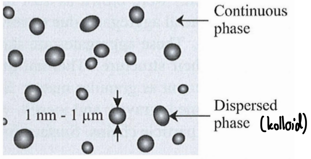
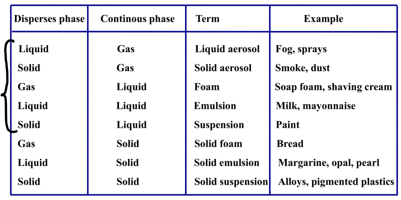
1. Introduksjon

Colloidal systems

- At least two components
- Uniform on macroscale, not microscale
- particles/drops/bubbles of one phase dispersed in another (matrix)
- Interphase: border between 2 phases
- 5 types: solid-liquid, solid-gas, solid-solid, liquid-gas, liquid-liquid
  - ↳ No gas-gas, gases aren't continous => get a solution
- At least one linear dimension from 1nm-1µm (diameter, length, interface)





This course

Disperses phase	Continous phase	Term	Example
Liquid	Gas	Liquid aerosol	Fog, sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Soap foam, shaving cream
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Suspension	Paint
Gas	Solid	Solid foam	Bread
Liquid	Solid	Solid emulsion	Margarine, opal, pearl
Solid	Solid	Solid suspension	Alloys, pigmented plastics

Distinctions between colloidal particles and larger particles

- Mobility due to thermal kinetic energy
- Negligible inertial effects, i.e. instant response to external fields.
- Negligible gravitational fields
- Long-ranged intermolecular interactions
- Thermodynamic propertres are size dependent
- Interaction with electromagnetic radiation.

Colloidal systems

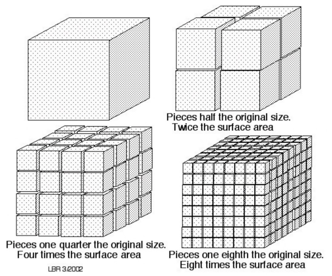
1. Colloidal dispersions
   - Lyophobic system. High surface free energy → Thermodynamically unstable, irreversible after separation.
2. Association colloids
   - self-assembled surfactants, micellar colloid. Thermodynamically stable, easily reversible
3. Macromolecutes (polymers/proteins)
   - True solutions, single lyophilic molecule. Thermodynamically stable, reversible

Surface

- Dividing line between two phases
- Chemically: A phase boundery with a thickness of molecular dimensions

Interface

- The dividing region between 2 phases.
- Colloidal dimensions lie between atomic and bulk dimensions
  - ↳ behaviour of colloidal systems largely determined by interfacial properties due to the high surface-to-volume-ratio.



Specific surface area (A_{sp})

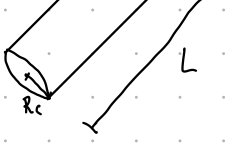
- Area of particles depend on amount of particles
  - ↳ Convenient with specific surface area: $A_{sp} = \frac{A_{tot}}{m_{tot}}$, A_{tot}: total surface area, m_{tot}: total particle mass

Special cases:

Sphere: $A_{sp} = \frac{3}{\rho R_s}$

Thin rod: $A_{sp} \approx \frac{2}{\rho R_c}$

Flat disk: $A_{sp} \approx \frac{2}{\rho L}$



Stability of colloidal systems

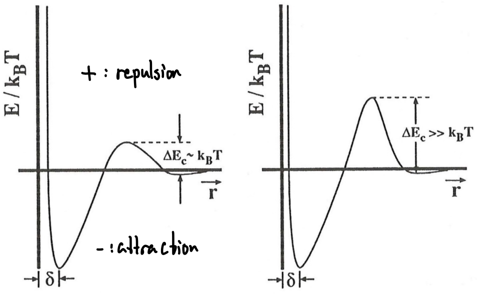
- Colloidal dispersions are thermodynamically or kinetically stable

1. Thermodynamic stability

   - Colloidal dispersions form spontaneously upon contact between solute and solvent.
   - Indefinite stability
   - True solutions - lyophilic (solvent loving) colloids
   - Examples: Macromolecules, micellar solutions

2. Kinetic stability

   - Does not spontaneously form colloid dispersion when phases are brought into contact
     ↳ requires energy added to the system.
   - Phase separation happens spontaneously
   - Lyophobic (solvent hating) colloids
   - Example : oil and water mixtures (emulsions)
   - Colloidal dispersions in technical systems are often kinetically stabilized.
     ↳ Kinetic stability have a broad time range (seconds to years)



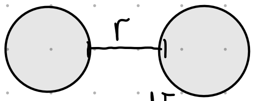
Kinetically *Unstable*

Kinetically *Stable*

Destabilisation of colloidal dispersions

- Destabilisation of kinetically stable dispersions can occur through coarsening processes:
  ↳ Spontaneous change into a smaller number of larger particles

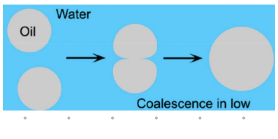
  · Coarsening processes:
    - Coalescence (koalesens)
    - aggregation (aggregering)
    - flocculation (flokkulering)



$$F = -\frac{dE}{dr}$$

Coalescence

- Drops/bubbles fuse to form a single, larger drop/bubble
  ↳ reduces total surface area
- As drop sizes increase, gravitational forces come into play, and the phases separate



Aggregation

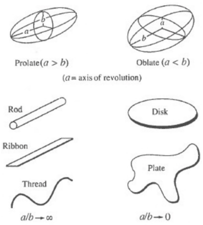
- Particles clump together, but does not fuse into a new particle
  ↳ total surface area is not significantly reduced.
- The process is often called coagulation (koagulering) when the destabilisation is caused by salts or charge neutralisation.

Flocculation

- Particles forms loose, easily reversible networks of particles (flocculates)
- Often referred to as secondary energy minimum.

Physical Chararistics of colloids

- Particle shape
  1. High degree of symmetry
     - sphere
     - approximation to spheres
  2. Low degree of symmetry
     - Ellipsoid of revolution, described by axial ratios
       - $a >> b$: prolate ellipsoid ~ cylinder (rod-shaped particles)
       - $a << b$: oblate ellipsoid ~ disc shape (clay platelets)



- Particle size
  - Monodisperse systems
    - Particles have one size
  - Polydisperse systems
    - Particle size varies in the system
    - Particle size distribution can vary

Polydispersity

- Particle size divided into classes
- Averages: "average" = $\sum_i$ (weighing factor)$_i$ (quantity being averaged)$_i$
- Number average: $\bar{d}_n = \sum_i \frac{n_i}{\sum_i n_i} \cdot d_i$
- Surface average: $\bar{d}_s = \sqrt{\frac{\sum_i n_i d_i^2}{\sum_i n_i}}$
- Volume average: $\bar{d}_v = \sqrt[3]{\frac{\sum n_i d_i^3}{\sum n_i}}$
- Monodisperse systems: $\bar{d}_n = \bar{d}_s = \bar{d}_v$
- Polydisperse systems: $\bar{d}_n < \bar{d}_s < \bar{d}_v$

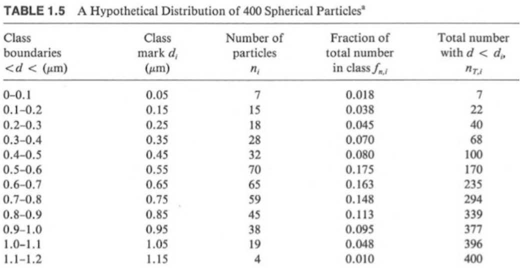


TABLE 1.5 A Hypothetical Distribution of 400 Spherical Particles[a]

Class boundaries $<d<$ (μm)	Class mark d_i (μm)	Number of particles n_i	Fraction of total number in class $f_{n,i}$	Total number with $d < d_i$, $n_{T,i}$
0–0.1	0.05	7	0.018	7
0.1–0.2	0.15	15	0.038	22
0.2–0.3	0.25	18	0.045	40
0.3–0.4	0.35	28	0.070	68
0.4–0.5	0.45	32	0.080	100
0.5–0.6	0.55	70	0.175	170
0.6–0.7	0.65	65	0.163	235
0.7–0.8	0.75	59	0.148	294
0.8–0.9	0.85	45	0.113	339
0.9–1.0	0.95	38	0.095	377
1.0–1.1	1.05	19	0.048	396
1.1–1.2	1.15	4	0.010	400

2. Intermolecular and interparticle forces

- All interfacial phenomenal (interfacial tension, wettebility...) are influenced by forces originating from molecular level interactions.
- Forces between molecules (vacuum)
- Scale-up to forces between colloidal particles (vacuum)
- Account for solvent

Intermolecular forces

- Total energy of a molecule:
  - Kinetic energy: $\propto k_B . T$
  - Potential energy: Depending on position and forces

Representation of intermolecular/interparticle forces:

$$F(r) = \underset{\substack{\nearrow \\ \text{attractive}}}{-} \frac{dV(r)}{dr} \leftarrow \text{potential energy-distance function}$$

- Different intermolecular forces
  - Coloumbic forces: 100 - 600 kJ/mol
  - Hydrogen bond: 10 - 40 kJ/mol
  - Van der Waals forces: < 1 kJ

Coulomb's law: $F = -\frac{q_1 q_2}{4\pi r^2 \varepsilon_r \varepsilon_0} = -\frac{dV}{dr}$

$$\Rightarrow V_{12} = \frac{q_1 q_2}{4\pi \varepsilon_r \varepsilon_0 r}$$

Van der Weals forces

(Formulas: p. 15 new book)

- Attractive forces, from induced or permanent dipoles in atoms/molecules
- Three types:
  1. Polar (Keesom) interactions: permenent dipole - permanent dipole

$$V_{12}^{p} = -\frac{1}{3}\left[\frac{\mu_1^2 \mu_2^2}{k_B T (4\pi\varepsilon_0)^2}\right] r^{-6}$$

  2. Debye interactions: permanent dipole - induced dipole

$$V_{12}^{ind} = -\left[\frac{\alpha_{01}\mu_2^2 + \alpha_{02}\mu_1^2}{(4\pi\varepsilon_0)^2}\right] r^{-6}$$

  3. Dispersion interactions: Induced dipole - induced dipole (always present)

$$V_{12}^{disp} = -\left[\frac{3\alpha_{01}\alpha_{02}}{2(4\pi\varepsilon_0)^2}\right]\left[\frac{I_1 I_2}{I_1 + I_2}\right] r^{-6}$$

- All molecules: dipole moment and polerizability, all three interactions <u>can</u> operate between a pair of molecules

$$V_{12} = V_{12}^{p} + V_{12}^{ind} + V_{12}^{disp} = -C_{12} r^{-6}$$

Fractional contribution: $f_D + f_K + f_L = 1$

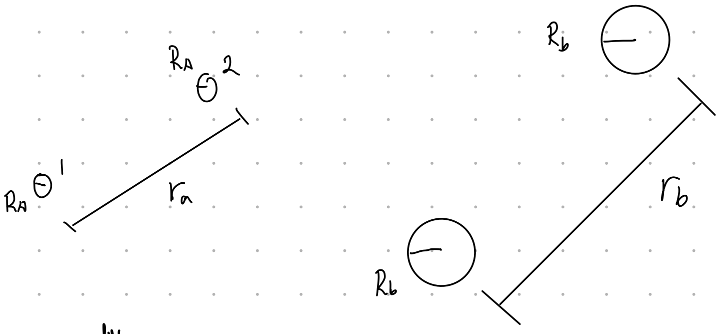
London interactions are the largest contribution for most molecules.

Van der Waals forces for colloids

- Considering 2 spherical particles of the same composition

a : Spheres of radius R_a

b: Spheres of radius R_b



$R_b = f R_a$, $f > 1$

$r_b = f r_a$

a: $V_{11}^{vdW}(a) = -C_{11} r^{-6}$

$\#\text{atoms}/cm^3 = \frac{\rho N_A}{M}$

In volume element: $\frac{\rho N_A}{M} \cdot dV_{1a}$

Number of pairwise interactions between 2 volume elements

$$= \underset{\substack{\uparrow \\ \text{Each pairwise interaction is counted twice}}}{\frac{1}{2}} \left(\frac{\rho N_A^2}{M}\right)^2 dV_{1a} \, dV_{2a}$$

$$dV_A(a) = \underbrace{-C_{11} r_a^{-6}}_{\substack{\text{Interaction} \\ \text{per pair}}} \cdot \underbrace{\left(\frac{1}{2}\left(\frac{\rho N_A}{M}\right) dV_{1a} \, dV_{2a}\right)}_{\text{Number of pairs}}$$

$$\Rightarrow V_A(a) = -\frac{1}{2}\left(\frac{\rho N_A}{2}\right)^2 \cdot C \cdot \iint r_a^{-6} \, dV_{1a} \, dV_{2a}$$

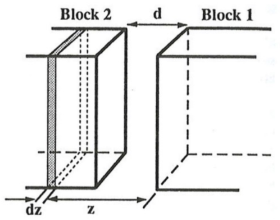
b: $V_A(b) = -\frac{1}{2}\left(\frac{\rho N_A}{M}\right)^2 C \iint r_b^{-6} \, dV_{1b} \, dV_{2b}$

$= -\frac{1}{2}\left(\frac{\rho N_A}{M}\right)^2 C \iint (\cancel{f} r_a)^{-6} \, d(\cancel{f^3} V_{1a}) \, d(\cancel{f^3} V_{2a})$

$= V_A(a)$

=> Identical => Scaling up depends on the geometries of the interacting bodies.

Attraction between blocks of material



$$V_A = -\left(\frac{\rho N_A}{M}\right)^2 \frac{C\pi}{12d^2}$$

Hamaker constant: $A = \left(\frac{\rho N_A \pi}{M}\right)^2 C$

$$V_A = -\frac{A}{12\pi d^2}$$

vdW for different geometries

- Spheres of equal radius R_s : $V_A = -\frac{AR_s}{12d}$, $R_s >> d$

d = distance between particles

- Spheres of radii $R_1 \neq R_2$: $V_A = -\frac{A}{6d} \cdot \frac{R_1 R_2}{R_1 + R_2}$ $R_1, R_2 >> d$
- Sphere and planar surface: $V_A = -\frac{AR_s}{6d}$

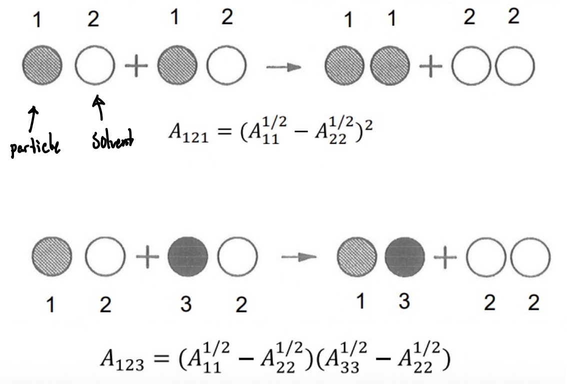
vdW forces characteristics

- Attractive in most cases
- Long ranged
- Strong at short distances

Effect of Solvent

Accounting for solvent => Hamaker constant A_{ijk}

If $A_{123} < 0$, no attraction between particles.



$$A_{121} = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

$$A_{123} = (A_{11}^{1/2} - A_{22}^{1/2})(A_{33}^{1/2} - A_{22}^{1/2})$$

3. Surface/Interfacial tension

Surface Tension, definitions

- As a force:
  - The force F required to keep the wire from moving "2D-system"

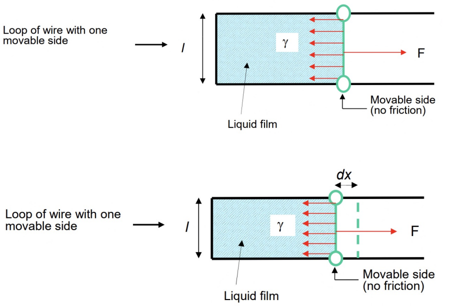
    Surface tension $\gamma = \frac{F}{2L}$ [mN/m]

- As gibbs free energy
  - Increase in G to create more surface

$$\Rightarrow dG = dW = F \cdot dx = \gamma(2L)\,dx = \gamma\, dA$$

$$\Rightarrow \gamma = \left(\frac{dG}{dA}\right)_{T,P} \Rightarrow \Delta G \approx \gamma \Delta A, \quad \Delta A = A_{final} - A_{initial}.$$

$\Delta G = 0 \Rightarrow$ Equilibrium
$\Delta G > 0 \Rightarrow$ Need work
$\Delta G < 0 \Rightarrow$ Sponteneous



Generally, increasing T decreases γ

Molecular origin of surface tension

Unbalance in the intermolecular forces at the surface

- surface is in a state of tension, due to there being less gas molecules than in the liquid, the molecules at the surface will be directed into the bulk of the liquid
- This means that the surface will spontaneously try to reduce its area.

