LECTURE 11: COLLOIDS AND INTERPARTICLE POTENTIALS

Outline :

Objectives: To derive mathematically the sphere-surface potential and to understand other long-range interparticle forces and how they determine colloidal stability

Readings: "Colloidal Processing of Ceramics", J. A. Lewis, *J. Am. Ceram. Soc.* **83** (10) 2341-59. 2000.

Multimedia : Podcast : Briscoe, et al. Nature 2006 444, 191 - 194. It can wait until Spring Break if you want→won't be covered on exam, but will be on next pset which will be due a week or so after Spring break.

MIDTERM: Everything up through today's lecture will be covered on exam.

MOLECULE-PLANAR SURFACE INTERACTIONS

-**Motivation** : Molecular Origins of Biocompatibility

-Calculation of the Net Potential for Interacting Bodies; Volume Integration Method; procedures and assumptions

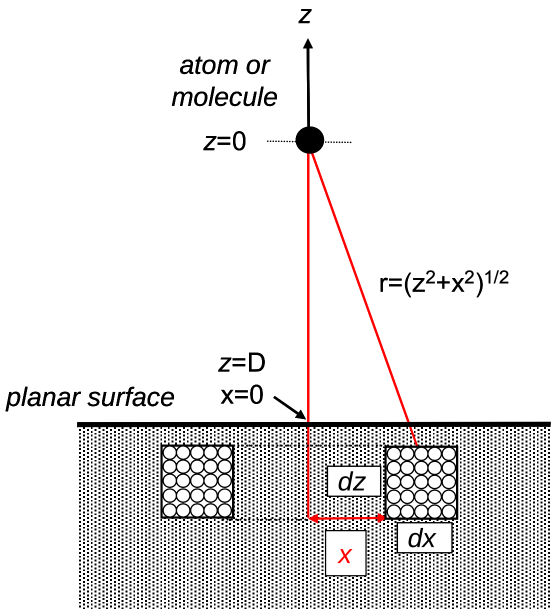
1) **Choose the mathematical form** of the interatomic/ionic/molecular potential, $w(r)$ (e.g. assume an arbitrary power law : $w(r) = -Ar^{-n}$)

2) **Set up the geometry** of the particular interaction being derived (e.g. molecule-surface, particle-surface, particle-particle, etc.)

3) **Assume "pairwise additivity"**; i.e. the net interacion energy of a body is the sum of the individual interatomic/intermolecular interactions of the constituent atoms or molecules which make up that body

4) A solid **continuum** exists : the summation is replaced by an integration over the volumes of the interacting bodies assuming a number density of atoms/molecules/m^3, ρ

5) **Constant material properties** : ρ and A are constant over the volume of the body→volume integration : $W(D) = \iiint w(r) \bullet \rho \, dV$



Geometry :

z = direction perpendicular to the sample surface

D (nm) = normal molecule-surface separation distance

x (nm) = direction parallel to sample surface = circular ring radius (m)

A = infinitesimal cross-sectional area (m^2) = dx dz

V = ring volume (m^3)= 2πx (dxdz)

N = # of atoms within the ring = ρ (2πx) dx dz

ρ = number density of atoms in the material constituting the surface (atoms/m^3)

r = distance from molecule to differential area

$$W(D)_{MOL\text{-}SFC} = \frac{-2\pi A\rho}{(n-2)(n-3)D^{n-3}}$$

n = *determined by the type of interaction; related to the range of the interaction*

A = *molecular level parameter; related to strength of the interaction*

ρ = *atomic density*

$$W(D)_{MOL\text{-}SFC} = \frac{-2\pi A\rho}{(n-2)(n-3)D^{n-3}}$$

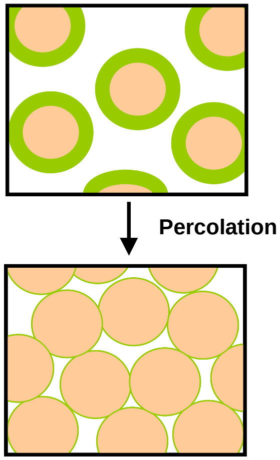
$$\text{London Dispersion Interactions } n = 6 \; ; W(D)_{MOL\text{-}SFC} = \frac{-\pi A\rho}{6D^3}$$

$$F(D)_{MOL\text{-}SFC} = \frac{\partial W(D)}{\partial D} = \frac{-\pi A\rho}{2D^4}$$

