EXAM
SOFT CONDENSED MATTER
June 23rd, 2009

1. Phase behaviour and structure of colloid-polymer mixtures

Sterically stabilized colloidal spheres can be modeled as hard spheres with a diameter σ.

a. Calculate the second virial coefficient for a fluid of hard spheres with diameter σ.

b. Is there gas-liquid and/or liquid-solid coexistence in the phase diagram of pure hard spheres? Motivate your answer.

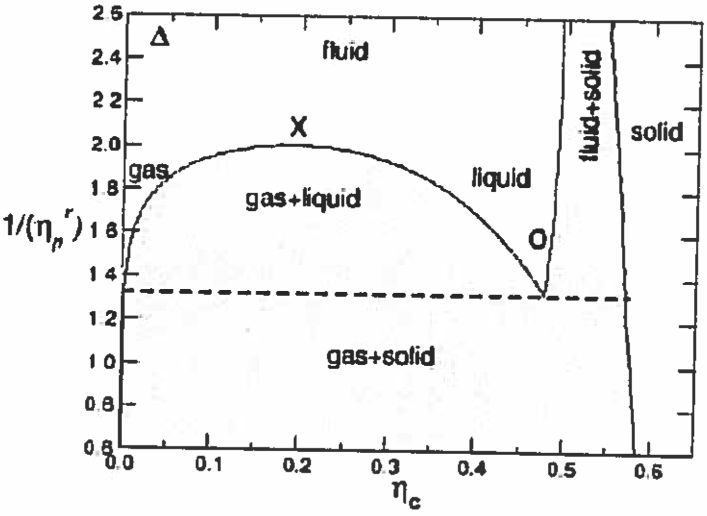


Figure 1: Phase diagram of a colloid-polymer mixture.

The addition of non-adsorbing polymer to a suspension of sterically stabilized colloids induces an effective attraction between the colloids. The strength of the attraction increases upon increasing the polymer reservoir packing fraction. Hence the polymer reservoir packing fraction η_p^r plays a similar role as the inverse temperature in simple liquids. Fig. 1 shows the phase diagram of a colloid-polymer mixture as a function of $1/\eta_p^r$ and the colloid packing fraction η_c. We distinguish one-phase regimes in which the system is a colloidal gas, a colloidal liquid, or a colloidal solid, as well as regimes where the system exhibits phase coexistence (the grey areas in Fig. 1).

c. Give, on the basis of Fig. 1, a reasonable estimate of the critical polymer reservoir packing fraction $\eta_{p,c}^r$ and the triple-point polymer reservoir packing fraction $\eta_{p,tr}^r$.

In the three state points, labeled in Fig. 1 by Δ, ×, and ○, scattering experiments have been performed to determine the structure factor $S(k)$,

where k is the scattering wavenumber. The results of these experiments are shown in Fig. 2 (a), (b), and (c).