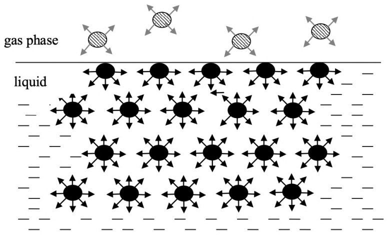
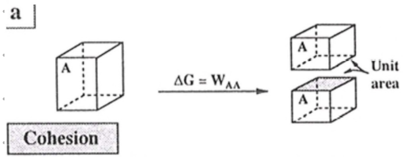


Fig. 3.1 Illustration of the intermolecular attractive forces (arrows) acting on molecules in the gas phase, the surface and the liquid phase, respectively.

Work of cohesion

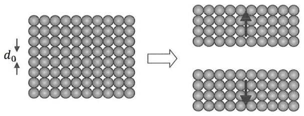
- Work done hypothetically to divide liquid element of pure fluid into 2 elements, generating 2 new lq/air interfaces

$$W_{AA} = W_C = \Delta G = 2\gamma_A$$



- Is a measurement of attraction between the molecules of the liquid
- Surface energy and the hamaker constant

d_0: Equilibrium spacing between molecules of the bulk material



Expression for attractive van der Weals forces between 2 planer surfaces: $V_A = -\frac{A}{12\pi d^2}$

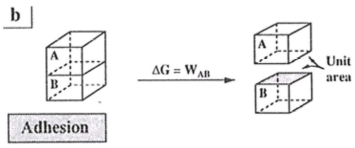
Pulling apart 2 elements results in $\Delta V_A = V_\infty - V_0 = 0 - \left(-\frac{A}{12\pi d_0^2}\right) = W_C = 2\gamma$

$$\Rightarrow \gamma = \frac{A}{24\pi d_0^2}$$

Work of adhesion

- Work done in hypothetical reversible process to separate two completely insoluable liquids
- 1 AB interface → 1A + 1B surface

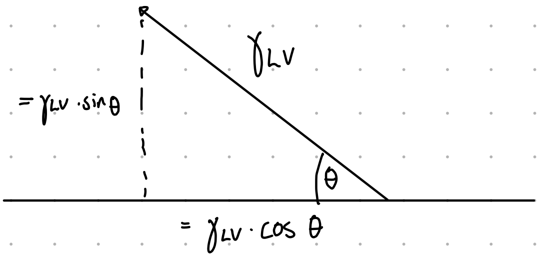
$$W_{AB} = W_{ab} = \Delta G = \underbrace{\gamma_A + \gamma_B}_{\text{Surface tensions}} - \underbrace{\gamma_{AB}}_{\text{Interfacial tensions}}$$

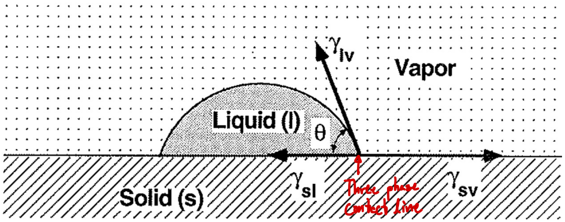


- Is a measurement of the attraction between two different phases

Contact angle/ wettability

- The angle at which the liquid-gas interface meets the solid-liquid interface is called the contact angle.

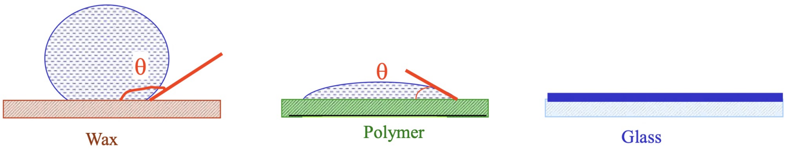




"Force balance" in horizontal direction: $\gamma_{SL} + \gamma_{LV} \cdot \cos\theta = \gamma_{SV}$, equilibrium condition $\sum \gamma_{\text{horizontal}} = 0$

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$ (Young's equation)

- How much a drop spreads on a surface is called wetting



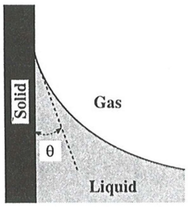
θ > 90°: Non-wetting (drop)

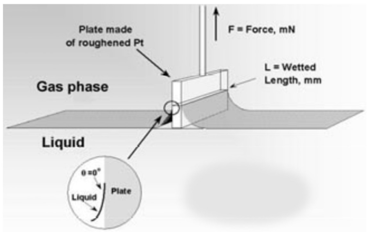
θ < 90°: Wetting (lense)

θ = 0: Complete wetting

Measuring surface tension/ Contact angle

- Wilhelmy plate method
  - A plate in liquid
  - We measure the force/pull on the plate





$$\gamma = \frac{F}{P \cdot \cos\theta}$$, where P = cross-sectional area length·width of the plate

Models for estimating interfacial tension

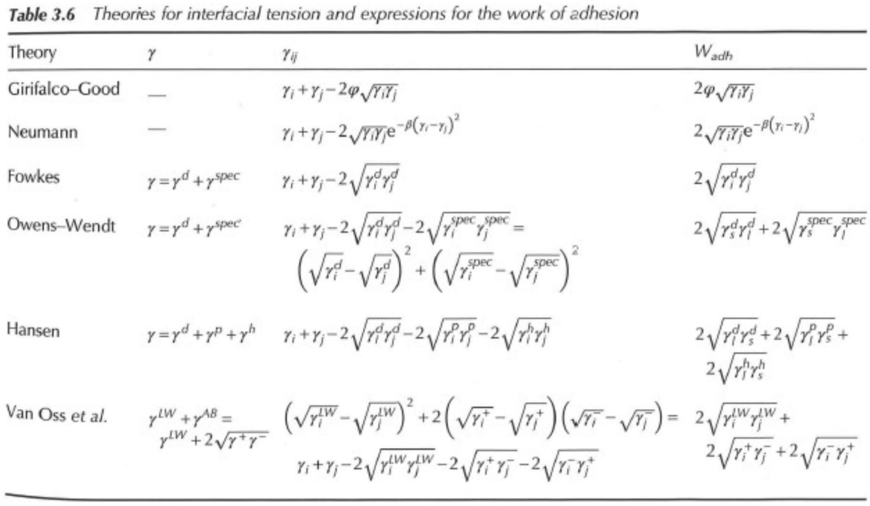


Table 3.6 Theories for interfacial tension and expressions for the work of adhesion

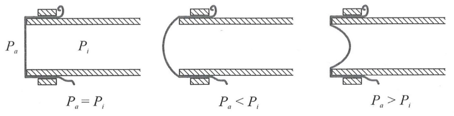
Theory	γ	γ_{ij}	W_{adh}
Girifalco–Good	—	$\gamma_i+\gamma_j-2\varphi\sqrt{\gamma_i\gamma_j}$	$2\varphi\sqrt{\gamma_i\gamma_j}$
Neumann	—	$\gamma_i+\gamma_j-2\sqrt{\gamma_i\gamma_j}e^{-\beta(\gamma_i-\gamma_j)^2}$	$2\sqrt{\gamma_i\gamma_j}e^{-\beta(\gamma_i-\gamma_j)^2}$
Fowkes	$\gamma=\gamma^d+\gamma^{spec}$	$\gamma_i+\gamma_j-2\sqrt{\gamma_i^d\gamma_j^d}$	$2\sqrt{\gamma_i^d\gamma_j^d}$
Owens–Wendt	$\gamma=\gamma^d+\gamma^{spec}$	$\gamma_i+\gamma_j-2\sqrt{\gamma_i^d\gamma_j^d}-2\sqrt{\gamma_i^{spec}\gamma_j^{spec}}=$ $\left(\sqrt{\gamma_i^d}-\sqrt{\gamma_j^d}\right)^2+\left(\sqrt{\gamma_i^{spec}}-\sqrt{\gamma_j^{spec}}\right)^2$	$2\sqrt{\gamma_s^d\gamma_l^d}+2\sqrt{\gamma_s^{spec}\gamma_l^{spec}}$
Hansen	$\gamma=\gamma^d+\gamma^p+\gamma^h$	$\gamma_i+\gamma_j-2\sqrt{\gamma_i^d\gamma_j^d}-2\sqrt{\gamma_i^p\gamma_j^p}-2\sqrt{\gamma_i^h\gamma_j^h}$	$2\sqrt{\gamma_l^d\gamma_s^d}+2\sqrt{\gamma_l^p\gamma_s^p}+$ $2\sqrt{\gamma_l^h\gamma_s^h}$
Van Oss et al.	$\gamma^{LW}+\gamma^{AB}=$ $\gamma^{LW}+2\sqrt{\gamma^+\gamma^-}$	$\left(\sqrt{\gamma_i^{LW}}-\sqrt{\gamma_j^{LW}}\right)^2+2\left(\sqrt{\gamma_i^+}-\sqrt{\gamma_j^+}\right)\left(\sqrt{\gamma_i^-}-\sqrt{\gamma_j^-}\right)=$ $\gamma_i+\gamma_j-2\sqrt{\gamma_i^{LW}\gamma_j^{LW}}-2\sqrt{\gamma_i^+\gamma_j^-}-2\sqrt{\gamma_i^-\gamma_j^+}$	$2\sqrt{\gamma_i^{LW}\gamma_j^{LW}}+$ $2\sqrt{\gamma_i^+\gamma_j^-}+2\sqrt{\gamma_i^-\gamma_j^+}$

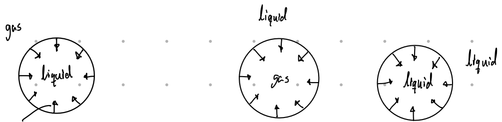
4. Fundamental equations in colloid and surface science

Curved interfaces

- For the dispersed phase in colloidal systems, drops/bubbles/particles, it is common to have a curved interface.

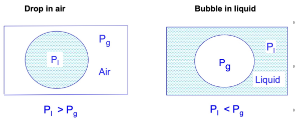
- There is always a pressure difference across curved interfaces.





Surface tension => $P_{bubble} > P_{gas}$

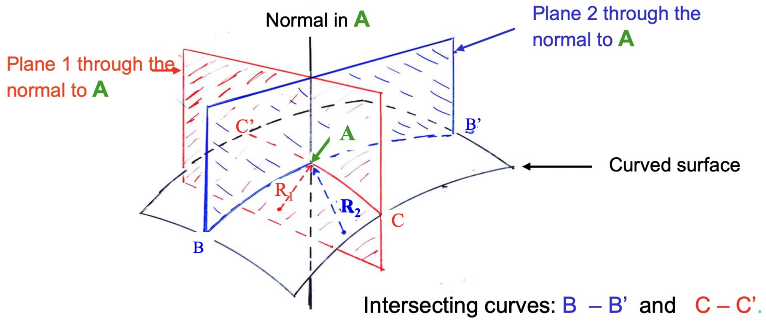
- The largest pressure is always on the concave side of the interface



- Radii of curvature

  - Measure of how much the curvature of a given object deviates from a flat surface.

  - Any point on a curved surface can be inscribed



Radii of curvature in point A: R_1 (for C-C') and R_2 (for B-B')

- To separate between cases of liquid bubbles in gas and gas bubbles in liquid, we make 2 definitions.

  1. We define the pressure difference as $\Delta P = P_{liquid} - P_{gas}$

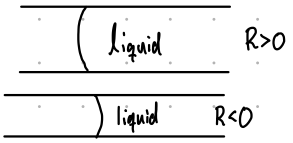
     ⓛ^{g}, $P_l > P_g \Rightarrow \Delta P > 0$

     ⓖ^{l}, $P_g > P_l \Rightarrow \Delta P < 0$

  2. By convention, the radius of curvature is measured in the liquid

     => R is positive for a liquid drop, and negative for a gas bubble

     - When the interface is curved toward the liquid, R is positive:
     - When the interface is curved away from the liquid, R is negative:



Young-Laplace equation

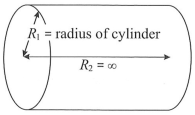
- $\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ where R_1 and R_2 are radii of curvature

- ΔP depends on surface tension and curvature (particle shape)

Special cases:

Spherical surface: $R_1 = R_2 = R_s \Rightarrow \Delta P = \frac{2\gamma}{R_s}$

Cylindrical surface:



$R_2 \to \infty$

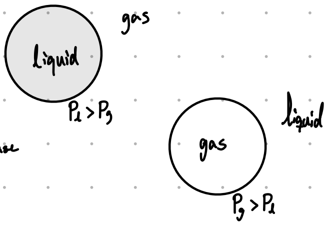
$\Rightarrow \Delta P = \frac{\gamma}{R_1}$

Planar surface:

- No curvature $\Rightarrow R_1 = R_2 \to \infty$, $\Delta P = 0$

Kelvin equation

- Relates phase equilibria to curved interfaces
- $\Delta P = 0$ across a planar surface $\Rightarrow P^{sat}$
- Curved interfaces: equilibrum vapour pressure change
  - ↳ drop, vapor pressure higher than flat surface. $P_l > P_g$. Molecules on the surface/interface more easily goes into gas phase
  - ↳ bubble, vapor pressure lower than flat surface. $P_g > P_l$. Molecules on the surface/interface more easily goes into liquid phase



- The quantitative change in vapor pressure is described by the Kelvin equation

$$RT \ln\left(\frac{P}{P^{sat}}\right) = \gamma V^L \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

or $$\ln\left(\frac{P}{P^{sat}}\right) = \frac{V^L}{RT} \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{M}{\rho_L RT} \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

P: Vapor pressure of curved phase
P^{sat}: Vapor pressure of flat interface
V^L: Molar volume of liquid

- Spherical droplet

$$RT \ln\left(\frac{P}{P^{sat}}\right) = \frac{2\gamma V^L}{R_S} = \frac{2M\gamma}{\rho R_S} \Rightarrow P = P^{sat} \cdot \exp\left(\frac{2M\gamma}{\rho R_S}\right)$$

- Spherical bubble in liquid:

$$RT \ln\left(\frac{P}{P^{sat}}\right) = -\frac{2\gamma V^L}{R_S}$$

Curvature effects: *relatively unimportant in μm range, but significant in nm range*

R_S(m)	P/P^{sat} (water droplets, 20°C)	P/P^{sat} (bubbles in water, 20°C)
10^{-6}	1,0011	0,9989
10^{-7}	1,0184	09893
10^{-8}	1,1139	0,8976
10^{-9}	2,94	0,339

Ostwald ripening

- Destabilisation mechanism

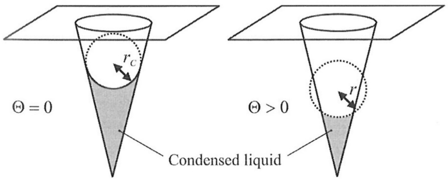
(- Happens to liquids) Dispersed phase

- Small droplets, bubbles and particles evaporates/dissolves, and condenses on the larger drops
- Can be viewed as diffusion of substance from smaller drops into larger drops
- The process continues until we have a single "large drop", meaning a complete phase separation
- The driving force is the difference in partial molar free energy between droplets of different size.
- Bigger drops grow at the expense of smaller ones
- Kelvin equation for solubility. Relates solubility of flat surface and spherical surface: $\ln\left(\frac{S(r)}{S(r \to \infty)}\right) = \frac{V_S}{RT} \cdot \frac{2\gamma}{R_S}$

Capillary condensation (Kelvin equation)

- Condensation of vapor inside pores will occur at lower vapor pressure than P^{sat}, $P_{vapor} < P^{sat}$.
- Normally condensation happens when $P > P^{sat}$, f.eks over flat surface:

$P > P^{sat} \Rightarrow$ Condensation



$$RT \ln\left(\frac{P}{P^{sat}}\right) = -\frac{2\gamma V^l}{r_C}$$

- The radius at which the system reach equilibrium is denoted r_c. Then the meniscous is constant.

