

Introduction to Colloid and Surface Chemistry

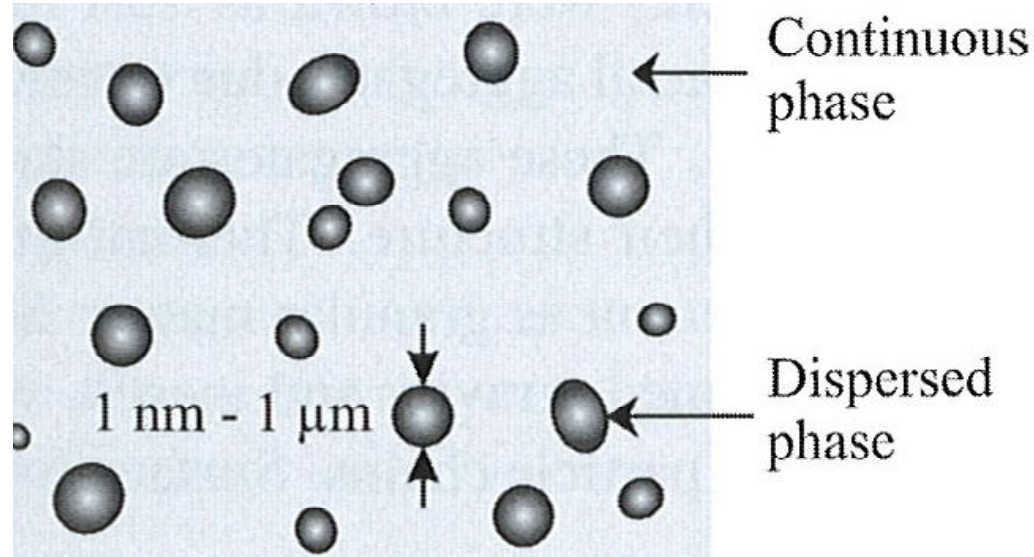
Basic definitions

Classifications of colloidal systems

Physical characteristics

Colloidal systems

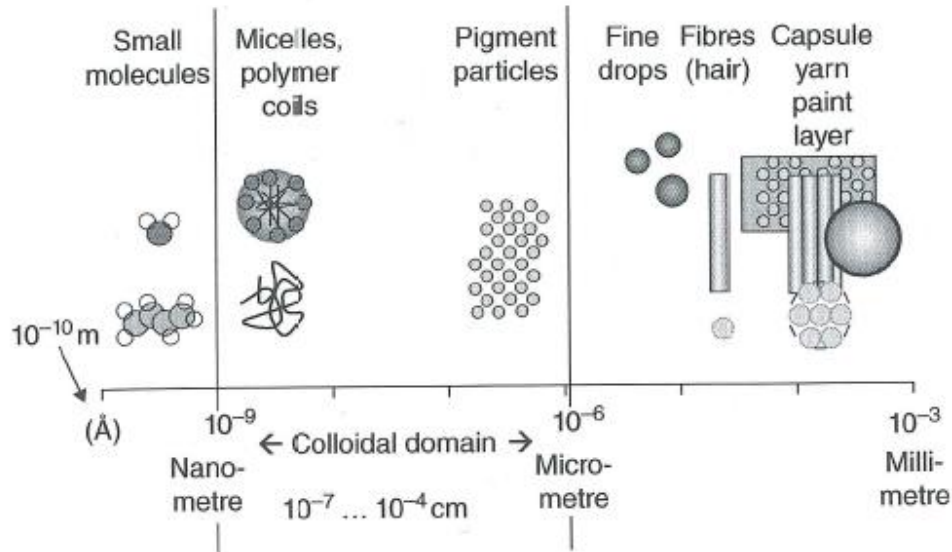
At least two components



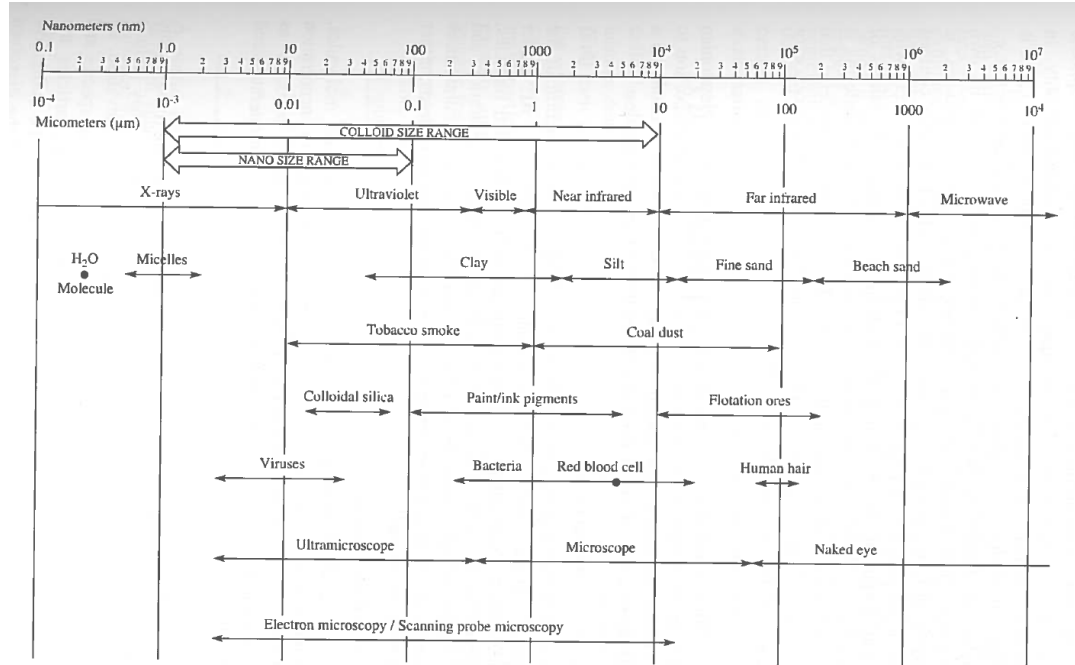
- uniform on macroscopic scale, but not on microscopic scale
- consists of particles/drops/bubbles of one phase dispersed in a matrix of another phase

Colloidal systems

At least one linear dimension between 1nm and 1 μ m (10^{-9} and 10^{-6} m)



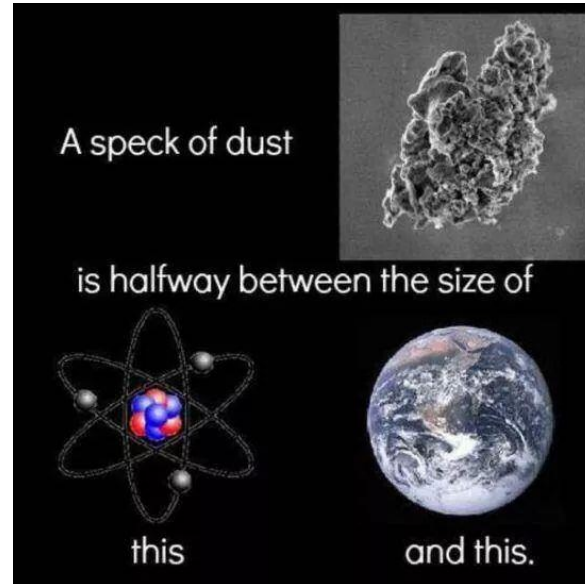
Colloidal systems



Nanostructure: Objects with at least one dimension between 1 and 100 nm

Colloidal systems

Colloidal dimensions lie between atomic and bulk dimensions





Colloidal systems

Important 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 effects
- Long-ranged intermolecular interactions
- Thermodynamic properties are size dependent
- Interaction with electromagnetic radiation

Colloidal systems



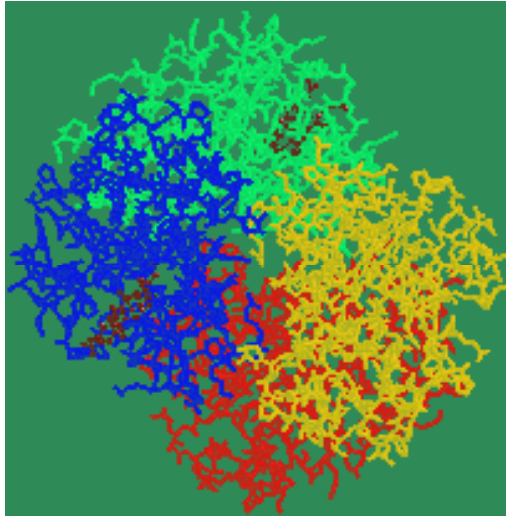
Disperses phase	Continuous phase	Term	Example
Liquid	Gas	Liquid aerosol	Fog, sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Soap foam, shaving cream
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Suspension	Paint
Gas	Solid	Solid foam	Bread
Liquid	Solid	Solid emulsion	Margarine, opal,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