COLLOIDS : DEFINITION AND APPLICATIONS

Colloid; Definition : Particles that possess at least one dimension 10 nm -1 μm, usually dispersed in a fluid medium, called a "**colloidal suspension**" (e.g. smoke, paint, cosmetics, fog, dust, milk, blood, pharmaceutical powders)→ contact area between particles and the dispersing medium is large→interparticle surface forces determine macroscopic behavior

"**Colloidal Inks**"- highly concentrated, stable, dispersed colloidal suspension with appropriate viscoelastic properties so that it can flow through a nozzle attached to a robotic set-up used to print 3D structures. After the ink exits from the nozzle, it will "set" via a fluid-to-gel transition induced by a variety of stimuli such as drying, pH, ionic strength, or solvent quality.



This involves the concept of "**percolation**"- critical volume fraction above which the system is capable of sustaining a stress, continuous pathway through entire material→ **processes final and mechanical properties tailored by interparticle surface forces**

Photos removed due to copyright restrictions.
See Figure 7 in Smay, et al. Langmuir 2002, 18, 5429.

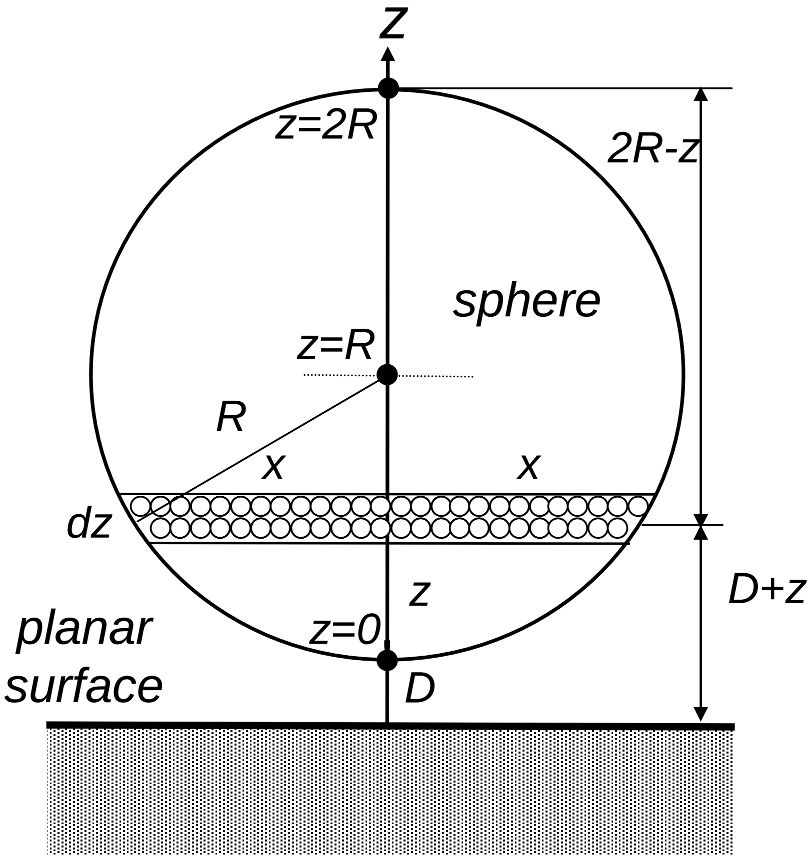
SEM images of 3D Periodic structures composed of colloidal "building blocks."