- Two cases:

1. Complete wetting $\theta = 0$

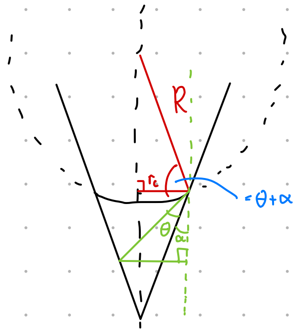
   $-R = r_c$

   $$RT \ln\left(\frac{P}{P^{sat}}\right) = -\frac{2\gamma V_m^l}{r_c}$$

2. Partial wetting (by condensed liquid on surface) $0 < \theta < 90°$

   $\Rightarrow$ The interface is shaped as part of a hemisphere

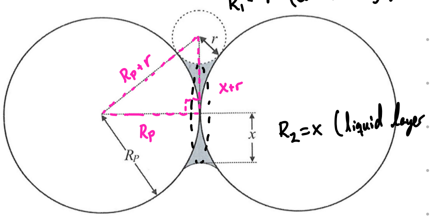
   $$R = \frac{r_c}{\cos(\theta + \alpha)} \underset{\substack{\uparrow \\ \text{for cylinder}}}{=} \frac{r_c}{\cos\theta}$$



Capillary force

- Consequence of capillary condensations

$R_1 = -r$ (curved away from liquid)



$R_2 = x$ (liquid layer is "inside"

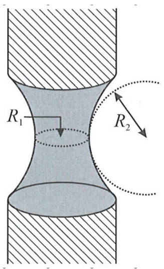
$$\Delta P = \Delta P_l - \Delta P_g = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$
$$= \gamma\left(-\frac{1}{r} + \frac{1}{x}\right)$$

Assuming $x >> r$

$$\Delta P = -\frac{\gamma}{r}$$

$$P_l = P_g - \frac{\gamma}{r}$$

Analogue to:
but $R_2 < R_1$

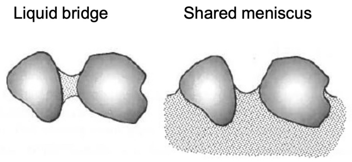


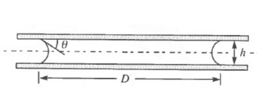
Capillary force: $F_\gamma = -A \cdot \Delta P = -\pi x^2 \cdot \left(-\frac{\gamma}{r}\right) \underset{\uparrow}{=} 2\pi\gamma R_p$

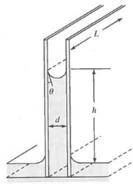
$(R_p + r)^2 = R_p^2 + (x + r)^2$, $x >> r$

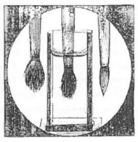
$x^2 = R_p^2 - 2R_pr + r^2 - R_p^2 = 2\pi R_pr$

Capillary interactions





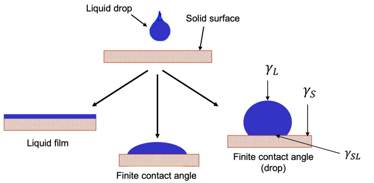




Young equation

- Relates surface tension and contact angle
- Used for liquid on solid surfaces
- Solid surfaces are more complex than liquids: Roughness, Chemical heterogenity, Impurities

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

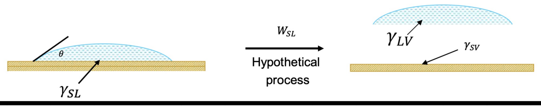


Equilibrium: condition with largest reduction of surface free energy.

$$dG_{tot} = \sum^{i} \gamma_i \, dA_i = \gamma_L dA_L + \gamma_S dA_S + \gamma_{SL} dA_{SL}$$

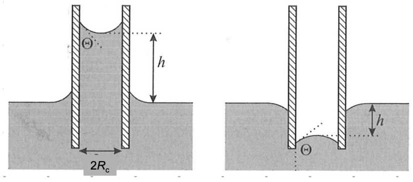
- For work of adhesion, we imagine a hypothetical process where we separate the liquid from the surface

Then, $W_{SL} = \gamma_{LV}(1+\cos\theta)$ (Young-Dupre equation)



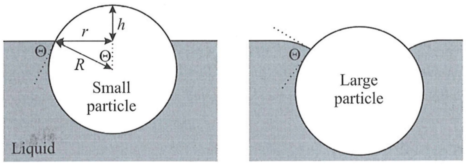
Wetting geometries

- Capillary rise



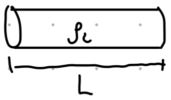
$$h = \frac{2\gamma_{LV}\cos\theta}{R_c \cdot g \cdot \rho}$$

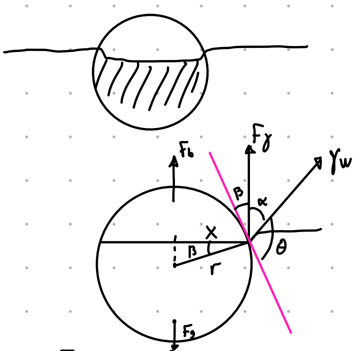
- Particles at liquid-gas or liquid-liquid interfaces



Can use Young's equation

- Cylinder





$$F_\gamma = \gamma_w \cos(180-\theta-\beta)(4r\cos\beta + 2L)$$

F_b: bouyancy force, $= \rho_w (A \cdot L) \cdot g$

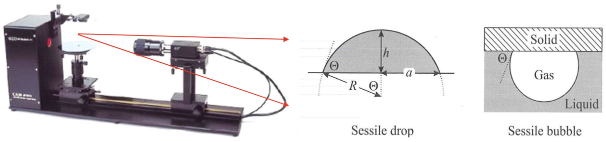
F_g: gravity, $mg = \pi \cdot r \cdot L \cdot \rho_c \cdot g$

cross-sectional area below water

$$A = \left[\pi \cdot \frac{90+\beta}{180} + \sin\beta\cos\beta\right] r^2$$

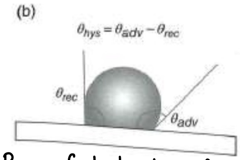
Measuring contact angle

Sessile drop/bubble method



Hysterisis

- Contact angle is different at the different contact points (tilted plate)



θ_{adv} : advancing contact angle

θ_{rec} : receding contact angle

- Reasons for hysteresis: surface roughness, not at equllibrium, surface contamination, surface undergo changes during contact with liquid, spreading coffecient may be low for low contact anghes

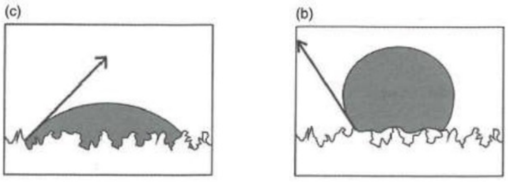
Surface roughness

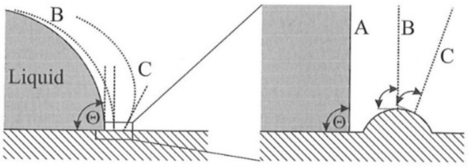
- Wenzel equation

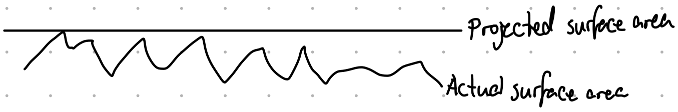
$$\cos \theta_{app} = R_{rough} \cos \theta$$

$$\hookrightarrow \text{where } R_{rough} = \frac{\text{Actual surface area}}{\text{projected/observed surface area}} \geq 1$$

$= 1$: Ideal surface

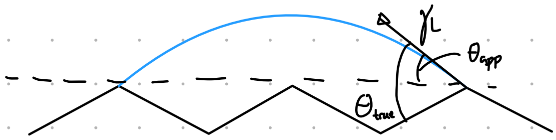






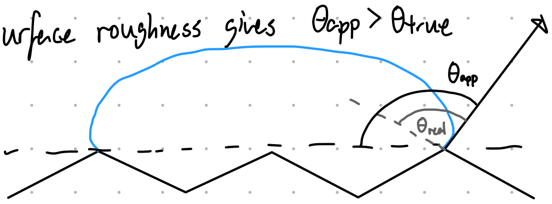
Partial wetting: $\theta < 90°C$

Surface roughness will give $\theta_{app} < \theta_{true}$



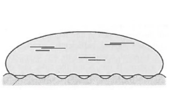
For $\theta > 90°$

Surface roughness gives $\theta_{app} > \theta_{true}$



Lotus effect

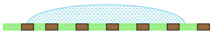
- Due to the surface roughness, the surface becomes hydrophobic, and repels water
- Usually, contact angle > 150° and contact angle hysteresis < 5°

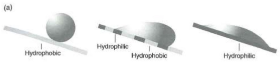


Chemical heterogenity

- The surface consist of areas or spots with different chemical compositions
- Cassie baxter equation

$$\cos \theta_{app} = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

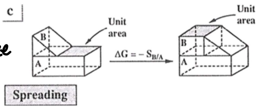




Spreading

- Spreading of B on A:

  $\hookrightarrow$ 1 A → 1 B + 1 AB surface



- We get that for the process, $\Delta G_{B/A} = \gamma_{AB} + \gamma_B - \gamma_A$
- We define the spreading coefficent as: $S_{B/A} = -\Delta G_{B/A} = \gamma_A - \gamma_B - \gamma_{AB}$
- If $S < 0$: The process is not spontaneous, and we get a finite contact angle
- If $S > 0$: The process is spontaneous, and we get complete spreading (no contact angle)

- Liquid spreading on liquid:

$$S_{O/W} = \gamma_{WA} - \gamma_{OA} - \gamma_{OW} = W_{adhesion,OW} - W_{cohesion,O}$$

On figure, if $S_{W/G} > S_{H/G}$, then water will expel the hexane

if $S_{W/G} < S_{H/G}$, then hexane will expel the water

Gibbs adsorption equation

- Relates interfacial tension and surface excess solute, or number of moles and chemical potential of components at the interface.

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln c}\right)_T \leftarrow \text{for ionic surfactants or dissociating ones, use } \frac{1}{2RT} \text{ instead}$$

- Works for Gibbs (soluble) monolayers
  - ↳ Adsorption onto liquid-liquid interfaces (Gibbs adsorption isotherm)
  - ↳ Adsorption onto solid-liquid interface (Langmuir adsorption isotherm)
- Langmuir (insoluble) monolayers
- 2-component system:

1: Solvent

2: Solute

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2$$

$\Gamma_i = \frac{n_i^\sigma}{A}$ - surface excess of component i.

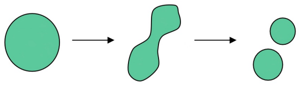
We define ideal interface so that $\Gamma_1 = 0 \Rightarrow d\gamma = -\Gamma_2 d\mu_2$

$$\frac{d\ln c}{dc} = \frac{1}{c} \Rightarrow d\ln c = \frac{dc}{c}$$

$$\Rightarrow \Gamma_2 = -\frac{c}{RT}\left(\frac{d\gamma}{dc}\right)$$

- Applications of Gibbs isotherm:
  - Determine surface excess from surface tension and concentration measurements
  - Calculate molecular area from surface excess
  - Calculate molecular weights from surface pressure

- Plotting γ against $\ln c$ gives Γ_2
- If $\left(\frac{d\gamma}{d\ln c}\right) < 0 \Rightarrow \Gamma_2$ is positive, adsorption of solute from surface
- If $\left(\frac{d\gamma}{d\ln c}\right) > 0 \Rightarrow \Gamma_2$ is negative, depletion of solute from surface



$$\Delta p = \frac{2\gamma}{R_s}$$

Partial molar quantities

- Describes contribution of one component to total property
- Ex volume

$$V_i = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_{j\neq i}}$$

n_i: amount of component i

$n_{j\neq i}$: amounts of other components than i kept constant.

- 2 comp system

$$dV = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_j} dn_i + \left(\frac{\partial V}{\partial n_j}\right)_{p,T,n_i} dn_j = V_i dn_i + V_j dn_j$$

- Chemical potential / partial molar Gibbs free energy

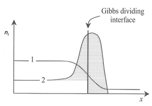
$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}}$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \sum\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j} dn_i$$

$$\text{Const } T, p \Rightarrow dG = \sum\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j} dn_i$$

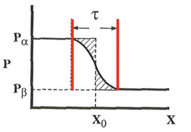
Interfaces

- All extensive parameters of a system is affected by an interface
- Ideal interface, $V_s = 0$, no thickness of interface. In reality, there is a gradient

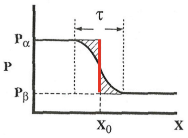


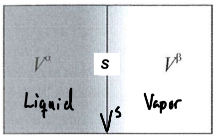
Define ideal interface so that $\Gamma_1 = 0$:

Real situation:



Ideal situation:





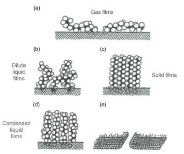
Gibbs ideal interface

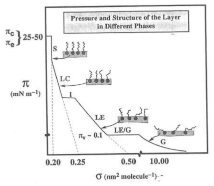
Ideal: $V^s = 0$

$\Rightarrow V = V^\alpha + V^\beta$

Monolayers + films

- Langmuir monolayers
  - Thin film that is one molecule in width
  - substances on liquid substrates





- Langmuir-Blodgette films
  - Several monolayers stacked into a multilayered film

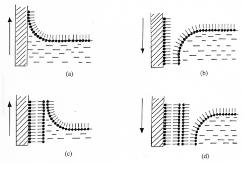
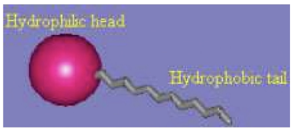


Figure 5.12 Producing a Langmuir-Blodgett film by repeated dipping.

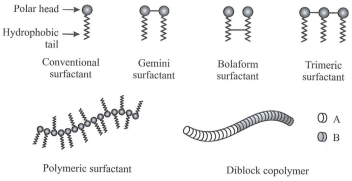
5. Surfactants and self assembly

Surfactants

- Surfactants (amphiphiles, tensids, emulgator) are surface active agents, that adsorb on liquid-air and oil-water interfaces.
- Decrease surface and interfacial tension and the corresponding works of adhesion
- Consists of a hydrophilic head, and a hydrophobic tail (usually a hydrocarbon chain)



- Classified according to the head group:
  - Anionic - Negatively charged head
  - Cationic - Positively charged head
  - Non-ionic - No charge on the head
  - Zwitterionic - The head has different areas with different charges
- There are 3 main types of tail groups:
  - Alkyl chain (single, double, triple): $CH_3(CH_2)_n$ -
  - Aromatic moieties within the chain $CH_3(CH_2)_n$ - Ph -
  - Flouronated hydrocarbon chain: $CF_3(CF_2)_n$ -



CMC

- Critical micelle concentration
- The concentration at which micelles start to form
- Adding surfactants to a solution happens in this order:
  1. Pure interface
  2. As surfactants is added the interfacial tension decreases
  3. Interface is covered by surfactants - interfacial tension does not decrease anymore. We are at CMC
  4. Micelle formation - aggregation of surfactants

Influenced by:

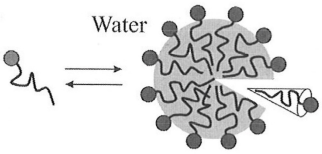
- Hydrophobic chain length
- Type of head group (ionic or nonionic)
- Electrolytes (ionic surfactants)
- Temperature (nonionic surfactants)
- Organic additives (solubilisation)

- During micelle formation, the following equilibrium establishes in the solution:

Monomers (single molecules) in solution ⇌ micelles (aggregates of surfactants)

$$nS \rightleftharpoons S_n$$

n - number of surfactants
S - surfactant monomer
S_n - micelle with n degree of aggregation



At CMC, many properties in the solution changes, while som become constant even while adding more surfactant

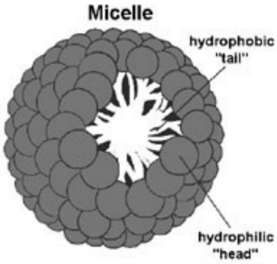
- Turbidity, solubilization, detergency and conductivity increase after CMC
- Surface tension and osmotic pressure becomes a constant at CMC

Krafft point

- The minimum temperature required for the creation of micelles
- Can be viewed as the melting point of the hydrocarbon chain of the surfactant, as micelles are liquid-like

Micelles

- In a water-solution, the tails are the core, and the heads are the interface towards the water
- Highly dynamic systems
  - Surfactant exchange between micelles: 10 μs
  - Formation and disintegration of micelles: ms



Micellization

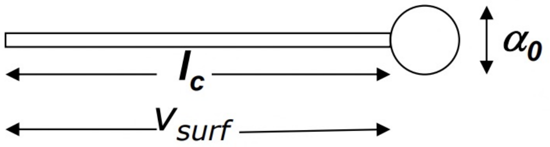
- Formation of micelles
- Driven by an increase in entropy
- Is a balance between opposing forces:
  - a) Attractive forces between hydrocarbon chains
    - tend to decrease effective headgroup area
  - b) Repulsive forces between neighbouring head groups
    - electrostatic repulsion (ionic surfactants)
    - steric repulsion (often, hydrophilic groups are hydrated)
    - Tend to increase effective headgroup area

} effective headgroup area: balance between a) and b)

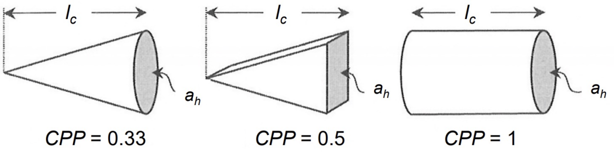
CPP

- Critical packing parameter
- Relates the structure of surfactant to the micelle structure

$$CPP = \frac{V_{surf}}{\alpha_0 l_c}$$



α_0 : Optimal head group area
l_c : Chain length
V_{surf} : volume of the chain



More structure on p. 99+100 of the new book + p.18 + 19 on pptx. 05

- The number of surfactants in a micelle is called "aggregation number"

$$N_{agg} = \frac{V_{micelle}}{V_{surfactant}} = \frac{A_{micelle}}{A_{surfactant}}$$

V_{mic} and A_{mic} can be found from geometric relations once the structure is known. For sphere $r \approx l_c$

