

Physical Chemistry of Colloids and Surfaces – Final Exam Review 4-30-02

**Material covered on the final exam: Evans 5.1-5.2, 7.1.1-7.1.4, 7.4, 8.1-8.4
+ notes from 3-19-02 to end of course**

The Derjaguin Approximation

-For interacting, curved particles whose curvature is much larger than their separation distance, the interaction *force* between curved surfaces can be obtained by summing the interaction *energy* between flat surfaces. This is the *Derjaguin approximation*.

$$F_{ss}(h) = 2p \left(\frac{R_1 R_2}{R_1 + R_2} \right) U_{ww}(h) \quad (\text{sphere-sphere})$$

$$F_{sw}(h) = 2pR U_{ww}(h) \quad (\text{sphere-wall})$$

$$F_{xc}(h) = 2p\sqrt{R_1 R_2} U_{ww}(h) \quad (\text{crossed cylinders})$$

Recalling that:

$$F(h) = -\frac{dU(h)}{dh}; \quad U(h) = \int_h^{\infty} F(h') dh'$$

we can obtain interaction energies and forces for many different geometries given the force or energy of interaction between flats.

The Hamaker Constant

-If we assume that intermolecular interactions are pairwise additive, we can obtain interaction energies between particles (U) by integration.

$$U_{sw}(h) = -p^2 C r_1 r_2 \frac{R}{6h} \quad (\text{sphere/wall})$$

-The prefactor is lumped together as a single constant, the *Hamaker constant* (H_{12}).

$$U_{sw}(h) = -\frac{H_{12} R}{6h} \quad (\text{sphere/wall})$$

-While pairwise additivity is not valid for van der Waals interactions, this lumped-parameter approach describes experimental data well.

-For other geometries:

$$U_{ww}(h) = -\frac{H_{12}}{12ph^2} \quad (\text{wall/wall, per unit area})$$

$$U_{ss}(h) = -\frac{H_{12}}{6h} \left(\frac{R_1 R_2}{R_1 + R_2} \right) \quad (\text{sphere/sphere})$$

-Effective Hamaker constants can be estimated using *combining relations*. They are only strictly valid for London interactions, and should be considered approximate for real systems.

$$H_{12} \cong \sqrt{H_{11} H_{22}} \quad (\text{dissimilar materials "1,2"})$$

$$H_{131} \cong H_{313} \cong H_{11} + H_{33} - 2H_{13} \quad (\text{similar materials "1" across a medium "3"})$$

$$H_{132} = (\sqrt{H_{11}} - \sqrt{H_{33}})(\sqrt{H_{22}} - \sqrt{H_{33}}) \quad (\text{dissimilar materials "1,2" across a medium "3"})$$

- H_{132} is negative when the Hamaker constant of the intermediate material is between that of the other two.

-When interacting over long ranges, van der Waals interactions are weakened by *retardation effects* due to equivalent time scales for electron density fluctuations and the time for EM radiation to travel between particles.

DLVO theory and colloidal stability

-The idea that VDW and EDL forces can be summed to describe colloidal stability has been called *DLVO theory*.

-DLVO theory has been used to verify the Schulze-Hardy rule, which has the critical coagulation concentration (CCC) proportional to $1/z^6$. This was accomplished by approximating the CCC using equilibrium data. Here, we assume that the DLVO curve with barrier height = 0 represents the CCC condition:

$$CCC \cong \frac{10^5 (\mathbf{e}_r \mathbf{e}_o)^3 (kT)^5 G_o^4}{z^6 e^6 H^2} \quad (\text{high surface charge density, symmetric electrolyte})$$

$$CCC \cong \frac{400 (\mathbf{e}_r \mathbf{e}_o)^3 kT F_o^4}{z^2 e^2 H^2} \quad (\text{low surface charge density, symmetric electrolyte})$$

-For asymmetric electrolytes, the coagulation behavior is determined by the charge-reversing ion, so as a good approximation its valency can be used in the above equations.

Stability ratio (W)

-Colloidal stability is really a kinetic process, so we define the *stability ratio* (W):

$$W = \frac{\text{rate of rapid flocculation}}{\text{rate of slow flocculation}}; 1 < W < \infty$$

-*Rapid flocculation* is diffusion-limited, and *slow flocculation* has a kinetic barrier.

