LECTURE 11: COLLOIDS AND INTERPARTICLE POTENTIALS

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


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 interaction 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, \( \rho \)

5) Constant material properties: \( \rho \) 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) = \( 2\pi x \, (dx \, dz) \)
- \( N \) = # of atoms within the ring = \( \rho \, (2\pi x) \, dx \, dz \)
- \( \rho \) = number density of atoms in the material constituting the surface (atoms/m^3)
- \( r \) = distance from molecule to differential area

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

\( n \) = determined by the type of interaction; related to the range of the interaction
\( A \) = molecular level parameter; related to strength of the interaction
\( \rho \) = atomic density

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

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

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

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

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

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

$$W(D)_{SPHERE:SFC} = \int_{z=0}^{z=2R} \frac{W(D)_{MOL:SFC}(D + z)}{\rho \pi} \pi \rho (2R - z)dz$$

Potential of each atom/molecule with all atoms/molecules of planar surface

$\rho$ = number of atoms in sphere surface

$$W(D)_{MOL:SFC} = \frac{-2\pi \alpha}{n-2(n-3)D^{n-3}}$$

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

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

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

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

$n = 6 (VDW) = \frac{-\pi^2 A \rho^2 R}{6D}$
SPHERE-PLANAR SURFACE VDW INTERACTION AND HAMAKER CONSTANT

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

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

"Hamaker Constant":

\[ A = \pi^2 A \rho^2 \text{ (sphere and surface are the same material)} \]

\[ A = \pi^2 A \rho_1 \rho_2 \text{ (sphere and surface are different materials)} \]

\[ A \sim 10^{-19} \text{ J} \]

\[ W(D)_{\text{SPHERE-SFC}}(VDW, n = 6) = -\frac{AR}{6D} \]

\[ F(D)_{\text{SPHERE-SFC}}(VDW, n = 6) = -\frac{\partial W(D)}{\partial D} = -\frac{AR}{6D^2} \]
### ANALYTICAL FORMULAS FOR VDW INTERACTIONS FOR OTHER GEOMETRIES

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Schematic</th>
<th>Interaction Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>atom-atom molecule-molecule</td>
<td><img src="atom-atom-molecule.png" alt="Schematic" /></td>
<td>( w(r) = -Ar^{-6} )</td>
</tr>
<tr>
<td>two parallel chain molecules</td>
<td><img src="two-parallel-chain.png" alt="Schematic" /></td>
<td>( w(r) = \left( \frac{3\pi AL}{8\sigma^2} \right) r^{-5} )</td>
</tr>
<tr>
<td>atom-planar surface molecule-planar surface</td>
<td><img src="atom-planar-molecule.png" alt="Schematic" /></td>
<td>( W(D) = -\frac{\pi A \rho}{6D^3} )</td>
</tr>
<tr>
<td>molecule-planar surface</td>
<td><img src="molecule-planar.png" alt="Schematic" /></td>
<td>( W(D) = -\frac{A R}{6D} ) → ( A ) can be a fitting parameter for example in a Force vs. Distance AFM experiment</td>
</tr>
<tr>
<td>sphere-planar surface</td>
<td><img src="sphere-planar.png" alt="Schematic" /></td>
<td>( W(D) = -\frac{AR}{6D} )</td>
</tr>
<tr>
<td>sphere-sphere</td>
<td><img src="sphere-sphere.png" alt="Schematic" /></td>
<td>( W(D) = -\frac{A R_1 R_2}{6D (R_1 + R_2)} )</td>
</tr>
<tr>
<td>planar surface-planar surface</td>
<td><img src="planar-surface.png" alt="Schematic" /></td>
<td>( W(D) = -\frac{A}{12\pi D^2} ) per unit area</td>
</tr>
<tr>
<td>two parallel cylinders</td>
<td><img src="two-parallel-cylinders.png" alt="Schematic" /></td>
<td>( W(D) = -\frac{AL}{12\sqrt{2D^{3/2}}} \left( \frac{R_1 R_2}{R_1 + R_2} \right)^{3/2}, W(D) = -\frac{A\sqrt{R_1 R_2}}{6D} )</td>
</tr>
<tr>
<td>two crossed cylinders</td>
<td><img src="two-crossed-cylinders.png" alt="Schematic" /></td>
<td></td>
</tr>
</tbody>
</table>

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"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 (actually 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 (\( \delta \)=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.
"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 $>> k_B T$

**Weakly Flocculated** : well depth $\sim 2-20 \ k_B T$

**Strongly Flocculated** : deep primary minimum

-e.g. Dispersion of nanotubes

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**Figure by MIT OCW.**