Agglomeration, Deposition, and Aggregation

Lecture 9
Theoretical principles
Sphere-sphere interaction

Electrostatic repulsion:

\[
\frac{2\pi a_1 a_2 n_{\infty} kT}{(a_1 + a_2) \kappa^2} \left( \Phi_1^2 + \Phi_2^2 \right) \left[ \frac{2\Phi_1 \Phi_2}{\Phi_1^2 + \Phi_2^2} \ln \left( \frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right) - \ln \left( 1 - e^{-2\kappa h} \right) \right]
\]

Dispersion force attraction:

\[
-\frac{Aa_1 a_2}{6h(a_1 + a_2)} \quad \text{Sphere-sphere}
\]

\[
-\frac{A}{6} \left[ \frac{a}{h} + \frac{a}{h + 2a} + \ln \left( \frac{h}{h + 2a} \right) \right] \quad \text{Sphere-plate}
\]

Small \( \Phi_i \)  
Small surface potentials

\( h \ll a_i \)  
Particles close together

\( \kappa a_i \gg 1 \)  
Particles large compared to double layers

Elimelech et al, Tables 3.2 & 3.3
Colloidal hydrodynamics

Dispersion attraction and electrostatic repulsions are short range (order of the particle size.)

The processes that bring particles together are:

- Brownian motion
- Frictional drag of fluid motion
- Motion of one particle affecting another
- External forces – e.g. gravity, centrifugation, electric fields
Brownian Motion is diffusion

The Einstein relation between particle size and its diffusion coefficient is:

$$D = \frac{kT}{6\pi\eta a}$$

However gravitational sedimentation tends to pull the particle to the bottom. When these two tendencies are in equilibrium, the concentration of particles is given by:

$$n = n_0 \exp\left(-\frac{h}{h_0}\right)$$

$$h_0 = \frac{3kT}{4\pi a^3 \Delta\rho g}$$

For a 500 nm radius particle, 2 gm/cm³ in water at 25°C, $h_0$ is about 1000 nm.

But Brownian motion is not the source of dispersion stability.

$D$ is the diffusion constant
$k$ is the Boltzmann constant
$T$ is temperature
$\eta$ is viscosity
$a$ is particle radius
$n$ is particle concentration
$n_0$ is the particle concentration at the bottom
$h$ is the height
$h_0$ is the characteristic height
$\Delta\rho$ is the particle-liquid density difference
$g$ is the gravitation constant
Frictional drag of fluid motion

The ratio of inertia to viscous drag is the Reynolds number:

\[ R_e = \frac{\rho L_0 U_0}{\eta} \]

where \( \rho \) is the density difference, \( L_0 \) is a characteristic length, \( U_0 \) is the local velocity, and \( \eta \) is the viscosity.

A Reynolds number less than one means the flow is laminar.

The Reynolds number is always small for submicron particles.
Convection versus Diffusion

The Peclet number is the relative strength of convection and Brownian diffusion:

\[ Pe = \frac{U_0 a}{D_0} \]

where \( U_0 \) is the velocity
\( a \) is the particle radius
\( D \) is the diffusion constant

The velocity has been calculated for flows near collectors: a rotating disc, a stagnation-point flow, a plate in uniform flow … (Table 4.1 in Elimelech et al.)
Concentration dependence

The viscosity for hard spheres with no charge:

\[ \eta = \eta_0 \left( 1 + 2.5\Phi \right) \]

where \( \eta_0 \) is the solvent viscosity

and \( \Phi \) is the volume fraction of particles

For hard spheres with low charge:

\[ \eta = \eta_0 \left[ 1 + \left( 2.5 + \frac{6\varepsilon^2 \varepsilon_0^2 \zeta^2}{\lambda \eta a^2} \right) \Phi \right] \]

where \( \varepsilon \) is the dielectric constant of the liquid

\( \varepsilon_0 \) is the permittivity of free space

\( \zeta \) is the zeta potential of the particles

\( \lambda \) is the specific conductivity
Trends in the diffusion coefficient

(a) Ionic strength, (b) zeta potential, (c) ion size, (d) fluid velocity

van de Ven, p.89.
## Characteristic times and forces

### Characteristic times (seconds)

<table>
<thead>
<tr>
<th>Force</th>
<th>Time scale</th>
<th>Sphere radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownian</td>
<td>$a^2 / D$</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>Viscous</td>
<td>$\rho a^2 / \eta$</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>Convection</td>
<td>$a / U$</td>
<td>$10^2$</td>
</tr>
</tbody>
</table>

### Characteristic forces (N/m$^2$)

<table>
<thead>
<tr>
<th>Force</th>
<th>Force scale</th>
<th>Sphere radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownian</td>
<td>$kT/D$</td>
<td>$10^{-13}$</td>
</tr>
<tr>
<td>Viscous</td>
<td>$6\pi\eta a U$</td>
<td>$10^{-20}$</td>
</tr>
<tr>
<td>Dispersion</td>
<td>$A/a$</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>$\varepsilon \varepsilon_0 \zeta_0^2$</td>
<td>$10^{-12}$</td>
</tr>
</tbody>
</table>

$A$ = Hamaker constant  
$D$ = Diffusion coefficient  
$kT$ = Boltzmann factor  
$\rho$ = density  
$\eta$ = viscosity  
$U$ = fluid velocity  
$\varepsilon_0$ = permittivity of free space  
$\zeta_0$ = zeta potential
Models
The hydrodynamics of the rotating disk is relatively simple.

