Colloidal gels
Multiscale approaches to their structure and rheology

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Lab Navier — École des Ponts
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Overview and schedule

Course goal: Highlight the key physical phenomena driving colloidal gelation and gel properties and discuss experimental methods to study their structure and rheology, with an emphasis on methods that enable an understanding of the connections between different length scales.

### LECTURE 1
1. Colloidal suspensions
   - Characteristics of the colloidal domain
2. Colloidal interactions
   - van der Waals interactions
   - Electrostatic interactions
     - polar liquids
     - non-polar liquids
   - Grafted and adsorbed polymers and surfactants
   - Model interactions

Reading:
- Israelachvili, chapter X

### LECTURE 2
3. Colloid motion
   - Mobility and resistance
   - Hydrodynamic interactions
   - Brownian motion
4. Equilibrium
   - Equilibrium phases of repulsive colloids
   - Equilibrium phases of attractive colloids
   - Non-equilibrium states – glasses and gels

Reading:
- Furst and Squires, chapters 2, 3

### LECTURE 3
5. Strongly flocculated suspensions
   - Colloidal interactions of strongly flocculated suspensions
   - Kinetics of flocculation
   - Quiescent structure of flocculated suspensions – fractal gels
6. Gel rheology
   - Elastic modulus
   - Yielding

### LECTURE 4
7. Weakly flocculated suspensions
   - Colloidal interactions of weakly flocculated suspensions
   - Structure of weakly flocculated suspensions and gels
8. Sedimentation, settling, and redispersion
   - Delayed collapse
   - Poroplastic compaction

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Overview

LECTURE 5

9. Methods for characterizing micro-scale structure and dynamics
   a. Scattering
   b. Microscopy
   c. Dynamics of fractal gels
   d. Dynamics of dense suspensions

10. Micromanipulation and particle interaction measurements
    a. Surface and colloidal force measurements
    b. Laser tweezers
    c. Mechanics of colloidal bond rupture
    d. Bond mechanics of strongly flocculated suspensions

LECTURE 6

11. Multiscale models of gel rheology
    a. Strong gels and the fractal model
    b. Failure of fractal models and motivation for new multiscale models
    c. Cluster gels

12. Gel structure under shear
    a. Compaction
    b. Startup of steady shear
    c. Thixotropy
Colloid science
What is a colloid?

The IUPAC definition of a colloid is a ‘`state of subdivision such that... particles dispersed in a medium have at least one dimension between approximately 1 nm and 1 μm…’”

A colloid is large enough to be much larger than the atoms or molecules around it (or inside it), but small enough that it exhibits some properties of the molecular scale (e.g. Brownian motion).

12 nearest neighbors in an fcc crystal (0.74)

$$\frac{4}{3} \pi (2a)^3 - \frac{4}{3} \pi a^3 = \frac{28}{3} \pi a^3$$

How many H$_2$O molecules if $2a = 1 \, \mu m$?

$$\bar{V} = 3 \times 10^{-29} \, m^3$$

$$V/\bar{V} = 1.2 \times 10^{11} \, \text{molecules}$$

$$\bar{V}^{-1/3} \sim 3.1 \, \text{Å}$$
What is a colloid?

The IUPAC definition of a colloid is a `state of subdivision such that... particles dispersed in a medium have at least one dimension between approximately 1 nm and 1 μm…`

A colloid is large enough to be much larger than the atoms or molecules around it (or inside it), but small enough that it exhibits some properties of the molecular scale (e.g. Brownian motion).

Therefore:

- Continuum mechanics (inside and outside)
- Continuum electrodynamic properties (dielectric constant, index of refraction, etc.)
Brownian motion

Optically trapped colloids 10μm

Scale-Human hair
Time scales

<table>
<thead>
<tr>
<th></th>
<th>( 2a = 100 \text{ nm} )</th>
<th>1 ( \mu \text{m} )</th>
<th>10 ( \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vorticity</td>
<td>( \tau_\eta = \frac{a^2}{\nu} = \frac{a^2 \eta_s}{\rho_s} )</td>
<td>2.5 ns</td>
<td>250 ns</td>
</tr>
<tr>
<td>Inertial</td>
<td>( \tau_I = \frac{2\rho_p}{9\rho_s} \tau_\eta )</td>
<td>0.6 ns</td>
<td>60 ns</td>
</tr>
<tr>
<td>Brownian</td>
<td>( \tau_B = \frac{\pi \eta a^3}{kT} )</td>
<td>0.1 ms</td>
<td>100 ms</td>
</tr>
</tbody>
</table>

\[ \nu \approx 10^6 \text{ m}^2/\text{s} \]

\[ kT = 4.1 \times 10^{-21} \text{ J} \]
Force and energy scales

\[ kT = 4.1 \times 10^{-21} \text{ J} \]

