Worksheet 3
Electrostatic screening and polymer properties

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Important remarks

- You can access the ICP web page to download important materials via the username **icp** and the password **icp**.
- Due date: **Monday, December 9^{th}, 2013, 12:00**
- You can either send a PDF file to Jens Smiatek (smiatek@icp.uni-stuttgart.de), Stefan Kesselheim (Stefan.Kesselheim@icp.uni-stuttgart.de) or submit a hand-written copy.
- Please write your name on each page and make sure that the pages are easily readable.
- If you have further questions, contact Jens Smiatek (smiatek@icp.uni-stuttgart.de) or Stefan Kesselheim (Stefan.Kesselheim@icp.uni-stuttgart.de).
- The solutions will be discussed on Thursday, December 12^{th}, 2013 at 8:00.

1 Short questions - short answers (6 points)

Please give precise and short answers to the questions.

1. Use the virial expansion to give an approximation of the free energy of a real gas.
2. What is Manning condensation? What is the definition of the Manning parameter ξ? What is the qualitative difference between $\xi < 1$ and $\xi > 1$?

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3. What is overcharging? Can Poisson-Boltzmann theory explain it?

2 Gibbs-Donnan equilibrium

The Gibbs-Donnan equilibrium describes the partition of an electrolyte solution in the presence of a semipermeable membrane. This situation is encountered, for example, in living cells, which can exchange ions with the surrounding medium, but not proteins.

Task 1: Cell wall permeable only to cations

We assume a cell filled with KCl solution that is immersed in a KCl solution of a different concentration c_o. Only K^+ ions can permeate the cell wall, and the density of Cl^- ions remains constant at c_i. If $c_i > c_o$, potassium ions will diffuse out of the cell, until a potential builds up across the cell membrane, the Donnan potential.

Calculate the Donnan potential.

You can approximate the chemical potential of the K^+ ions by

$$\mu_+ = k_B T \log \frac{c_+}{c_o} + \Phi.$$

Assume electroneutrality $c_{i,+} = c_{i,-}$, and assume that the chemical potential of the potassium ions is identical inside and outside the cell. What is the osmotic pressure of a cell with $c_i = 0.1$ mol/l in a solution of $c_o = 0.001$ mol/l?

Task 2: Cell was permeable to small anions and cations

Assume that the cell is filled with a number density of n proteins with charge Z. The cell walls shall be penetrable for both ion species, potassium and chloride. Assume the following form for the chemical potential of the chloride ions.

$$\mu_- = k_B T \log \frac{c_-}{c_o} - \Phi.$$

Calculate the Donnan potential with these assumptions. Hint: Look at the chemical potential of a pair of ions $\mu_+ + \mu_-$.

3 Van-der-Waals equation

For this task, it is helpful to use standard statistical mechanics or thermodynamics books. We have scanned the relevant pages of Hansen, Barrat, *Basic Concepts for Simple and Complex Liquids*, Cambridge University Press, Cambridge (2003), which contains a brief but very helpful overview. Please check our website.

Many substances can be realistically described by the van-der-Waals equation of state

$$\left(p + a\frac{N^2}{V^2}\right)(V - Nb) = N k_B T.$$

Virial expansion and free energy

Solve the equation for the pressure and expand this expression in a Taylor series of the density. What is the second virial coefficient. What is its sign, and what does this mean?

Free energy and phase coexistence

Plot the van-der-Waals equation of state in a p-ρ diagram. Plot several subcritical isotherms, a supercritical isotherm and try to find the critial isotherm. Calculate the (Helmholtz) free energy of a van-der-Waals Gas. Plot the free energy as a function of the density for the same parameters you used in the plot before. How can you graphically find coexisting phases?