Collective term: Colloidal dispersions

Colloidal systems

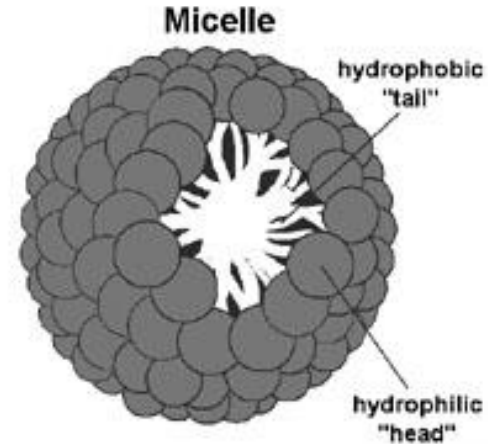
Macromolecules (polymers/proteins)

– true solutions



Association colloids

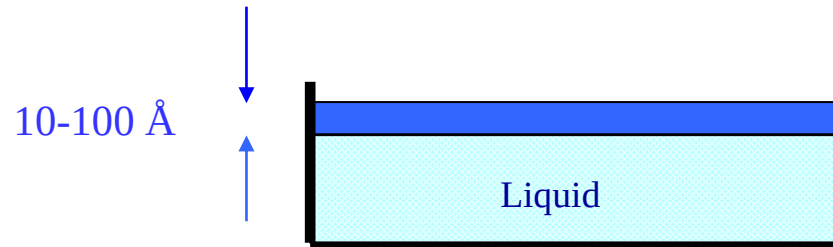
- self-assembled surfactants



Colloids and surfaces

Surface: Often considered as a dividing line between two phases

Chemically: A phase boundary with a thickness of molecular dimensions

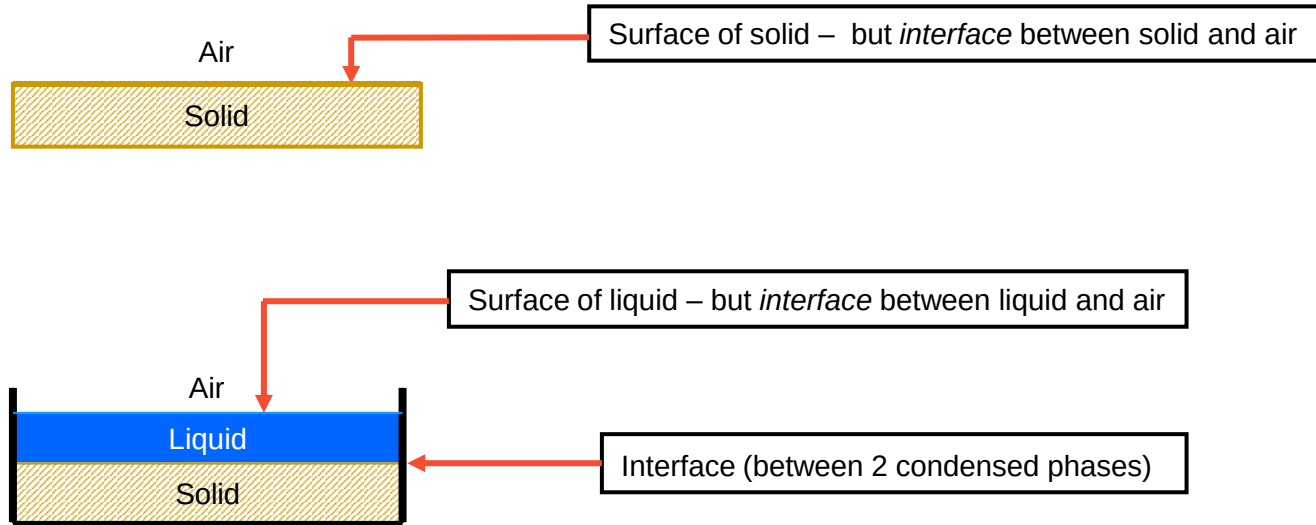


Colloids and interfaces



Interface (grenseflate):

The dividing region between 2 phases

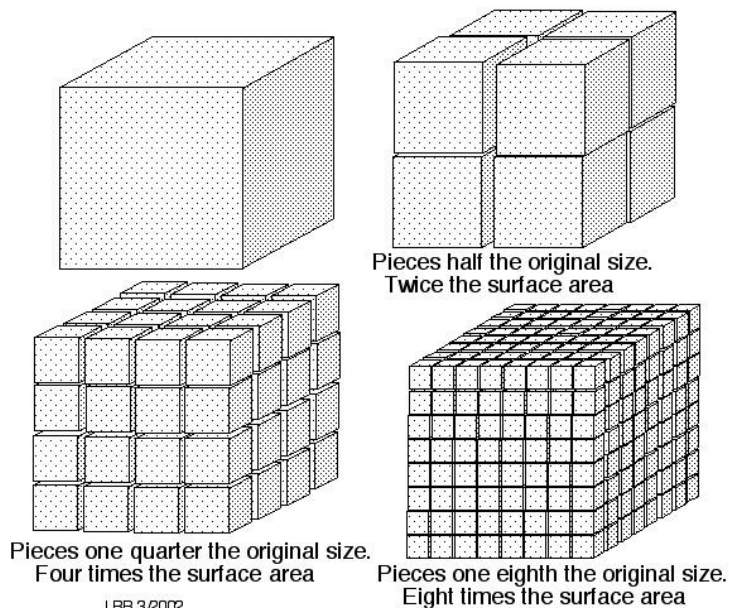


Colloids and interfaces



Colloidal dimensions lie between atomic and bulk dimensions

⇒ behaviour of colloidal systems largely determined by *interfacial properties*



LBR 3/2002



Specific surface area (A_{sp})

The area of particles will depend on the amount of particles

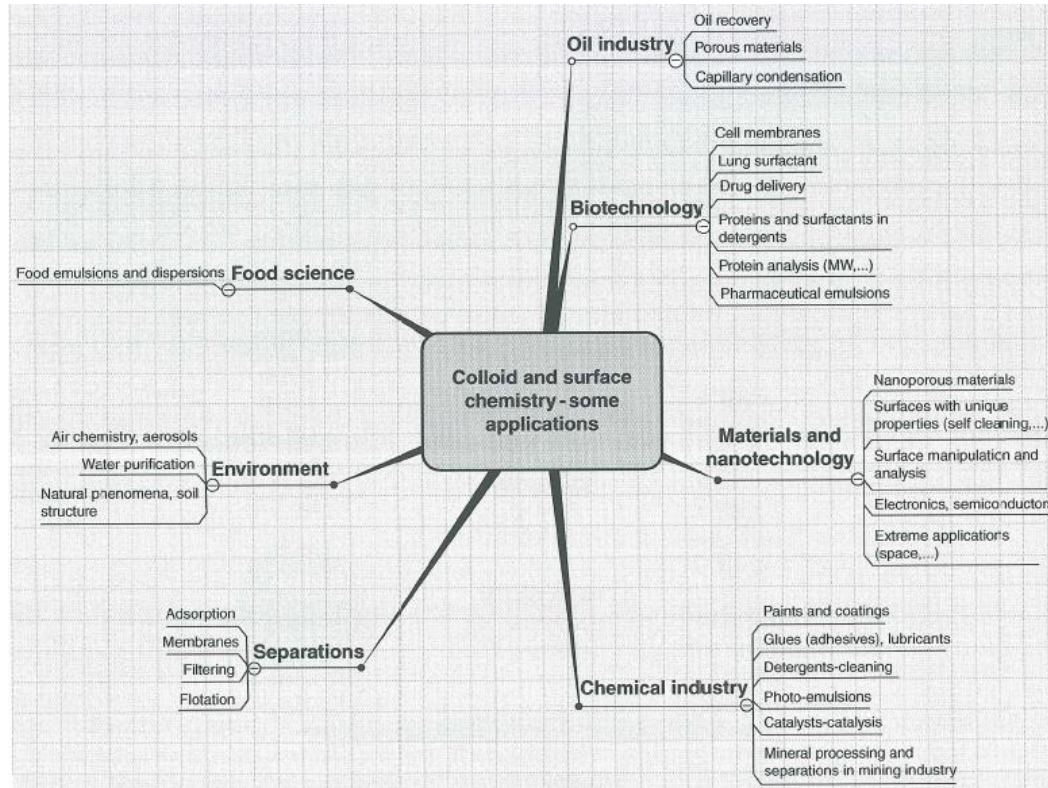
⇒ Convenient to define *specific surface area*: $A_{sp} = \frac{A_{tot}}{m_{tot}}$

