Dispersion systems

Dispersion system = dispersed phase in a continuum phase (medium)
s/l, l/l, ...

According to the size of the dispersed phase:

- coarse dispersion (suspension), > 1 μm
- colloid 1 μm–1 nm
  - heterogeneous (micelles, precipitates,...)
  - homogeneous (solutions of macromolecules)
- solutions

Examples: polymer solutions, asphalt concrete, starch, milk, fresh precipitate...
Properties of dispersions

- Coarse dispersions: turbidity (look as a haze), milk-like size $\gg \lambda$: white/gray (if particles are not colored)
size $\approx \lambda$: Tyndall phenomenon, blue is scattered more (red Sun in dust)
size $\ll \lambda$: Rayleigh scattering, blue is scattered more
elastic scattered – photon energy does not change

- Colligative properties – measurable only in fine dispersions

- Brownian motion, diffusivity decreases as the size increases
  \[ D = \frac{k_BT}{6\pi\eta R} \]

- Viscosity – bigger than the fluid medium, often non-Newton
  – plasticity = a minimum stress needed
to flow, viscosity decreases with the shear strain
  – dilatancy = viscosity increases with flow speed/shear strain
    (starch + water)

- Density – in between both phases

- Surface tension – often lower

Credit: http://www.physics.emory.edu/~weeks/squishy/
# Dispersion systems

<table>
<thead>
<tr>
<th>Dissolved or dispersed phase</th>
<th>Continuous medium</th>
<th>Solution: Homogeneous mixture: Dissolved phase &lt; 1 nanometer</th>
<th>Colloid: Dispersed phase between 1 nanometer and 1 micrometer</th>
<th>Coarse dispersion (Suspension): Heterogeneous mixture: Dispersed phase &gt; 1 micrometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Gas</td>
<td>Gas mixture: <strong>air</strong> <em>(oxygen and other gases in nitrogen)</em></td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Liquid</td>
<td>Gas</td>
<td>None</td>
<td><strong>Aerosol</strong>: fog, mist, vapor, hair sprays</td>
<td><strong>Aerosol</strong></td>
</tr>
<tr>
<td>Solid</td>
<td>Gas</td>
<td>None</td>
<td><strong>Solid aerosol</strong>: smoke, cloud, air particulates</td>
<td><strong>Solid aerosol</strong>: dust</td>
</tr>
<tr>
<td>Gas</td>
<td>Liquid</td>
<td><strong>Solution</strong>: oxygen in water</td>
<td>Foam: whipped cream, shaving cream</td>
<td>Foam</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td><strong>Solution</strong>: alcoholic beverages</td>
<td><strong>Emulsion</strong>: miniemulsion, microemulsion</td>
<td><strong>Emulsion</strong>: milk, mayonnaise, hand cream</td>
</tr>
<tr>
<td>Solid</td>
<td>Liquid</td>
<td><strong>Solution</strong>: sugar in water</td>
<td><strong>Sol</strong>: pigmented ink, blood</td>
<td><strong>Suspension</strong>: mud <em>(soil, clay or silt particles are suspended in water)</em>, chalk powder suspended in water</td>
</tr>
<tr>
<td>Gas</td>
<td>Solid</td>
<td><strong>Solution</strong>: hydrogen in metals</td>
<td><strong>Solid foam</strong>: aerogel</td>
<td>Foam: dry sponge, styrofoam, pumice</td>
</tr>
<tr>
<td>Liquid</td>
<td>Solid</td>
<td><strong>Solution</strong>: amalgam <em>(mercury in gold)</em>, hexane in paraffin wax</td>
<td><strong>Gel</strong>: agar, gelatin, silicagel, opal</td>
<td>Wet sponge</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td><strong>Solution</strong>: alloys, plasticizers in plastics</td>
<td><strong>Solid sol</strong>: cranberry glass</td>
<td><strong>Gravel, granite</strong></td>
</tr>
</tbody>
</table>

*credit: wikipedia*
**Classification**

Shape of particles:
- globular, isometric particles ($r_x \approx r_y \approx r_z$)
- laminar, anisometric particles ($r_x \approx r_y \gg r_z$)
- fibrillar, anisometric particles ($r_x \gg r_y \approx r_z$)

