EXAM 2
SOFT CONDENSED MATTER
June 26th, 2012

- *This is an open book exam. You can use the syllabus and the handouts provided by the lecturers.*
- *Use a new sheet of paper for each of the problems.*
- *Constants:*

Boltzmann:		$k_B = 1.38\times10^{-23}$ J/K
vacuum permittivity:		$\varepsilon_0 = 8.854\times10^{-12}\ \mathrm{C^2/N\cdot m^2}$
Avogadro's number:		$N_{Av} = 6.022\times10^{23}\ \mathrm{mol^{-1}}$
elementary charge:		$e = 1.602\times10^{-19}$ C

1. The Flory-Huggins expression for a polymer blend is given by

$$f_m(\phi) = \frac{1}{N_A}\phi\ln\phi + \frac{1}{N_B}(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)$$

a. Indicate which terms in the expression are of entropic and which are of energetic origin.

b. What is the definition of the chi-parameter (χ) in this case and on which parameters does it depend?

c. Can you give qualitative arguments (i.e. without calculating anything) whether a blend will mix easily or not?

d. Explain why the critical point is determined by the conditions

$$f_m''(\phi_{cr}) = 0$$
$$f_m'''(\phi_{cr}) = 0$$

e. Use these conditions to calculate the value of the critical volume fraction ϕ_{cr} and critical chi-parameter (χ_{cr}) and discuss the result in case (a) $N_B = N_A$ and (b) $N_B = 1$.

2. The standard-chemical potential of a surfactant molecule in a micellar aggregate of size n in principle depends on the occupied area per surfactant molecule, a. A primitive way to take that dependence into account is by writing

$$\bar{\mu}_n^0 = \gamma a + k / a, \qquad (1)$$

where the chemical potential here is related to the one defined above Eq. (2.10) in chapter 6 of the syllabus by $\bar{\mu}_n^0 = \mu_n^0 / n$.

a. Provide (a) possible interpretation(s) of the two terms in $\bar{\mu}_n^0(a)$.

b. Show that the optimal area per molecule, a_0, is given by

$$a_0 = \sqrt{k / \gamma} \qquad (2)$$

Provide an interpretation of this result. *Hint*: consider the function $\bar{\mu}_n^0(a)$.

c. Show that Eq. (1) can be written as

$$\bar{\mu}_n^0 = 2\gamma a_0 + \frac{\gamma}{a}(a - a_0)^2. \qquad (3)$$

Hint: make use of Eq. (2) to write the chemical potential of a surfactant molecule at optimum headgroup area as $\bar{\mu}_n^0(a_0) = 2\gamma a_0$.

d. Show that the fraction of molecules with headgroup area a relative to the optimal area a_0 is approximately given by

$$\frac{x_a}{x_{a_0}} = exp\left(\frac{-\gamma}{a}(a - a_0)^2 / k_B T\right) \qquad (4)$$

What assumption(s) have you made?

3. Consider a mixture of two polymer species with radius of gyration R_1 and R_2 for species 1 and 2, respectively.

a. Calculate the Helmholtz free energy $F(N_1, N_2, V, T)$ of such a binary mixture consisting of $N_1 \gg 1$ and $N_2 \gg 1$ polymer coils in a volume V and at a temperature T under the assumption that the polymers can be treated as ideal point particles. Calculate also the pressure p, the chemical potential μ, and the internal energy E of this mixture.

The equation of state of a colloidal suspension can be approximated by

$$\frac{p}{k_B T} = \rho - \frac{a}{k_B T}\rho^2 + b^2\rho^3 \qquad (1)$$

where $\rho = N/V$ is the number density, p the pressure, T the temperature, N the number of particles, V the volume, k_B Boltzmann's constant and $a,b > 0$ phenomenological constants.

b. Sketch the equation of state, i.e., p as a function of ρ, for sufficiently high and low temperature. Do you expect gas-liquid coexistence at high temperature and at low temperature? Motivate your answer.

c. Calculate the critical pressure p_c, critical density ρ_c, and critical temperature T_c.

d. What are the conditions for phase coexistence? Describe how gas-liquid equilibrium coexistence can be determined from $\mu(\rho, T)$ and $p(\rho, T)$ for $T < T_c$?

The chemical potential $\mu(\rho, T)$ can be derived from the equation of state $p(\rho, T)$ using thermodynamic integration.

e. Show that the chemical potential reads

$$\mu(\rho, T) = k_B T \log\left(\rho\Lambda^3\right) + \int_0^{\rho} \frac{1}{\rho'}\left(\frac{\partial\left(p - \rho' k_B T\right)}{\partial \rho'}\right)_T d\rho'$$

where Λ denotes the thermal wavelength.

f. Calculate the chemical potential $\mu(\rho, T)$ using the equation of state (1).