The goal is to deduce the magnitude of colloidal forces. Typical experiments vary zeta potentials and ionic strengths.

Particles gather at the center, top of the stagnation-point collector.

Elimelech, p. 116-133.
Perikinetic flocculation (1):
Driven by Brownian motion

\[ J_{ij} = k_{ij} n_i n_k \] is the number of collisions per unit volume and time

\[ k_{ij} = \frac{2kT (a_i + a_j)^2}{3\eta a_i a_j} \] second order rate constant

where \( kT \) is the Boltzmann factor
\( \eta \) is the viscosity
\( a_i \) and \( a_j \) are the particle radii

Different sized particles flocculate faster.
Perikinetic flocculation (2): Driven by Brownian motion

For equal sized particles and interaction potential $U$:

$$n = \frac{n_0}{1 + \frac{4kT}{3\eta W} n_0 t}$$

is the particle concentration

$$t_{1/2} = \frac{3\eta W}{4kTn_0} = \frac{\eta \pi a^3 W}{\Phi kT}$$

is the half-life

$$W = 2a \int_0^\infty \exp\left(\frac{U(H)}{kT}\right) \frac{dH}{H^2}$$

is the Stability Ratio
Orthokinetic agglomeration: Collisions by fluid motion

With laminar flow, shear rate = $G$

$$n = n_0 \exp \left( \frac{-4G\Phi}{\pi} t \right)$$

For turbulent flow, an model based on power input gives:

$$\bar{G} = \sqrt{\frac{\varepsilon \rho}{\eta}}$$

where $\varepsilon$ is the power input per unit mass
$\rho$ is the fluid density
$\eta$ is the fluid viscosity
A comparison of rates (1)

Perikinetic

\[ k_{ij} = \frac{2kT}{3\eta} \left( \frac{a_i + a_j}{a_i a_j} \right) ^2 \]

Orthokinetic

\[ k_{ij} = \frac{4}{3} G \left( a_i + a_j \right) ^3 \]

Differential settling

\[ k_{ij} = \left( \frac{2\pi g}{9\eta} \right) \left( \rho_s - \rho \right) \left( a_i + a_j \right) ^3 \left( a_i - a_j \right) \]

where \( g \) is gravitational acceleration
\( \rho_s \) is the particle density
\( \rho \) is the liquid density
A comparison of rates (2)

Figure 6.3  Comparison of collision rate constants for different transport mechanisms (see text)

Elimelech, p. 170.
Mechanisms of flocculation

• Charge neutralization
  (Ion adsorption, pH change, charged polymers)

• Double layer compression (ccc)

• Irregular charge distribution

• Polymer insolubility
  (temperature or solvent composition)

• Desorption of polymer

• Polymer bridging
Add a polymer that will “bridge” between two particles:

If a polymer is adsorbed and if the particles are not completely covered, then the polymer acts as a flocculant!

The efficiency of flocculation goes roughly as $\approx \Theta(1 - \Theta)$

If the coverage is large, the polymer acts as a stabilizer.

Elimelech, p. 194.
Adsorption at a solid surface is a slow process.

The adsorption of surfactants is much slower than is estimated by molecular diffusion.

Time is required for molecules to rearrange at the solid/liquid interface.
Experimental methods
Measure particle size distributions*

Want number distributions for understanding.

Therefore any technique that “counts”:
- Microscopy
- Sensing zones (optical and electrical)

Light scattering:
- Rayleigh scattering – get weight average, if small
- Mie scattering – not practical
- QELS – only very dilute, get weight average and 1\textsuperscript{st} moment
- Fraunhoffer – most practical but not accurate

Sedimentation:
- Easy but tricky data analysis
- Hindered settling is an issue
- Measure concentration as a function of height

*Much easier said then done!
Measure particle deposition rates

**Rotating disk:** Particles are collected on a microscope coverglass attached to disk G and counted after removal from tank.

**Stagnation-point flow:** Observation is on B of the liquid flowing up through tube A.

**Parallel-plate channel:** Particles deposited as a function of time can be seen from either side with a microscope.

Elimelech, pp 296-303
Bibliography


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Russel, W.B. *The dynamics of colloidal systems*; University of Wisconsin Press: Madison; **1987**.

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