Week # 4
MR Chapter 5
Colloids and Fine Particles

• Tutorial #4
• MR #5.3, 5.5, 5.6.
• To be discussed on Feb. 20, 2019.
• By either volunteer or class list.

Drag force \( \sim x \)

Surface area / Volume = \( \frac{\pi x^2}{\frac{6}{x}} = \frac{6}{x} \)

\( x \) is the particle diameter (1nm – 10\( \mu \)m)

Body force \( \sim x^3 \)

Other surface forces: van der Waals, electrical double layer, bridging and steric forces

MARTIN RHODES (2008)
Introduction to Particle Technology, 2nd Edition.
Publisher John Wiley & Son, Chichester, West Sussex, England.
Brownian motion

Robert Brown (1827)

Thermal energy from environment causes the molecules of the liquid to vibrate.

These vibrating molecules collide with each other and with the surface of the particles.

Illustration of the random walk of a Brownian particle. The distance the particle has moved over a period of time is $L$. 
\[
\bar{v} = \sqrt{\frac{3kT}{m}}
\]

\[
\frac{3}{2} kT = \frac{1}{2} mv^2
\]

Random thermal energy
Ignoring drag, collision and other factors

(Einstein, 1956)

Based on statistical analysis of 1-D random walk to determine root mean square distance traveled.

\[
L = \sqrt{2\alpha t}
\]

\[
\alpha f = kT
\]

k: Boltzmann constant = \(1.381 \times 10^{-23}\) J/K
f: friction coefficient = \(F_d/U\)

\[
f = 3\pi x \mu
\]

x is the particle diameter

\[
\alpha = kT/3\pi x \mu
\]

\[
L = \sqrt{\frac{2kT}{3\pi x \mu}} t
\]

Extension to 3D case:

\[
L = \sqrt{6\alpha t}
\]
Surface forces

\[ F = -\frac{dV}{dD} \]

Figure 5.2 Schematic representations of interparticle potential energy \((V)\) and force \((F)\) versus particle surface to surface separation distance \((D)\). (a) Energy versus separation distance curve for an attractive interaction. The particles will reside at the separation distance where the minimum in energy occurs. (b) Force versus separation distance for the attractive potential shown in (a). (The convention used in this book is that positive interparticle forces are repulsive.) The particles feel no force if they are at the equilibrium separation distance. An applied force greater than a maximum is required to pull the particles apart. (c) Energy versus separation distance curve for a repulsive interaction. When the potential energy barrier is greater than the available thermal and kinetic energy the particles cannot come in contact and move away from each other to reduce their energy. (d) Force versus separation distance for the repulsive potential shown in (c). There is no force on the particles when they are very far apart. There is a maximum force that must be exceeded to push the particles into contact.
• Van der Waals Forces

A group of electrohydrodynamic interactions that occur between the atoms in two different particles.

Figure 5.3 Schematic representation of the dipole–dipole attraction that exists between the instantaneous dipoles of two atoms in two particles. The + represents the nucleus of the atom and the – represents the centre of the electron density. Because the centre of electron density is typically not coincident with the nucleus, a dipole moment exists between the two separated opposite charges in each atom. Application of Coulomb’s law between the charges indicates that the lowest free energy configuration is as shown in the figure. The resulting position of positive and negative charges leads to an attraction between the two atoms, again due to Coulomb’s law

\[ V_{vdW} = -Ax/24D \]

\[ F_{vdW} = -Ax/24D^2 \]
Notation used to indicate the type of material for each particle and the intervening medium.

Dielectric properties of medium 2 is between materials 1 & 3.