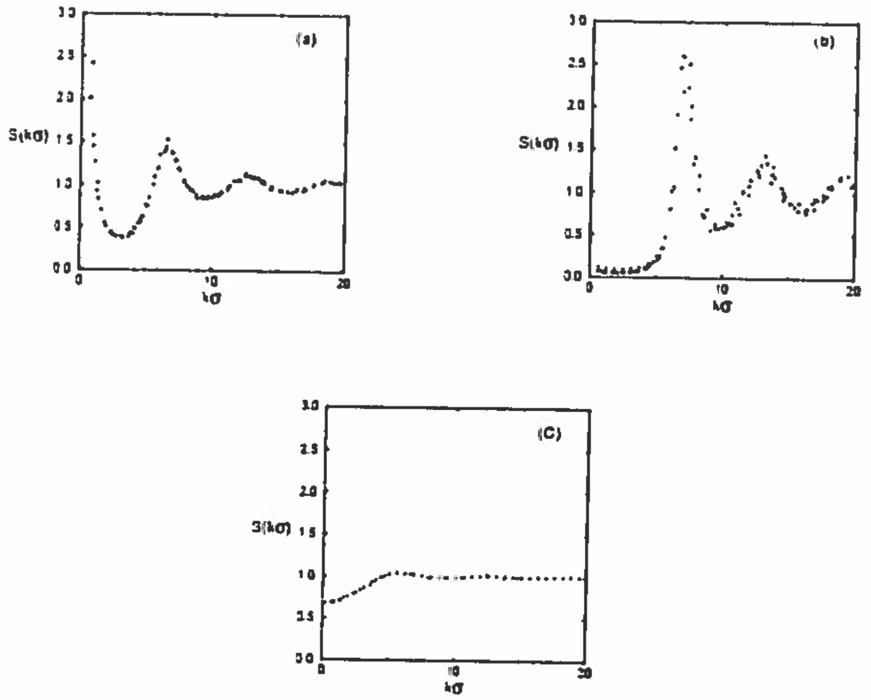


Figure 2: Structure factors of a colloid-polymer mixture.

d. Identify for each of the three state points Δ, $\times$, and $\circ$ the corresponding structure factor [(a), (b), or (c)]. Motivate your answer briefly.

We focus now on the colloidal gas and colloidal liquid phase of the system. Consider a system of N_c colloids in a volume V (with density $\rho_c = N_c/V$). The Helmholtz free energy is given by

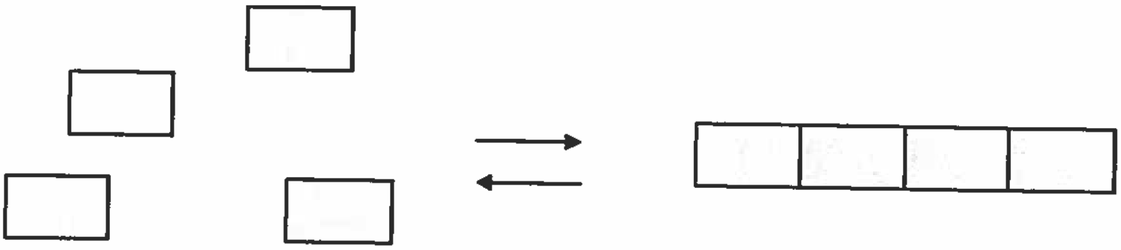
$$F(N_c, V, \eta_p^r, T) = N_c kT \log\left[\frac{N_c \Lambda^3}{V - N_c b}\right] - a(\eta_p^r)\frac{N_c^2}{V}, \tag{1}$$

with Λ the thermal wavelength, k Boltzmann's constant. Note that only the positive constant a depends on η_p^r, which describes the attraction between the colloids due to the presence of the non-adsorbing polymer. b is a positive constant that is related to the finite size of the colloids.

e. Determine the pressure $p(\rho_c)$ and the chemical potential $\mu(\rho_c)$ for fixed η_p^r (and temperature T).

f. Determine $(\partial p/\partial \rho_c)_{\eta_p^r,T}$ and $(\partial^2 p/\partial \rho^2)_{\eta_p^r,T}$, and the critical density ρ_c.

2. Consider a model of equilibrium, one-dimensional aggregation. Such a model is relevant in so-called 'living polymers', where linear aggregates may contain ANY number of monomers, n. An example of a special case n=4 in equilibrium with 4 monomers has been sketched below.



a. Argue, referring to the assumptions that underlie the derivation in the handout, that the size distribution of the one-dimensional aggregates ('the *n*-mers') is given by Eq. (2.10) (but with the correct sign!) in the handout, i.e.,

$$x_n = x_1^n \exp\left(\frac{-(\mu_n^0 - n\mu_1^0)}{kT}\right).$$

(so: no derivation is required, only a discussion whether the underlying assumptions in the handout apply to this 1-dimensional case!)

b. Argue that in this one-dimensional case, $\mu_n^0 - n\mu_1^0 \approx (n-1)\varepsilon$ with ε the interaction energy between the 'sticky sites' of two objects that are in close contact. Suppose this interaction energy is very short-range.

c. Prove that the concentration (mole fraction) of objects in the form of monomers is given by

