

## Answers Homework 7 Properties of Materials

- 1) a) Obtain an expression for the sedimentation velocity using a force balance between viscous drag and gravity

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Equate  $mg$  gravitational force with  $\xi v$  drag force:

$$(\rho_s - \rho_1) \frac{4}{3} \pi R^3 g = 6\pi v R \eta$$

solve for velocity yields

$$v = \frac{2(\rho_s - \rho_1)g R^2}{9\eta}$$

- b) Use a similar force balance and the definition of mobility to obtain an expression relating mobility and the zeta potential.

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Define mobility as

$$u = \frac{v}{E}$$

for a charged particle of charge  $q$  the electrostatic force in a field  $E$  is  $F = qE$ . At steady state (acceleration = 0) this is just balanced by the drag force  $F = \xi v$ . Using Stokes Law for the friction factor an expression for the mobility by equating the forces and using the definition of the mobility is

$$u = \frac{q}{6\pi\eta R}$$

The zeta potential is the charge difference between the Debye screening layer and the particle layer, when the screening layer is small compared to the particle diameter then the zeta potential is defined as,

$$\zeta = \frac{q}{4\pi\epsilon R}$$

substituting in to the expression for mobility yields

$$u = \frac{\zeta\epsilon}{\eta}$$

- c) Explain what the streaming potential is and how the zeta potential can be obtained from electro-osmotic measurements.

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The streaming potential is the potential that builds up when a colloidal fluid with charged particles flows through a narrow capillary. It is given by

$$E = \frac{\epsilon \Delta p \zeta}{\eta k_0}$$

where  $\Delta p$  is the pressure drop across the capillary and  $k_0$  is the conductivity of the electrolyte. This equation is arrived at by a balance between the current associated with electrolyte conduction and flow of the charged particles.

d) How can colloidal particle size be obtained using static light scattering or neutron scattering?

$I = G \exp(-q^2 R_g^2/3)$  Guinier's Law

$I$  is the scattered intensity,  $G$  is a constant proportional to the weight average molecular weight of the colloid,  $R_g$  is the radius of gyration (a measure of the size of the particles for monodisperse spheres Diameter =  $2.6 R_g$ ) and  $q$  is the scattering vector which is a reduced angle equal to  $2\pi/d$  where  $d$  is the d-spacing from Bragg's law.

e) How can colloidal particle size be obtained using dynamic light scattering?

<http://www.eng.uc.edu/~gbeauca/Classes/Properties/HiemenzRajagopalanDLS.pdf>

Fluctuation of light scattered in a static scattering measurement can be analyzed to obtain the diffusion coefficient. The faster the fluctuations the larger the diffusion coefficient associated with the particles. The diffusion coefficient can be related to the hydrodynamic radius of the particles using the Stokes-Einstein relationship.

2) In class the relationship between the Boltzmann equation and the Debye screening equation was discussed.

a) The equation  $S = k \log W$  is carved on Boltzmann's grave in the Central Grave Yard of Vienna.  $W$  is the number of states that a system can have. How was the Boltzmann equation used in class and how does the form shown in Vienna relate to the form used in class?

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Eqns. 3.3 and 3.4 are a form of the Boltzmann equation. The issue is to relate concentration with probability or number of states.

$$c_+ = c_0 \exp\left(\frac{-ze\Phi}{k_B T}\right) \quad (3.3)$$

and

$$c_- = c_0 \exp\left(\frac{+ze\Phi}{k_B T}\right) \quad (3.4)$$

For a system with no enthalpic interactions the Gibbs free energy is  $\Delta G = -T\Delta S$ . This is a system governed by statistics only, there are no biasing interactions. From Boltzmann's grave we have  $\Delta G = -kT \ln W$  and for a charged particle of charge  $ze$  subjected to a field  $\Phi$ , the Free energy is  $\Delta G = \pm ze\Phi$  depending on the sign of the ion charge. For a random system of particles or ions the probability of finding a particle is the same as the volume concentration,  $c$ , for a system with multiple states the probability of finding one state is  $1/W$ .  $\ln W = -\ln(1/W)$ .  $1/W$ ,  $c$  and probability all reflect the probability of finding one state among many in a random system, i.e. they are interchangeable and which is used depends on the particular system you are considering. So we have  $\pm ze\Phi = -kT \ln(c_{\pm})$ . Taking the exponential of this expression yields eqns. 3.3 and 3.4.

b) The Gaussian function (bell shaped curve or normal distribution) is another exponential distribution function. Give the Gaussian function and explain why it is a symmetric function. Is the Debye screening equation a symmetric function?