Special cases: Sphere: $A_{sp} = \frac{3}{\rho R_S}$

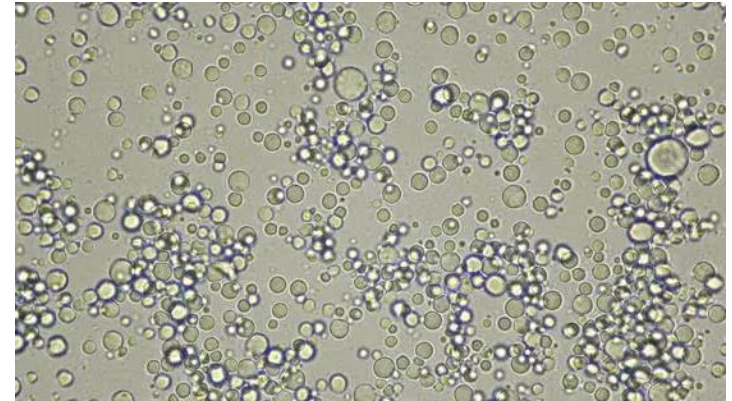
Thin rod: $A_{sp} \approx \frac{2}{\rho R_C}$

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

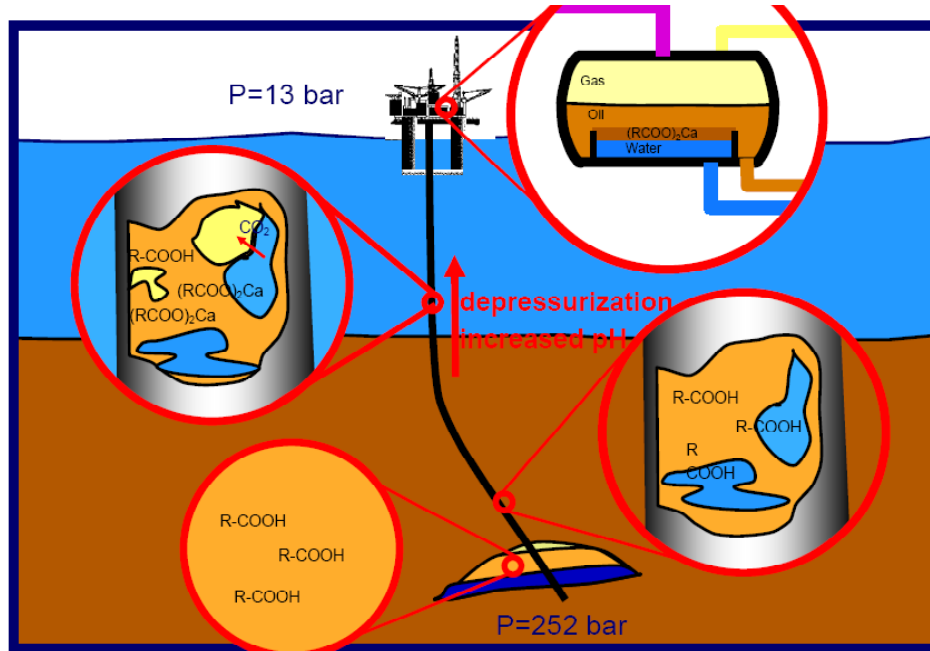
Applications



Food industry



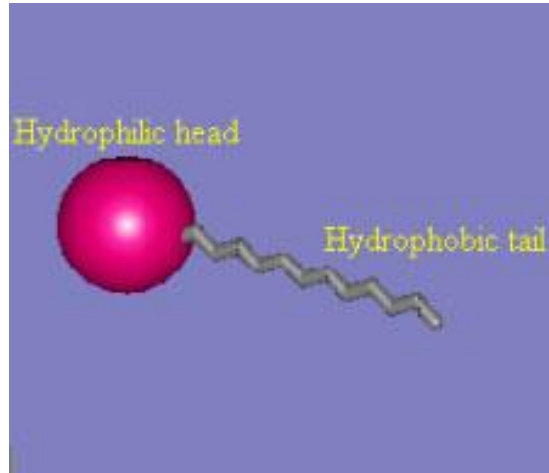
Petroleum industry



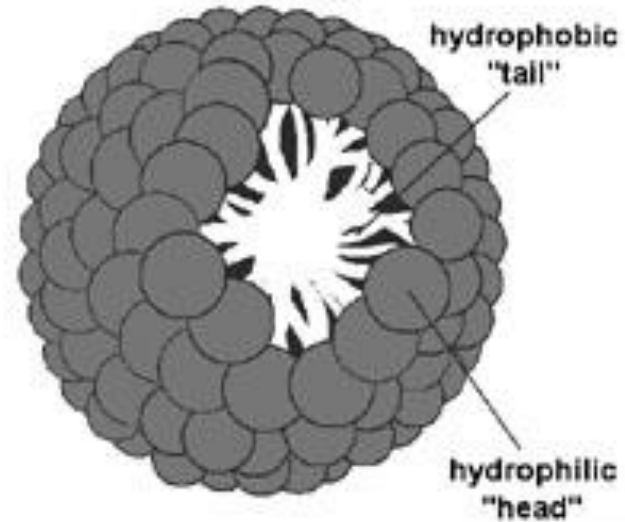
Detergency



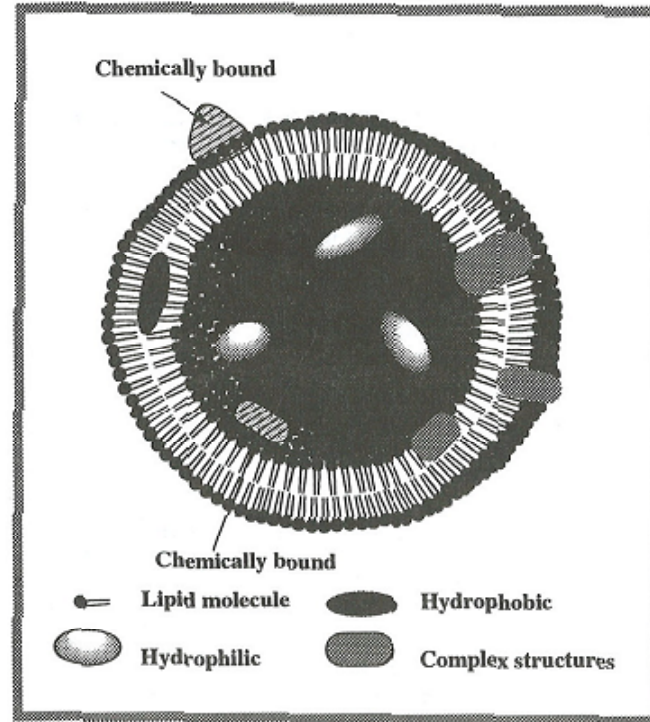
Surfactant



Micelle



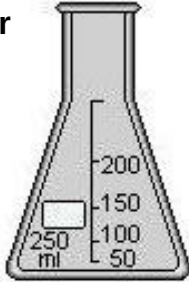
Pharmaceutical industry



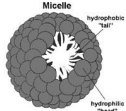
Materials technology



Silica
precursor



Micelle solution



Sol-gel route:

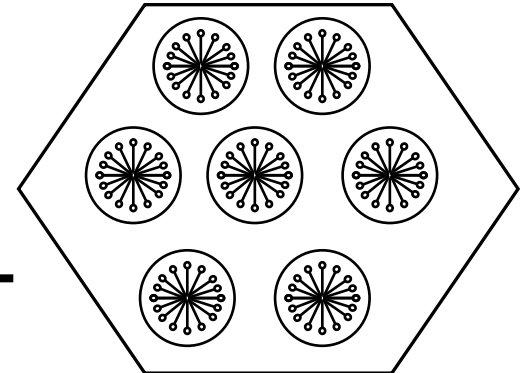
Hydrolysis: $\equiv\text{Si-OR} + \text{H}_2\text{O} \leftrightarrow \equiv\text{Si-OH} + \text{ROH}$

Water condensation: $\equiv\text{Si-OH} + \equiv\text{Si-OH} \leftrightarrow \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O}$

