficiently strong, so that the chance of breaking the bond is 50 %?
c. What will be the difference if we bring the pair of ions in water? Calculate a. and b. for this case.
d. How many water molecules are approximately needed to separate two ions far enough so that the thermal energy and the interaction strength are approximately equal?

Thus the Coulombic interactions are long ranged, but the dielectric properties of a medium can greatly shorten the interaction length. In addition, the presence of other ions may also influence the total interaction energy. In what follows, we will see how this comes about.

9.
Now we seek to understand the interactions that hold a salt together. Below is a picture of the crystal structure of table salt (NaCl), which we will use here as an example. We can assume that the distance between two ion contact pairs is given by the sum of the radii and that the crystal is placed in vacuum.

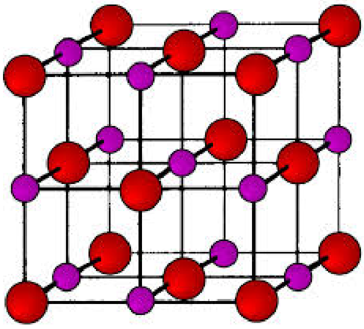

Fig. 1: *Crystal lattice of table salt.*

a. Which colors represent Na^+ / Cl^- ions?

b. Taking r for the distance between two nearest neighbors show that for the interaction energy we can write the following series:

$$\mu_i = \frac{-e^2}{4\pi\varepsilon_0 r}\left\{6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \cdots\right\} = 1.748\,\frac{-e^2}{4\pi\varepsilon_0 r}$$

Start with the definition for the interaction energy and determine the number and distance between the nearest neighbors, as well for the next closest neighbors, etc.

c. Do you expect the series to depend on the material?

d. What is the molar lattice energy or cohesive energy (U)?

Calculate the number both in terms of kJ/mol and kT. What is the sign of U?

e. Two NaCl crystals that are placed with a separation of 10 μm do not attract each other, even though the pair potential has only a 1/(distance) dependence. Explain the reason for this observation.

Ions in solutions - introduction

As we have seen in Chapter 3 the interactions between ions are governed by the Coulomb interaction, which has an electrostatic potential ψ(r) that decays as ~1/r. However, the distribution of ions can introduce a different dependence of the potential on the distance. For instance, the stacking of the anions and cations in a crystal lattice leads to a much steeper decay of the electric potential outside the crystal than the ~1/r law.

In an aqueous solution, we have a scenario that is in between an ordered and a random distribution of ions. Positive ions prefer being surrounded by negative ions, and because they are free to move they will approach each other. However, entropy maximization will ensure that a certain amount of disorder can be reached with the aid of the available thermal energy. Therefore, there is no strict ion organization, but only a statistical deviation from randomness. Figure 1 shows an illustration of the distribution of ions in a liquid. This non-random distribution of counter ions leads to a decay of the electrostatic potential that is much steeper than the 1/r term in the Coulombic interaction.

In order to understand this behavior and the underlying interactions, we will first derive the theory that explains this behavior in an approximate way (exercise 10) and then check its properties to get a feel for the behavior of ionic distributions (exercise 11). The theory also has applicability to predict the changes in solubility of ions and macromolecules. The material of this exercise will be aided by the lecture and the notes that will be handed out. Later in the course we will encounter Debye-Hückel theory again to understand the structuring and stability of interfaces.

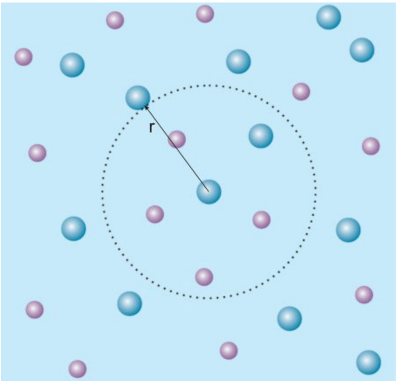

Figure 1*: Ions in solution.*

Derivation of Debye-Hückel theory

10.

In the following exercise, we will work out the expressions that Debye and Hückel have derived in the early years of the 20th century for the electrostatic potential $\psi(r)$ and charge density $\rho(r)$ around a single ion that is surrounded by co- and counter ions in a solution. We define r as the distance from the center of our ion to a point of interest in the solution (see Fig. 1). Thus, our aim is to **find the electrostatic potential $\psi(r)$ and charge density $\rho(r)$ around a single ion that is surrounded by co- and counter ions in an aqueous solution.** In order to follow the approach of Debye and Hückel we need to do the following:

1. We first need to know which solution parameters can be used as input, and we need to define useful parameters.
2. We need to determine which equations can be used as a starting point.
3. We need to combine expressions, make approximations and find solutions for the electrostatic potential and the charge density around a single ion in solution.

Note that this is the same scheme we have identified in Lecture 1 as necessary to solve a problem analytically.