<table>
<thead>
<tr>
<th>Material 1</th>
<th>Material 2</th>
<th>Material 3</th>
<th>Hamaker constant (approximate) (J)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Air</td>
<td>Alumina</td>
<td>$15 \times 10^{-20}$</td>
<td>Oxide minerals in air are strongly attractive and cohesive</td>
</tr>
<tr>
<td>Silica</td>
<td>Air</td>
<td>Silica</td>
<td>$6.5 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>Zirconia</td>
<td>Air</td>
<td>Zirconia</td>
<td>$20 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>Titania</td>
<td>Air</td>
<td>Titania</td>
<td>$15 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td>Water</td>
<td>Alumina</td>
<td>$5.0 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>Water</td>
<td>Silica</td>
<td>$0.7 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>Zirconia</td>
<td>Water</td>
<td>Zirconia</td>
<td>$8.0 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>Titania</td>
<td>Water</td>
<td>Titania</td>
<td>$5.5 \times 10^{-20}$</td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td>Water</td>
<td>Metals</td>
<td>$40 \times 10^{-20}$</td>
<td>Conductivity of metals makes them strongly attractive</td>
</tr>
<tr>
<td>Air</td>
<td>Water</td>
<td>Air</td>
<td>$3.7 \times 10^{-20}$</td>
<td>Foams</td>
</tr>
<tr>
<td>Octane</td>
<td>Water</td>
<td>Octane</td>
<td>$0.4 \times 10^{-20}$</td>
<td>Oil in water emulsions</td>
</tr>
<tr>
<td>Water</td>
<td>Octane</td>
<td>Water</td>
<td>$0.4 \times 10^{-20}$</td>
<td>Water in oil emulsions</td>
</tr>
<tr>
<td>Silica</td>
<td>Water</td>
<td>Air</td>
<td>$-0.9 \times 10^{-20}$</td>
<td>Particle bubble attachment in mineral flotation, weak repulsion</td>
</tr>
</tbody>
</table>
Electrical double layer forces

\[
M-OH + H^+ \rightarrow_{K_a} M-OH_2^+
\]
\[
M-OH + OH^- \rightarrow_{K_b} M-O^- + H_2O
\]

(a) vacuum

(b) water (at IEP)

(c) low pH

(d) high pH

Figure 5.5 Schematic representation of the surface of metal oxides (a) in vacuum. Unsatisfied bonds lead to positive and negative sites associated with metal and oxygen atoms, respectively. (b) The surface sites react with water or water vapour in the environment to form surface hydroxyl groups (M-OH). At the isoelectric point (IEP) the neutral sites dominate, and the few positive and negative sites present exist in equal numbers. (c) At low pH the surface hydroxyl groups react with H\(^+\) in solution to create a positively charged surface composed mainly of (M-OH\(_2^+\)) species. (d) At high pH the surface hydroxyl groups react with OH\(^-\) in solution to create a negatively charged surface composed mainly of (M-O\(^-\)) species.
Number density per unit area of neutral (M-OH), positive (M-OH$_2^+$) and negative (M-O$^-$) surface sites as a function of pH
A measure of the counterion cloud (thus the range of the repulsion) is the Debye length, $k^{-1}$

$$\kappa = 3.29 \sqrt{[c]} \, \text{(nm}^{-1}\text{)}$$

Approximate EDL potential energy

$$V_{\text{EDL}} = \pi \varepsilon \varepsilon_0 x \Psi_0^2 e^{-\kappa D}$$
Zeta potential of alumina particles as a function of pH and salt concentration
• Adsorbing polymers, bridging and steric forces

Schematic representation of (a) bridging flocculation and (b) steric repulsion
- **Net interaction force**  

**DLVO Theory:**

- **Figure 5.9**  
  (a) Force versus distance curves for alumina at different pH values calculated from Equations (5.8) and (5.11) with parameters as detailed in Franks *et al.* (2000). At pH 9 the van der Waals attraction dominates. As pH is decreased the range and magnitude of the EDL repulsion increases as zeta potential increases (see Figure 5.8). At very small separation distances the van der Waals attraction always dominates the EDL repulsion. 
  (b) Force versus distance curves for silica particles interacting with an adsorbed polymer (Zhou *et al.*, 2008). Upon approach, the adsorbed polymer provides a weak steric repulsion. Upon separation (retraction) the polymer creates a strong long range attraction because chains are adsorbed on both surfaces. The van der Waals only interaction is shown for comparison.
• Result of surface forces on behaviour in air and water

Low zeta potential (near IEP)
High salt (coagulation)
Bridging polymers

High zeta potential (away from IEP)
Low salt
Polymer cushions (steric repulsion)