- We can estimate l_c and V_{surf} from:

$$l_c = 0{,}154 + 0{,}1265n$$
$$V_{surf} = (0{,}0274 + 0{,}0269n)m$$

Where n is the number of carbons in the carbon chain, and m is the number of chains in the tail group
The values are in nm (10^{-9} m)

- The CPP and the structure can be influenced by many parameters
  Ex. adding electrolyte/ions to ionic surfactant.
    - ↳ The (counter-) ions are attracted to the head groups, and moves between the head groups
    - ↳ This causes screening/shielding of the repulsive forces between the head groups
    - ↳ The head groups can pack closer
      - ⇒ α_0 decreases
      - ⇒ CPP increases
    - ↳ We move toward inverted structures
- Other parameters that influences the micelle structure

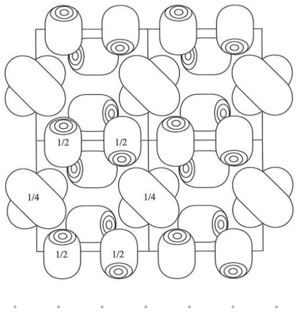
a_h can be changed by:
- electrolyte concentration (ionic surfactants)
- pH - degree of dissociation of head groups (ionic surfactants)
- temperature (nonionic surfactants)

V_c and l_c can be changed by:
- Increasing chain length
- Increasing number of chains
- Introduce branching in chains
- Unsaturated hydrocarbon chains

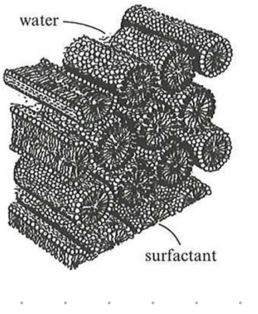
Liquid crystalline phases

- In very concentrated solutions of surfactants, the micelles may go from being small aggregates to arrange themselves in "infinetely" large micellar structures called "liquid crystalline phases"

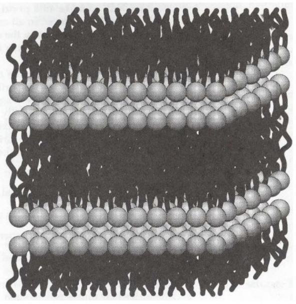
Micellar cubic phase (I_1):
Regular packing of micelles



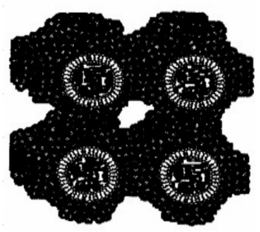
Hexagonal Phase (E):
Infinitely long cylindrical micelles arranged in a hexagonal pattern



Lamellar Phase (D):
Bilayers of surfactants alternating with water layers



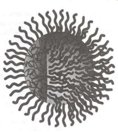
Bicontinuous phases (I_1, V_1):
Several different structures forming 3-D connected structures
- Connecting rod-like/branched micelles
- Bilayer structures



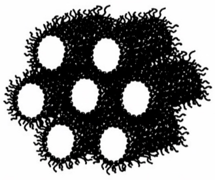
Reversed phases

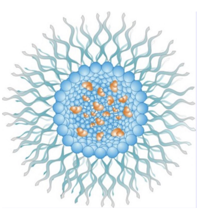
- Has the head groups pointing inwards, and the tailgroups outwards
- Happens in oil solution, where water is enclosed inside the micelles

Water droplets (L_2)



Hexagonally packed water cylinders (F)

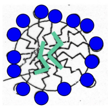




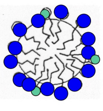
Reverse micelle

Solubization

- Above CMC, non-polar or semi-polar compounds can dissolve extensively in surfactant solution
- The compound is dissolved in the micelle
- The polarity of the solubilisate (what is dissolved) determines its location in the micelles
- There is an upper limit to the amount of compound that can dissolve into micelle solutions



Hydrocarbons



Polar compounds (Alcohol)

Detergency

- Removal of oily drop/dirt from a surface
- Spreading can be shown like so:

Wetting $\theta<90°$

Non-polar textiles (poly ester)

- Less efficient

Non-wetting $\theta>90°$

Polar textiles (cotton)

- Effective

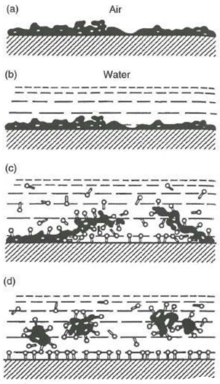
- The removal in terms of adhesion:

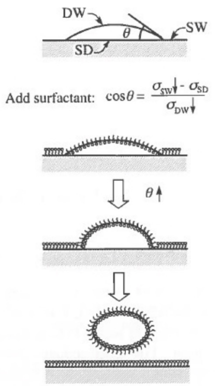
$$\Delta G = W_{ad} = \gamma_{ow} + \gamma_{sw} - \gamma_{os}$$

S: surface
W: water
O: oil

↳ the process is sponteneous if $\Delta G<0$

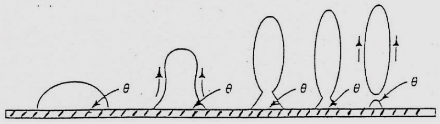
=> Want to decrease γ_{ow} or γ_{sw}





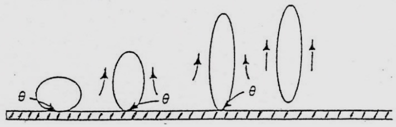
- In terms of θ

On the figures, the arrows indicate the reeling mechanism caused by water streams during washing



$\theta<90°$

Leaves residue



$\theta>90°$

Completely removes the oil

The contact angle is given by $\cos\theta = \frac{\gamma_{sw} - \gamma_{os}}{\gamma_{ow}}$

Decreasing γ_{sw} so that it is lower than γ_{os}

=> $\cos\theta < 0$ => $\theta > 90$

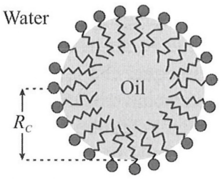
- In both cases we want to decrease γ_{sw} and γ_{ow} => Add surfactant. Decreases γ_{ow} an γ_{sw} by adsorbing on surface/interface.
  - ↳ The adsorbed surfactants on the surface prevents redisposition.

This is an entirely different mechanism

- In order to prevent redisposition onto surface, we want the oil/dirt to solubilize into micelles.
  - ↳ Having micelles in the solution allows for diffusion of oil from the surface into micelles in the surrounding water phase.
  - ↳ This also lead to removal, and happens independently of the surface properties
  - ↳ This is a thermodynamically spontaneous process, and forms microemulsions.

Microemulsions

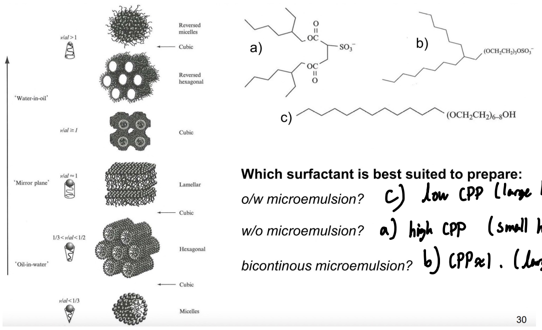
- Forms in 3 component systems (oil, water, surfactant)
- Often, we also have a 4th component as well (co-surfactant)
- General properties
  - Thermodynamically stable, properties does not change with time, respond to changes in temperature and composition
  - Volume fraction of surfactant is often significant
  - Drop sizes: 10 - 100 nm range
  - Transparent



- Can be considered as swollen micelles - similar curvature:
  - Highly curved towards oil - o/w microemulsion (micelle, picture ↗)
  - Highly curved towards water - w/o microemulsion (inverted micelle)
  - Zero mean curvature - bicontinous microemulsions:

← Interdispersed oil and water nanodomains separated by flexible monolayers of surfactants.

- The packing parameter can be useful for microemulsions as well



Which surfactant is best suited to prepare:

o/w microemulsion? c) low CPP (large headgroup, small Vc)

w/o microemulsion? a) high CPP (small headgroup, high Vc)

bicontinous microemulsion? b) CPP≈1. (large headgroup and Vc)

Self-assembly

See pptx for nanoparticles and synthesis of materials.

- By looking at phase diagrams (or microscope), we can decide structures of micelles.
- They self-assemble into the most stable structure spontaneously.
- Above CMC, surfactants interact and create structures by themselves. Monomers ⇒ Micelles

---

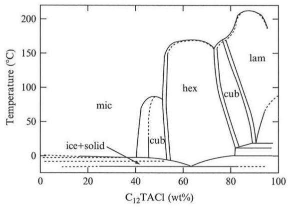
Phase diagrams

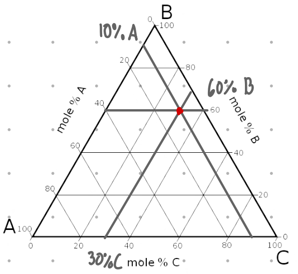
Determined experimentally and contains information about:

- How many phases are formed
- Which phases are formed
- Composition of the phases

Binary phase diagram :

- Micellar solution up to high surfactant concentration (~40 wt%)
- Cubic phase of globular micelles
- Packing restrictions ⇒ deformation of micelles and transition into hexagonally phase
- Second cubic phase, bicontinuous
- Lamellar phase
- Solid hydrated surfactant

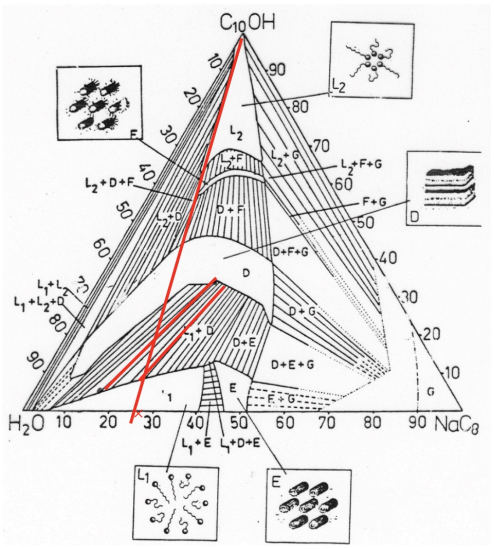




● = 10% A, 60% B, 30% C

Ternary phase diagrams

Ternary phase diagrams are"maps" of phase behaviour of 3 component systems



6. Adsorption in colloid and surface science

Applications

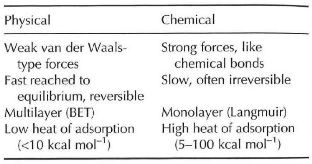
- Stabilization of colloidal systems (i.e. polymers adsorbed on particles causing steric hindrance)
- Cleaning
- Heterogenous catalysis
- Surface modification

⋮

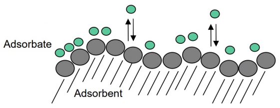
- Amount of adsorbed gas as function of pressure can be used to determine
  - Specific surface area of solid, A_{sp}
  - Pore size & volume of porous solids

Adsorption of gases on solids

- Chemisorption: formation of chemical bonds, irreversible
- Physisorption: Van der Waals interactions, reversible
- Adsorbent: surface where adsorptions occur
- Adsorbate: specie adsorbed at the adsorbent



Physical	Chemical
Weak van der Waals-type forces	Strong forces, like chemical bonds
Fast reached to equilibrium, reversible	Slow, often irreversible
Multilayer (BET)	Monolayer (Langmuir)
Low heat of adsorption (<10 kcal mol^{-1})	High heat of adsorption ($5–100$ kcal mol^{-1})



- Langmuir adsorption isotherm

$$\Theta = \frac{V}{V_m} = \frac{Bp}{1+P}$$

Θ : Fraction of molecules at the interface

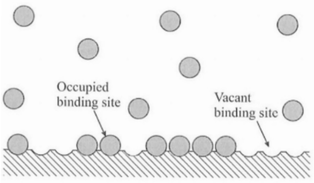
V : Volume of the adsorbed layer

V_m: Volume of the monolayer

B: Affinity parameter

P : Pressure of the gas

Assumptions
- Homogenous surface
- Only monolayer adsorption
- No solute-solvent or solute-solute interactions



Linearizing gives

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{BV_m}$$

Allowing V_m and B to be determined from linear regression

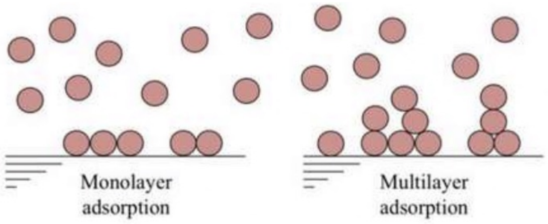
$$\text{Slope} = \frac{1}{V_m}, \quad \text{Intercept} = \frac{1}{BV_m}$$

- Θ is defined as fraction of filled sites

If $\Theta = 1$ ⇒ Monolayer coverage

$\Theta < 1$ ⇒ Sub-monolayer coverage

$\Theta > 1$ ⇒ Multilayer coverage



Monolayer adsorption   Multilayer adsorption

- BET isotherm

$$\Theta = \frac{V}{V_m} = \frac{C\,(P/P_0)}{(1-P/P_0)[1+(C-P/P_0)P/P_0]}$$

- V: Total volume of adsorbed gas
- V_m: Volume of adsorbed gas at monolayer
- C: Temperature dependent constant
- P_0: Normal vapor pressure of the liquid used in measurements (typically nitrogen 77 K)
- P : Pressure in system

Linearized BET equation:

$$\boxed{\frac{P}{V(P_0-P)}} = \frac{1}{CV_m} + \frac{C-1}{CV_m}\boxed{\left(\frac{P}{P_0}\right)}$$

Experimental data

$$\text{Slope} = \frac{C-1}{CV_m} \qquad \text{Intercept} = \frac{1}{CV_m}$$

- Determine A_{sp} (specific surface area of solid)

After finding volume of adsorbed gas that would saturate the surface if adsorption were limited to a monolayer, V_m, we can determine A_{sp}:

$$A_{sp} = \frac{V_m \cdot N_A}{V_g} A_0$$

N_A : Avogadros number - $6{,}022 \cdot 10^{23}$ mol^{-1}
V_g : Molar gas volume at STP - 22, 414 L/mol
A_0 : Area occupied by one gas molecule, usually N_2 at 77K - $16{,}2 \cdot 10^{-20}$ m^2

Adsorption from solution

- Lanmuir adsorption isotherm
  - Similar to the gas case, but some differences
  - Uses the exact same assumptions

$$\Theta = \frac{\Gamma}{\Gamma_{max}} = \frac{kC}{1+kC}$$

Linearized form

$$\frac{C}{\Gamma} = \frac{C}{\Gamma_{max}} + \frac{1}{k\Gamma_{max}}, \quad A_{sp} = \Gamma_{max} N_A A_0$$

We also use that

$$\Gamma = \frac{n^{sat}}{A_{tot}} = \frac{n^{sat}}{m_{tot} \cdot A_{sp}}$$

$$\Gamma_{max} = \left(\frac{n^{sat}}{A_{tot}}\right)_{max} = \frac{1}{N_A \cdot A_0}$$

- The solvent makes adsorption from solution more complex than for gases

Measured indirectly:

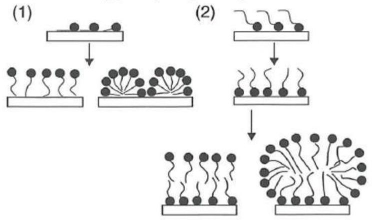
A solution is put in contact with a solid surface.
The solute adsorb at the solid-liquid interface.
The concentration of solute in the bulk solution will be reduced.

The change in concentration of solute in the bulk solution is determined (spectroscopic methods).
When specific surface area of the solid is known, the amount of solute adsorbed per unit area solid can be calculated (surface excess).

Adsorption of surfactants

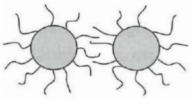
- Depends on surface properties and interactions between surfactants
- Non-polar surfaces: adsorption is related to CCP
- Polar surfaces: adsorption requires interactions between head group and surface

Surfactants adsorb (1) with hydrocarbon part on non-polar surfaces
(2) with polar part on polar surfaces



Adsorption of polymers

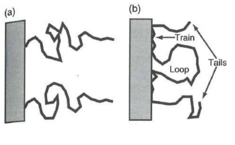
- Important in many applications
  - Stabilisation of colloidal dispersions - steric stabilisation (peint, food, cosmetics, pharmaceuticals,...)



↳ Best if
- Thick and dense layers
- Extended conformations - good solvent
- Strong adsorption - poor solvent
- Complete particle coverage

  - Promote destabilisation - flocculation (water treatment, mineral processing,...)

