

Materials 218/UCSB: Addendum to Class III: Forces between colloidal particles

You will not be tested on this addendum

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The source for the material in these notes is: J. Prost and F. Rondelez, *Structures in colloidal physical chemistry, Nature Supplement* **350** (18th April 1991) 11-23. Also see Israelachvili.

- Colloids are systems with a characteristic length scale between 10 nm and 1,000 nm.
- For experiments on colloidal interactions, a nice system to work with are cross-linked polymer spheres of uniform size. Usually, these particles are modified so that they have ionizable surface groups.
- The Deryaguin-Landau-Verwey-Overbeek ¹ (DLVO) theory describes suspended colloidal particles in solution based on the principal interactions which are:

The van der Waals attraction: Usually written $-H/r^6$ where r is the distance between two particles and H is the so-called Hamaker constant. H is related to the polarizability of the material.

The Coulomb repulsion: Since the particles have like charges, they repel. However, ions in the solvent medium *screen* the repulsion so it does not take the usual $1/r$ form, but instead, takes the form $\exp(-r/\lambda)/r$, where λ is the Debye screening length, and comes from the Debye-Hückel theory for electrolytes. The complete DLVO potential looks something like:

$$U(r) = \frac{z^2 e^2}{\epsilon} \left[\frac{\exp(\lambda a)}{1 + \lambda a} \right]^2 \frac{\exp(-r/\lambda)}{r} - \frac{H}{r^6}$$

Where z is the number of charges, a is the radius of the sphere within which the charge resides (approximated to the radius of the particle) and ϵ is the dielectric constant of the solvent.

- By tuning λ through changing the concentration of salt in the solution, the interaction potential can be tuned.
- The system of polymer spheres in water is characterized by three parameters, d , a and λ :
 - $d/\lambda \gg 1$; $d/a \approx 1$ The system behaves like a collection of hard spheres of radius equal to the screening length λ . When the system crystallizes, the structures formed are typical of hard spheres (*eg.* hcp, fcc).
 - $d/a \gg 1$; $d/\lambda \ll 1$ The system behaves like a one-component plasma in a uniform background of neutralizing charges. The system crystallizes as a bcc array.
- The DLVO theory explains why rivers (fresh water) silt up at the mouths (water is salty). Colloidal clay particles attract, but in fresh water, the repulsive Coulombic forces dominate. When the amount of salt in the water increases, the Debye screening length λ becomes very small, and the particles no longer repel as strongly. The van der Waals attraction dominates and the particles coagulate, and then precipitate.

¹The spellings vary: Boris Vladimirovich Derjaguin (1902-1994); Lev Davidovich Landau (1908-1968); Evert Johannes Willem Verweij (1905-1981); J. Th. G. Overbeek (???)