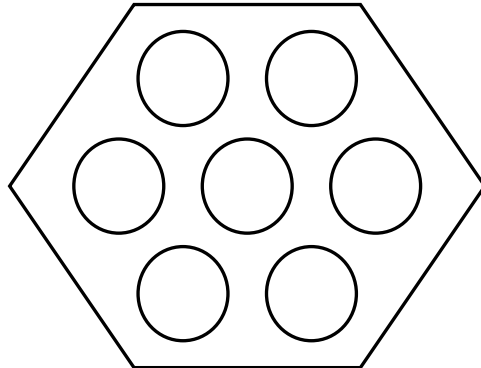
Alcohol condensation: $\equiv\text{Si-OR} + \equiv\text{Si-OH} \leftrightarrow \equiv\text{Si-O-Si}\equiv + \text{ROH}$

Self-assembly and

Charge Density Matching



Calcination or Extraction



Stability of colloidal systems



Colloidal dispersions: thermodynamically stable 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

Stability of colloidal systems



2. Kinetic stability:

No *spontaneous* formation of a colloid dispersion when two phases are brought into contact

⇒ *Energy* is required to form the dispersion

Phase separation will occur spontaneously

Lyophobic (solvent hating) colloids

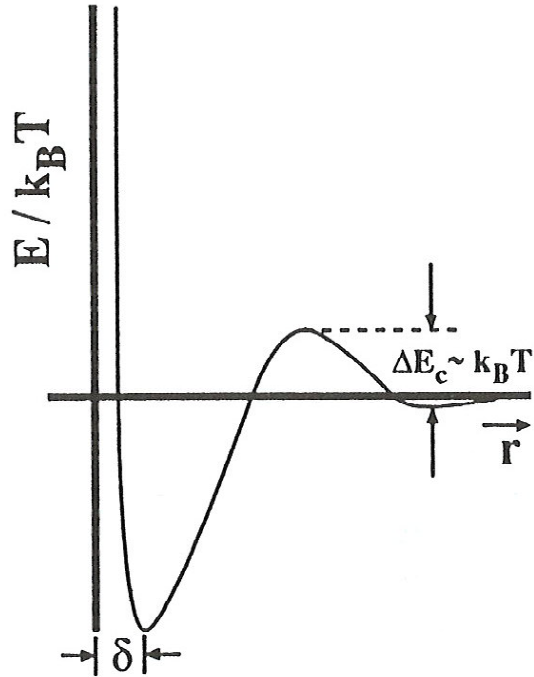
Example: oil and water mixtures (emulsions)



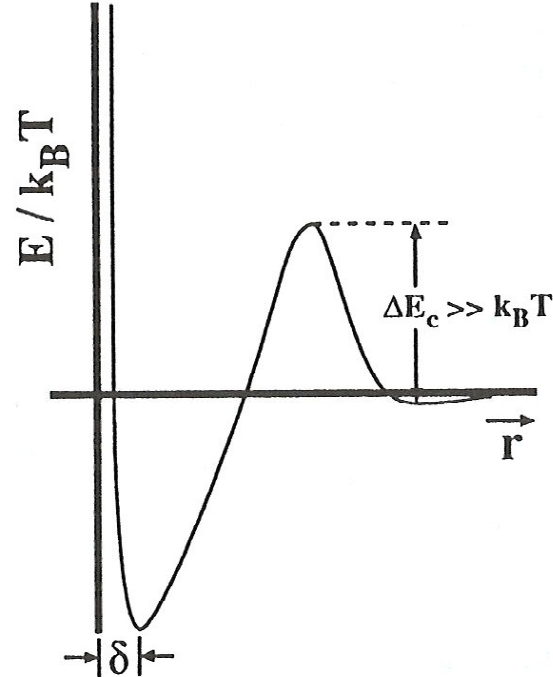
Colloidal dispersions in technical systems are often *kinetically stabilised*.

Kinetic stability have broad time range (seconds to years)

Stability of colloidal systems



Kinetically Unstable



Kinetically Stable

Destabilisation of dispersions

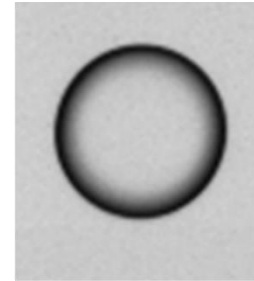
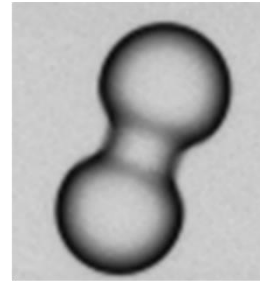
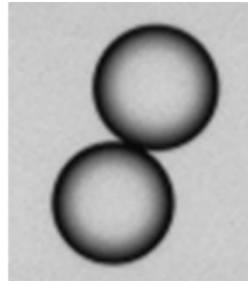
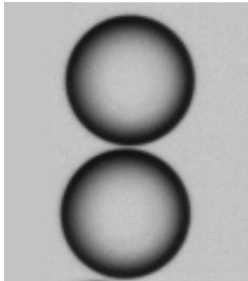
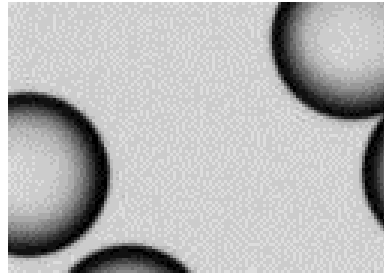
Destabilisation of kinetically stable dispersions can occur through coarsening processes:
Spontaneous change into a smaller number of larger particles

Coarsening processes:

- coalescence (*koalesens*)
- aggregation (*aggregering*)
- flocculation (*flokkulering*)

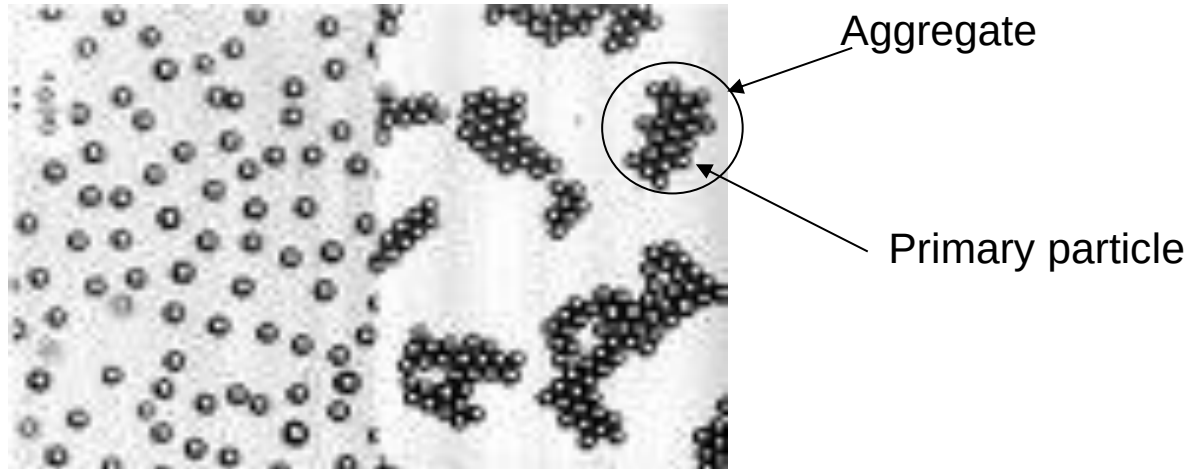
Coalescence

Drops/bubbles fuse together to a larger drop/bubble $\Rightarrow$ *total surface area is reduced*



Aggregation

Particles "clump together", but do not fuse into a new particle
 $\Rightarrow$ *total surface area is not significantly reduced*



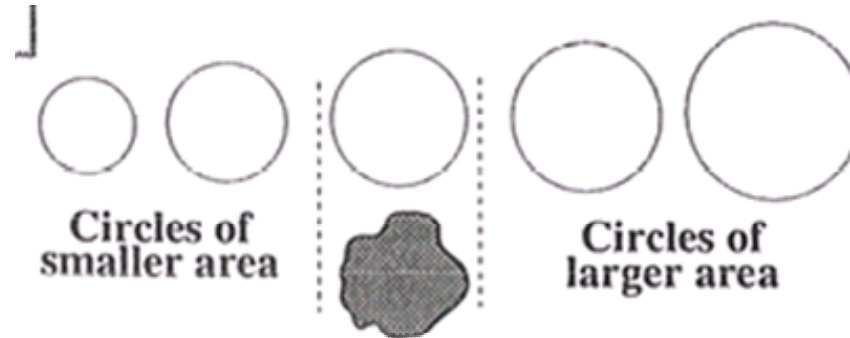
Aggregation is often called coagulation ([koagulering](#)) when destabilisation is caused by salts or charge neutralisation