The Gaussian function is a function of the form  $P(x) = K \exp(-(x-\mu)^2/2\sigma^2)$  where  $K$  is a normalization constant (determined by setting the integral of  $P(x)$  between  $\pm$  infinity to 1) and  $\mu$

is the mean value (often taken to be 0 by definition).  $P(x)$  is the probability of finding a value  $x$ . In a grade distribution following the bell shaped curve  $x$  would be a grade and  $\mu$  would be the average grade. The function is symmetric about  $\mu$  because positive and negative deviations from  $\mu$  have equal probability, that is, it is symmetric about the mean giving rise to a bell shape. The Debye screening function,  $\exp(-\kappa x)$  is not symmetric since positive and negative values of  $x$  are not equivalent, it only works for positive  $x$ .

- c) The Gaussian function (normal distribution function) is used to describe the probability of finding a metal atom about a crystal lattice position due to thermal motion of the atom where the standard deviation is a function of temperature. (This is called Debye thermal broadening of an XRD peak). Explain why you think that this symmetric function is needed to describe thermal motion in a crystal while it is not appropriate to describe charge distribution due to thermal motion at an interface.

The atom must be symmetrically contained within a crystal lattice site since the forces in any direction are equivalent. For a particle surface the forces are not balanced in this way. On one side of the interface there is a DVLO type potential and on the other is the particle where the Debye equation does not apply at all.

- d) Explain how the Debye screening length relates to the exponential decay function.

The Debye screening length is the inverse of the parameter  $\kappa$  in the exponential decay function.

- e) Describe the relationship between the Debye screening length and the ability to hold a conversation in a crowded room.

For two charged particles or ions a force exists associated with an electrostatic interaction. If similar charged ions or particles are introduced they serve to screen the interaction. This is similar to two people holding a conversation in a large room. They can hear each other when the room contains only the two people even when they are at opposite ends of the room. When the room becomes crowded such as at a party, they need to be closer to hear. The more crowded the room the closer the two must be so the screening length becomes smaller with increasing concentration of the charged species. At some point the interactions between charged particles can be described by a “mean-field” or background noise and no real communication is occurring.

- 3). a) Give an expression for the DLVO theory describing the potential between two spherical particles.

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$$V = \frac{64\pi R k_B T c_0 \Gamma_0^2}{\kappa^2} \exp(-\kappa b) - \frac{A_H R}{12b} \quad (3.21)$$

the first term reflects the Debye exponential decay and the second term the Hamaker interaction term for spheres.

- b) Could a colloidal system be made stable by adjusting the Hamaker constant in DLVO theory? Explain using the equation in part a.

Yes, by decreasing  $A_H$  the potential becomes more repulsive and the system becomes more stable.

- c) Could a colloidal system be made stable by adjusting the electrolyte concentration? Explain using the equation in part a.

Yes,  $c_0$  in the first term is the electrolyte concentration, also  $\kappa$  depends on electrolyte concentration as does  $\Gamma_0$ .

d) Define the critical coagulation concentration.

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forces is reduced. Coagulation can occur at an electrolyte concentration such that the repulsive double-layer interaction is reduced sufficiently to enable attractive interactions to predominate. This occurs at a critical coagulation concentration (c.c.c.). Using the potential defined in Eq. (3.21), it is straightforward to show (see Q. 3.9) that at the c.c.c. ( $V = 0$  and  $F = 0$ ) the interparticle separation is

$$b = \frac{1}{\kappa} \quad (3.23)$$

The critical coagulation concentration can then be estimated by substituting  $\kappa b = 1$  into Eq. (3.21) and determining  $\kappa$  (Q. 3.9). This can be equated to the Debye length  $\kappa$  defined in Eq. (3.8) to determine the c.c.c. The approximate concentration (moles/unit volume) is

$$\text{c.c.c.} = \frac{9.85 \times 10^4 \varepsilon^3 (k_B T)^5 \Gamma_0^4}{N_A e^6 A_H^2 z^6} \quad (3.24)$$

or, for an aqueous dispersion at 25°C,

$$\text{c.c.c.} = \frac{3.84 \times 10^{-39} \Gamma_0^4}{(A_H/J)^2 z^6} \text{ mol dm}^{-3} \quad (3.25)$$

The striking feature of this result is the strong dependence on the valence of the electrolyte (i.e. sixth-power dependence) at high potentials where  $\Gamma_0$  tends to unity. This strong dependence on electrolyte charge is in agreement with the Schulze-Hardy rule. In contrast, the c.c.c. is essentially independent of the specific nature of the ions.

e) Explain the following terms: bridging flocculation, steric stabilization, depletion flocculation, depletion stabilization.

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Bridging flocculation: polymer adsorbs to multiple particles and cause the particles to flocculate

Steric Stabilization: Polymer adsorbs or is grafted to one particle and the polymer chains interfere with the DVLO interactions at short range preventing coagulation.

Depletion Flocculation is an osmotic effect caused by the absence of polymer chains between particles leading to an osmotic vacuum that makes particles flocculate.

Depletion stabilization is the stabilization of a colloidal suspension by osmotic pressure created by free polymer chains between colloidal particles.