Attraction
Repulsion

Flocculated or aggregated

Dispersed or stabilized

Aggregation
Rapid sedimentation
Low density sediments (high moisture)
High viscosity and yield stress

Individual particles
Slow settling
Dense sediments (low moisture)
Low viscosity

Figure 5.10 The top section of the figure gives examples of how the solution conditions influence the forces between particles. The bottom section shows how attractive and repulsive forces influence some behaviour of suspensions.
Influences of particle size and surface forces on solid/liquid separation by sedimentation

\[ L = \sqrt{\frac{2kT}{3\pi \kappa \mu}} \frac{(\rho_p - \rho_f) x^2 g}{18 \mu} t \]

\[ t = \frac{216kT \mu}{\pi g^2 (\rho_p - \rho_f)^2 x^5} \]

Figure 5.11 (a) Repulsive colloidal particles result in stable dispersions that only form sediments after extended periods. The sediment is quite concentrated. (b) When a flocculant is added to a stable dispersion, the resulting attraction causes aggregation of the particles and rapid sedimentation of the flocs. The sediment in this case is quite open.
• Suspension rheology

Figure 5.12  Equilibrium volume fraction as a function of consolidation pressure in a filter press (data from Franks and Lange, 1996) for 200 nm diameter alumina. At pH 4 the strong repulsion between particles results in consolidation to high densities over a wide range of pressures. At pH 9, the IEP of the powder, the strong attraction produces difficult to consolidate and pressure-dependent filtration behaviour. The weak attraction at pH 5, with added salt results in intermediate behaviour.
\[ \mu_s = \mu_1(1 + 2.5\phi) \]

Einstein (1906), < 7% volume solids

\[ \mu_s = \mu_1(1 + 2.5\phi + 6.2\phi^2) \]

Batchelor (1977), 7-15%, volume solids

Relative viscosity \( (\mu_s / \mu_i) \) of hard sphere silica particle suspensions (black circles) and Einstein’s relationship (line)
The transition from Brownian dominated random structures to preferred flow structures as shear rate is increased is the mechanism for the shear thinning behaviour of concentrated suspensions of hard sphere colloids.
\[ \mu_s^* = \mu_l \left(1 - \frac{\phi}{\phi_{\text{max}}} \right)^{-2} \]

Figure 5.15  Relative viscosity ($\mu_s/\mu_l$) at low shear rate of hard sphere silica suspensions (circles). Quemada’s model (solid line) with $\phi_{\text{max}} = 0.631$; Batchelor’s model (dashed line) and Einstein’s model (dotted line). (Data from Jones et al., 1991)
Figure 5.16 Map of typical rheological behaviour of hard sphere suspensions as a function of shear rate for suspensions with volume fractions between about 40 and 55 vol % solid particles. The dashed lines indicate the approximate location of the boundaries between Newtonian and non-Newtonian behaviour.
Influences of surface forces on suspension flow

- Repulsive forces

\[ \phi_{\text{eff}} = \frac{\text{volume of solid + excluded volume}}{\text{total volume}} \]

Figure 5.17 (a) Illustration of suspension of particles with volume fraction 0.4 (grey circles) with repulsive interaction extending to the dotted line, resulting in an effective volume fraction of 0.57. (b) Relative viscosity of suspensions of repulsive particles (black dots and dotted line) as a function of actual volume fraction. When the rheological results are plotted as a function of effective volume fraction (open dots) the data maps onto the Quemada model (solid line)
• Attractive forces

Figure 5.18 Comparison of typical shear thinning behaviour of attractive particle network with less pronounced shear thinning of hard sphere suspensions. The attractive particle network is broken down into smaller flow units as the shear rate is increased.
Figure 5.19  Yield stress of 25 vol % alumina suspensions (0.3 μm diameter) as a function of pH and salt concentration. (Data from Johnson et al., 1999)

\[ \tau_Y \propto \frac{\text{Number of bonds}}{\text{Unit volume}} \times \text{Strength of bond} \]

Strength of bond \( \propto x \)
Figure 5.20  Yield stress of alumina suspensions at their IEP as a function of particle size. The best fit line has a slope of −2.01, correlating quite well with the predicted inverse square particle size dependence as per Equation (5.22). (Data from Zhou et al., 2001).
WORKED EXAMPLE 5.1

Brownian Motion and Settling

Estimate the amount of time that each of the following suspensions will remain stabilized against sedimentation due to Brownian motion at room temperature (300K).