Physical characteristics of colloids

Particle shape

1. High degree of symmetry

- Spheres
- Approximation to spheres



Physical characteristics of colloids

Particle shape

2. Low degree of symmetry

Ellipsoid of revolution, described by axial ratios

- $a \gg b$: prolate ellipsoid
~cylinder (rod-shaped particles)
- $a \ll b$: oblate ellipsoid
~disc shape (clay platelets)

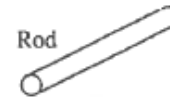


Prolate ($a > b$)



Oblate ($a < b$)

(a = axis of revolution)



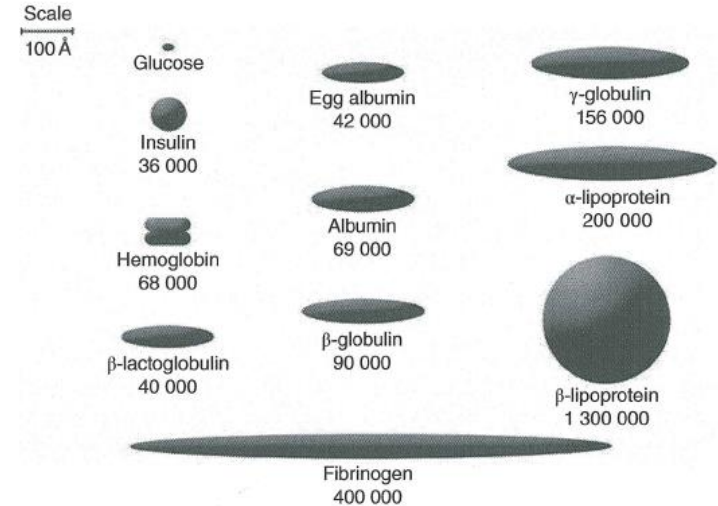
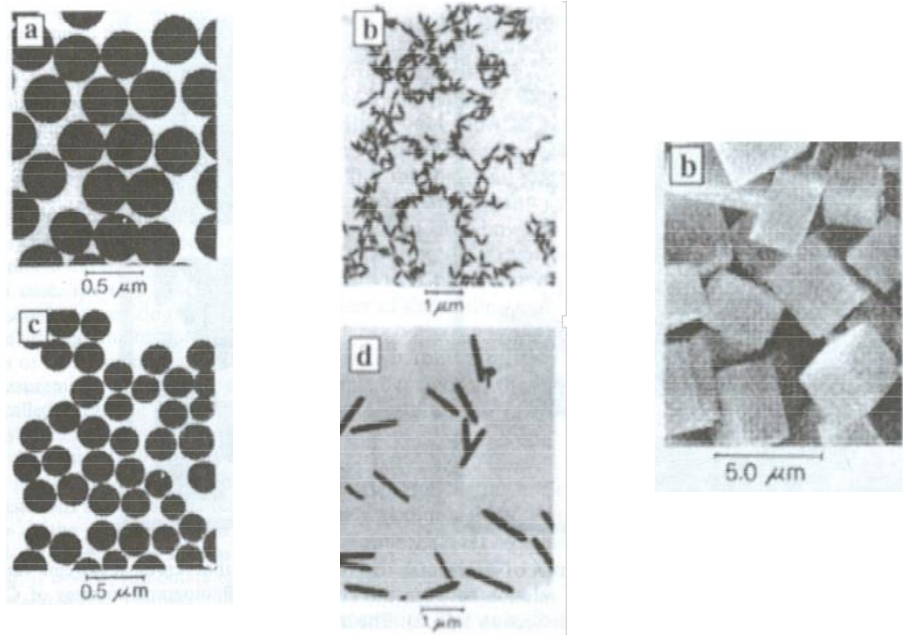
$a/b \rightarrow \infty$



$a/b \rightarrow 0$

Physical characteristics of colloids

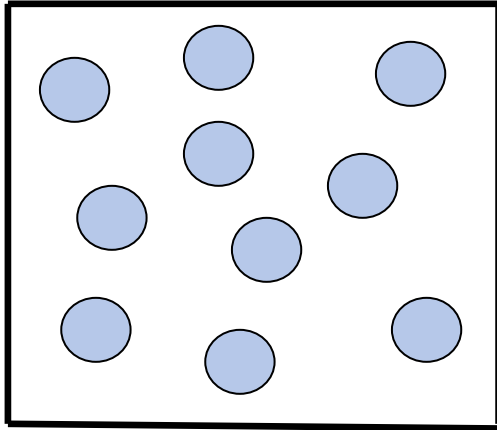
Particle shape



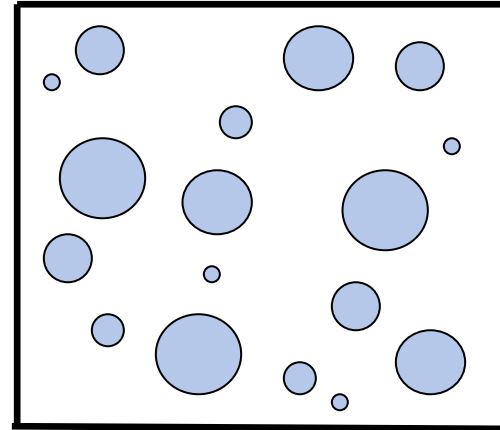
Physical characteristics of colloids

Particle size

Monodisperse system

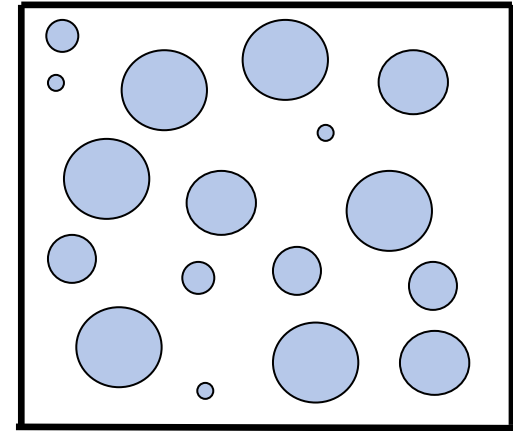
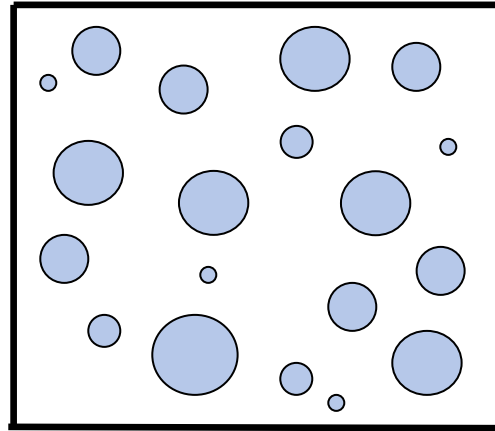
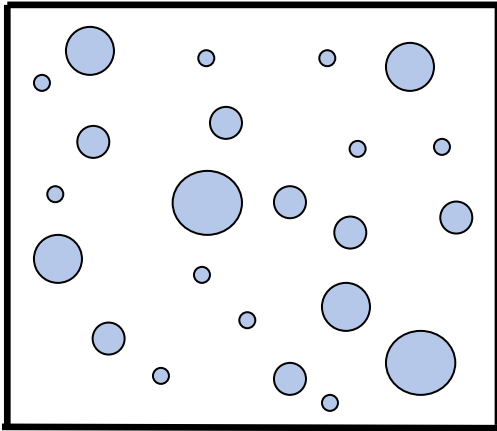


Polydisperse system



Physical characteristics of colloids

Particle size distribution can vary in a polydisperse system:



Physical characteristics of colloids

Polydispersity

Particle size is divided into classes

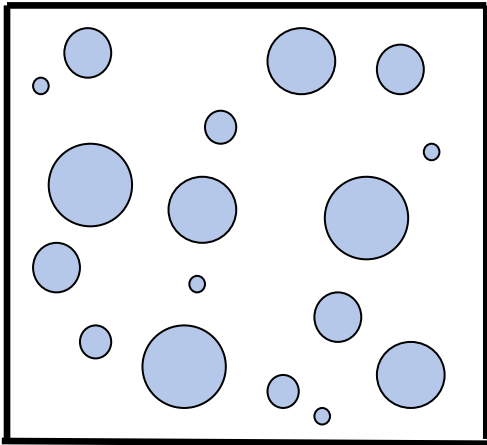


TABLE 1.5 A Hypothetical Distribution of 400 Spherical Particles^a

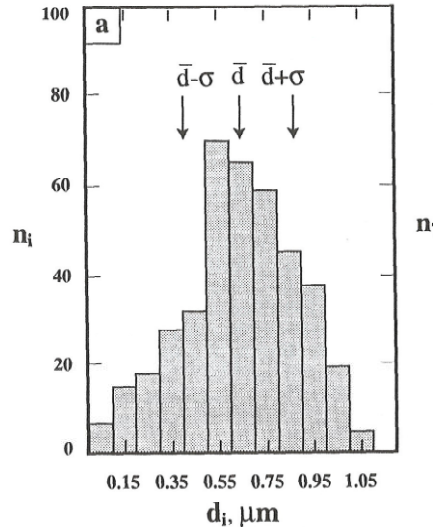
Class boundaries $<d < (\mu\text{m})$	Class mark d_i (μm)	Number of particles n_i	Fraction of total number in class $f_{n,i}$	Total number with $d < d_p$ $n_{T,i}$
0–0.1	0.05	7	0.018	7
0.1–0.2	0.15	15	0.038	22
0.2–0.3	0.25	18	0.045	40
0.3–0.4	0.35	28	0.070	68
0.4–0.5	0.45	32	0.080	100
0.5–0.6	0.55	70	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

