Colloid Science Exam Part I (Philipse) April 21, 2021

1. The electrical double-layer (EDL) repulsive energy for two flat plates at distance *h* is, within the weak-overlap approximation, given by equation (5.60) from the Colloidal Dispersions lecture notes:

$$\frac{A_{\text{rep}}}{kT} = 64\rho_s \kappa^{-1} \tanh^2(\Phi_0/4)\ \exp[-\kappa h] \ ;\ \Phi_0 = \frac{ze\Psi_0}{kT} \ , \qquad (5.60)$$

   a) What is the (quantitative) criterion for the "weak-overlap approximation' to apply? [5]

   b) Show that the LHS and the RHS in (5.60) have the same unit.[5]

   c) An EDL-repulsion like (5.60) is sometimes also referred to as an *electrostatic* repulsion. Defend or criticize this terminology. [10]

   d) Write down the DLVO potential $A_{\text{tot}}(h)/kT$ as the sum of (5.60) and the Van der Waals attraction (in units of m^{-2}) between the two flat surfaces. [5]

   e) Let ρ_{floc} be the salt concentration needed to 'aggregate' the two surfaces (that is, by thermal motion they come in contact and irreversibly stick together). Show how ρ_{floc} for the DLVO potential from d) depends on ion valency z and surface potential Ψ_0. [20]

   f) Consider for your result in e) for ρ_{floc}, the two limiting cases of high surface potential $(\tanh(\Phi_0) \sim 1)$ and the Debye-Hückel case of low potential $(\tanh(\Phi_0) \sim \Phi_0)$. [15]

   g) In e) we employ the EDL-repulsion valid for the case of weak EDL- overlap, to a situation where the plates are getting into close proximity. Defend or criticize this approach. [10]

2. Consider a solution of charged colloids and a large salt reservoir solution (with constant salt concentration) separated by a semi-permeable membrane (Figure 2).

   a) What, precisely, is a Donnan equilibrium? [9]

   b) What are the assumptions one has to make to apply the Donnan equilibrium and calculate, for example, the osmotic pressure drop (the "Donnan pressure') across the membrane in Figure 2 ? [9]

   c) Discuss for each of these assumptions whether their validity increases, decreases or remains unaffected when:

   1. more colloids are added to the 'cell' in Figure 2
   2. the charge number density σ on the colloids increases.
   3. more salt is added to the reservoir solution
   4. the cell in Figure 2 is so small that only *one* colloid fits into it.
   5. the reservoir solution is much smaller than the cell
   6. the valency of ions is doubled [12]

   d) What is the maximal Donnan pressure across the membrane in Figure 2, for a colloid number density ρ_c with valency z? Explain in words why the Donnan pressure decreases upon increasing the salt concentration in the reservoir. [10]

3. Suppose silica colloids homogeneously nucleate and grow in an aqueous silicate solution (with supersaturation *S*) in the form of amorphous discs (Figure 3) with diameter *L* and thickness *d*. γ is the surface tension of the silica-water interface and v_{m} is the volume contribution per (silicate) molecule to the disc volume.

a) Give an expression for the formation Gibbs energy ΔG of a silica disc as function of L and d. Check the units (which should be identical left and right of the equality sign). [10]

b) Thickness *d* can only grow spontaneously *above* a certain critical disc diameter $L = L^*$. Why is that the case? [6]

c) Derive an expression for L^* and show that indeed $\partial \Delta G / \partial d < 0$ for $L > L^*$. [15]

d) Suppose that (due to some Ostwald ripening process) a silica disc with dimensions $L = 1\ \mu\mathrm{m}$ and $d = 10\ \mathrm{nm}$ transforms to a silica sphere with radius *R* (Figure 3). Will this transformation be a spontaneous or non-spontaneous process? Why? [6]

e) Calculate the Gibbs energy change (in Joule) for this transformation (take $\gamma \approx 0.05\ \mathrm{Nm}^{-1}$). Hint: assume that the silica volume does not change, and neglect the contribution of the disc edge area πdL to the surface Gibbs energy of the thin disc.[15]

f) Any prediction for the nucleation rate of silica colloids from classical nucleation theory is bound to be very inaccurate. Discuss the reason(s) why. [8]