(4 zeptajoules)

\[ 2a = \begin{array}{c} 1 \text{ nm} \\ 1 \mu\text{m} \end{array} \]

Brownian force \[ F_B = \frac{kT}{a} \]

10^{-12} \text{ N} \quad 10^{-15} \text{ N}

Brownian stress \[ \sigma_B = \frac{kT}{a^3} \]

10^3 \text{ Pa} \quad 10^{-6} \text{ Pa}
A colloid?
Examples of colloids

- **Monodisperse latex**
- **“FEP”**
- **Latex dumbbells**
- **Titania needles**
- **Zeolite**
- **Stöber silica**
- **Solid wax**
- **Carbon black**

**Acicular, prolate**
- Precipitated CaCO₃
- SiC whiskers
- Fumed silica
- Fe₂O₃(OH) (Goethite)
- Al₂O₃ (Gibbsite)
- Precipitated CaCO₃

**Plate-like, oblate**
- Kaolin
- Oblate SiO₂
- Lead sulfide

**Irregular, faceted**
- Precipitated CaCO₃

**Rough / smooth**
- Monodisperse / polydisperse
- Isotropic / anisotropic
- Uniform / patchy
- Prolate / oblate
What is a colloidal gel?

- An elastic solid with a yield stress composed of...
- Percolated microstructure
- and (incompressible) solvent
Colloidal gels


Swan and Varga, MIT
Fundamental and economic significance

- Colloidal suspensions with attractive interparticle interactions include colloid-polymer mixtures, colloids with screened electrostatic interactions, protein solutions at low temperatures.

- Exhibit a wide range of equilibrium and non-equilibrium behavior

- This affects the stability and shelf-life of consumer products, foods, agrochemicals, pharmaceuticals, coatings, paints, etc.

- Generalizable / predictable behavior to aid development and engineering?

Examples of equilibrium and non-equilibrium behavior

<table>
<thead>
<tr>
<th>Phase separation</th>
<th>Thickening / gelation</th>
<th>Consolidation / sedimentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable, homogeneous dispersion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Colloidal interactions and stability
Colloidal interactions

van der Waals interactions

Related to the polarizability of molecules

\[ u_{\text{ind}} = ql = \alpha E \]

\[ E_r = -2\alpha E/4\pi\varepsilon_0 r^3 = -2\alpha(ze)/(4\pi\varepsilon_0)^2 r^5 \]

\[ F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0)^2 r^5 \]

\[ w(r) = -\int_0^\infty Fdr = -\alpha(ze)^2/2(4\pi\varepsilon_0)^2 r^4 \]

Keesom interaction
angle-averaged dipole-dipole

\[ w(r) = \frac{-u_1^2 u_2^2}{3(4\pi\varepsilon\varepsilon_0)^2 kT} \left( \frac{1}{r^6} \right) \]

Debye interaction
rotating dipole-induced dipole

\[ w(r) = \frac{-u_1^2 \alpha_0}{(4\pi\varepsilon\varepsilon_0)^2} \left( \frac{1}{r^6} \right) \]

London interaction
induced dipole-induced dipole

\[ w(r) = \frac{-3\alpha_0^2 \hbar \nu}{4(4\pi\varepsilon\varepsilon_0)^2} \left( \frac{1}{r^6} \right) \]
London dispersion interaction

\[ w(r) = \frac{-3\alpha_0^2 h\nu}{4(4\pi \varepsilon_0)^2} \left( \frac{1}{r^6} \right) \]

- "Long-range" interaction 0.2-10 nm
- Usually attractive, special cases repulsive
- Brings together molecules and weakly aligns
- Not pairwise additive

Bohr atom

\[ -q \quad +q \]

\[ O(10^{-16}) \text{s} \]

\[ E = \frac{1}{4\pi \varepsilon_0 r^3} (3\vec{\alpha} \cdot \vec{u} - I) \cdot \vec{u} \]

\[ \nu \sim 3.3 \times 10^{15} \text{s}^{-1} \]

\[ I = h\nu \]

First ionization potential of Bohr atom based on its "orbital frequency"

