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<u>Exam in Soft Matter Physics TIF015/FIM110</u>
Time: Friday January 18, 2013, 14-18.00.
Examiner: Aleksandar Matic (0730-346294)
Allowed material: Physics Handbook or equivalent, dictionary and pocket calculator approved by Chalmers (Chalmersgodkänd räknare)
Grading: 24 points, is required for a passed.
Note: <u>All answers must be in English.</u> Motivate all answers carefully. Answers without motivation give no credit.

1. For a binary mixture of liquids, the free energy of mixing, according to the Flory-Huggins model, is

$$\frac{\Delta F_{mix}}{k_B T} = \frac{\Delta U_{mix}}{k_B T} - \frac{\Delta S_{mix} T}{k_B T}$$
$$= \phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi \phi_A \phi_B ,$$

where ϕA and ϕB are the volume fractions of the two species respectively, and χ is determined by the interaction between particles in the mixture.

a) For which values of the interaction parameter χ is the mixture stable for all possible volume fractions of the two species? (5 p)

b) Sketch the free energy curve for a globally stable, and for a phase separated mixture respectively, and indicate the stable compositions in the latter case. (5 p)

2. a) When a mixture in an unstable state phase separates, it does so via a process of so called uphill diffusion. Describe how uphill diffusion differs from normal diffusion. (3 p)

b) A mixture in a metastable state can also phase separate, but by a different mechanism. What is it called? (1 p)

c) When a metastable mixture phase separates, the free energy will have to overcome a barrier expressed as

$$\Delta F(r) = \frac{4}{3}\pi r^3 \Delta F_v + 4\pi r^2 \gamma$$

Describe the two competing terms in the right hand side of the equation. (4 p)

d) If the second term in the above equation is too large, the system will not separate. What can we do to make it smaller, and hence make the mixture separate? (2 p)

3. A surfactant solution consists of the anionic surfactant sodium tetradecyl sulphate ($NaC_{14}SO_4$) in water. The size of the surfactant can be estimated by the parameters: $l_c=(0.154+0.127\cdot n)$ nm, $v=(0.0274+0.0269\cdot n)$ nm^3, $a_0=0.65$ nm^2

a) Determine the shape of the micelles formed in the solution and the association number. Motivate the answer and the calculations (6 p)

b) Explain what might happen to the shape of the micelles and the association number if you add salt to the solution. Carefully motivate your answer. (4p)

4. Consider a polymer mixture of molten polyethylene chains $-(CH_2)_n$ with 50% of the chains having a molecular weight of of 12.000 and 50% of the chains having a molecular weight of 24.000.

a) Calculate number average, M_n, weight average, M_w and dispersion. (4p)

b) Sketch the G(t) – the stress relaxation modulus of the two polymer melts mentioned above (mark the curves) with arbitrary units on the axes (now the polymers are not mixed) (3p)

c) G(t) decreases rapidly at the terminal time τ_T which depends strongly on molecular weights (N). Using simple reptation arguments calculate the ratio of τ_T (molecular weight 12.000) to τ_T (molecular weight 24.000) (3p)

5. The distribution of end-to-end distances (R) in an ensemble of random polymer coils is Gaussian. The Gaussian probability function is:

$$P(\overline{R}) = \left(2\pi Na^2/3\right)^{-3/2} \exp\left(\frac{-3\overline{R}^2}{2Na^2}\right)$$

As can be seen from the function above the probability decreases monotonically with increasing R (one end is attached at origin). The radial distribution g(R) is obtained by multiplying with $4\pi R^2$

a) Sketch (coarsely) P(R) and g (R) assuming chains with N= 10000 and a = 1 Å. (4p)

b) Calculate the most probable end-to-end distance R_{mp} of a Gaussian chain. (6p)

6. A colloidal suspension is formed by polystyrene spheres (radius 150 nm) dispersed in an aqueous electrolyte solution (the salt is NaCl) at room temperature. To decrease the influence of salt concentration the particles are covered by a polymer layer. The polymer is polyethylene oxide (PEO, $[-CH_2-O-CH_2-]_n$) with M_w=14000. Estimate the salt concentration range you can work with in order so that the system can be regarded as a hard sphere system! (10 p)

You can assume that we are at theta conditions for this particular combination of polymer and solvent at this temperature and a step length of a=0.56 nm for the polymer. A relation that might be of use is the Debye screening length:

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2e^2 n_0 z^2} \right)^{1/2}$$