-Hydrodynamic forces effectively limit W to no smaller than 2. In practice, attractive forces do not cause W to approach zero as predicted here due to hydrodynamic forces.

Rapid Flocculation

-The *Smoluchowski analysis* predicts the rapid flocculation rate for monodisperse particles:

$$\frac{d[P]}{dt} = -k_r[P]^2; k_r = 8pDR = \frac{4kT}{3m}$$

-Or, in terms of the reaction half-life t ,

$$\frac{[P]}{[P]_o} = \frac{1}{1 + t/t}; t = \frac{1}{k_r[P]_o}$$

-For growing particles, follow the previous law by analogy, one particle size at a time:

$$\sum_j [P_j] = \frac{[P]_o^{tot}}{1 + t/t}$$

whose series solution is:

$$[P_k] = [P]_o^{tot} \left(\frac{t}{t}\right)^{k-1} \left(1 - \frac{t}{t}\right)^{-k-1}$$

-Stirring increases the flux of larger particles, increasing the flocculation rate, and nonspherical particles flocculate more rapidly than spherical ones as they take up more space by rotation.

Slow Flocculation

-Slow flocculation can be considered “hindered” diffusion, or diffusion in a repulsive force field.

-The rate of flocculation depends on the interparticle potential $U(h)$, where h is the interparticle separation distance:

$$\frac{d[P]}{dt} = \frac{-4pD[P]^2}{\int_{2R}^{\infty} \frac{1}{h^2} \exp\left(\frac{U(h)}{kT}\right) dh}$$

-The stability ratio (W) can be expressed in terms of $U(h)$, demonstrating the connection between surface forces and colloidal properties:

$$W = 2R \int_0^{\infty} \frac{1}{h^2} \exp\left(\frac{U(h)}{kT}\right) dh$$

-Plots of W vs. [salt] show a fairly abrupt kink, which is a better measure of the CCC than the DLVO prediction is.

-The *fractal dimension* (D_f) of a floc can be used to identify their mechanisms of formation:

$$\text{Mass} \propto r^{D_f}; D_f \cong 1.7 \quad (\text{rapid flocculation})$$

Electrokinetic phenomena

-*Electrophoresis* is the motion of a charged particle in electrolyte in response to an applied electric field. It is very useful for the deposition of molecules (paints, displays), biomolecule separation, and colloidal characterization, especially the prediction of surface charge.

-Migration of charged particles in an electric field occurs due to relative motion of the particle and its counterion cloud. In an electrophoresis experiment, the mobility (u) is the measured quantity:

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

where E is the electric field and v is the particle velocity. The *zeta potential* (ζ) is the potential at the slip plane (typically very near the surface), where the flow of particle and

counterions separate. It can be obtained from mobility data using the following expressions, where \mathbf{m} is the electrolyte viscosity.

$$u = \frac{2e_r e_0 z}{3\mathbf{m}} \quad (\text{Hückel limit, low } kR)$$

Physically speaking, the Hückel limit assumes the electric field directly forces the charged particle.

$$u = \frac{e_r e_0 z}{\mathbf{m}} \quad (\text{Smoluchowski limit, high } kR)$$

Physically speaking, the Smoluchowski limit assumes the particles are forced indirectly by the electric field. The field pulls EDL ions, which drag solvent along with them. The resulting shear stress is transferred to the particle.

In reality, both physical effects are important, but these are approximate limits for extreme kR . For intermediate kR , the zeta potential can be obtained by through the prefactor (C) graphically using O'Brien-White theory.

-*Electroosmosis* is the flow of electrolyte induced by an electric field in a capillary. The counterions near the charged wall are pushed by the electric field, carrying solution with them. The volumetric flow rate (Q) under electro-osmotic conditions can be calculated in terms of the electroosmotic potential (f_{eo}) or the current (I).

$$Q = \frac{e_r e_0 z p R^2 f_{eo}}{\mathbf{m}} \quad Q = \frac{e_r e_0 I z}{\mathbf{m}(k_b + 2k_s / R)}$$

Electroosmotic flow always contributes to electrophoresis experiments, and needs to be considered to obtain accurate information. Electroosmotic flow approximates plug flow in most cases.