**Interactions:**
- lyophilic dispersions (medium wets the particles, $\theta < 90^\circ$)
  - in water: hydrophilic
- lyophobic dispersions (does not wet)
  - in water: hydrophobic
Preparation of dispersions

- polymerization
- oversaturation of a solution (ouzo, anise drink)
- oversaturation of a micellar colloid (over CMC = critical micellar concentration)
- mechanically (grinding, ultrasound)
- electrically (electric arch, cathodic sputtering)
- precipitation reactions – insoluble product (AgBr in a photographic “emulsion”)

Microcrystals of a precipitate may be aggregated (flocculated), because the electric double layer is thin in a concentrated ionic solution (according to the DLVO theory), rinsing out the ions stabilizes the colloid (peptization).

Aggregation caused by weak forces:

\[
\text{free dispersed particles} \xrightleftharpoons{\text{flocculation}} \xleftarrow{\text{peptization}} \text{weakly bound aggregates}
\]
**Distribution functions**

E.g., **mass (differential) distribution function** $F_w(m)$: ratio (prob = count/(total number)) of particles of masses in interval $(m, m + dm)$ is $F_w(m)dm$.

Normalization:

$$\int_0^\infty F_w(m) dm = 1$$

Cumulative (integrated) distrib. function = ratio of particles of masses $< m$:

$$I_w(m) = \int_0^m F_w(m') dm', \quad Q_w(m) = \int_m^\infty F_w(m') dm' = 1 - I_w(m)$$

Similar: Distribution function of particle volumes, ...

- **Monodisperse system** – all particles of the same size (peak on $F_w(m)$); may form crystals
  - Spheres: fcc 74%, “random close packing” 64%

- **Polydisperse systems**: e.g. asphalt concrete (example of random fractal) *try to guess the fraction of mineral filling*

Fraction = group of particles of approx. the same size (filtering, ...)
Potential of external force (e.g., gravity) = $U$
External force: $\vec{F} = -\text{grad } U$

**Forces of gravity** (acceleration = $g$):

$$F = -mg, \quad U = mhg$$

**Forces in a centrifuge:**

$$F = mR\omega^2, \quad U = -\frac{1}{2}m(R\omega)^2, \quad \omega = 2\pi \nu = \frac{2\pi}{\tau}$$

$\omega$ = angular (circular) frequency
$\nu$ = frequency (in Hz or RPM, 1 RPM = $\frac{1}{60}$ Hz)
$R$ = radius of rotation
$\tau$ = period
Speed of sedimentation

Density of particles = $\rho_1$
Density of dispersion medium = $\rho$
Viscosity of dispersion = $\eta$
Particle volume = $V_1$
Friction coefficient = $f$
Sedimentation speed = $v$

**In the field of gravity:**
The force must be corrected for the buoyant force (Archimedes’ principle):

$$ F = V_1(\rho_1 - \rho)g, \quad v = \frac{F}{f} = \frac{V_1(\rho_1 - \rho)g}{f} $$

Spherical particles: $V_1 = \frac{4}{3}\pi r^3$, $f = 6\pi\eta r$ (Stokes)

$$ v = \frac{2r^2}{9\eta}(\rho_1 - \rho)g $$

**In a centrifuge:** use $R\omega^2$ instead of $g$
(typical $1000g – 10,000g$, ultracentrifuge up to $10^6g$)

Small particles sediment slowly. Molecules sediment, too (very slowly): uranium enrichment by centrifugation of UF$_6$(g)
From Boltzmann probability

Ideal solution: concentration $\propto$ Boltzmann probability $\Rightarrow$

$$c(\vec{r}) = c_0 \exp \left( \frac{-U(\vec{r})}{k_B T} \right)$$

In a gravitational field this is the barometric formula:

$$c(h) = c(0) \exp \left( \frac{-V_1(\rho_1 - \rho)gh}{k_B T} \right)$$

In a centrifuge of angular frequency $\omega = 2\pi \times$ frequency:

$$c(r) = c(0) \exp \left( \frac{\frac{1}{2}V_1(\rho_1 - \rho)(R\omega)^2}{k_B T} \right)$$