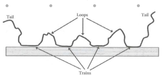
  - Surface modification (food processing, bioapplications,...)
  - Surface functionalisation (bio-tech applications,...)
  - Changing properties (rheology, foaming,...)
- Influence of molecular weight; adsorption increases with molecular weight
- Role of polymer extension (radius of gyration) at surface
  - ↳ Polymers change configuration upon adsorption



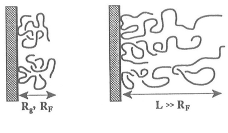
- Role of solvent

"Ideal" solvent: Interactions between monomer subunits equal to interactions with solvent
"Good" solvent: Repulsive forces acts between monomers, polymer swells
"Bad" solvent: Monomers attract each other, polymer shrink
Temperature dependent transition between "good" and "bad" solvent
- Ideal polymer behaviour at a given temperature

- Interactions during stable destabilisation are influenced by two main factors:
  1. Type of solvent
     - "Good" solvent - repulsive forces (polymer extends into solution)
     - "Bad" solvent - attractive forces



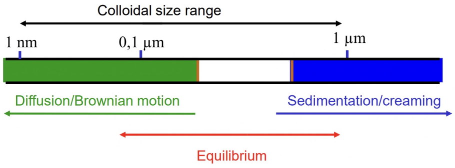
  2. How much polymer at interface



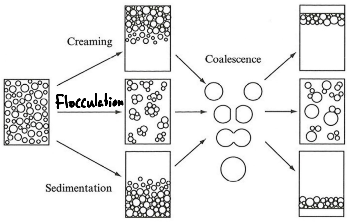
7. Kinetic properties and rheology

What is it?

- Motion of dispersed phase in:
  - gravitational field
  - centrifugal field
  - Brownian motion (thermal forces)



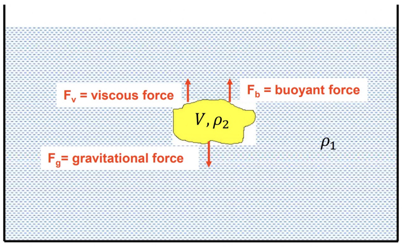
Sedimentation and brownian motion



We also have ostwald ripening, where large drops grow at the expense of small

Gravitational sedimentation

- The direction of the particles are decided by the density:
  - $\rho_2 > \rho_1$ => Downwards = Sedimentation
  - $\rho_1 > \rho_2$ => Upwards = Creaming



- The velocity of the particles, u, can be estimated by (using a force balance)

$$u = \frac{m_2}{f}\left(1 - \frac{\rho_1}{\rho_2}\right), \quad \frac{m}{f}: \text{mass-to-friction-factor}$$

η = viscosity of liquid

R_s = radius of particle

f can be found from:

1. Assuming spherical particles (stokes): $f = f_0 = 6\pi\eta R_s$
2. Evaluate f in combination with diffusion studies: $f = \frac{k_B \cdot T}{D}$

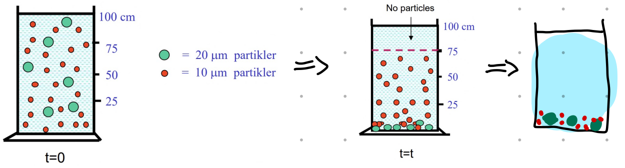
(3. Frictional ratio chart, find $\frac{f}{f_0}$ => Get f)

- Stoke's law: $F_v = 6\pi\eta R_s u = f \cdot u$, inserting into force-balance equation gives:
- Stokes (sedimentation) equation

$$u = \frac{2}{9}\frac{R_s^2(\rho_2 - \rho_1)g}{\eta} = \frac{d_s^2(\rho_2 - \rho_1)g}{18\eta}$$

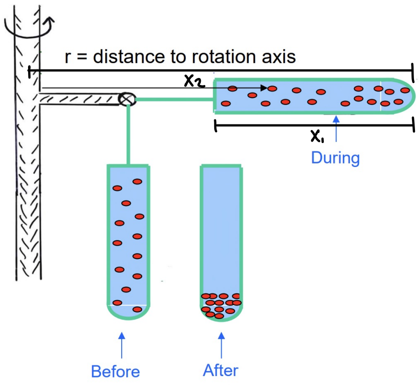
diameter of particle

- Distance moved is calculated by $x = u \cdot t$
- Sedimentation happens in 2 steps: fractionation (if there are multiple types of particles) and phase separation



Centrifugal sedimentation

- Centrifugal acceleration > gravitational acceleration - ultracentrifuge



Sedimentation coefficient s [seconds]:

$$s = \frac{dx/dt}{\omega^2 x} = \frac{\ln(x_2/x_1)}{\omega^2(t_2 - t_1)}$$

$$s = \frac{m}{f}\left(1 - \frac{\rho_1}{\rho_2}\right)$$

ω = angular velocity rad/s

2π radians per revolution

$\Rightarrow rps = \frac{\omega}{2\pi}$ and $rpm = 60 \cdot rps = \frac{60\omega}{2\pi}$

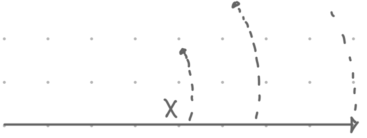
Stokes (sedimentation) equation still apply, but we must remember that g must be replaced by the centrifugal field.

The reason for the differenticl is that as X changes, so does the particle speed (the length it must travel per rotation increases)

X_1 is the starting point of a particle at t_1 (usually the top)

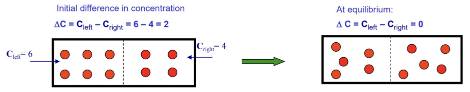
X_2 is the ending point of a particle at t_2 (usually we look at the bottom)

m is the mass of a single particle/molecule



Diffusion

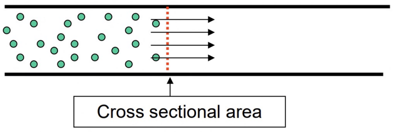
- Particles with non-uniform distribution experience a force to obtain uniform distribution, this transport of matter is called diffusion.



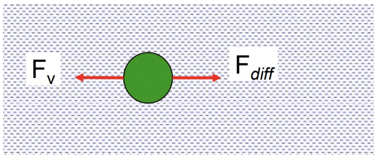
Macroscopically: uniform system

Molecular level: local fluctuations (*Brownian motion*)

- Fick's laws of diffusion
  - Quantitative descriptions of diffusion
  - 1st law: $J = -D\frac{dc}{dx}$
  - 2nd law: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$
  - D: Diffusion coefficient (m^2/s)

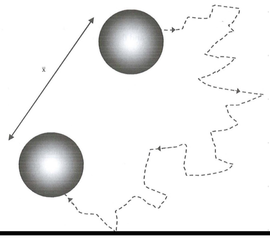


- Friction factor
  - Einstein's diffusion law: $D = \frac{k_B T}{f}$
  - Stokes-einstein relationship: $R_s = \frac{k_B T}{6\pi\eta D}$ (spherical particles)
  - At equilibrium, $F_v = F_{diff} \Rightarrow f \cdot u = -\frac{k_B \cdot T}{c} \cdot \frac{dc}{dx} \Rightarrow D = \frac{k_B \cdot T}{f}$



Brownian motion

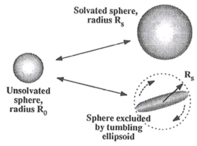
- Small/colloid particles move randomly due to collisions with other particles

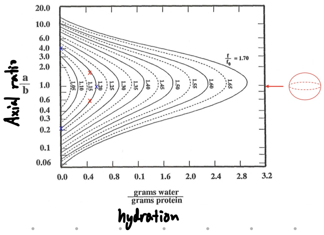


"Root mean square" displacement, $\bar{x} = \sqrt{2Dt}$

Effect of solvation and asymmetry

- Deviations from stokes model
- Hydrated particles (solvated) grow due to water molecules "attaching" on the surface. (Also different density)
- Non-spherical particles obviously has another resistance/friction than spheres.
- We use $\frac{f}{f_0}$ = friction factor as a measurement for the deviation from unsolvated spheres.
- For proteins, we can use a contour plot if we have additional information.

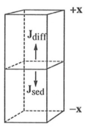


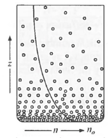


Sedimentation and diffusion in equilibrium

- While in equilibrium, no macroscopic changes

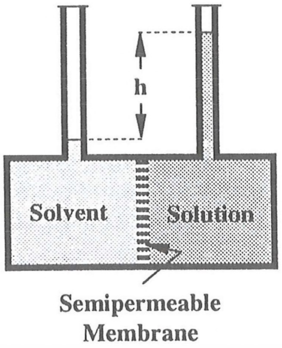
$$J_{sed} = J_{diff}$$





- However, the phases will still separate. The brownian motion will lead to aggregation/coalescence which gives bigger particles. For which J_{sed} is dominant.

Osmotic pressure



Also: $M = \frac{R_{ig} T}{\lim_{c\to 0}(\pi/c)}$

- Solvent = løsemiddel
- Solution (løsning) = solute (løst stoff) + solvent
- Semipermeable membrane: only permeable for solvent

- Solvent will flow from left to right through the membrane to try to equalize the concentration difference
- Diffusion does not occur as the solute cannot pass through the membrane
- Osmotic pressure is defined as the pressure needed to stop the flow. $\pi = \rho \cdot g \cdot \Delta h$

OR

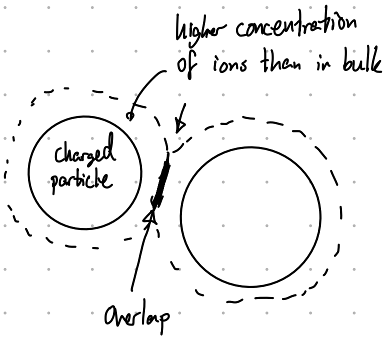
- The concentration difference represents a difference in chemical potential, and the osmotic pressure counteracts the diff.

$$\pi = -\frac{RT \ln a_i}{\bar{V}_i}$$

Van't hoffs eq

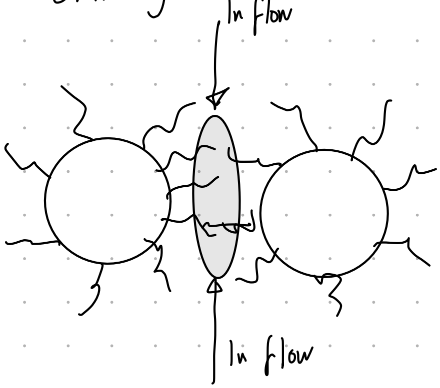
$$\pi = \frac{C_2 RT}{M}$$

π: osmotic pressure
a_i: activity of component i
$\bar{V}_i$: partial molar free energi of component i
M: molecular weight of solute
C_2: concentration of solute



Osmotic pressure makes water flow in to cancel concentration gradient => Stabilizing/equalizing the chemical potential. leads to separation of the particles

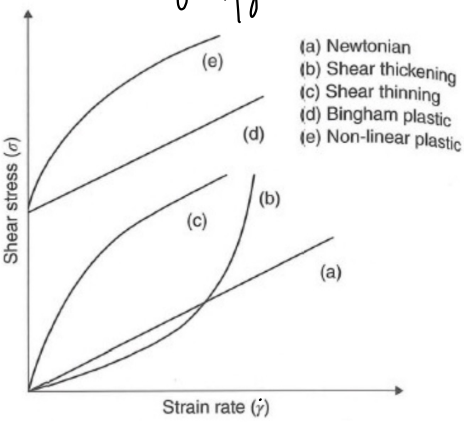
Similarily



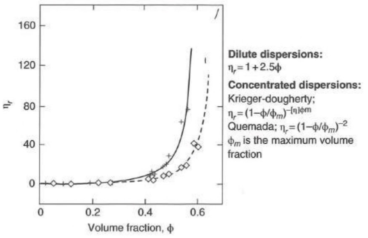
Rheology of colloidal dispersions

- Characteristics for rheology of dispersions
  - Huge difference between dilute and concentrated solution
  - Depends on continous phase viscousity, concentration, size and shape of particles, interactions between particles-dispersion medium, polydispersity.
  - Large effect of adsorbed polymers and/or double layers
  - Gives (in) direct information on structure and forces of the dispersions

$\sigma = \eta \dot{\gamma}$



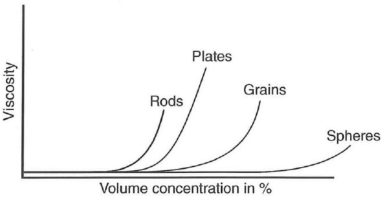
Particle concentration



Dilute dispersions:
$\eta_r = 1 + 2.5\phi$

Concentrated dispersions:
Krieger-dougherty;
$\eta_r = (1 - \phi/\phi_m)^{-[\eta]\phi m}$
Quemada; $\eta_r = (1 - \phi/\phi_m)^{-2}$
ϕ_m is the maximum volume fraction

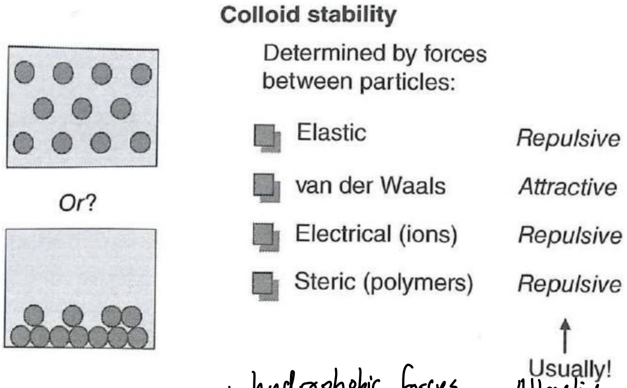
Particle shape



8. Colloidal stability - van der Waals and electrical forces

Colloidal stability

- Balance between attractive and repulsive forces


Colloid stability

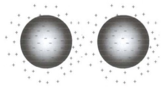
Determined by forces between particles:

Elastic	*Repulsive*
van der Waals	*Attractive*
Electrical (ions)	*Repulsive*
Steric (polymers)	*Repulsive*
+ hydrophobic forces	Attractive
+ hydration forces	Repulsive

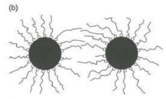
Usually!

We can provide stabilization in two ways

Electrostatic stabilisation



Polymer induced/
steric stabilisation



- Colloidal stability: small particles that does not aggregate

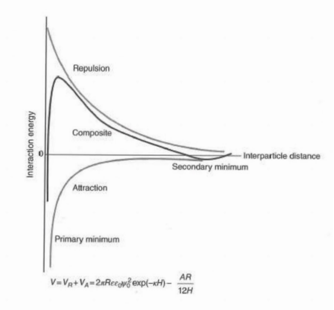
Potential energy curves

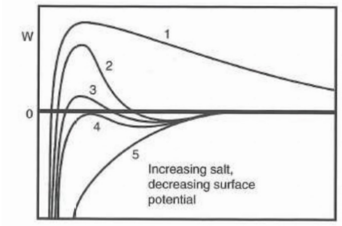
- Describe the interaction between 2 particles as a function of distance
- Net interaction energy = attractive + repulsive interaction energies
- DLVO theory - repulsive part only due to electrostatic stabilization (overlapping electrical double layers):

$$V = V_R + V_A = 2\pi R \varepsilon \varepsilon_0 \psi_0^2 \exp(-\kappa H) - \frac{AR}{12H}$$

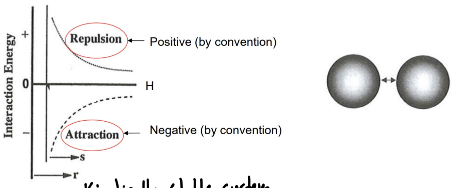
(two equal-sized spherical particles)

- Attraction and repulsion dominate in different regions
  - Secondary minimum:
    Flocculation (reversible)
  - Primary minimum:
    Coagulation (irreversible)
  - Energy barrier:
    Obstacle to coagulation

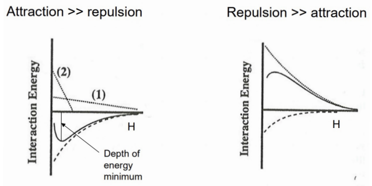




1. Strong repulsion - colloids remain stable
2. Colloids "stable" in secondary minimum, but easily redispersed
3. Colloids come into secondary minimum and coagulate slowly
4. Colloids come into secondary minimum and coagulate rapidly (or redisperse)
5. Colloids rapidly coagulate or coalesce.