Physical characteristics of colloids

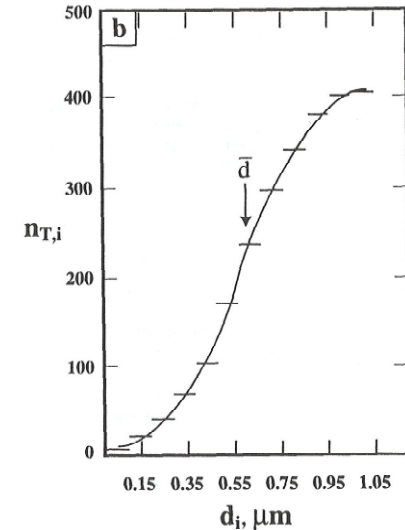
Polydispersity

Various graphical representations:

Histogram



Cumulative curve





Physical characteristics of colloids

Polydispersity

Definition of average: $\text{"average"} = \sum_i (\text{weighting factor})_i (\text{quantity being averaged})_i$

Number average

(antallsgjennomsnitt):

$$\bar{d}_n = \sum_i \frac{n_i}{\sum_i n_i} d_i$$

Surface average

(overflategjennomsnitt):

$$\bar{d}_s = \sqrt{\frac{\sum_i n_i d_i^2}{\sum_i n_i}}$$

Volume average

(volumgjennomsnitt):

$$\bar{d}_v = \sqrt[3]{\frac{\sum_i n_i d_i^3}{\sum_i n_i}}$$



Physical characteristics of colloids

Polydispersity

Polydisperse systems: $\bar{d}_n < \bar{d}_S < \bar{d}_V$

Monodisperse systems: $\bar{d}_n = \bar{d}_S = \bar{d}_V$



Physical characteristics of colloids

Example:

A suspension contains totally $n = 4 \times 10^{13} \text{ particles/dm}^3$

The total volume of particles is $V_{tot} = 4 \times 10^{-6} \text{ m}^3$

The dispersion is bidisperse (contains two types of monodisperse particles, A and B),
where $n_A = 3n_B$ and $d_B = 2d_A$

What is the volume average diameter?

Home experiment - mayonnaise



Materials:

- large jar with lid
- two egg yolks
- measuring cups
- 1/4 cup vinegar
- salad oil
- 1/4 cup salad oil
- water
- one small cup or bowl

Recording procedure:

1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no



Procedure:

Part 1

1. Measure two - three cups of water and pour into a large jar.
2. Measure out two - three cups of salad oil and pour into the jar.
3. Shake the contents
4. Leave it to rest for 5 minutes
5. Observe and explain what happens

Part 2

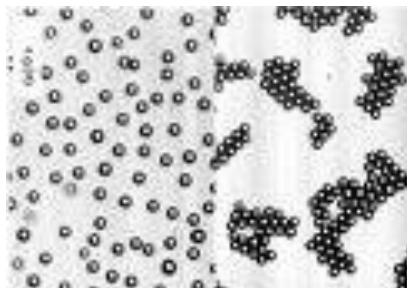
1. Pour the vinegar into your jar, after emptying it.
2. Pour the salad oil into the jar and put on the lid.
3. Shake the contents very hard for 5 minutes, then leave it to rest for about 5 min.
4. Observe and explain what happens

Part 3

1. Put the egg yolks into the small cup or bowl.
2. Beat the yolks until they are liquid.
3. Pour the beaten yolks into the jar with the oil and vinegar and close the lid.
4. Shake the contents very hard for 5 minutes.
5. Observe and explain what happens.

Intermolecular and Interparticle forces

All interfacial phenomena (interfacial tension, wettability,...) are influenced by forces originating from molecular level interactions



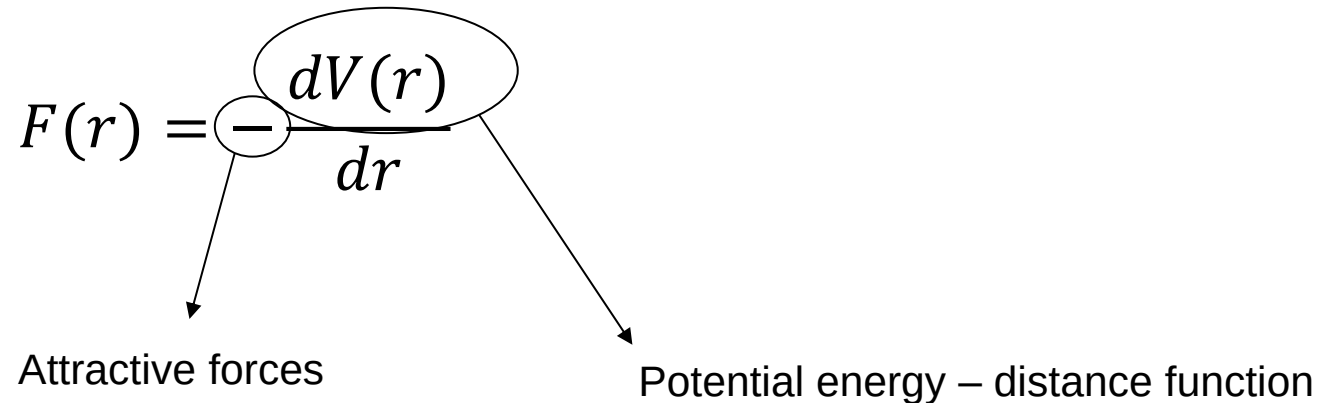
- Forces between molecules (in vacuum)
- Scale-up to forces between colloidal particles (in vacuum)
- Account for solvent

Intermolecular forces

Total energy of molecules:

- Kinetic energy (proportional to $k_B T$)
- Potential energy (depend on position and forces)

Useful representation of intermolecular (and interparticle) forces:

$$F(r) = - \frac{dV(r)}{dr}$$


Attractive forces

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/mol
(Covalent bonds	150 – 900 kJ/mol)



Van der Waals forces – molecular origin

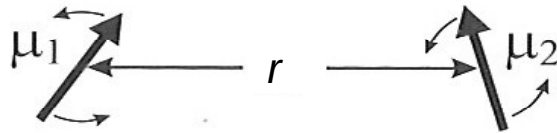
Attractive forces originating from induced or permanent dipoles in atoms/molecules

Three contributions:

1. Polar (Keesom) interactions (permanent dipole/permanent dipole)
2. Induced (Debye) interactions (permanent dipole/induced dipole)
3. Dispersion (London) interactions (induced dipole/induced dipole)

Van der Waals forces – molecular origin

Polar (Keesom) interactions: permanent dipole - permanent dipole



$$V_{12}^p = -\frac{1}{3} \left[\frac{\mu_1^2 \mu_2^2}{k_B T (4\pi\epsilon_0)^2} \right] r^{-6}$$

Debye Interactions: permanent dipole - induced dipole

Molecule with permanent dipole induce a dipole in the second molecule

$$V_{12}^{ind} = - \left[\frac{\alpha_{01} \mu_2^2 + \alpha_{02} \mu_1^2}{(4\pi\epsilon_0)^2} \right] r^{-6}$$



Van der Waals forces – molecular origin

Dispersion interactions: induced dipole - induced dipole

$$V_{12}^{disp} = - \left[\frac{3\alpha_{01}\alpha_{02}}{2(4\pi\epsilon_0)^2} \right] \left[\frac{I_1 I_2}{I_1 + I_2} \right] r^{-6}$$

No permanent dipole is necessary for attraction to occur
- *dispersion forces are always present*



Van der Waals forces – molecular origin

All molecules: dipole moment and polarizability,
i.e. all three interactions *can* operate between any pair of molecules

The net van der Waals interaction (pair of molecules):