(a) 200 nm diameter alumina ($\rho = 3980 \text{ kg/m}^3$) in water (typical ceramic processing suspension);

(b) 200 nm diameter latex particles ($\rho = 1060 \text{ kg/m}^3$) in water (typical paint formulation);

(c) 150 nm diameter fat globules ($\rho = 780 \text{ kg/m}^3$) in water (homogenized milk);

(d) 1000 nm diameter fat globules ($\rho = 780 \text{ kg/m}^3$) in water (non-homogenized milk).

Solution

The time that the suspension remains stable against gravity can be approximated by equating the average distance moved by a particle due to Brownian motion to the distance settled due to gravity. This time is presented in Equation (5.13) as follows:

$$ t = \frac{216kT\mu}{\pi g^2(\rho_p - \rho_f)^2x^5} $$

where $k = 1.381 \times 10^{-23} \text{ J/K}$, $\mu_{\text{water}} = 0.001 \text{ Pa s}$, $g = 9.8 \text{ m/s}^2$, $\rho_{\text{water}} = 1000 \text{ kg/m}^3$.

then

$$ t = \frac{216(1.381 \times 10^{-23} \text{ J/K})300 \text{ K}(0.001 \text{ Pa s})}{\pi(9.8 \text{ m/s}^2)^2(\rho_p - 1000 \text{ kg/m}^3)^2x^5} $$

$$ t = \frac{2.96 \times 10^{-24} \text{ kg}^2 \text{ s/m}}{(\rho_p \text{ kg/m}^3 - 1000 \text{ kg/m}^3)^2x^5\text{m}^5} $$
(a) For the alumina suspension

\[ t = \frac{2.96 \times 10^{-24} \text{ kg}^2 \text{s/m}}{(3980 \text{ kg/m}^3 - 1000 \text{ kg/m}^3)^2 (200 \times 10^{-9})^5 \text{ m}^5} = 1042 \text{ s} = 17.4 \text{ min} \]

(b) For the latex particles in paint

\[ t = \frac{2.96 \times 10^{-24} \text{ kg}^2 \text{s/m}}{(1060 \text{ kg/m}^3 - 1000 \text{ kg/m}^3)^2 (200 \times 10^{-9})^5 \text{ m}^5} = 2.57 \times 10^6 \text{ s} = 30 \text{ days} \]

(c) For the homogenized milk

\[ t = \frac{2.96 \times 10^{-24} \text{ kg}^2 \text{s/m}}{(780 \text{ kg/m}^3 - 1000 \text{ kg/m}^3)^2 (150 \times 10^{-9})^5 \text{ m}^5} = 8.06 \times 10^5 \text{ s} = 9.3 \text{ days} \]

(d) For the non-homogenized milk

\[ t = \frac{2.96 \times 10^{-24} \text{ kg}^2 \text{s/m}}{(780 \text{ kg/m}^3 - 1000 \text{ kg/m}^3)^2 (1000 \times 10^{-9})^5 \text{ m}^5} = 61 \text{ s} \]

These characteristic times correspond best with the time for the first particle to settle out. The time for all the particles to settle out depends upon the height of the container. Nonetheless, one can understand the reasons why the alumina suspension needs to be mixed to keep all of the particles suspended for extended periods of time, why latex paints must be stirred if kept for a month and why milk is homogenized to prevent cream from forming while the milk is in your fridge for a week or two.
**WORKED EXAMPLE 5.2**

van der Waals and EDL Forces

Use the DLVO equation, \( F_T = \pi \varepsilon_0 x \Psi_0^2 \kappa e^{-\kappa D} (Ax/24D^2) \), to plot the total interparticle force \( (F_T) \) versus interparticle separation distance \( (D) \) for two alumina particles and for two oil droplets under the following conditions. The particles are spherical, 1 \( \mu \)m in diameter and suspended in water that contains 0.01 M NaCl. Plot three conditions for each material: (a) at the IEP; (b) with \( \zeta = 30 \text{ mV} \); and (c) with \( \zeta = 60 \text{ mV} \). Comment on the differences in the behaviour of the two different materials. Which particles are easier to disperse and why?