-A *streaming potential* is created by the pressure-induced flow of electrolyte past a charged wall. Counterions in the EDL are displaced from one vessel to another, creating an electrical current. Back-flow of charge through the solution and capillary balances this current to yield a steady-state streaming potential (f_{str}):

$$f_{str} = \frac{e_0 e_r z D p}{\mathbf{m}(k_b + 2k_s / R)}$$

Non-DLVO forces – Hydration forces

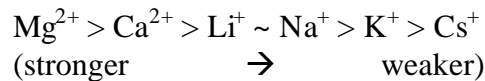
-*Hydration forces* are short-range repulsive forces felt by polar surfaces interacting in aqueous systems. They arise from the extra energy required to squeeze out adsorbed water molecules.

-*Primary hydration forces* arise from water adsorbed directly on the surface. *Secondary hydration forces* arise from hydrated ions adsorbed from solution.

$$F_{ww}(h) = C_o \exp\left(-\frac{h}{I}\right)$$

where I is a characteristic decay constant, about the size of a water molecule (~0.2 nm).

-The strength of secondary hydration force follows a *lyotropic series*:



-Higher ionic strength leads to stronger hydration forces as more ions adsorb by mass action.

Non-DLVO Forces - Polymer-induced Forces

-A *polymer* is a long molecule composed of short subunits linked together in a stepwise fashion.

-In solution, polymers assemble into a spherical blob called a *random coil*, minimizing its free energy. In poor solvents, the enthalpy of monomer-monomer contacts dominates the free energy while in good solvents, the configurational entropy dominates. When both effects exactly cancel, the polymer chain is described by random walk statistics (“theta solvent”).

-The size of a polymer is described by its *radius of gyration* (R_g). For a theta solvent:

$$R_g = \sqrt{\frac{N_p l_m l_p}{6}} \propto M_w^{0.5}$$

N_p is the degree of polymerization, l_m is the monomer length, and l_p is the persistence length, or the contour length required to achieve a 90 degree bend in the chain. The theta condition is observed in real systems when excluded-volume and monomer-monomer attraction effects cancel each other.

-Polymer/solvent interactions are described by the *Flory-Huggins* parameter (χ). For $\chi < 0.5$, we have a good solvent, for $\chi > 0.5$ we have a poor solvent, and for $\chi = 0.5$ we have a *theta solvent*.

$$R_g \propto M_w^{0.6} \text{ (good solvent)}$$

$$R_g \propto M_w^{0.333} \text{ (poor solvent)}$$

-In general, most polymers adsorb to surfaces since only a few monomers need to stick to hold the entire chain in place. This leads to a *loop-train-tail* configuration for homopolymer adsorption.

-Polymers can also be attached to surfaces by chemical grafting or through the use of a *block copolymer* with one adsorbing block.

-A *polymer mushroom* is a sparsely populated (low grafting density) adsorbed monolayer for which the layer thickness less than $2R_g$.

-A *polymer brush* is an adsorbed monolayer of polymer for which the layer thickness (L) is significantly greater than $2R_g$ (high grafting density). The repulsive interaction between polymer brushes can be described by the *Alexander-de Gennes model*:

$$F_{ww}(h) \cong \frac{kT}{s^3} \left[\left(\frac{2L}{h} \right)^{9/4} - \left(\frac{h}{2L} \right)^{3/4} \right]; \quad h < 2L$$

where s is the mean distance between attachment points.

-*Steric stabilization* prevents the flocculation of a colloid by attaching polymers to the particle surface. This is a very useful method, since it provides strong stabilization even at high salt conditions. Often times, the flocculation can be reversible using steric stabilization. While steric stabilization can have an enthalpic or entropic origin, the repulsive force typically arises from the restriction of polymer configurational entropy on the approach of two polymer layers. This is favored with high grafting densities and good solvents.

-*Bridging attraction* occurs when there are sites available for adsorption on multiple particles, and chains attach to two particles at once. The attraction is strongest at intermediate grafting density. This is favored with low grafting densities and poor solvents.

-*Depletion attraction* is flocculation brought about by non-adsorbing polymers based on differences in osmotic pressure in the tiny gaps between particles.