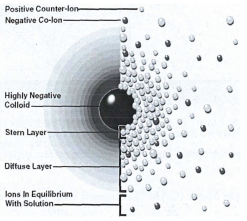
Kinetically stable system

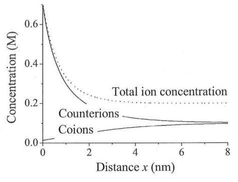

Attraction >> repulsion

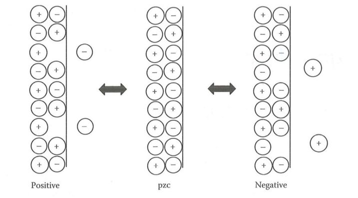
Repulsion >> attraction

The electrical double layer

- Electrical field originating from a charged surface: - Attracts counter-ions
  - Repels co-ions
- The layer of surface charge + the diffuse layer of counter-ions together is known as the electrical double layer.
- Overlapping electrical double layers causes repulsion by amongst others, osmotic pressure (see previous page)
- The surface can be charged by several mechanisms p.221 new book:
  - Dissociating -COOH groups: $-COOH \rightleftharpoons -COO^- \quad H^+$
  - Differential loss of ions from ion lattice: $AgI \longrightarrow I^- \quad Ag^+$
    - ↳ Ag^+ (and most cations) have a higher affinity for water than the larger than the larger I (anions) therefore, more I^- is on the surface, giving a negatively charged surface.
    - ↳ Increasing $[Ag^+]$ will decrease the negative charge until and past pzc.
    - ↳ Increasing $[I^-]$ will increase the negative charge



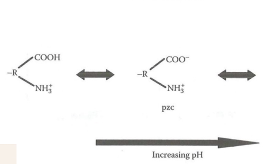




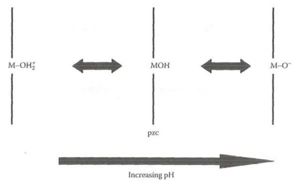
Potential determining ions: change charge of surface
Indifferent ions: do not change charge of surface
pzc: point of zero charge

- Oxides, proteins, water solouble polymers:
  - ↳ Amphoteric surfaces - take up or release proton depending on pH
  - ↳ Potential determining ions: H^+ and OH^-

Proteins:



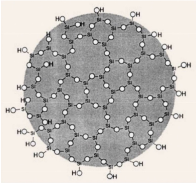
Oxides:



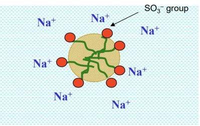
- Silica

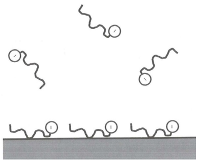
$$Si-OH + OH^- \rightarrow Si-O^- + H_2O$$

$$Si-OH + H^+ \rightarrow Si-OH_2^+$$



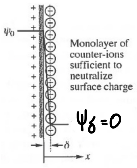
- Hydrophobic particles and emulsion droplets
  - ↳ Adsorption of ionic surfactants

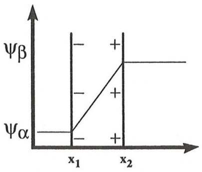




EDL - Capacitor model

- Variation in ion density near a charged surface
- We want to describe how the electrical potential varies near a charged surface
- The capacitor model can be used from the surface to the centre of the counter ions in the first layer.
  - ↳ Only electrostatic interactions
  - ↳ Poor model for the entire EDL
  - ↳ Does not consider temperature effects on ions



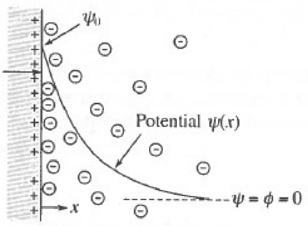


$$\Delta\psi = \underbrace{\psi_0 - \psi_\delta}_{\text{Defined as positive - negative ?}} = \frac{\sigma_0}{\varepsilon_r \varepsilon_0}\delta$$

σ_0 : charge density C/m^2
ε_r : relative permittivity
ε_0 : permitivity of vacuum $8,854 \cdot 10^{-12}\ C^2 \cdot J^{-1} \cdot m^{-1}$
δ : separation distance

EDL - Gouy-Chapman model

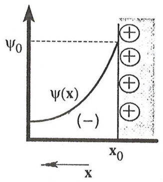
- Accounts for thermal motion of ions
- Charge density varies with distance from interface
- Starting from poisson eq, assuming planar surface, and using boltzmanns equation:



$$\left(\frac{d^2\psi}{dx^2}\right) = -\frac{e}{\varepsilon}\sum z_i n_{i\infty} \exp\left(\frac{-z_i e \psi}{k_B \cdot T}\right)$$

$\varepsilon = \varepsilon_r \varepsilon_0$
T: Temperature in kelvin
z_i: Valence number of the ion
$n_{i\infty}$: concentration of ions in bulk
e: the elementary charge: $1,60 \cdot 10^{-19}$ C
k_B: Boltzmanns constant: $1,38 \cdot 10^{-23}$ J/K

- The solution using the Debye-Hückel approximation
  - ↳ Assuming low potentials $z_i e \psi_0 < k_B \cdot T$ or $\frac{|z\psi_0|e}{2k_B \cdot T} \ll 1$
  - ↳ Using conditions $\psi \rightarrow \psi_0$ as $x \rightarrow 0$
    $\psi \rightarrow 0$ as $x \rightarrow \infty$
  - ↳ We get:



$$\psi = \psi_0 \exp(-\kappa x), \text{ where } \kappa = \sqrt{\frac{e^2}{\varepsilon \cdot k_B \cdot T} \cdot \sum_i z_i^2 n_{i\infty}} = \sqrt{\frac{1000 e^2 N_A}{\varepsilon_r \varepsilon_0 k_B \cdot T} \sum_i z_i^2 c_i} = \sqrt{\frac{2000 e^2 N_A}{\varepsilon_r \varepsilon_0 k_B \cdot T} \cdot I}$$

ions/m³ mol/L

C_i : concentration of ion i in the bulk solution

Where I is the ionic strength, $I = \frac{1}{2}\sum_i z_i^2 c_i$

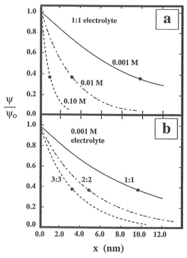
if we have water, $\varepsilon_w = \varepsilon_{r,w}\varepsilon_0 = 6,95\ 10^{-10}$ F/m $\Rightarrow \kappa = 3,28 \cdot 10^9 \underbrace{\sqrt{I}}_{\text{In mol/L}}$ $[m^{-1}]$

if we have something else than water

$$\kappa = \sqrt{\frac{\varepsilon_{r,w}}{\varepsilon_{r,new}}} \cdot 3,28 \cdot 10^9 \sqrt{I}$$

- ↳ Using $|\psi| = \frac{k_B \cdot T}{z \cdot e}$, we find velidity of appoximation (25°C):
  - Monovalent $\psi < 25,7$ mV
  - Divalent $\psi < 12,9$ mV
  - In practice, valid until 50-80 mV

- κ is known as the Debye-Hückel parameter. The debye length, $\frac{1}{\kappa}$, gives the extension of the double layer
  - ↳ $\frac{1}{\kappa}$ decrease with increased electrolyte concentration, and increasing valency of ions.



- Solution without the D-H assumption

$$\ln\left\{\frac{[\exp(\frac{ze\psi}{2k_BT})+1][\exp(\frac{ze\psi_0}{2k_BT})-1]}{[\exp(\frac{ze\psi}{2k_BT})-1][\exp(\frac{ze\psi_0}{2k_BT})+1]}\right\}=\kappa x$$

- Potential near charged surface depends on the number of charged groups at the surface
  - ↳ Graheme equation: relates surface charge (σ_0) and surface potential (ψ_0)
    - Planar surface (D-H approx): $\sigma_0 = \varepsilon_r \varepsilon_0 \psi_0 \kappa$
- Solution for sphericel surface (using D-H approx):

$$\psi = \psi_0 \frac{R_s}{r} e^{-\kappa(r-R_s)}$$, R_s = particle radius

r = distance from point in EDL to center of sphere

- The corresponding Grahame equation:

$$\sigma_0 = \frac{\varepsilon_r \varepsilon_0 \psi_0 (1+\kappa R_s)}{R_s}$$

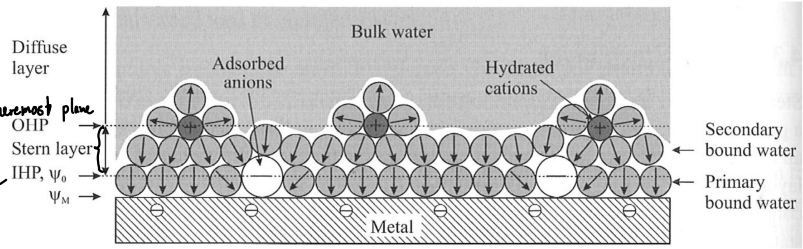
Stern model

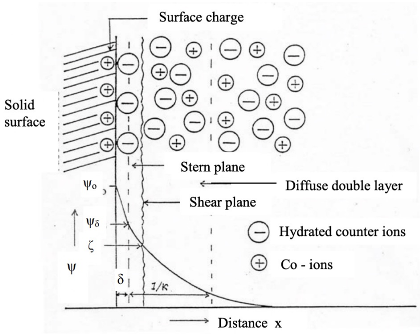
- While the Gouy-Chapman model considers all ions to be mobile, the stern model divides the EDL into 2 parts:
  - Inner part (immobile ions - specific adsorption) - Stern layer
  - Outer/diffuse part (mobile ions) - Gouy-Chapman layer

Positive

Outer heremost plane

Negative - Inner





Indifferent ions adsorb directly at surface

- specific adsorption (Stern adsorption)

↑

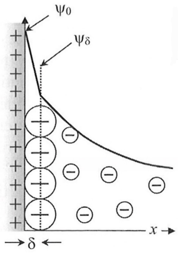
for the system feels london interactions

(↓) = water

kations are hydrated, and can't come closer than OHP, closest that counterions can come

Capacitor model from IHP to OHP

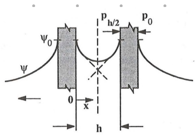
- Inner layer (IHP to OHP)



Due to size and hydration, there is a limit to how close ions can approach the solid surface - indifferent ions

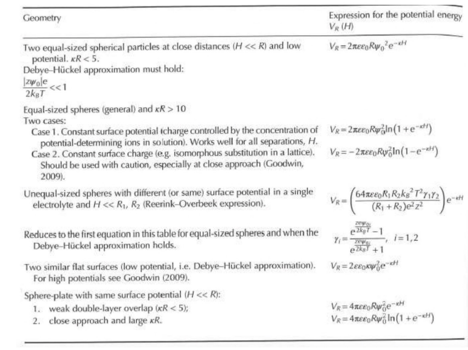
- Overlapping double layers
  - ↳ Origin of repulsive forces between surfaces
  - ↳ Repulsion between planar double layers at separation distance h, bulk concentration n_∞, surface potential ψ_0.

At equilibrium: all forces (osmotic + electrostatic) must balance



Repulsive force: $F_R \approx 64\, k_B T n_\infty \Upsilon_0^2 \exp(-h\kappa)$

Repulsive interaction energy $V_R = 64\, k_B T n_\infty \kappa^{-1} \Upsilon_0^2 \exp(-h\kappa)$



Geometry	Expression for the potential energy $V_R\,(H)$
Two equal-sized spherical particles at close distances ($H << R$) and low potential. $\kappa R < 5$. Debye–Hückel approximation must hold: $\frac{\lvert z\psi_0 \rvert e}{2k_BT} << 1$	$V_R = 2\pi\varepsilon\varepsilon_0 R\psi_0{}^2 e^{-\kappa H}$
Equal-sized spheres (general) and $\kappa R > 10$ Two cases:	
Case 1. Constant surface potential (charge controlled by the concentration of potential-determining ions in solution). Works well for all separations, H.	$V_R = 2\pi\varepsilon\varepsilon_0 R\psi_0^2 \ln(1+e^{-\kappa H})$
Case 2. Constant surface charge (e.g. isomorphous substitution in a lattice). Should be used with caution, especially at close approach (Goodwin, 2009).	$V_R = -2\pi\varepsilon\varepsilon_0 R\psi_0^2 \ln(1-e^{-\kappa H})$
Unequal-sized spheres with different (or same) surface potential in a single electrolyte and $H << R_1, R_2$ (Reerink–Overbeek expression).	$V_R = \left(\frac{64\pi\varepsilon\varepsilon_0 R_1 R_2 k_B{}^2 T^2 \gamma_1\gamma_2}{(R_1+R_2)e^2 z^2}\right) e^{-\kappa H}$
Reduces to the first equation in this table for equal-sized spheres and when the Debye–Hückel approximation holds.	$\gamma_i = \frac{e^{\frac{ze\psi_{0i}}{2k_BT}}-1}{e^{\frac{ze\psi_{0i}}{2k_BT}}+1},\quad i=1,2$
Two similar flat surfaces (low potential, i.e. Debye–Hückel approximation). For high potentials see Goodwin (2009).	$V_R = 2\varepsilon\varepsilon_0\kappa\psi_0^2 e^{-\kappa H}$
Sphere-plate with same surface potential ($H << R$): 1. weak double-layer overlap ($\kappa R < 5$); 2. close approach and large κR.	 $V_R = 4\pi\varepsilon\varepsilon_0 R\psi_0^2 e^{-\kappa H}$ $V_R = 4\pi\varepsilon\varepsilon_0 R\psi_0^2 \ln(1+e^{-\kappa H})$

Electrophoresis

- Some definitions
  - Electrokinetics: Combined effects of motion and charge
    (colloidal particles: motion affected by electrical double layer phenomena)
  - Outcome of electrokinetic measurements: Zeta potential
  - Two ways of measuring electrokinetics:
    - Solution moves relative to surface in an applied electrical field
      (electro-osmosis, streaming potential)
    - Colloids move in solution in an applied electrical field (electrophoresis)
- eletcrophoretic mobility (u)
  (velocity of a charged colloid in an externally applied electrical field)
  ↳ We need u to get zeta potential
- Generally, the relationship between electrophoretic mobility and zeta potential is given by Henrys equation:

$$\mu = \frac{\varepsilon \zeta}{\eta} f(\kappa R_s)$$

μ: electrophoretic mobility $\left[\frac{m^2}{V \cdot s}\right]$

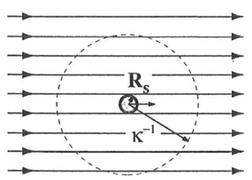
$\varepsilon = \varepsilon_r \varepsilon_0$

η: Viscosity of medium kg/m·s

R_s: Radius of sphere

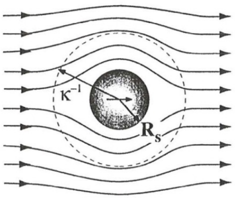
Obs: Sometime μ is written u

- We have two extreme cases of spherical particles:



Small particle size compared to "thickness" of double layer

$\kappa R_s < 0{,}1$



Particle size is large compared to "thickness" of double layer

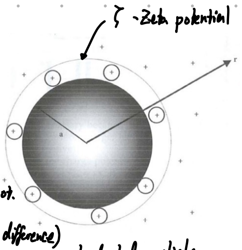
$\kappa R_s > 100$

$\mu = \frac{2}{3} \frac{\varepsilon \zeta}{\eta}$ (Hückel equation)

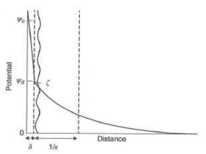
$\mu = \frac{\varepsilon \zeta}{\eta}$ (Smoluchowski equation)

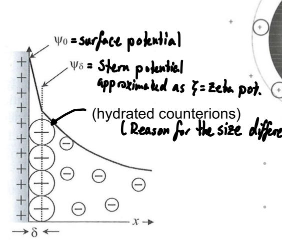
As many case fall outside of the rules, we use Hückels eq for $\kappa R_s < 10$ and Smoluchowski for $\kappa R_s > 10$

- Electrophoretic mobility & zeta potential
  - During electrophoresis = motion of charged colloids in an electrical field, the zeta potential is measured at the surface of shear, inside there is no motion of solution relative to surface, but outside there is.



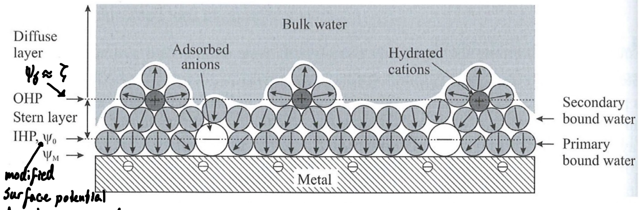
  - Usually we approximate $\psi_\delta \approx \zeta$, sometimes $\psi_0 \approx \zeta$





hydrated particle everything inside boundary is moving with the particle

  - Zeta potential is affected by:
    - potential determining ions
    - ionic strength (indifferent ions)
    - specific adsorption
  - Iso electric point (IEP): $\zeta = 0$ (hydrodynamic surface)
  - Point of zero charge (PZC): $\psi_0 = 0$ (solid-liquid interface)
  - At high or low ζ, $|\zeta| \gtrsim 40$ mV, the system is quite stable.



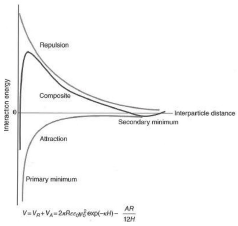
modified surface potential due to specific adsorption

9. Colloidal stability - DLVO theory: Kinetics of aggregation

DLVO theory

- Looks at the stability of colloids
- Considers electrostatic stability, using attractive vdW forces and repulsive electrostatic interaction energies

$$V = V_A + V_R$$



$V = V_R + V_A = 2\pi R\varepsilon\varepsilon_0\psi_0^2\exp(-\kappa H) - \frac{AR}{12H}$

Hamaker Constant

- We can control the hamacker constent by choosing solvent and composition of dispersed phase carefully

A_{11} = Hamaker constant for component 1, interactions between particles of same composition. $A_{11} \approx 0$ for gas bubbles in liquid.