**Solution**

Assume the surface potential equals the zeta potential \( (\Psi_0 = \zeta) \).

Calculate the inverse Debye length \( (\kappa) \) with Equation (5.10).

\[
\kappa = 3.29 \sqrt{[c]} \text{ (nm}^{-1}) = 3.29 \sqrt{0.01 \text{ (nm}^{-1})} = 0.329 \text{ (nm}^{-1}) = 3.29 \times 10^8 \text{ m}^{-1}
\]

The relative permittivity of water \( (\varepsilon) \) is 80 and the permittivity of free space \( (\varepsilon_0) \) is \( 8.854 \times 10^{-12} \text{ C}^2/\text{J/m} \).
The diameter of the particles is $1 \times 10^{-6}$ m.

Then

$$F_T = \pi80(8.854 \times 10^{-12} \text{C}^2/\text{J/m})(1 \times 10^{-6} \text{m})\Psi_0^2(3.29 \times 10^8 \text{m}^{-1})e^{-(3.29 \times 10^8 \text{m}^{-1})D} \frac{A(1 \times 10^{-6})}{24D^2}$$

$$F_T = (7.32 \times 10^{-7} \text{C}^2/\text{J/m})\Psi_0^2e^{-(3.29 \times 10^8 \text{m}^{-1})D} \frac{(1 \times 10^{-6} \text{m})A}{24D^2}$$

where $\Psi_0$ is in volts and $D$ in meters.

From Table 5.1 the Hamaker constants ($A$) are:

For alumina $A = 5.0 \times 10^{-20} \text{J}$

For oil $A = 0.4 \times 10^{-20} \text{J}$

Then for alumina

$$F_T = (7.32 \times 10^{-7} \text{C}^2/\text{J/m})\Psi_0^2e^{-(3.29 \times 10^8 \text{m}^{-1})D} \frac{(1 \times 10^{-6} \text{m})(5 \times 10^{-20} \text{J})}{24D^2}$$

$$F_T = (7.32 \times 10^{-7} \text{C}^2/\text{J/m})\Psi_0^2e^{-(3.29 \times 10^8 \text{m}^{-1})D} \frac{5 \times 10^{-26} \text{J m}}{24D^2}$$

and for oil

$$F_T = (7.32 \times 10^{-7} \text{C}^2/\text{J/m})\Psi_0^2e^{-(3.29 \times 10^8 \text{m}^{-1})D} \frac{(1 \times 10^{-6} \text{m})(0.4 \times 10^{-20} \text{J})}{24D^2}$$

$$F_T = (7.32 \times 10^{-7} \text{C}^2/\text{J/m})\Psi_0^2e^{-(3.29 \times 10^8 \text{m}^{-1})D} \frac{0.4 \times 10^{-26} \text{J m}}{24D^2}$$
These equations can be plotted by a standard data plotting software such as Excel, KG, or SigmaPlot, but first the units and typical values must be checked by hand to insure no errors are made while writing the equation to the spreadsheet.

Unit analysis

\[ F_T = C^2 / J/m V^2 e^{m^{-1} \times m} - \frac{J m}{m^2} \] where \( V = J/C \)

\[ F_T = C^2 / J/m J^2 / C^2 e^{m^{-1} \times m} - \frac{J m}{m^2} \] so \( F_T = m^{-1} J - \frac{J}{m} = \frac{J}{m} \) and \( J = N \ m \) so

\( F_T \) is in newtons so the units are OK.

Figures 5W2.1 and 5W2.2 are the plotted results.

The difference between the two materials is that the Hamaker constant for the alumina is much greater than for the oil and thus the attraction between alumina particles is much stronger between alumina than between oil droplets. Thus, it is possible to just stabilize the oil droplets with 30 mV zeta potential, whereas when the alumina has 30 mV zeta potential, there is still attraction between the particles. Hence 60 mV is needed to stabilize the alumina to the same extent that 30 mV was able to stabilize oil droplets.
Force versus separation distance curves for alumina particles
Force versus separation distance curves for oil droplets