New applications :

- -Tissue Engineering
- -Advanced Ceramics
- -High performance Composites

(*Smay, et al. Langmuir 2002, 18, 5429)*

DERIVATION OF SPHERE-PLANAR SURFACE POTENTIAL



$$Chord\ Theorum = x^2 = (2R - z)z$$

$$Area = \pi x^2, Volume = \pi x^2 dz$$

$$N = number\ of\ atoms = \rho\pi x^2 dz = \rho\pi(2R - z)zdz$$

Photo of sphere on AFM tip removed due to copyright restrictions.

$$W(D)_{SPHERE\text{-}SFC} = \int_{z=0}^{z=2R} \underbrace{W(D)_{MOL\text{-}SFC}(D+z)}_{\text{Potential of each atom/molecule with all atoms / molecules of planar surface}} \underbrace{\rho\pi(2R-z)zdz}_{\text{number of atoms in sphere}}$$

$$W(D)_{MOL\text{-}SFC} = \frac{-2\pi A\rho}{(n-2)(n-3)D^{n-3}}$$

$$W(D)_{SPHERE\text{-}SFC} = \frac{-2\pi^2 A\rho^2}{(n-2)(n-3)} \int_{z=0}^{z=2R} \frac{(2R-z)zdz}{(D+z)^{n-3}}$$

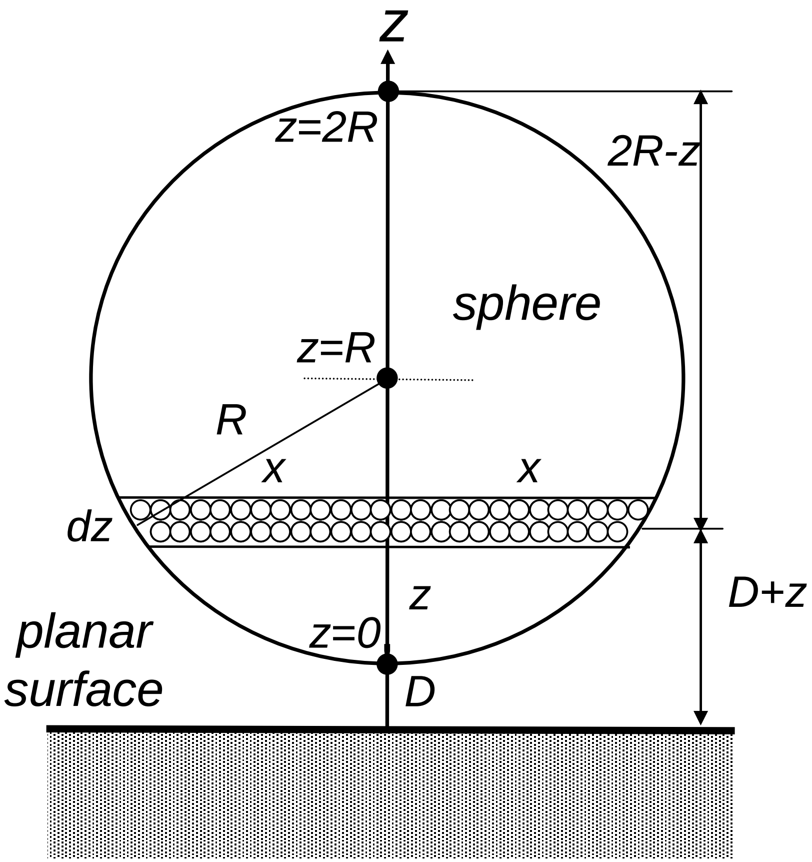
$$For\ D << R, only\ small\ values\ of\ z\ contribute\ to\ the\ integral$$

$$W(D)_{SPHERE\text{-}SFC} = \frac{-2\pi^2 A\rho^2}{(n-2)(n-3)} \int_{z=0}^{z=\infty} \frac{2Rzdz}{(D+z)^{n-3}}$$

$$W(D)_{SPHERE\text{-}SFC} = \frac{-4\pi^2 A\rho^2 R}{(n-2)(n-3)(n-4)(n-5)D^{n-5}}$$

$$n = 6\ (VDW) = \frac{-\pi^2 A\rho^2 R}{6D}$$

SPHERE-PLANAR SURFACE VDW INTERACTION AND HAMAKER CONSTANT



$$W(D)_{SPHERE\text{-}SFC}(VDW, n=6) = \frac{-\pi^2 A\rho^2 R}{6D}$$

$$w(r) \sim r^{-6}, W(D)_{MOL-SFC} \sim D^{-3}, W(D)_{SPHERE-SFC} \sim D^{-1}$$

"Hamaker Constant" :