A_{12} = particle of type 1 interacting with particle of type 2 (f.ex solvent) (pptx bruker denne som A_{12})

A_{121} = particles of type 1 interacting with themselves in medium of type 2

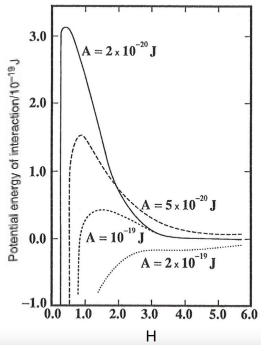
A_{123} = particles of type 1 interacting with particles of type 3 in medium of type 2

$$A_{12} = A_{121} = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

Usually: $A_{12} \approx (A_{11}A_{12})^{1/2}$ (geometric mean)

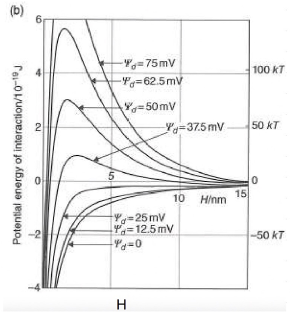
$$A_{123} = (A_{11}^{1/2} - A_{22}^{1/2})(A_{33}^{1/2} - A_{22}^{1/2})$$

- Plays a huge role in the interaction energy

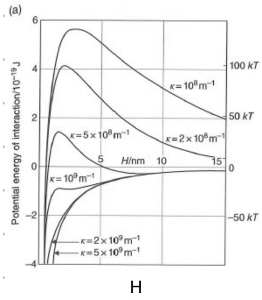


Other effects on the interaction energy

- Surface/stern/zeta potential



- Ionic strength



- For stability of the dispersion, we want:
  - High
    - Debye length, κ^{-1}
    - High permittivity of medium, $\varepsilon = \varepsilon_r\varepsilon_0$
    - High potential (surface/stern/zeta), $\psi_0 \approx \psi_\delta \approx \zeta$
  - Low
    - Salt/electrolyte concentration, C } Ionic strength I
    - Valency of salt ions, z } Ionic strength I
    - Hamaker constant (if possible, negative values are preffered), A
    - Temperatures

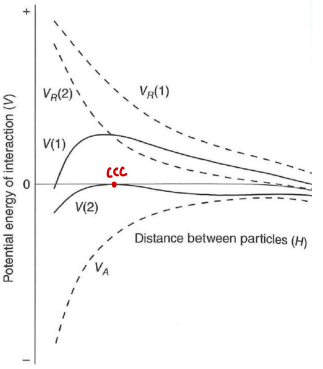
- High surface/zeta potential => Large/high repulsion between particles
- Low electrolyte concentration => Repulsion at long distances (due to large double layer extension)
- Small hamaker constant => Small attraction between particles
  ↳ Negative?, repulsion between particles, due to higher affinity for medium.

Critical coagulation concentration

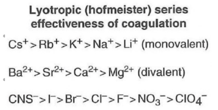
- CCC
- The electrolyte concentration necessary to induce coagulation
- Good example of CCC calculations on p.231-232 in new book.
- Where $V = \frac{dV}{dH} = 0$ (see figure)
- Schulze-Hardy rule

$$CCC \propto z^{-6}$$, where z is the valency of the counterions

- Only estimate/trend, does not account for specific adsorption



- Different ions coagulate better than others, we can use the hofmeister series to look at trends:


Lyotropic (hofmeister) series
effectiveness of coagulation

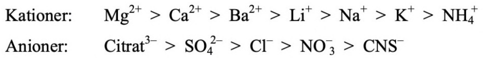
$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (monovalent)

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ (divalent)

$CNS^- > I^- > Br^- > Cl^- > F^- > NO_3^- > ClO_4^-$

Lytropic = solvent loving

Li^+ has higher CCC than Cs^+ (series range which ion coagulate first)

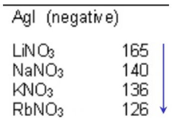

Kationer: $Mg^{2+} > Ca^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+ > NH_4^+$

Anioner: $Citrat^{3-} > SO_4^{2-} > Cl^- > NO_3^- > CNS^-$

Opposite order compared to the picture on the left

Mg^{2+} is more easily hydrated, and therefore less likely to coagulate compared to Ca^{2+}.

CCC (mmol/L)



AgI (negative)	
$LiNO_3$	165
$NaNO_3$	140
KNO_3	136
$RbNO_3$	126 ↓

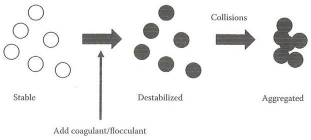
Coagulation in dilute dispersions

- All kinetically stabilised systems are unstable over time
- Stability determined by rate of coagulation (or coalescence)
- Rate of coagulation is determined by:
  1. Particle collision frequency
  2. Probability that particles stick together upon collison
- Fuch's stability ration: $W = \frac{k_2^0}{k_2}$ (quantify colloidal stability), where

  k_2^0: rate constant of rapid coagulation (no repulsive interactions, diffusion controlled)

  k_2: rate constant of slow coagulation (interaction controlled collisions)

  - W is a function of properties affecting interparticle interactions (energy barrier)



- Initially, the coagulation can be described by:

  $$\frac{dN}{dt} = -k_2 N^2$$, where N is the number of particles in the solution

- $t_{1/2}$: When half of the initial particles have coagulated. At $t_{1/2}$, $N = \frac{1}{2} N_0$

Rapid coagulation

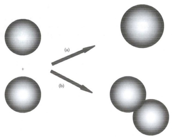
- No repulsive barrier
- Particles stick together after contact => Doublet formation or coalescence (adhere)
- The collision frequency is:

  $$Z = 8\pi R_s D N^{2?}$$ p. 250 old book

  D: Diffusion coefficient
- The rate constant is:

  $$k_2^0 = \frac{4 k_B T}{3\eta}$$
- As every collision leads to adhesion:

  $$\frac{dN}{dt} = -k_2^0 \cdot N^2 = -Z$$



$$\frac{dN}{dt} = -k_2^0 N^2 \Rightarrow \int_{N_0}^{N} -\frac{dN}{N^2} = \int_0^t k_2^0 \, dt$$

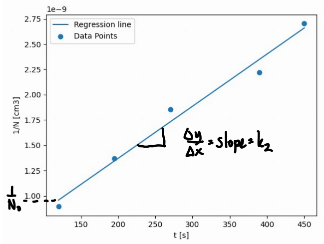
$$\left[\frac{1}{N}\right]_{N_0}^{N} = k_2^0 \cdot t$$

$$\boxed{\frac{1}{N} - \frac{1}{N_0} = k_2^0 t}$$

Slow coagulation

- There is an energy barrier
- Collision frequency is now reduced by the interaction potential:

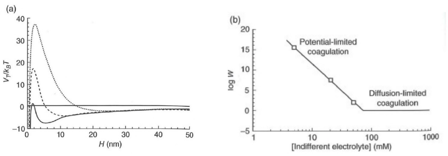
  $$Z = \frac{8\pi D R_s N}{\int_s^\infty e^{\frac{p(s)}{k_B T}} \frac{ds}{(s+2)^2}}$$
- The coagulation rate is given by: $\frac{dN}{dt} = -k_2 N^2$
- As Z (and k_2) is difficult to calculate, we use linear regression on $\frac{1}{N} = k_2 \cdot t + \frac{1}{N_0}$ (using experimental data) to find k_2



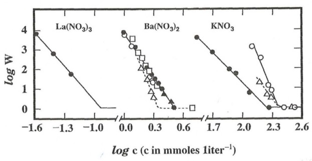
Stability ratio and CCC

- $\log W = K_1 \log c + K_2$

  log, not ln!
- At $\log W = 0$ there is a break
  ↳ $\log W = 0 \Rightarrow W = 1$ ⇒ We have coagulation, and are at CCC. (diffusion limited coagulation)

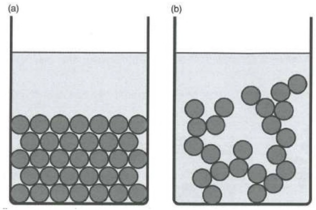


AgI dispersions:



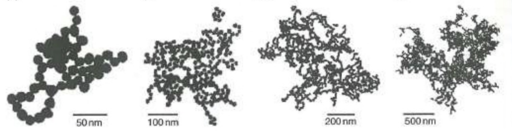
Aggregates

- Aggregates can have many different structures



Aggregate, "impossible" to disperse

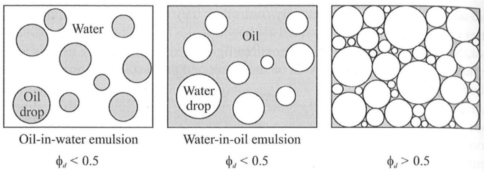
Flocculents, Can be dispersed by adding small amounts of energy



10. Emulsions

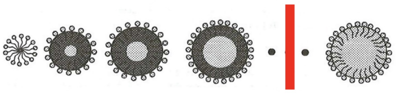
Emulsions

- Mixtures of two immicible liquids
- Separates rapidly without stabilization
- Is kineticclly stabilized (needs energy to form)
- 2-phase system
- W/O (water in oil) or O/W emulsions
- Polydisperse drops, average size: 0,1 - 10 μm
- Surfactants adsorb on the o-w interface and orient as monolayers



Microemulsions vs. emulsions

- Generally microemulsions contain droplets at least on order of magnitude lower than for emulsions
- Microemulsions are clear, emulsions are cloudy - milk is not clear => emulsion, not microemulsion
- Microemulsions form spontaelusly, emulsions require energy input
- Microemulsions: thermodynamically stable, emulsions: kinetically stable
- Microemulsions are highly dynamic systems, emulsions are relatively static systems (in terms of surfactants)



No continuum from micelles/microemulsions to emulsions

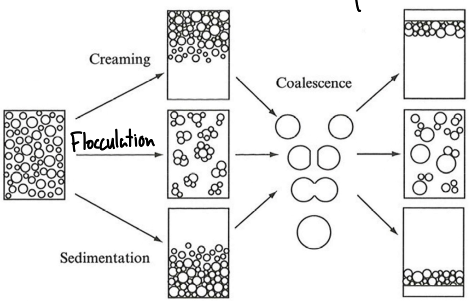
Important: main difference is *not* drop size

– microemulsion can be a misleading term!

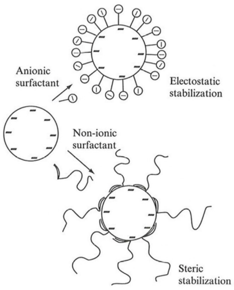
Stability of emulsions

- Interaction energy between dispersed droplets
  - Attractive part: vdW interactions
    - long ranged
    - Strong at small distances
    - always present
  - Repulsive part: provided in 2 ways
    - Electrostatic interactions (repulsion due to EDL)
      ↳ Electrostatic stabilisation (DLVO)
    - Polyme induced stability (masked van der Waals attraction)
      ↳ Steric stabilization

Destabilisation: $u = \frac{2}{9}\frac{R_S^2(\rho_2-\rho_1)g}{\eta}$



- Also, ostwald ripening



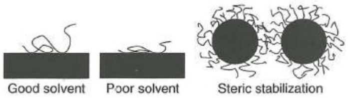
Factors enhancing stability:

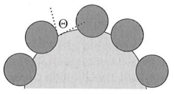
- Low interfacial tension
- A mechanically strong and elastic interfacial film
- Eletrical double layer repulsions
- Relatively small volume of dispersed phase
- Narrow droplet size distribution

- Steric stabilization

Requirements for surfactants:
- Reduce the o-w interfacial tension
- Rapid diffusion to newly created interfaces

- Low molecular weight surfactants are superior when creating emulsions
- High molecular weight polymers, particles, proteins and liquid crystals diffuse slowly to the interface, may play a larger role in stabilisation





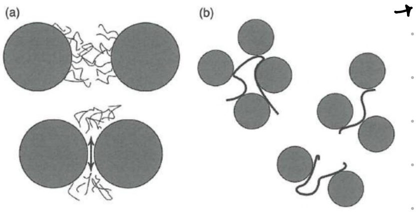
Particle stabilisation

- $\Delta G_{mix} = \Delta H_{mix} - T \cdot \Delta S_{mix}$ applies, increasing the temperature will lead to destabilization. $\Delta G < 0$ => spontaneous coagulation

- Destabilisation by polymers:

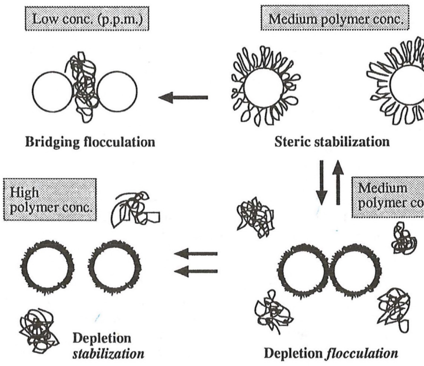
Depletion floucculation

Bridging flocculation



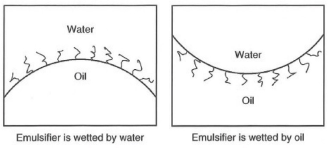
→ Small concentration of polymer, leads to partial coverage => allows different parts of the polymer to adsorb on different particles, creating bridges, which gives rise to flocculation.

↳ Small concentrations of lyophilic polymers (does not really adsorb). They move a lot around. As particles approach, the entropy of the polymers decrease due to less space. Therefore, the will detach and go into the bulk. This creates a low concentration of polyme between the particles => Osmotic pressure => Solute will flow from in between particles into bulk, creating an attractive force between the particles.



Emulsion design

- We need to design the emulsion so that it has the right properties
- Bancrofts rule
  - water-soluble surfactants: o/w emulsions
  - oil-soluble surfactants: w/o emulsions



Emulsifier is wetted by water

Emulsifier is wetted by oil

- HLB: Hydrophilic - Lipophilic Balance
  - Gives a rough idea of the applications of an emulsion. Even with several surfactants.
  - Relationship between HLB-number, solubility and application

HLB	Behavior of emulsifier in water	HLB	Applications
1-4	Not dispersible	3-6	W/O emulsions
3-6	Poorly dispersible	7-9	Wetting agents
6-8	Unstable milky dispersion	8-15	O/W emulsions
8-10	Stable milky dispersion	13-15	Detergents
10-13	Semi transparent dispersion/solution	15-18	Solubilization
13→	Transparent solution		

↑ hydrophobic

↓ hydrophilic

↳ Rough rule: $HLB < 8 \Rightarrow$ W/o emulsion

$HLB > 8 \Rightarrow$ o/w emulsion

- For mixtures of emulsifiers: $HLB_{mix} = \sum_{i=1}^{n} W_i \cdot HLB_i$, where W_i is the weight percentage of emulsifier i in the total emulsifier mixture, and HLB_i is it's HLB value.

