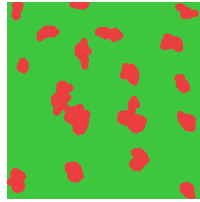## Dispersion systems

Dispersion system =
dispersed phase in a continuum phase (medium)

s/l, l/l, . . .

According to the size of the dispersed phase:

⬤ coarse dispersion (suspension), $> 1\,\mu m$

⬤ colloid $1\,\mu m$–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
  $(D = k_B T/6\pi\eta R)$

⬤ 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

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

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, $\theta < 90°$)
  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 el. double layer is thin in a concentrated ionic solution (according to the DLVO theory), rinsing out the ions stabilizes he colloid (peptization).

Aggregation caused by weak forces:

$$\text{free disperged particles} \underset{\text{peptization}}{\overset{\text{flocculation}}{\rightleftarrows}} \text{weakly bound aggregates}$$

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, . . .)

Sedimentation

Potential of external force (e.g., gravity) = U
External force: $\vec{F} = -\text{grad}\,U$
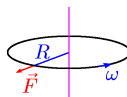
asphalt concrete:
95 % mineral filling
5 % bitumen

Forces of gravity (acceleration = g):

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

Forces in a centrifuge:

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

ω = angular (circular) frequency
ν = frequency (in Hz or RPM, 1 RPM = $\frac{1}{60}$ Hz)
R = radius of rotation
τ = period

Speed of sedimentation

Density of particles = ρ_1
Density of dispersion medium = ρ
Viscosity of dispersion = η
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 $10^6 g$)

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 $\Delta m = V_1(\rho_1 - \rho)$

From the speeds of sedimentation and diffusion

$$v_{\text{sedimentation}} = \frac{F}{f} = -\frac{\nabla U}{f}$$

$$v_{\text{diffusion}} = \frac{J}{c} = -\frac{D\nabla c}{c} = -D\nabla \ln c = -\frac{k_B T}{f}\nabla \ln c$$

$$v_{\text{sedimentation}} + v_{\text{diffusion}} = 0 \quad \Rightarrow \quad c = c_0 \exp\left(-\frac{U}{k_B T}\right)$$

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

$$\mu = \mu_0 + k_B T \ln(c/c^{\text{st}}) \quad \Rightarrow \quad v_{\text{diffusion}} = -\frac{1}{f}\nabla\mu$$

Thus

$$v_{\text{sedimentation}} + v_{\text{diffusion}} = 0$$

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 $0.997\,\text{g cm}^{-3}$, the density of oil is $0.920\,\text{g cm}^{-3}$.

42 nm

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 $1.35\,\text{g cm}^{-3}$, the viscosity of water is $0.891\,\text{mPa s}$.

$V_1 = 2.46 \times 10^{-26}\,\text{m}^3,\ r = 1.8\,\text{nm},\ v = 0.32\,\text{mm h}^{-1},\ a = 3220\,0g$

Dispersions are thermodynamically metastable (large interface)

- sedimentation ($\downarrow$), creaming ($\uparrow$)
- flocculation (reversible), coagulation (irreversible)
- coalescence (of droplets)
- Ostwald ripening (small $\rightarrow$ large, Kelvin equation)
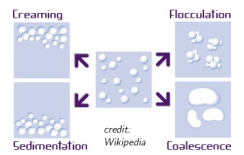
Stabilization:

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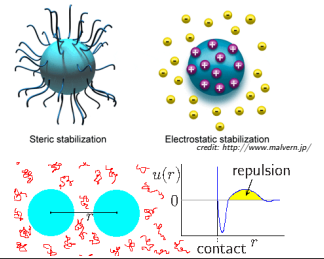
Deryagin (Дерягин, Derjaguin) + Landau (Ландау),
Verwey + Overbeek.

- 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 $\phi e/k_B T$:

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

Surface charge $= -$ layer charge

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

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

ϵ/λ = capacity of the Gouy–Chapman double layer (per unit area)

Energy (per unit area) of the surface charge σ in potential ϕ_0 is (in the superposition approximation, that's why multiplied by 2)

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

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

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
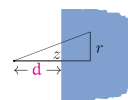- London force for $r \gg 1\mu m$: $u \propto 1/r^7$.

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

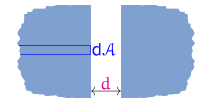Contributions from atom pairs are considered as independent (valid to $\sim$ 80–90 %)

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

Point–surface (half-space) first:

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

Then a column of area $d\mathcal{A}$:

$$E_{\text{vdW}} = -\frac{\pi\mathcal{N}^2 C}{12d^2} = -\frac{A}{12\pi d^2}$$
(per unit area)

$\mathcal{N} = N_A n/V$ = number density

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

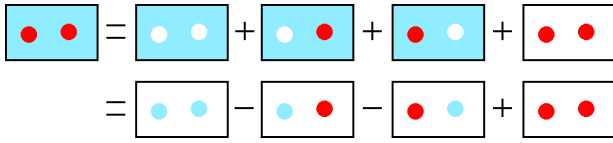Two R-balls d apart, first term of the expansion in $d \ll R$: $E_{\text{vdW}} = -\frac{AR}{12\pi d}$

DLVO: colloid in a medium

Cross interaction between both media,

$$u_{12}(r) = -\frac{C_{12}}{r^6}, \quad A_{12} = \pi^2 \mathcal{N}_1 \mathcal{N}_2 C_{12}$$

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

$$A_{1/2} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2$$

DLVO: case study

TiO_2 in a ⊙ of NaCl.
$A(TiO_2) = 19.5 \times 10^{-20}$ J, $A(H_2O) = 3.7 \times 10^{-20}$ J, $\Rightarrow A \approx 6.2 \times 10^{-20}$ J

- flat interface formulas
- energy expressed in k_BT per 100 nm^2
- figure: $\phi_0 = 0.15$ V, $c = 0.1$ mol dm^{-3}
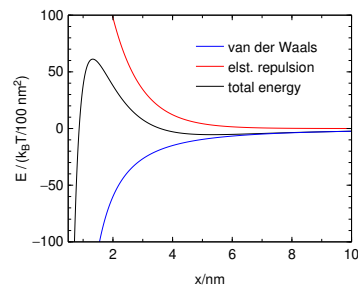
k_BT = thermal "quantum"

barrier 60 k_BT/100 nm^2
$e^{-E/k_BT} = e^{-60} = 1 \times 10^{-26}$

⇓

cubes of side 10 nm will be stable

Rule of the thumb:
stable for barrier > 25k_BT

$e^{-25} \approx 10^{-11}$

DLVO: case study – instability halftime

- Diffusivity of a spherical particle of diameter $2R = 10$ nm (Stokes formula):

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

- 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)