$\mathbf{A} = \pi^2 A\rho^2$ *(sphere and surface are the same material)*

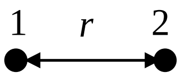
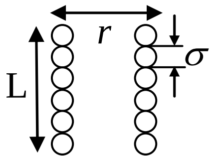
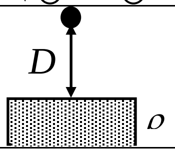
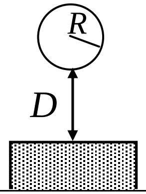
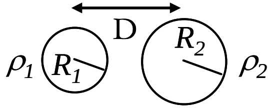
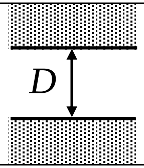
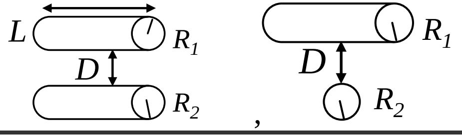
$\mathbf{A} = \pi^2 A\rho_1\rho_2$ *(sphere and surface are different materials)*

$\mathbf{A} \sim 10^{-19}\,\mathrm{J}$

$$W(D)_{SPHERE\text{-}SFC}(VDW, n=6) = \frac{-\mathbf{A}R}{6D}$$

$$F(D)_{SPHERE\text{-}SFC}(VDW, n=6) = -\frac{\partial W(D)}{\partial D} = \frac{-\mathbf{A}R}{6D^2}$$

ANALYTICAL FORMULAS FOR VDW INTERACTIONS FOR OTHER GEOMETRIES

Type of Interaction	Schematic	Interaction Potential
atom-atom molecule-molecule		$w(r) = -Ar^{-6}$
two parallel chain molecules		$w(r) = -\left(\frac{3\pi AL}{8\sigma^2}\right) r^{-5}$
atom-planar surface molecule-planar surface		$W(D) = -\frac{\pi \mathbf{A}\rho}{6D^3}$
sphere-planar surface		$W(D) = -\frac{AR}{6D}$ → **A** can be a fitting parameter for example in a Force vs. Distance AFM experiment
sphere-sphere		$W(D) = -\frac{\mathbf{A}}{6D}\frac{R_1R_2}{(R_1+R_2)}$
planar surface-planar surface		$W(D) = -\frac{\mathbf{A}}{12\pi D^2}$ per unit area
two parallel cylinders two crossed cylinders		$W(D) = -\frac{\mathbf{A}L}{12\sqrt{2}D^{3/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}, W(D) = -\frac{\mathbf{A}\sqrt{R_1R_2}}{6D}$

COLLOIDAL STABILITY : OTHER LONG RANGE FORCES

$$W(D)=W(D)_{VDW}+W(D)_{ELECTROSTATIC}+W(D)_{STERIC}+W(D)_{STRUCTURAL}-W(D)_{DEPLETION}$$

"**Electrostatic Double Layer Repulsion**" : for charged particles, this force arises from a diffuse, highly mobile surface layer of counterions; an exponential repulsion exists on compression since which is entropic in origin (actuallly not electrostatic) since the counterions want to retain their translational mobility

$$W(D)=W(D)_{VDW}+W(D)_{ELECTROSTATIC}$$

"DLVO Theory"-Derjaguin, Landau, Verwey and Overbeek

"**Steric Repulsion**": For macromolecules attached to a colloid, they maintain some equilibrium conformation, any deviation away from this equilibrium conformation, for example upon compression, results in a nonlinear repulsion. For stabilization, the macromolecular layers must be of sufficient thickness and density to overcome VDW forces (δ=layer thickness)

"***Electrosteric***" interactions→polyelectrolytes (electrostatics and sterics both contribute and in fact, are coupled to each other)- **USED IN BIOLOGY**

"**Structural Repulsion**"→ repulsion arising from other nonadsorbed species in the media, e.g. small nanoparticles