How strong? Consider two atoms with

\[ \frac{\alpha_0}{4\pi \varepsilon_0} = 1.5 \times 10^{-30} \text{m}^3 \]

\[ I = h\nu = 2 \times 10^{-18} \text{J} \]

\[ r \sim \sigma \approx 0.3 \text{nm} \]

\[ w(\sigma) = -4.6 \times 10^{-21} \text{J} \]

\[ \approx 1 \text{kT} \]
van der Waals interactions

FIGURE 11.2 Methods of summing (integrating) the interaction energies between molecules in condensed phases to obtain the interaction energies between macroscopic bodies. (a) Molecule near a flat surface or “wall.” (b) Spherical particle near a wall \((R \gg D)\). (c) Two planar surfaces \((L \gg D)\).
### van der Waals attraction

#### Geometry of bodies with surfaces $D$ apart ($D \times r$)

| Two atoms or small molecules |  
|---|---|
| Energy, $W$ | $-C/r^6$ |
| Force, $F$ = $-dW/dD$ | $-6C/r^7$ |

| Two flat surfaces (per unit area) |  
|---|---|
| $W_{flat} = -A/12\pi D^2$ | $A/6\pi D^3$ |

| Two spheres or macromolecules of radii $R_1$ and $R_2$ |  
|---|---|
| $W_{flat} = -A/6\pi (R_1 + R_2)$ | $-A/6\pi D^3$ |

| Sphere or macromolecule of radius $R$ near a flat surface |  
|---|---|
| $W_{flat} = -AR/6D$ | $-AR/6D^2$ |

| Two parallel cylinders or rods of radii $R_1$ and $R_2$ (per unit length) |  
|---|---|
| $W_{flat} = -A/12\sqrt{2D^3} (R_1 + R_2)$ | $-A/12\sqrt{2D^3} (R_1 + R_2)$ |

| Cylinder of radius $R$ near a flat surface (per unit length) |  
|---|---|
| $W_{flat} = -A/12\sqrt{2D^3} R$ | $-A/12\sqrt{2D^3} R$ |

| Two cylinders or filaments of radii $R_1$ and $R_2$ crossed at $90^\circ$ |  
|---|---|
| $W_{flat} = -A/12\sqrt{2D^3} R$ | $-A/12\sqrt{2D^3} R$ |

### Interaction between spheres (more rigorous)

$$A_H = \frac{\pi^2 C \rho_1 \rho_2}{d}$$

$$w(r) = -\frac{C}{r^6}$$

$$A_H = (0.4-4) \times 10^{-19} \text{ J}$$

### Reference

FIGURE 13.1 Van der Waals interaction energy $W$ and force $F$ between macroscopic bodies of different geometries in terms of their Hamaker Constant, $A$. Negative $F$ implies attraction ($A$ positive); positive $F$ means repulsion ($A$ negative). The Hamaker constant $A$ is defined as $A = \frac{\pi^2 C \rho_1 \rho_2}{d}$, where $\rho_1$ and $\rho_2$ are the number of atoms per unit volume in the two bodies and $C$ is the coefficient in the atom-atom pair potential (top row). More rigorous methods for calculating Hamaker constants are described in Sections 13.4 and 13.5. For other geometries, see Peresegian (2006).
### Table 13.2 Nonretarded Hamaker Constants for Two Identical Media Interacting in a Vacuum (Inert Air) at Room Temperature