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



Van der Waals forces – molecular origin

Fractional contributions to the total interactions: $f_D + f_K + f_L = 1$

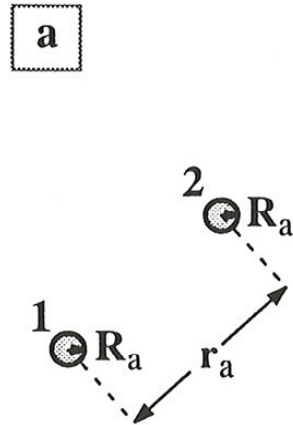
Compound	μ (debye)	$\frac{\alpha}{4\pi\epsilon_0} \times 10^{30}$ (m ³)	$\beta \times 10^{77}$ (J m ⁶)	Percentage contribution of		
				Keesom (permanent- permanent)	Debye (permanent- induced)	London (induced- induced)
CCl ₄	0.00	10.70	4.41	0.0	0.0	100.0
Ethanol	1.73	5.49	3.40	42.6	9.7	47.6
Thiophene	0.51	9.76	3.90	0.3	1.3	98.5
<i>t</i> -Butanol	1.67	9.46	5.46	23.1	9.7	67.2
Ethyl ether	1.30	9.57	4.51	10.2	7.1	82.7
Benzene	0.00	10.50	4.29	0.0	0.0	100.0
Chlorobenzene	1.58	13.00	7.57	13.3	8.6	78.1
Fluorobenzene	1.35	10.30	5.09	10.6	7.5	81.9
Phenol	1.55	11.60	6.48	14.5	8.6	76.9
Aniline	1.56	12.40	7.06	13.6	8.5	77.9
Toluene	0.43	11.80	5.16	0.1	0.9	99.0
Anisole	1.25	13.70	7.22	5.5	6.0	88.5
Diphenylamine	1.08	22.60	14.25	1.5	3.7	94.7
Water	1.82	1.44	2.10	84.8	4.5	10.5

London interactions: largest contribution for *most* molecules

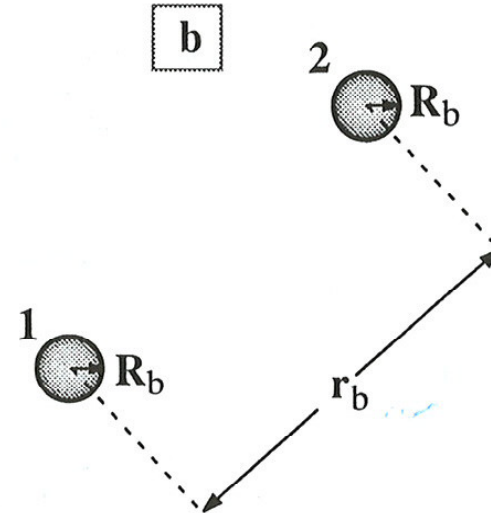
van der Waals forces - colloids

Consider 2 spherical particles of the same composition

a: Spheres of radius R_a



b: Spheres of radius R_b

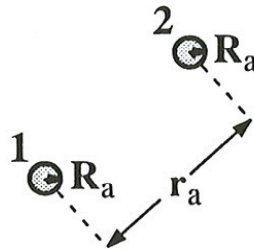


Radii are related: $R_b = f R_a$, where $f > 1$

van der Waals forces - colloids

Situation a:

a

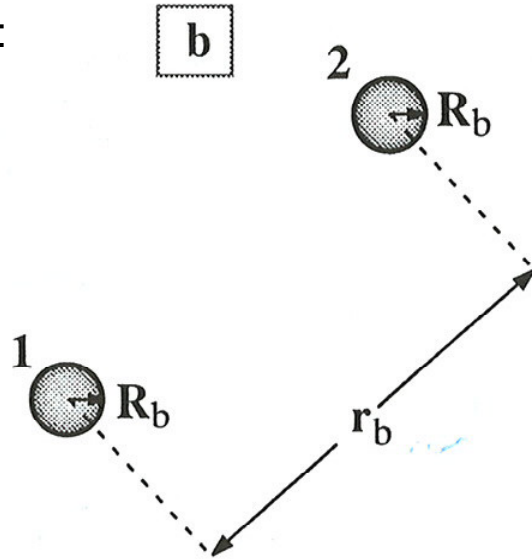


Assume that every atom in sphere 1 attracts every atom in sphere 2 with the total attractive energy:

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

van der Waals forces - colloids

Situation b:



Spheres larger by a factor f

Distance between centers also larger
a factor f : $r_b = fr_a$

Total interaction potential:
$$V_A(b) = -\frac{1}{2} \left(\frac{\rho N_A}{M} \right)^2 C \int \int r_b^{-6} dv_{1b} dv_{2b}$$



van der Waals forces - colloids

$$V_A(a) = V_A(b)$$

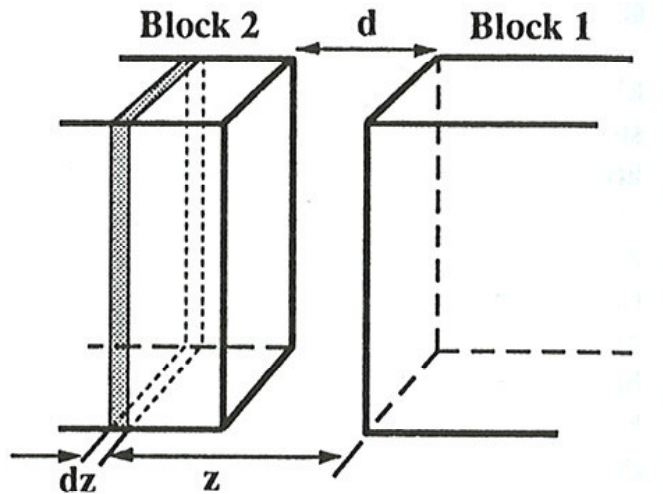
Attractive interaction energy is *identical* for the two situations

Two molecules 0,3 nm in diameter and 1 nm apart interact with exactly the same energy as two spheres of the same material that are 30 nm in diameter and 100 nm apart

Scaling up vdW interactions depend on geometry of interacting bodies

van der Waals forces - colloids

Attraction between two blocks of material:



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

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

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



van der Waals forces - colloids

Spheres of equal radius R_S :

$$V_A = -\frac{AR_S}{12d} \quad R_S \gg d$$

Spheres with radii R_1 and R_2 :

$$V_A = -\frac{A}{6d} \cdot \frac{R_1 R_2}{R_1 + R_2} \quad R_1 \text{ and } R_2 \gg d$$

Sphere and planar surface:

$$V_A = -\frac{AR_S}{6d}$$



Van der Waals forces - characteristics

- In most cases attractive
- Long-ranged
- Strong at short distances

Magnitude of Hamaker constants:

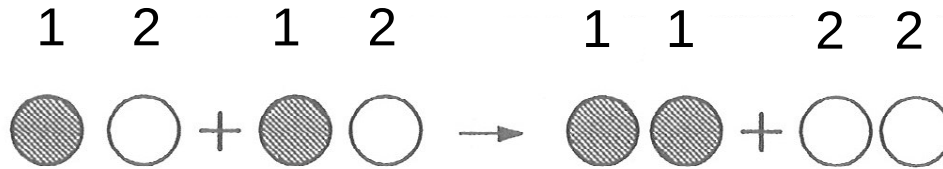
TABLE 10.3 Hamaker Constants for Selected Materials

Material	$A \times 10^{20}$ Joules	Source
Acetone	4.2	Croucher and Hair
Alumina	15.4	Bargeman and van Voorst Vader
Gold	45.3	Bargeman and van Voorst Vader
Magnesia	10.5	Bargeman and van Voorst Vader
Metals	16–45	Visser
Natural rubber	8.58	Croucher and Hair
Polystyrene	7.8–9.8	Croucher and Hair ; Croucher
Silver	39.8	Bargeman and van Voorst Vader
Toluene	5.4	Croucher and Hair
Water	4.35	Bargeman and van Voorst Vader

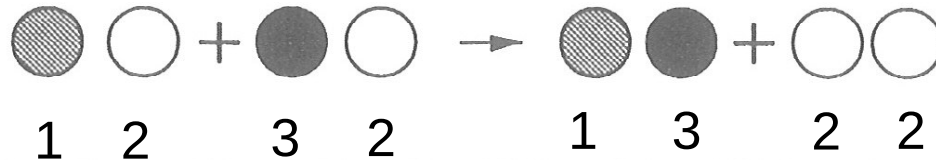
Van der Waals forces – effect of solvent



Model for accounting for solvent - defining a Hamaker constant A_{ijk} :