where $\Delta m = V_1(\rho_1 - \rho)$
Sedimentation equilibrium

From the speeds of sedimentation and diffusion

\[ \nu_{\text{sedimentation}} = \frac{F}{f} = -\frac{\nabla U}{f} \]

\[ \nu_{\text{diffusion}} = \frac{J}{c} = -\frac{D \nabla c}{c} = -D \nabla \ln c = -\frac{k_B T}{f} \nabla \ln c \]

\[ \nu_{\text{sedimentation}} + \nu_{\text{diffusion}} = 0 \Rightarrow c = c_0 \exp \left( -\frac{U}{k_B T} \right) \]

Let \( \mu \) be per particle (not mole), infinite dilution approximation:

\[ \mu = \mu_0 + k_B T \ln \left( \frac{c}{c^{\text{st}}} \right) \Rightarrow \nu_{\text{diffusion}} = -\frac{1}{f} \nabla \mu \]

Thus

\[ \nu_{\text{sedimentation}} + \nu_{\text{diffusion}} = 0 \]

is equivalent to

\[ U + \mu = \text{const} \]

Some time ago, we used the assumption of \( U + \mu = \text{const} \) to derive \( D = k_B T / f \).
Example. The equilibrium concentration of monodisperse oil droplets in a cuvette 10 cm tall is twice as large near the surface than at the bottom. Calculate the diameter of oil droplets. The temperature is 25 °C, the density of water is 0.997 g cm\(^{-3}\), the density of oil is 0.920 g cm\(^{-3}\).

Example. Consider a globular protein of molecular weight of 20 kDa. What is the speed of sedimentation in a centrifuge of 24000 RPM at a point 5 cm from the axis? The density of the protein is 1.35 g cm\(^{-3}\), the viscosity of water is 0.891 mPa s.
Dispersions are thermodynamically metastable (large interface)

- sedimentation (↓), creaming (↑)
- flocculation (reversible), coagulation (irreversible)
- coalescence (of droplets)
- Ostwald ripening (small → large, Kelvin equation)

**Stabilization:**

- by electric double layer
  DLVO theory (see below)
- steric (adsorption of macromolecules in a good solvent)
- depletion (macromolecules in between particles)
- electrosteric
- kinetic (in a very viscous medium)
DLVO theory

Deryagin (Дерягин, Derjaguin) + Landau (Ландау),
Verwey + Overbeek.

- repulsion of charged surfaces (screened by a Gouy–Chapman (diffusion) layer) stabilizes a colloid
- attractive dispersion (London) forces tries to stick particles together

Stability is a result of a competition between both forces

- surface charge increases stability
- dispersion forces decrease stability
Diffusion (Gouy–Chapman) layer, 1:1 electrolyte, small $\phi e/k_BT$:

$$\phi = \phi_0 e^{-x/\lambda}, \quad \text{where} \quad \lambda = \sqrt{\frac{\varepsilon RT}{2cF^2}}$$

Surface charge = $-\text{layer charge}$

$$\sigma = -\int_0^\infty (\rho_+ - \rho_-)dx = -\int_0^\infty cF \left\{ \exp\left[ -\frac{\phi(x)e}{k_BT} \right] - \exp\left[ \frac{\phi(x)e}{k_BT} \right] \right\} dx$$

For small $\frac{\phi(x)e}{k_BT}$: $\sigma \approx \int_0^\infty 2cF \frac{\phi(x)e}{k_BT} dx = 2\lambda cF \phi_0 e = \frac{\varepsilon}{\lambda} \phi_0$

$\varepsilon/\lambda = \text{capacity of the Gouy–Chapman double layer (per unit area)}$

Energy (per unit area) of the surface charge $\sigma$ in potential $\phi_0$ is (in the superposition approximation, that’s why multiplied by 2)

$$E_{\text{elst}} = 2\sigma \phi_0 e^{-d/\lambda} = 2\frac{\lambda \sigma^2}{\varepsilon} e^{-d/\lambda} = 2\frac{\varepsilon \phi_0^2}{\lambda} e^{-d/\lambda}$$

Formulas for curved interfaces are more complex, however, the leading term is always $e^{-d/\lambda}$
van der Waals forces