<table>
<thead>
<tr>
<th>Medium</th>
<th>Dielectric Constant $\varepsilon$</th>
<th>Refractive Index $n$</th>
<th>Absorption Frequency $\nu_\text{a}$ ($10^{15}$ s$^{-1}$)</th>
<th>Hamaker Constant $A$ ($10^{-20}$ J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid He</td>
<td>1.057</td>
<td>1.028</td>
<td>5.9</td>
<td>0.057</td>
</tr>
<tr>
<td>Water</td>
<td>80</td>
<td>1.333</td>
<td>3.0</td>
<td>3.7</td>
</tr>
<tr>
<td>$n$-Pentane ($C_5H_{12}$)</td>
<td>1.84</td>
<td>1.349</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>$n$-Octane</td>
<td>1.95</td>
<td>1.387</td>
<td>3.0</td>
<td>4.5</td>
</tr>
<tr>
<td>$n$-Dodecane</td>
<td>2.01</td>
<td>1.411</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>$n$-Hexadecane</td>
<td>2.05</td>
<td>1.423</td>
<td>2.9</td>
<td>5.1</td>
</tr>
<tr>
<td>Hydrocarbon (crystal)</td>
<td>2.25</td>
<td>1.50</td>
<td>3.0</td>
<td>7.1</td>
</tr>
<tr>
<td>Diamond</td>
<td>5.66</td>
<td>2.375</td>
<td>2.6</td>
<td>28.9</td>
</tr>
<tr>
<td>Cyclohexane ($C_6H_{12}$)</td>
<td>2.03</td>
<td>1.426</td>
<td>2.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Benzene ($C_6H_6$)</td>
<td>2.28</td>
<td>1.501</td>
<td>2.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Carbon tetrachloride ($CCl_4$)</td>
<td>2.24</td>
<td>1.460</td>
<td>2.7</td>
<td>5.5</td>
</tr>
<tr>
<td>Acetone ($CH_3CO$)</td>
<td>21</td>
<td>1.359</td>
<td>2.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Ethanol ($C_2H_5OH$)</td>
<td>26</td>
<td>1.361</td>
<td>3.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2.55</td>
<td>1.557</td>
<td>2.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Polivinyl chloride</td>
<td>3.2</td>
<td>1.527</td>
<td>2.9</td>
<td>7.5</td>
</tr>
<tr>
<td>PTFE (Teflon)</td>
<td>2.1</td>
<td>1.359</td>
<td>2.9</td>
<td>3.8</td>
</tr>
<tr>
<td>Silica ($SiO_2$)</td>
<td>3.8</td>
<td>1.448</td>
<td>3.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Mica</td>
<td>5.4–7.0</td>
<td>1.60</td>
<td>3.0</td>
<td>10</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>7.4</td>
<td>1.427</td>
<td>3.8</td>
<td>7.0</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>11.6</td>
<td>3.44</td>
<td>0.80</td>
<td>18</td>
</tr>
<tr>
<td>Silicon nitride ($Si_3N_4$)</td>
<td>8</td>
<td>1.98</td>
<td>2.45</td>
<td>17</td>
</tr>
<tr>
<td>Silicon carbide ($SiC$)</td>
<td>10.2</td>
<td>2.65</td>
<td>1.8</td>
<td>25</td>
</tr>
<tr>
<td>$\alpha$-Alumina, sapphire ($Al_2O_3$)</td>
<td>10.1–11.6</td>
<td>1.75</td>
<td>3.2</td>
<td>15</td>
</tr>
<tr>
<td>Zirconia ($n$-ZrO$_2$)</td>
<td>18</td>
<td>2.15</td>
<td>2.1</td>
<td>18</td>
</tr>
<tr>
<td>Zinc sulfide ($ZnS$)</td>
<td>8.5</td>
<td>2.26</td>
<td>1.6</td>
<td>16</td>
</tr>
<tr>
<td>Metals (Au, Ag, Cu)</td>
<td>$\infty$</td>
<td>—</td>
<td>3–5</td>
<td>25–40</td>
</tr>
</tbody>
</table>


*bExperimental values from Israelachvili and Tabor (1972), Derjaguin et al., (1978), and other literature sources.
Electrostatic repulsion

Negatively charged surface

counter ion  co-ion

Contact values

Poisson equation

$$-\varepsilon \varepsilon_0 \nabla^2 \psi = z e \rho$$

Boltzmann distribution

$$\rho = \rho_0 e^{-z e \psi / kT}$$

Poisson-Boltzmann equation

$$\nabla^2 \psi = - (z e \rho_0 / - \varepsilon \varepsilon_0) e^{-z e \psi / kT}$$


Interaction potential between spheres

Constant potential surfaces

\[ U_{e1}(h) = 2\pi\varepsilon\varepsilon_0 (kT/ze)^2 a \Psi_s^2 \ln \left[ 1 + e^{-\kappa h} \right] \]

Debye length

\[ \kappa^{-1} = \left( \frac{kT\varepsilon\varepsilon_0}{2Ie^2} \right)^{\frac{1}{2}} \]

 Ionic strength

\[ I = \frac{1}{2} \sum_{i=1}^{N} z_i^2 n_s,i \]

\[ n_s,i = 1000 N_A c_{s,i} \]

<table>
<thead>
<tr>
<th>NaCl (mM)</th>
<th>( \kappa^{-1} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>31</td>
</tr>
<tr>
<td>1</td>
<td>9.7</td>
</tr>
<tr>
<td>10</td>
<td>3.1</td>
</tr>
<tr>
<td>100</td>
<td>0.97</td>
</tr>
</tbody>
</table>