- To calculate HLB for a surfactant from it's chemical structure:

$$HLB = 7 + \sum_i n_i \, HLB_i$$

, where n_i is the number of the type of groups in the molecule, and HLB_i is the groups HLB value (tabulated)

- Some HLB values of common emulsifiers:

Chemical	Commercial name	HLB
Sorbitan monolaurate	Span 20	8.6
Sorbitan monostearate	Span 60	4.7
Sorbitan tristearate	Span 65	2.1
Sorbitan monooleate	Span 80	4.3
Polyoxyethylen(20) Sorbitan monolaurate	Tween(polysorbat) 20	16.7
Polyoxyethylen(20) Sorbitan monostearate	Tween(polysorbat) 60	14.9
Polyoxyethylen(20) sorbitan tristearate	Tween(polysorbat) 65	10.5
Polyoxyethylen(20) Sorbitan monooleate	Tween(polysorbat) 80	15.6

Table 11.5 HLB numbers of molecular groups

Chemical group	HLB	Chemical group	HLB
$-SO_4Na$	38.7	-O-	1.3
-COOK	21.1	-OH (sorbitan)	0.5
-COONa	19.1	$-(CH_2-CH_2-O)-$	0.33
$-SO_3Na$	11.0	$-(CH_2CH_2CH_2O)-$	-0.15
-N (tertiary amin)	9.4	$-CH_2-$, CH	-0.475
Ester (sorbitan ring)	6.8	$-CH_3$	-0.475
Phenol residue, $-C_6H_4-O-$	~ 6.5	$= CH_2-$	-0.475
Free ester group	2.4	$-CF_2-$	-0.87
-COOH	2.1	$-CF_3$	-0.87
-OH	1.9		

Obs! $-C_6H_4-$ (benzene ring) is viewed as 6 Carbons

$\Rightarrow HLB_i = 6 \cdot (-0{,}475) = -2{,}85$

- Structure of a few common surfactants:

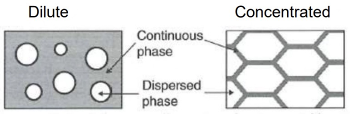
Category	Name	Structure
Anionic	Sodium stearate	$CH_3(CH_2)_{16}COO^-Na^+$
	Sodium oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^-Na^+$
	Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}SO_4^-Na^+$
	Sodium dodecyl benzene sulfonate	$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$
Cationic	Dodecylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$
	Hexadecyl(trimethyl)ammonium bromide (CTAB)	$CH_3(CH_2)_{15}N(CH_3)_3^+Br^-$
Non-ionic	Polyethylene oxides (C_xE_y or C_xEO_y)	$CH_3(CH_2)_{x-1}(OCH_2CH_2)_yOH$
	Nonylphenyl ethoxylates (X_{EO} is the number of ethylene oxide groups)	$CH_3(CH_2)_8-C_6H_4-(OCH_2CH_2)_{X(EO)}OH$

- PIT - phase inversion temperature
  - Temperature where non-ionic emulsifiers changes from o/w to w/o
  - Below PIT, the emulsifier is strongly polar, above, it interacts less with water
  - Temperature is not taken into account for HLB

11. Foams

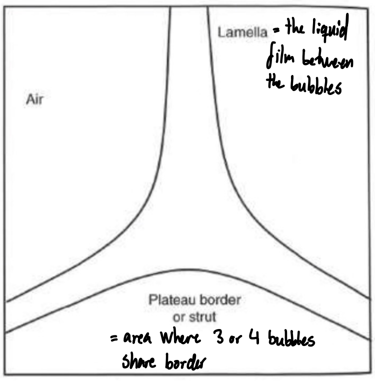
Foams

- Gas dispersed in liquid using a foaming agent; usually one or more surfactants



Volume fraction dispersed phase: 0.5-0.9
Sizes: 1 mm – several cm (but also nm)

- Froth, foam stabilized by solid particles
- Pure liquids do not foam, the presence of foam means that there is a least one surface active compound in the liquid.

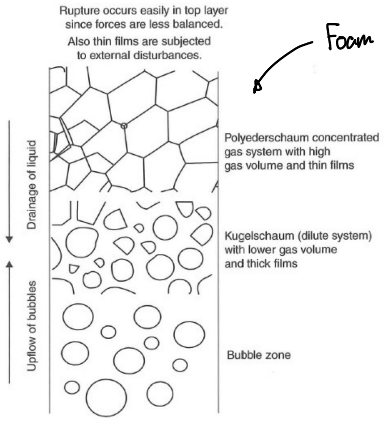


Lamella = the liquid film between the bubbles

= area where 3 or 4 bubbles share border

Lamella thickness:
30 μm in «young» foams
0.1 μm after gravitational drainage

Characterisation



Foam column

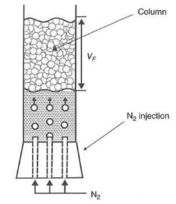
Foam number

$$F = \frac{V_F}{V_L} = \frac{V_G + V_L}{V_L} = 1 + \frac{V_G}{V_L}$$

V_F = Volume of foam
V_L = Volume of liquid in foam
V_G = Volume of gas in foam

Preparation

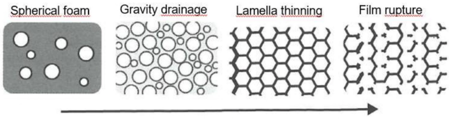
- Condensation of dissolved gas (pressure reduction of liquid supersaturated with gas) (Kelvin eq)
- Dispersion (injection) into liquid: (as on the figure)



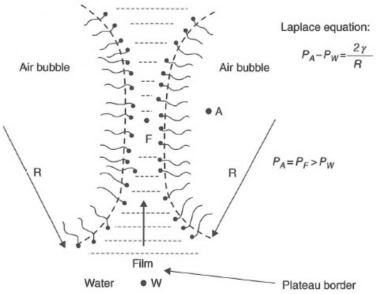
Bikerman column often used to characterise foams

Destabilization mechanisms

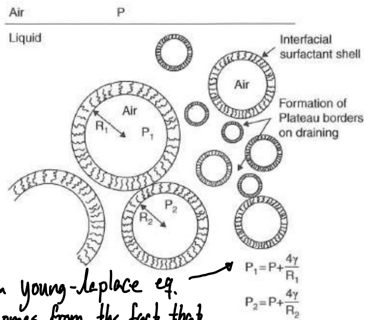
- There are 3 major mechanisms, which is important when depends on the systems state and properties



- Gas diffusion (ostwald ripening):



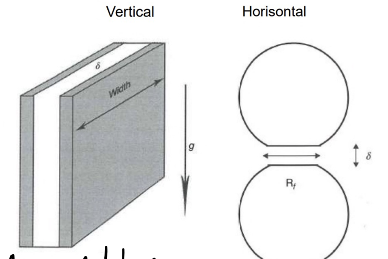
- We have a curved interface towards A
  - => $P_A > P_W$
- At point F, the interface is flat, meaning that $P_A = P_F$ (inside liquid film)
  - => $P_F > P_W$
- As F and W isn't separated, there will be a liquid flow from F to W to counteract the pressure difference.
- This is known as a capillary pump.
- The result is that the lameller film will become thinner.



- In addition, the pressure inside the air bubbles is larger than in the liquid or air phase.
- Also, the solubility of the bubbles in the liquid is larger for small bubbles than large.
- We therefore have a driving force for diffusion of small droplets into larger ones (or liquid bulk)

From young-laplace eq.
"4" comes from the fact that we have 2 interfaces for each bubble, inside and outside (only applicable for foams)

- Drainage
  - Vertical or horizontal
  - Usually the most rapid drainage
  - Gravity causes the liquid to flow downwards, draining the lamella.
  - Eventually, the lamella is not thick enough to support the pressure of the bubbles => Rupture.

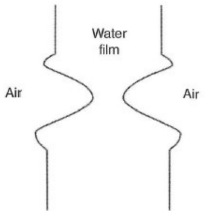


Approximated by a vertical slap

- Rupture (coalescence)
  - Surface waves that travel through the lamella makes it so that the lamella is thinner than its critical rupture thickness, hc, and the film ruptures => Coalescence
  - hc is calculated by:

$$h_c = 0{,}207\left(\frac{A_{121}^2\, R_B^2}{\gamma_{AL}\,\Delta P}\right)^{\frac{1}{7}}, \text{ where}$$

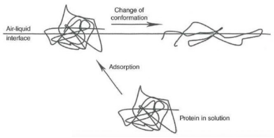
A_{121}: Effective Hamaker constant for air-liquid-air
R_B: Radius of the bubble
γ_{AL}: interfacial tension of air-liquid interface
ΔP: Excess capillary pressure, $\Delta P = \frac{2\gamma_{AL}}{R_B}$

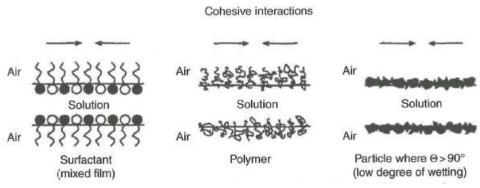


  - hc for
    - Pure water: 100-400 nm
    - Surfactant solutions: 5-15 nm
  - The surface waves are caused by disturbances, which can be: vibrations (sound/movement), drought, organic contaminants, dust, particles, temperature gradients, evaporation or heat.
  - Rupture can also happen without disturbances, by the previous thinning mechanisms.

Stabilization

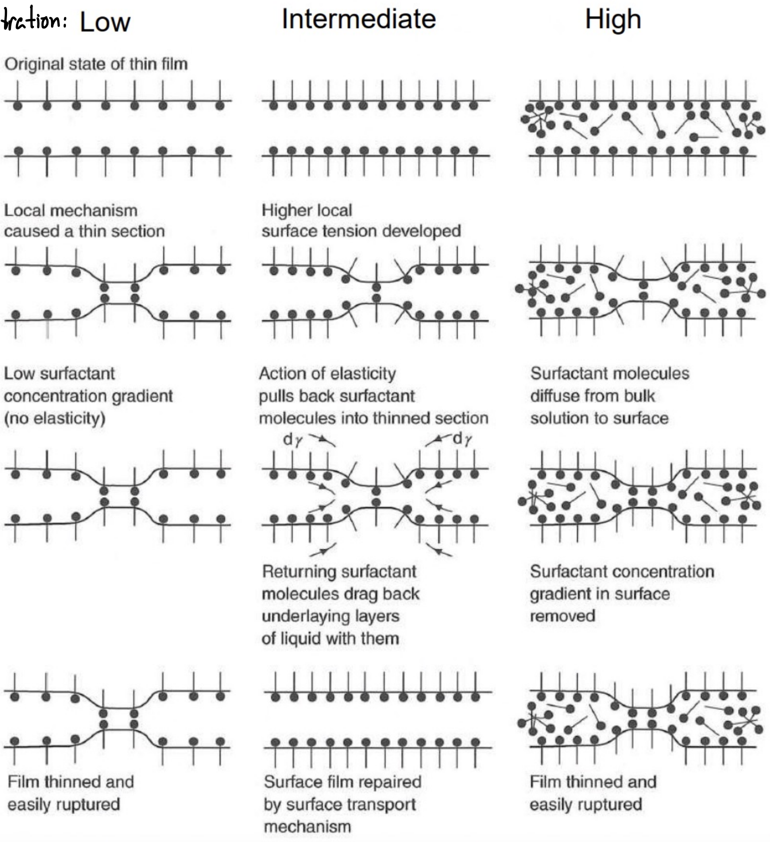
- We can achieve stabilization in 2 ways
- Increasing surface viscosity
  - Adding surfactants, polymers with high molecular mass or certain types of particles can increase surface viscosity
  - This is due to cohesion or adhesion between the additives.
  - The surface becomes more elastic => It can stretch more before rupture.
  - This also affects the drainage, as explained below.





- Increase surface elasticity, or self-healing
  - Adding surfactants allow for self-healing
  - Know as the Gibbs-Marangoni effect

- Surfactant concentration:



Original state of thin film

Local mechanism caused a thin section

Higher local surface tension developed

Low surfactant concentration gradient (no elasticity)

Action of elasticity pulls back surfactant molecules into thinned section

Surfactant molecules diffuse from bulk solution to surface

Returning surfactant molecules drag back underlaying layers of liquid with them

Surfactant concentration gradient in surface removed

Film thinned and easily ruptured

Surface film repaired by surface transport mechanism

Film thinned and easily ruptured

- Before drainage

- After/during drainge. The surfactants was pulled away with the water.
- Low concentration, the concentration gradient around the thinning is too low, so nothing more heppens

- Intermediate: Surfactants diffuse along the surface to the place with low concentration. They pull underlying liquid layers along with them. And the removed liquid is replaced, repairing the film.

- High: Surfactants diffuse from bulk solution, and no liquid is dragged into the film. No repairing.

From the exercises

Exercise 1

- Suspension: Solid particles suspended in continous phase (liquid or solid)
- Colloids are turbid (ikke gjennomsiktige), solutions are clear
- Particles lose size during degassing (heating in vacuum) due to volatile matter (adsorbed matter like water) desorbes and evaporates during heating
- Characteristic for van der Waals forces:
    - almost always attractive (but *might* be negative between particles with different composition)
    - long-ranged (compared to other surface forces)
    - strong at short distances
    - always present

Exercise 2

b. The vapour pressure of water is lower inside the pore than the normal vapour pressure for water. This means that water vapour will condense at the curved water film inside the pore at a lower pressure compared to a horizontal water film (capillary condensation).

Exercise 4

Assuming linearity

$$\Gamma_2 = -\frac{c}{nRT}\left(\frac{\gamma-\gamma_0}{c-c_0}\right),$$ where n depends on the system (2 for strong electrolytes, see book)
(2 if dissociation occurs)

Molecular area

$$A = \frac{1}{\Gamma \cdot N_A}$$

For anionic surfactant, adding ions decreases the molecular area as the ions can shield the surfactants, making them come closer and increasing the packing.
For non-ionic surfactant, adding ions shows no change as the ions do not affect the packing as the surfactant doesn't dissociate.

The ionic surfactant is bigger than non-ionic; this could be due to solvation of the ions and charge in the head group due to SDS will cause repulsion and will also result in a larger molecular area.

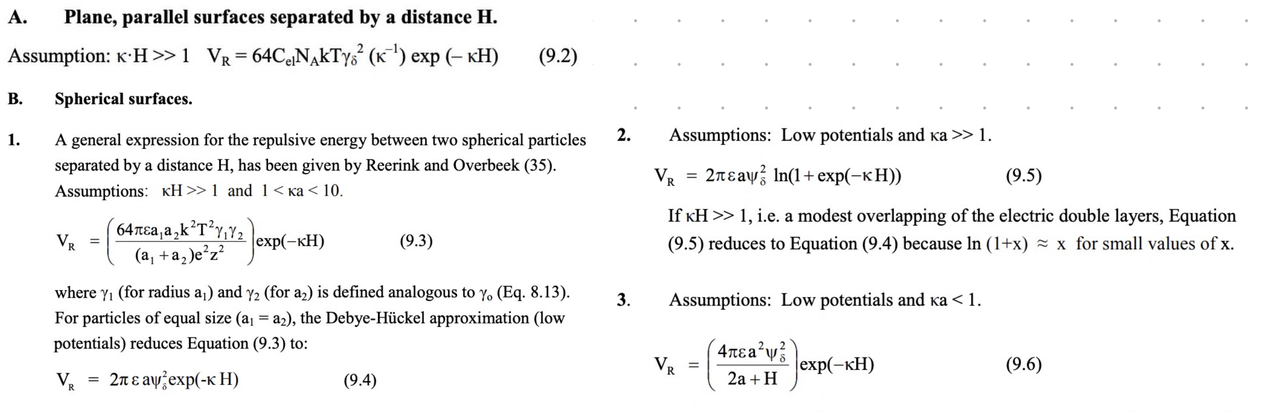
Exercise 5

b.
The results show that the area per molecule is lower for the short chained fatty acids (acetic acids and propionic acid) than for the long chained fatty acids (palmitinic acid and stearic acid). This means that the short chained fatty acids are much more densely adsorbed onto the Fe_2O_3 particles than the long chained fatty acids. Consequently, the 2-dimensional states are different between the short chained and long chained fatty acids. The short-chained acids are in a condensed state, while the long-chained acids are in a gaseous state (analogous to condensed and gaseous states of Langmuir monolayers).

d. The adsorption of surfactant increases with increase in CPP, irrespective of the surface. All factors that increases the CPP increase the adsorption on hydrophobic surfaces as high CPP will lead to cylindrical shape and cylindrical shaped surfactant are better adsorbed on to the surface. A similar trend, increase in adsorption while CPP increases, can also be seen when surfactants are adsorbed on polar surfaces.

Exercise 8

V_R expressions for different geometries:



A. Plane, parallel surfaces separated by a distance H.

Assumption: $\kappa \cdot H >> 1$ $V_R = 64C_{el}N_A kT\gamma_\delta^2(\kappa^{-1})\exp(-\kappa H)$ (9.2)

B. Spherical surfaces.

1. A general expression for the repulsive energy between two spherical particles separated by a distance H, has been given by Reerink and Overbeek (35). Assumptions: $\kappa H >> 1$ and $1 < \kappa a < 10$.

$$V_R = \left(\frac{64\pi\varepsilon a_1 a_2 k^2 T^2 \gamma_1 \gamma_2}{(a_1+a_2)e^2 z^2}\right)\exp(-\kappa H) \qquad (9.3)$$

where γ_1 (for radius a_1) and γ_2 (for a_2) is defined analogous to γ_o (Eq. 8.13). For particles of equal size ($a_1 = a_2$), the Debye-Hückel approximation (low potentials) reduces Equation (9.3) to:

$$V_R = 2\pi\varepsilon a\psi_\delta^2\exp(-\kappa H) \qquad (9.4)$$

2. Assumptions: Low potentials and $\kappa a >> 1$.

$$V_R = 2\pi\varepsilon a\psi_\delta^2 \ln(1+\exp(-\kappa H)) \qquad (9.5)$$

If $\kappa H >> 1$, i.e. a modest overlapping of the electric double layers, Equation (9.5) reduces to Equation (9.4) because $\ln(1+x) \approx x$ for small values of x.

3. Assumptions: Low potentials and $\kappa a < 1$.

$$V_R = \left(\frac{4\pi\varepsilon a^2\psi_\delta^2}{2a+H}\right)\exp(-\kappa H) \qquad (9.6)$$

This case is especially relevant for non-aqueous dispersions of small particles.

Exercise 9

Average vertical draining:

$$V_{AV} = \frac{g\rho_L \delta(t)^2}{8\eta_L}$$

Average rate of horizontel draining

$$\frac{d\delta}{dt} = -\frac{2\delta^3 \Delta P}{3\eta_L R_f^2}, \Delta P = \frac{2\gamma_{AL}}{R_B}$$

Explanations of the exam terms