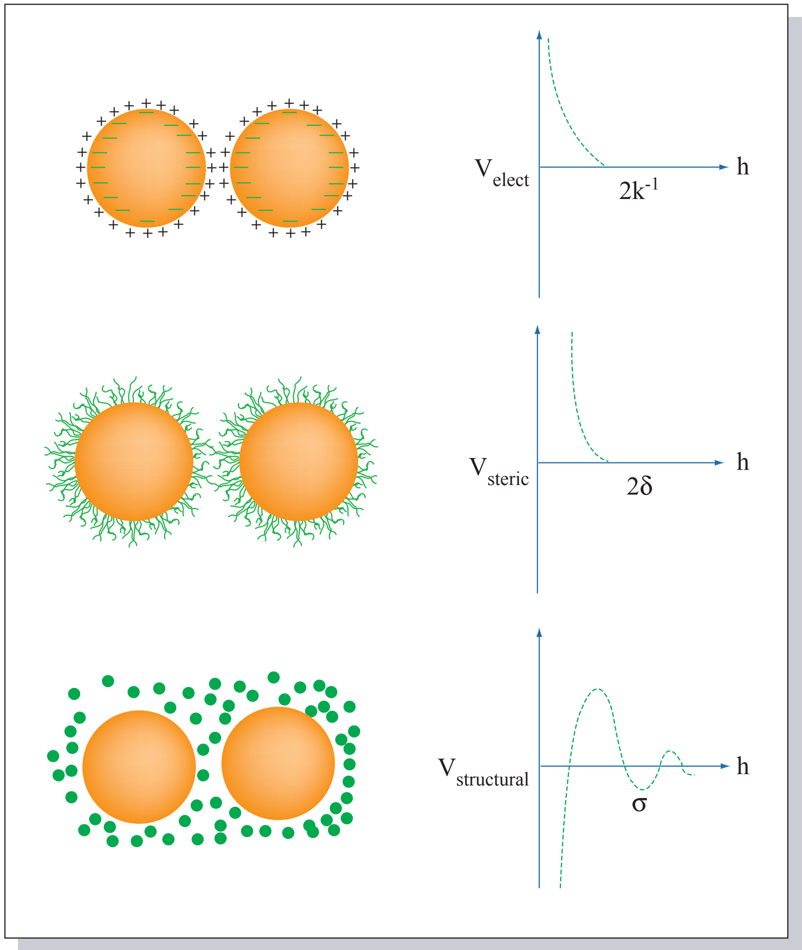
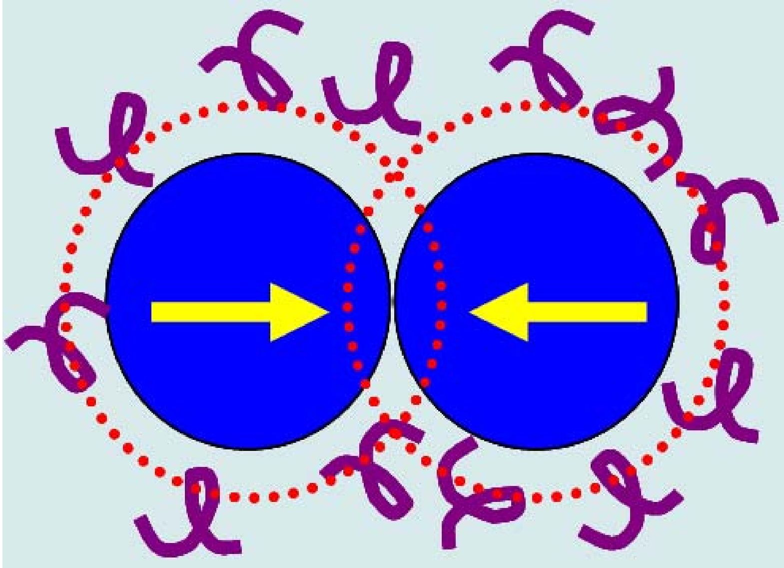


Figure by MIT OCW.
After Lewis. *J Am Ceram Soc* 83, no. 10 (2000): 2341-59.