Starting with the first point we typically know the compounds, the concentration, the volume, and the temperature of a solution. We can thus assume that we have a solution of monovalent ions A^+, and B^-, such as NaCl, or KCl. The total number of anions and cations in a volume V is equal and equal to the concentration*V. We can identify the total number of cations (anions) as N_+ (N_-) and we should then have number densities of n_+ (n_-) that correspond to $N_{+/-}/V$. We can also say that far away from our ion of interest the ionic distribution is random, so that $n_+=n_-=n_0$, where n_0 is again a number density. We can make the same statements about the charge density ρ. We can write ρ_+,ρ_-, ρ_0 as equivalents for n_+, n_-, n_0.

a. The probability to find a co- or counterion at a position r away from our central A^+ ion is determined by the interplay of electrostatic interactions and thermal effects. Which equation can we use as a starting point? Write down the expression for the density of cations ($n_+(r)$) and anions ($n_-(r)$) and the total ion density ($n_+(r) + n_-(r)$) in terms of $\psi(r)$. Do the same for $\rho_+(r)$, $\rho_-(r)$, $\rho_0(r)$. Do not try to find an explicit expression for $\psi(r)$, this will be done later.

b. Now we have one equation for two unknowns: $\rho(r)$ and $\psi(r)$. Show that by combining the differential form of Gauss law ($\nabla \cdot E = \frac{\rho}{\varepsilon_0 \varepsilon}$), with the definition for the electric field ($E = -\nabla\psi(r)$) we can get a second equation linking $\rho(r)$ and $\psi(r)$:

$$\nabla^2 \psi(r) = -\frac{\rho(r)}{\varepsilon_0 \varepsilon} \qquad (1)$$

This is the Poisson equation. Show that we can now combine the result of a. and (1) to obtain:

$$\nabla^2 \psi(r) = -\frac{e n_0}{\varepsilon_0 \varepsilon}\left(e^{-e\psi(r)/_{kT}} - e^{e\psi(r)/_{kT}}\right) \qquad (2)$$

This is called the Poisson-Boltzmann equation which can be solved to obtain a unique solution for the electrostatic potential around the central ion. The solution can often only be found numerically. However, in many cases we can find an approximate analytical expression by noting that the energy of the electrostatic interaction is (much) smaller than the thermal energy of the ions.

c. Show that

$$\rho(r) \cong -\frac{2e^2 n_0 \psi(r)}{kT} \qquad (3)$$

Hint: *Substitute $x = e\psi(r)/(kT)$ and consider using a Taylor expansion to simplify the expression. Definition: $f(x) = \sum_{n=0}^{\infty} \frac{f(0)^{n'}}{n!} x^n$.*

d. Show that:

$$\nabla^2 \psi(r) = \kappa^2 \psi(r) \qquad (4)$$

(using the previous equations) and show that the pre-factor on both sides of the equation has dimension of m^{-2}. What is the expression for κ? (We will come back to the meaning of κ later).

Now we have derived a *single* differential equation for a *single* parameter that can be solved easily. We can use the fact that the interactions are independent of the rotational angles between the ions, so that we can ignore this part of the differential and write for ∇^2:

$$\nabla^2 \psi(r) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi(r)}{\partial r}\right)$$

And we can rewrite this to:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi(r)}{\partial r}\right) = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi(r)) \qquad (5)$$

e. Using the above expressions show that the solution for the electrostatic potential is:

$$\psi(r) = \frac{Ae^{-\kappa r} + Be^{+\kappa r}}{r} \qquad (6)$$

by solving differential equation (4), using the given radial expression for ∇^2 (Eq. 5). Find values for A and B using the following boundary conditions:

- at infinity the electrostatic potential vanishes
- at the boundary of the ion (that has a radius a) the potential decays according to Coulombs law.

f. Having found the expression for the electrostatic potential we can go back to question a. and find an expression for the density of cations and anions. What is the expression for the density of cations and anions?

g. Sketch the functions for $\rho_+(r)$,$\rho_-(r)$ and $\psi(r)$.

Properties of Debye - Hückel theory and consequences for salt solutions

11.

a. The expressions we have derived are only valid under the condition that the energy of the interaction is (much) smaller than the thermal energy of the ions. Show that this means that the values that we can find by using the Debye-Hückel approximation are exact for electrostatic potentials < 26 mV, and that values > 26 mV are only approximate.

b. For a solution of monovalent ions, estimate the distance for which the electrostatic potential is smaller than 26 mV. Do not take the effect of the ion atmosphere into account. How many water molecules can fit in that distance?
Will this distance increase or decrease when we do take the effect of the ionic atmosphere into account?

From the exponential term in (6) and your answer of question 13g we see that κ influences the value and decay of the electrostatic potential. Now we want to examine this parameter κ.

The ionic strength I is defined by:

$I = \frac{1}{2}\sum c_i z_i^2$, where c_i is the ionic concentration in mol/L, z_i is the ion valency.

c. Calculate the ionic strength of a solution of 100 mM NaCl, 100 mM $AlCl_3$, and 100 mM of KCl and 100 mM $CaCl_2$.

d. Show that $\kappa = 3.3\sqrt{I}$ (nm^{-1}) at room temperature in water.

e. Calculate the Debye screening length $1/\kappa$ for a solution of 1 μM, 100 μM, 1 mM, 100 mM, and 1 M of NaCl

f. Show that the average distance between the centers of two ions in a solution assuming no interaction between them is given by $d=0.94/c^{1/3}$ [nm]. c is the concentration in mol/L.

g. Make a small table listing c, $1/\kappa$, d for 1 μM, 100 μM, 1 mM, 100 mM, 1 M. Compare the spacing d and the screening length $1/\kappa$. For which concentrations do the ions interact with each other? Will the solubility of ions be concentration dependent?