4. The trajectory followed by a sedimenting colloid is a superposition of a linear convective motion (vertical blue vector in Figure 1) and random fluctuations due to Brownian motion. We consider only fluctuations in the x-direction; Δx_j is the amplitude of the fluctuation on time t_j.

a) The colloid starts to sediment in the z-direction at $t = 0$ s. Which information do you need to calculate the typical time it takes for the colloid to achieve a stationary speed v? [6]

b) How large is the average amplitude $< \Delta x >$? [6]

c) Compute for colloids with diffusion coefficient $D = 10^{-6}\ \mathrm{m^2 s^{-1}}$, the average $< (\Delta x)^2 >$ when the colloids have been sedimenting for one minute. [11]

d) It takes t_{D} seconds for a colloidal sphere to diffuse a distance comparable to its own radius *R* ; it takes t_{v} seconds for the colloid to sediment that same distance. For which radius is the case that $t_{\mathrm{D}} = t_{\mathrm{v}}$? (You are asked for a formula, not a number). [12]

e) When sedimentation-diffusion equilibrium has been reached, the number density profile (for ideal colloids) is $\rho(z) = \rho(z=0)\exp[-z/\ell_g]$, where $\ell_g = kT / m_{\mathrm{B}} g$ is the gravitational length. Show how via this barometric profile one can find Van' t Hoff's osmotic pressure law. [15]

f) Another derivation of Van' t Hoff's law for ideal colloids is given in Section 11.3 of the Lecture Notes Brownian Motion. Where in that derivation is the assumption made that the colloids are ideal, non-interaction particles ? [10]

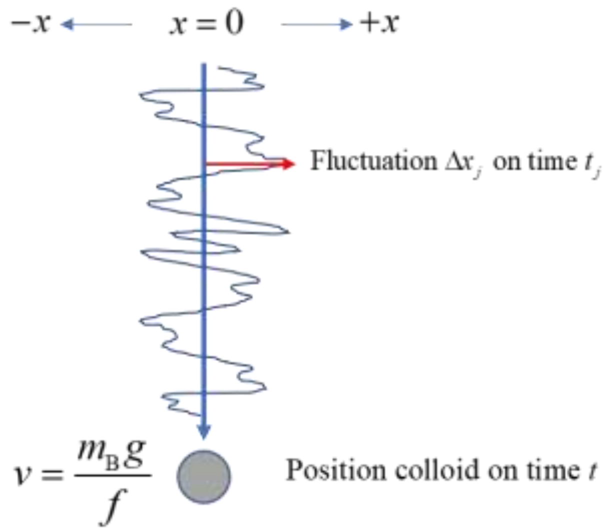

Figure 1 Trajectory of a sedimenting colloid comprises a linear part due to sedimentation and a random fluctuation due to Brownian motion. v is the stationary sedementation speed of a colloid with buoyant mass m_B and friction factor f.

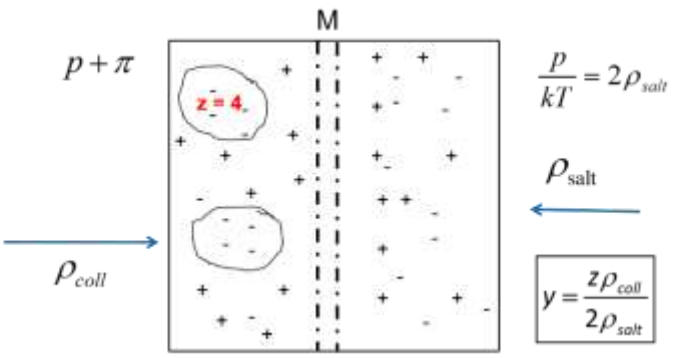

Figure 2 A suspension of charged colloids in an 'osmotic cell' (left) separated by a semi-permeable membrane M from a large reservoir salt solution (right); only solvent and ions can pass M.

Figure 3. A circular disc with diameter L and thickness d transforms to a sphere with radius R having the same volume as the disc.