COLLOIDAL STABILITY: EFFECT ON DISPERSION

"**Depletion Interaction**" : For entropic reasons the chains avoid the space between two close particles, or between a particle and a planar wall, and create an effective **attraction** among the colloid particles.



Dispersed state : repulsive energy barrier >>k_BT
Weakly Flocculated : well depth ~ 2-20 k_BT
Strongly Flocculated : deep primary minimum

-e.g. Dispersion of nanotubes

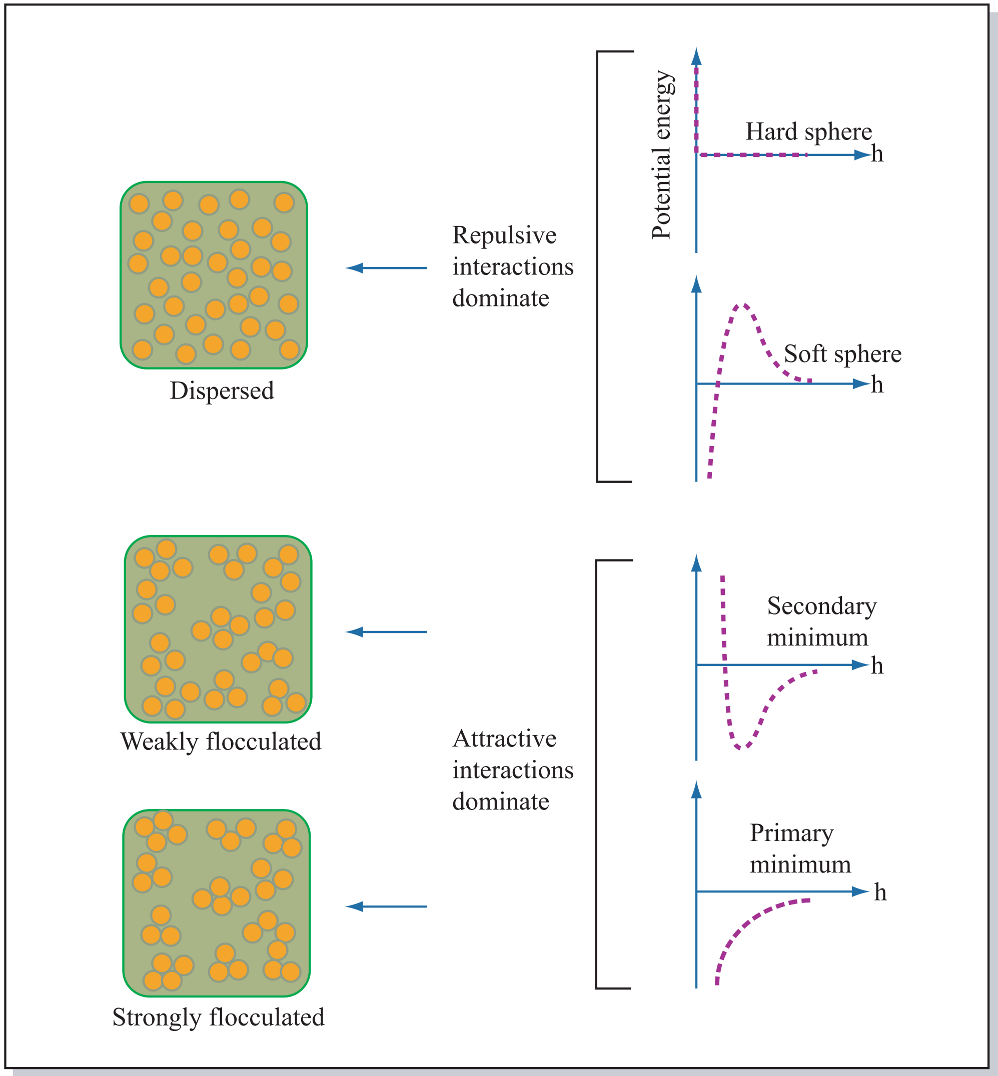


Figure by MIT OCW.
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