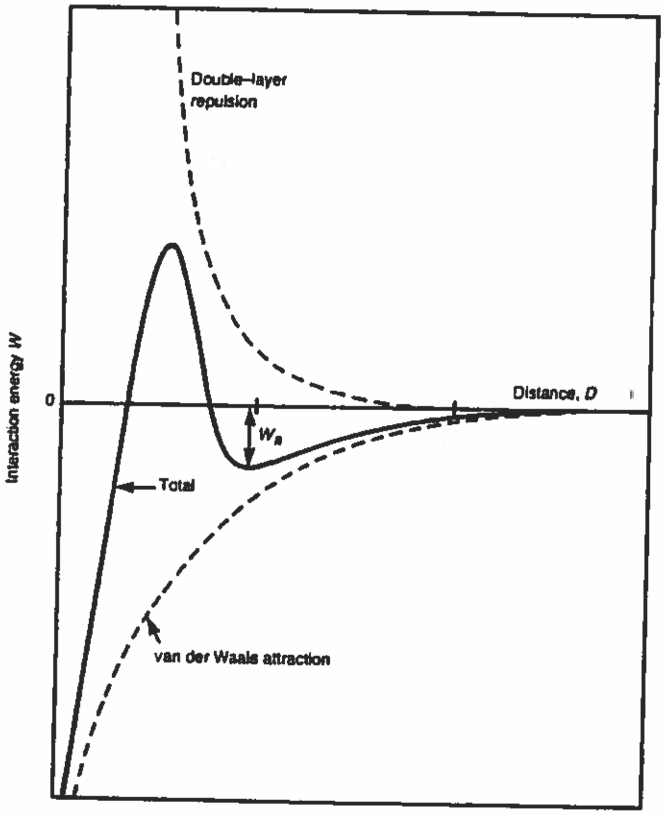
$$x_1 = \frac{1+2xe^{-\varepsilon/kT} - \sqrt{1+4xe^{-\varepsilon/kT}}}{2xe^{-2\varepsilon/kT}}$$

Here, x is the total (added) mole fraction of monomers, i.e., including those that are part of aggregates with $n>1$. Hint: make use of the geometrical series $\sum_{q=0}^{\infty} qy^q = \frac{y}{(1-y)^2}$ (for $y<1$).

d. Is the concentration of objects in the form of monomers, x_1, as a function of x consistent with the global behavior of micelles? In particular, is there a condition where $x_1 \approx x$? If so, identify that condition. Is there another condition or limit where x_1 is (at most) a slowly increasing function of x? Does the system have a cmc?

Hint: consider the Taylor series $\sqrt{1+y} = 1 + \frac{y}{2} - \frac{y^2}{8}$ ($y<<1$).

3. In the accompanying picture a schematic is given of the interaction potential between two gold particles (radius 400 nm) in water ($\varepsilon = 78$) with a background concentration of monovalent ions of 10^{-7} M. The surface charge on the colloids was measured to be 50 mV and is caused by citrate ions (negative ions from dissociated citric acid) adsorbed to the surface. Subsequently, in a titration a salt solution (NaCl) is added drop wise. When a concentration of salt of 3×10^{-6} M salt is reached the stable dispersion suddenly forms a colloidal crystal. Viewed through a microscope the colloidal particles on the colloidal crystal lattice sites still clearly perform Brownian motion around their equilibrium position on the lattice. In your answers make use of the fact that at room temperature in water for an ionic strength of 1.0×10^{-3} M (monovalent salt) gives a $1/\kappa = 9.6$ nm. The Hamaker constants of water $A_{w\text{-}w} = 4 \times 10^{-20}$ J, that of gold $A_{Au\text{-}Au} = 30 \times 10^{-20}$ J, that of silica $A_{S\text{-}S} = 7 \times 10^{-20}$ J.



a. Explain what happened.

Starting from the crystalline situation sketched above 1a), what will happen if:

b. if a very small amount of acetic acid is added. Explain your answer.

