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Tfy-0.3252 Soft Matter Physics / Pehmeän aineen fysiikka
Final exam 12.12.2013 (5 problems / 2 pages).
No auxiliary written material is allowed (tables, notes etc.) A standard calculator accepted in the Finnish matriculation examinations (yo-kirjoitukset) is allowed.
Since the language of the course was English, the exam problems are in English as well. You can write your answers either in English or Finnish.

Problem 1. (6 points)
Describe the basic physical molecular interactions in soft matter systems: what are their physical origins, relative magnitudes, directionalities, and distance dependences?
The convenient energy scale for interactions in soft matter systems is k_BT (where k_B is Boltzmann's constant and T is usually the "room temperature", something between 290 – 300 K). What is the significance of this in view of free energies of soft matter systems?

Problem 2. (6 points)
Consider a system of surfactants in water. We'll simplify the picture so that the surfactants exist in the solution only either as isolated molecules (unimers) or in micelles with a fixed aggregation number n.
a) Briefly explain the thermodynamic principles for determining the relation between molar fractions of the surfactant molecules as unimers, x_1, and in aggregates, x_n, when the system is at thermodynamic equilibrium.
b) Define the concept *critical micelle concentration (CMC)*.
c) Starting from the general expression of the chemical potential of an ideal solution, derive the relation between x_1 and x_n at thermodynamic equilibrium. With $n = 65$, $\mu_1^0 - \mu_n^0 = 22$ kJ/mol, and $T = 293$ K, provide a reasonable estimate for x_1 at CMC. What is the corresponding concentration in molars (1 M = 1 mol/liter)? Comment on your result.

Problem 3. (6 points)
Consider two very large ("semi-infinite") parallel walls, each having the same surface charge density $\sigma_{\text{surf}} < 0$, and separated by the distance D. Let the x-axis be normal to the wall surfaces, and the midplane between the walls be located at $x = 0$. This way, the other wall fills the space $x < -D/2$ and the other one, correspondingly, fills the space $x > D/2$. The region between the walls is filled with water, and the system is at thermodynamic equilibrium at $T = 293$ K. In order to have an electroneutral system, there are also counterions of ionic valency z between the planar walls.
a) Write the Poisson-Boltzmann equation for this system.
b) Determine the counterion concentration profile $c(x)$ with respect to the ionic concentration at the midplane between the walls, $c_0 \equiv c(0)$. (Hint: start with the derivative of $c(x)$ with respect to x.)
c) Considering the case that the counterion concentration at the midplane is negligible ($c_0 \approx 0$), calculate the concentration of monovalent counterions at a wall surface with $\sigma_{\text{surf}} = -0.02$ C/m^2. Moreover, estimate the charge density due to the monovalent counterions in a thin layer of thickness δ right next to the wall surface. Interpret your result.

Turn the page.

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Problem 4. (6 points)
Answer to the following multiple choice questions. Write your answer to each question on a separate line in your exam paper. A correct answer in each case may consist of one *or* several of the choices given. For each correct answer you will receive two points. No points will be given for incorrect or partially incorrect answers.

4-1. The free energy associated with solvating a hydrophobic solute molecule in water (the "free energy penalty"), ΔG_{solv}, is mainly determined by...
a) entropy at all solute sizes/local surface curvatures.
b) enthalpy at all solute sizes/local surface curvatures.
c) entropy for very small solutes or high local surface curvatures, and enthalpy for much larger solutes or low local surface curvatures.
d) enthalpy for very small solutes or high local surface curvatures, and entropy for much larger solutes or low local surface curvatures.

4-2. Consider the temperature dependence of the free energy associated with solvating a hydrophobic solute in water, ΔG_{solv}. Which of the following statement/statements is/are true?
a) For a solute of characteristic size $R = 0.3$ nm, increasing the temperature increases ΔG_{solv}.
b) For a solute of characteristic size $R = 0.3$ nm, increasing the temperature decreases ΔG_{solv}.
c) For a spherical solute of radius $R = 3$ nm, decreasing the temperature decreases ΔG_{solv}.
d) For a spherical solute of radius $R = 3$ nm, decreasing the temperature increases ΔG_{solv}.
e) There is no temperature dependence for ΔG_{solv} of a hydrophobic solute in water.

4-3. We have an aqueous dispersion of solid colloidal particles, on which there are covalently attached polymers. The density of the grafted polymer chains is relatively high, and the polymers are in extended conformations in the solvent (the so-called good solvent conditions). Consider now two such colloidal particles drifting close to each other, so that the regions of the extended polymer chains of the two particles begin to overlap. Which of the following statement/statements is/are true?
a) There is an effective repulsion between the colloidal particles.
b) There is an effective attraction between the colloidal particles.
c) The effective interaction between the particles increases with temperature.
d) The effective interaction between the particles decreases with temperature.

Problem 5. (6 points)
Give a short explanation of the following concepts. Use illustrations if possible.
a) Debye screening length
b) Surfactant packing parameter
c) Hamaker coefficient

Useful constants, equations etc.
Avogadro's number $N_A = 6.0221 \times 10^{23}$ mol^{-1}
Boltzmann's constant $k_B = 1.3807 \times 10^{-23}$ J/K
Elementary charge $e = 1.60218 \times 10^{-19}$ C
Permittivity of vacuum $\varepsilon_0 = 8.85419 \times 10^{-12}$ F/m
Molar mass of water: $M_{H_2O} = 18.015$ g/mol
Chemical potential of an ideal solution: $\mu_k(x_k, p, T) = \mu_k^0(p, T) + k_B T \ln x_k$