-*Polyelectrolytes* are charged polymers. They are potent steric stabilizers since their adsorbed layers repel each other by entropic and EDL interactions. They are potent electrostatic flocculants since they raise the ionic strength of the solution by adding polymer and counterions. The persistence length of polyelectrolytes is inversely related to the salt concentration due to Debye screening.

The Electric Double Layer (Review)

-Colloidal particles become charged due to dissociation of surface functional groups, adsorption of ions to the surface, and isomorphous substitution.

-In water, ions will collect near a charged surface to maximize their free energy. The surface and its associated ions is called an *electric double layer*, and has properties similar to a capacitor, with an electric *potential* whose absolute value decays with distance from the surface.

-The chemical potential of an ion in this potential (\mathbf{m}) is given by:

$$\mathbf{m}_i = z_i e \mathbf{f}(x) + kT \ln c_i^*(x) \quad (1\text{-dim.})$$

-The *Boltzmann distribution* describes the concentration of ions (c_i^*) in the potential:

$$c_i^*(x) = c_{i\infty}^* \exp\left(\frac{-z_i e \mathbf{f}(x)}{kT}\right) \quad (1\text{-dim.})$$

-The *Poisson equation* relates the variation of \mathbf{f} with the local charge density:

$$\frac{d^2 \mathbf{f}}{dx^2} = \frac{-z_i e c_i^*(x)}{\epsilon_r \epsilon_o} \quad (1\text{-dim.})$$

-The *Poisson-Boltzmann equation* is a differential equation that combines field effects with osmotic effects:

$$\frac{d^2 \mathbf{f}}{dx^2} = -\frac{z_i e c_{i\infty}^*}{\epsilon_r \epsilon_o} \exp\left(\frac{-z_i e \mathbf{f}}{kT}\right)$$

-Integration with suitable boundary conditions yields the Gouy-Chapman equation:

$$\mathbf{f}(x) = \frac{2kT}{ze} \ln \left\{ \frac{1 + G_o \exp(-kx)}{1 - G_o \exp(-kx)} \right\} \quad (\text{symmetric electrolytes only})$$

where:

$$G_o = \frac{\exp\left(\frac{ze\mathbf{f}_o}{2kT}\right) - 1}{\exp\left(\frac{ze\mathbf{f}_o}{2kT}\right) + 1} = \tanh\left(\frac{ze\mathbf{f}_o}{4kT}\right) \quad \frac{1}{k} = \sqrt{\frac{\epsilon_r \epsilon_o kT}{\sum_i (z_i e)^2 c_{i\infty}^*}}$$

-The quantity $1/k$ is called the *Debye screening length*, and is a characteristic measure of the size of the double layer. The Debye length will decrease with added salt.

-The surface potential (ψ_0) is related to the surface charge density by the *Graham equation*:

$$\sigma = \sqrt{8kTc_{\infty}^* \epsilon_r \epsilon_0} \left(\exp\left(\frac{ze\psi_0}{2kT}\right) - \exp\left(-\frac{ze\psi_0}{2kT}\right) \right) = \sqrt{8kTc_{\infty}^* \epsilon_r \epsilon_0} \sinh\left(\frac{ze\psi_0}{2kT}\right)$$

(symmetric electrolyte only)

-For small surface potential, can use the *linearized GC equation*:

$$\psi(x) = \frac{4kT}{ze} \tanh\left(\frac{ze\psi_0}{4kT}\right) \exp(-kx)$$

EDL Forces

-Charged surfaces in electrolyte repel each other due to a loss of counterion entropy as the two EDL's overlap – *osmotic pressure* (P_{os}) of counterions is the key property.

$$P_{os} \cong c^* kT$$

-By performing a force balance and applying a mathematical approximation to the linearized GC equation, we obtain an expression for the EDL repulsion between flat walls per unit area in the *weak overlap limit*:

$$F_{ww}(h) = 64kTc_{\infty}^* \left(\tanh\left(\frac{ze\psi_0}{4kT}\right) \right)^2 \exp(-kh) \quad (\text{weak overlap limit})$$

-This treatment ignores the finite sizes of ions, ion adsorption, double-layer polarization, and other effects.