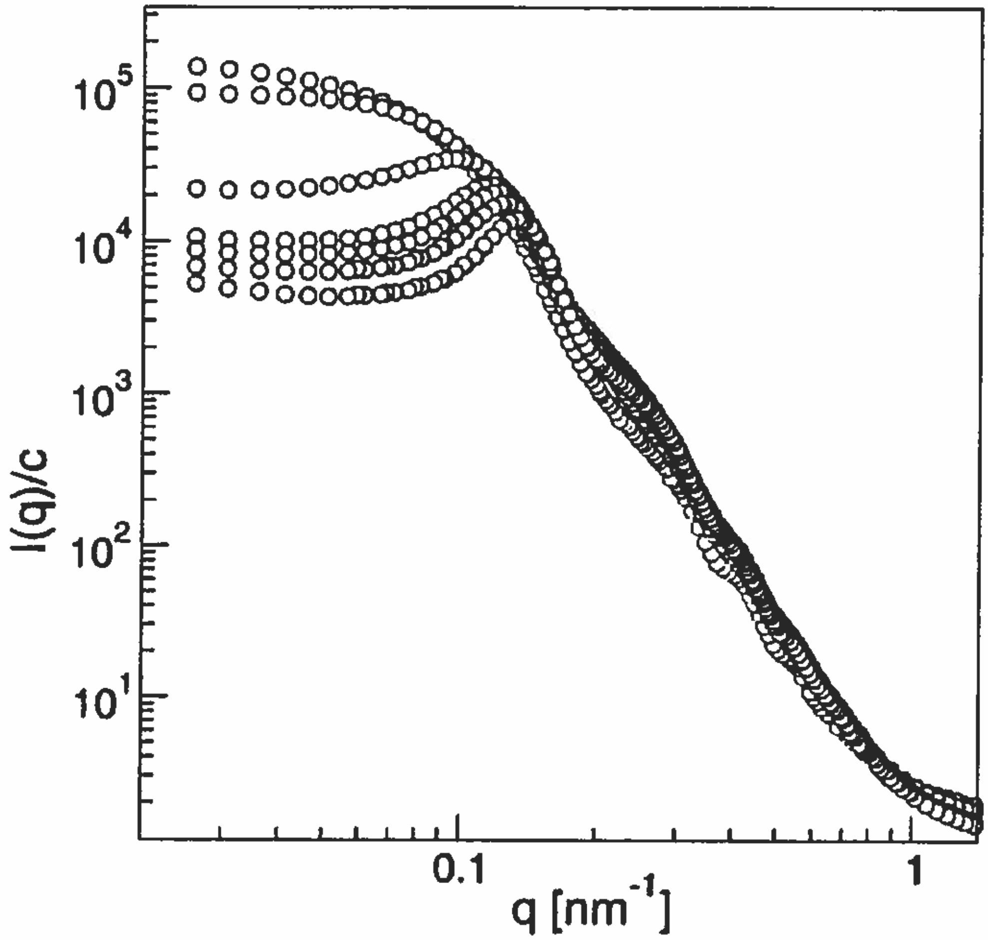
c. if 10^{-5} M of NaCl is added, explain.

d. if the particle material is changed to silica, while everything else stays the same (surface potential, salt concentration, etc.), explain.

e. if the solvent is changed to one with a dielectric constant of 8 (other conditions stay the same)? Explain.

f. For the conditions mentioned above question a (gold colloids), show by a numerical calculation that the secondary minimum is situated around $D = 50$ nm.

4. The figure below shows small angle neutron scattering data on suspensions of sterically stabilized polystyrene colloids dispersed in water [Zackrisson et al., Langmuir 21, 10835 (2005)]. The quantity plotted is the scattered intensity $I(q)$ at scattering vector q divided by the weight concentration c of colloids. The seven sets of data correspond to colloid concentrations of 0.40, 0.35, 0.33, 0.30, 0.21, 0.048, and 0.0042 g/mL.



a. Which set of data corresponds to which colloid concentration? Explain your answer.

b. Estimate the average distance between particles at the highest concentration.

c. From the low-q scattering data, prepare a plot of the inverse of the osmotic compressibility $\frac{1}{kT}\left(\frac{\partial \Pi}{\partial \rho}\right)$ versus the concentration c. Interpret the result.

d. Estimate the second virial coefficient B_2/V_0 of this colloidal system, given that the particle density is d=1.076 g/mL. Interpret the result.
Hint: The number density ρ and weight concentration c are simply related through $\rho = c/V_0 d$. V_0 is the volume of a particle.