For 2 molecules $r$ apart ($r \gg$ overlap of orbitals), the energy decays as $\propto 1/r^6$:

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

- charge–charge: $u \propto 1/r$
- dipole–charge: $u \propto 1/r^2$ (fixed dipole orientation)
- dipole–dipole: $u \propto 1/r^3$
- Freely rotating dipole–freely rotating dipole: $u \propto 1/r^6$
- Dipole–induced dipole: $u \propto 1/r^6$
- London (dispersion) force (fluctuating dipole–fluctuation dipole):
  fluctuation $\Rightarrow$ dipole $\Rightarrow$ el. field $\propto 1/r^3$ $\Rightarrow$ induced dipole $\propto 1/r^3$ $\Rightarrow$ $u \propto 1/r^6$
  Usually the most pronounced
- London force for $r \gg 1\mu$m: $u \propto 1/r^7$. 
DLVO theory: van der Waals forces

\[ u(r) = -\frac{C}{r^6} \]

Contributions from atom pairs are considered as independent (valid to \( \sim 80-90\% \))

For two bodies we make a sum (integral); e.g., for a slit:

Point–surface (half-space) first:

\[ u_{\text{wall}}(d) = -N C \frac{2\pi}{12d^3} \]

\[ N = N_A n/V = \text{number density} \]

\[ A = (\pi N)^2 C = \text{Hamaker constant} \text{ of given substance, } [A] = \text{J} \]

Two \( R \)-balls \( d \) apart, first term of the expansion in \( d \ll R \):

\[ E_{vdW} = -\frac{\pi N^2 C}{12d^2} = -\frac{A}{12\pi d^2} \] (per unit area)
Cross interaction between both media,

\[ u_{12}(r) = -\frac{C_{12}}{r^6}, \quad A_{12} = \pi^2 N_1 N_2 C_{12} \]

Particles of 2 in material 1 (0 = particles far away)

\[ A_{1/2} = A_{11} - 2A_{12} + A_{22} \]

Approximation (combining rule):

\[ A_{12} \approx \sqrt{A_{11}A_{22}} \]

Then

\[ A_{1/2} = (\sqrt{A_{11}} - \sqrt{A_{22}})^2 \]
TiO$_2$ in a ⊙ of NaCl. 

$A(\text{TiO}_2) = 19.5 \times 10^{-20}$ J, $A(\text{H}_2\text{O}) = 3.7 \times 10^{-20}$ J, ⇒ $A \approx 6.2 \times 10^{-20}$ J

° flat interface formulas

° energy expressed in $k_B T$ per 100 nm$^2$

° figure: $\phi_0 = 0.15$ V, $c = 0.1$ mol dm$^{-3}$

$k_B T =$ thermal “quantum”

barrier $60 k_B T/100$ nm$^2$

$e^{-E/k_B T} = e^{-60} = 1 \times 10^{-26}$

↓

cubes of side 10 nm will be stable

Rule of the thumb: 
stable for barrier $> 25k_B T$

$e^{-25} \approx 10^{-11}$
Diffusivity of a spherical particle of diameter $2R = 10$ nm (Stokes formula):

$$D_i = \frac{k_B T}{6 \pi \eta R_i} = \frac{1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}}{6 \pi \times 0.89 \times 10^{-3} \text{ m}^{-1} \text{ kg s}^{-1} \times 5 \times 10^{-9} \text{ m}} = 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$$

If the particles are about $r = R$ apart, the typical collision time is

$$\tau \approx \frac{r^2}{6D} = \frac{(5 \times 10^{-9} \text{ m})^2}{6 \times 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}} = 1 \times 10^{-7} \text{ s}$$

For the probability of barrier crossing of $\pi = e^{-25} = 10^{-11}$, the typical timescale of flocculation is:

$$\frac{\tau}{\pi} \approx 10000 \text{ s} \approx \text{hours}$$
DLVO: summary

- Surfaces close together (at contact): attraction (adhesion)
- Surfaces far away: fast decreasing attraction
- Medium distances (according to the potential): energy barrier

The barrier grows = stability increases for:
- Potential (surface charge) increases (in abs. value)
- Salt concentration decreases (longer Debye screening range)