In water, R.T.
DLVO potential

\[ U(h) = U_{vdw}(h) + U_{el}(h) \]

1 μm diameter polystyrene, -50mV

Israelachvili, 2007
Kinetic stability

$$t \sim \left( \frac{3\pi a^3 \eta}{k_B T} \right) \exp\left( \frac{\Phi_{\text{max}}}{k_B T} \right)$$

$$e^1 \approx 2.7$$
$$e^5 \approx 150$$
$$e^{10} \approx 2 \times 10^4$$

Brownian

$$\tau_B = \frac{\pi \eta a^3}{kT}$$

<table>
<thead>
<tr>
<th>$2a$</th>
<th>100 nm</th>
<th>1 $\mu$m</th>
<th>10 $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_B$</td>
<td>0.1 ms</td>
<td>100 ms</td>
<td>100 s</td>
</tr>
</tbody>
</table>
Cohesion

When particles come into contact, they are held by strong van der Waals forces

\[
W_{SL} = \frac{1}{2} W_{SS} + \frac{1}{2} W_{LL} - \gamma_{SL}
\]

Then

\[
W_{SL} = \gamma_S + \gamma_L - \gamma_{SL}
\]

Young equation

\[
\gamma_S = \gamma_{SL} + \gamma_L \cos \theta
\]

Young-Dupré equation

\[
W_{SL} = \gamma_L (1 + \cos \theta)
\]

Alternately,

\[
\gamma_S \approx \frac{A_H}{12\pi D_0^2}
\]
Adhesion between elastic particles

JKR Theory


\[ P_0 = 0 \quad a_c = \left[ \frac{3\pi a^2 W_{SL}}{2K} \right]^{1/3} \]

Surface adhesion energy:

\[ W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \]

where \( \theta_0 = 73.7 \pm 0.3^\circ \)

\[ \gamma_L \approx 72 - 73 \text{mN/m} \]

Elastic modulus:

\[ K = \frac{2E}{3(1 - \nu^2)} \]

\[ K \approx 2.5 \text{GPa} \]

2 Jarvis and Scheiman, J. Phys. Chem. 72, 74 (1968).
DMT and JKR theories

Derjaguin, B., Muller, V. & Toporov, Y., J. Colloid Interface Sci. 53, 314–326 (1975)

Contact radius

\[
a_c = \left( \frac{3\pi a^2 W}{2K} \right)^{1/3}
\]

JKR model

\[
\lambda = \left( \frac{2W^2a}{9K^2h^3} \right)^{1/3}
\]

Tabor #

\[
\lambda \gg 1, \quad \lambda \ll 1
\]

PMMA

40nm

1.9

K = 2.5 GPa

silica

10nm

0.4

K = 23 GPa

\[2a = 1\mu m, W \sim 100\text{mJ/m}^2, h \sim 0.3\text{nm}\]

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Energy holding particles together


\[ U(h = 0) \approx 4.7 \times 10^{-15} J \]

\[ U(h = 0) \approx 10^{-16} J \approx 10^3 \text{kT} \]

We should calculate the force!
Steric forces


Adsorbed and grafted polymers
Homopolymers and co-polymers

For chemically-grafted polymers:

\[
\Phi_p = \begin{cases} 
\Phi_0 \left[ -\ln y - \frac{9}{5} (1 - y) + \frac{1}{3} (1 - y^3) - \frac{1}{30} (1 - y^6) \right], & 0 < y < 1 \\
0, & y \geq 1 
\end{cases}
\]

\[y = \frac{h}{2L} = \frac{(r - 2a)}{2L}\]

\[\Phi_0 = \left( \frac{\pi L \sigma_p k_B T}{12 N_p l^2} \right) a L^2\]

- \(L\) contour length
- \(N_p\) degree of polymerization
- \(l\) segment length
- \(\phi_p\) surface graft fraction
Bridging interactions

Adsorbed polymer, protein at lower surface coverage

Depletion attraction


\[ \Pi = -nkT \oint n_i g dS_i \]

\[ \langle F \rangle_i = -nkT \oint n_i g dS_i \]

\[ \frac{U(r)}{k_BT} \approx \phi_p \left\{ 1 - \frac{3r}{4R(1 + R_g/R)} + \frac{1}{2} \left[ \frac{r}{2R(1 + R_g/R)} \right]^3 \right\} \]

Depletion potential