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



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

Surface/interfacial tension

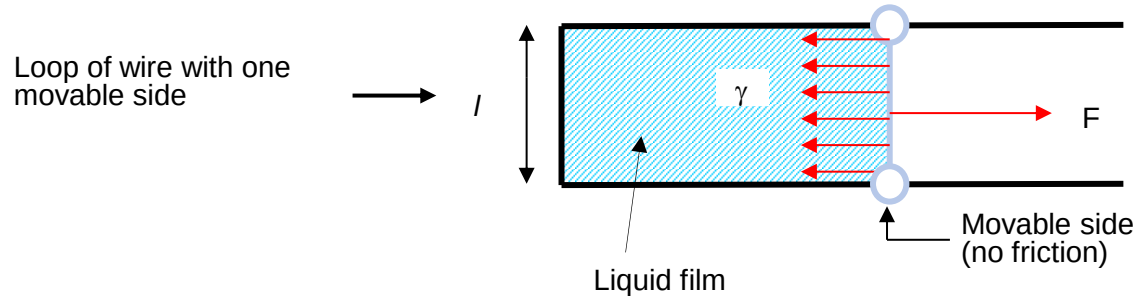


<https://www.youtube.com/watch?v=ynk4vJa-VaQ>

Surface Tension – definition 1



Surface tension as a force

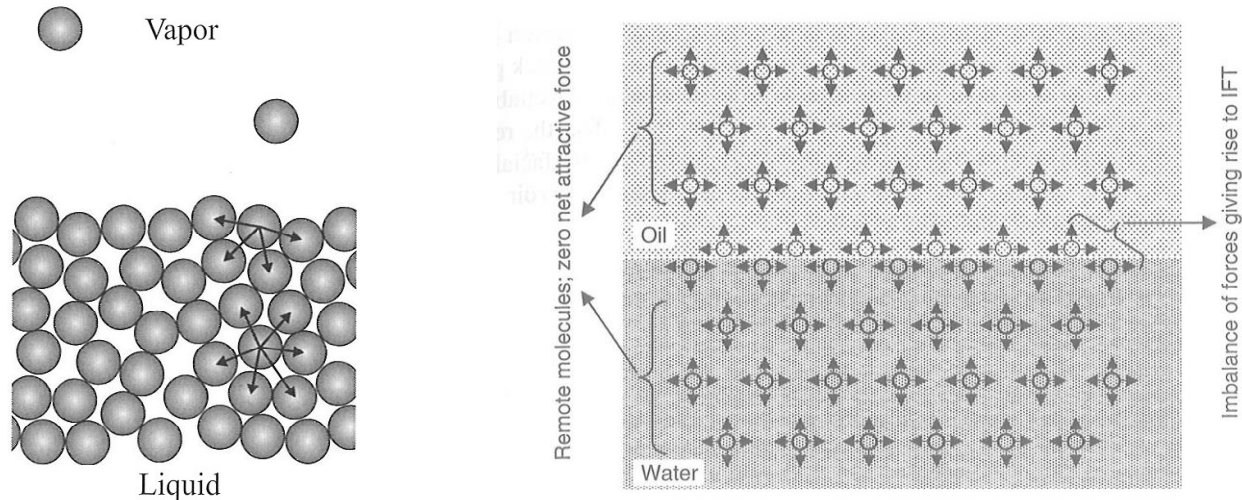


Force F needed
to prevent wire
moving

Surface tension: $\gamma = \frac{F}{2l}$ (mN/m) *also (dyn/cm)*

Process attid a minimum over flat area.
<http://web.mit.edu/nnf/education/wettability/slider.wmv>

Surface Tension – molecular origin



Unbalanced intermolecular forces at surfaces

⇒ surface is in a "state of tension"

⇒ surface will spontaneously try to reduce its area

Gibbs free energy:

ΔG : maximum work we can get from a process when
 $\Delta T = \Delta P = 0$

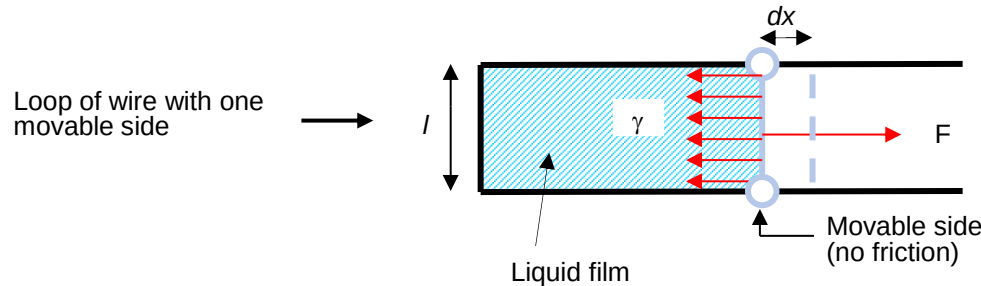
$\Delta G < 0$ = spontan process.

$\Delta G = 0$ likevekt

$\Delta G > 0$ ikke spontan.

Surface Tension – definition 2

Surface tension as Gibbs free energy



$$dW = \gamma dA \quad \Rightarrow \quad \gamma = \left(\frac{\partial G}{\partial A} \right)_{T,p} \quad (\text{J/m}^2) \quad (\text{Gibbs free energy of surfaces/ surface free energy})$$

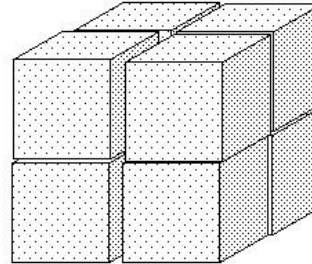
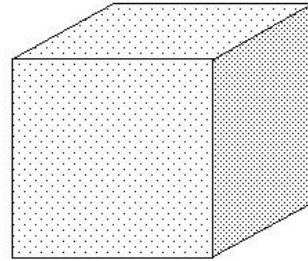
<http://web.mit.edu/nnf/education/wettability/surfacedeformation.wmv>

$$dW = Fdx = \gamma 2l dx = \gamma dA$$

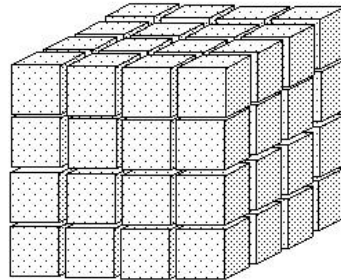
$$\Delta G = \gamma \Delta A$$

Interfacial tension

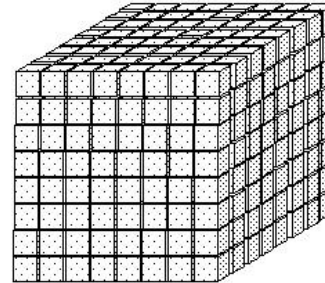
– importance for colloidal systems



Pieces half the original size.
Twice the surface area



Pieces one quarter the original size.
Four times the surface area



Pieces one eighth the original size.
Eight times the surface area

LBR 3/2002

Surface Tension – some values

Table 2.1: Surface tensions γ of some liquids at different temperatures T .

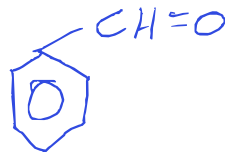
Substance	T	γ (mNm ⁻¹)	Substance	T	γ (mNm ⁻¹)
Water	10°C	74.23	Mercury	25°C	485.48
	25°C	71.99	Phenol	50°C	38.20
	50°C	67.94	Benzene	25°C	28.22
	75°C	63.57	Toluene	25°C	27.93
	100°C	58.91	Dichloromethane	25°C	27.20
Argon	90 K	11.90	<i>n</i> -pentane	25°C	15.49
Methanol	25°C	22.07	<i>n</i> -hexane	25°C	17.89
Ethanol	10°C	23.22	<i>n</i> -heptane	25°C	19.65
	25°C	21.97	<i>n</i> -octane	10°C	22.57
	50°C	19.89		25°C	21.14
1-propanol	25°C	23.32		50°C	18.77
1-butanol	25°C	24.93		75°C	16.39
2-butanol	25°C	22.54		100°C	14.01
Acetone	25°C	23.46	Formamide	25°C	57.03

dispersion
VdW
lenger fjelde
sterke elektroner

Interfacial tension – some values

Liquid (20° C)	Surface tension (mN/m) <i>Air</i>	Interfacial tension against water (mN/m) <i>Not air</i>
Water	72,8	–
Benzaldehyd	40,0	5,5
n-hexan	18,4	51,1
n-octan	21,8	50,8
Hexadecan	27,5	53,8
Ethanol	22,7	soluble
Mercury	485	426

Benzaldehyd:



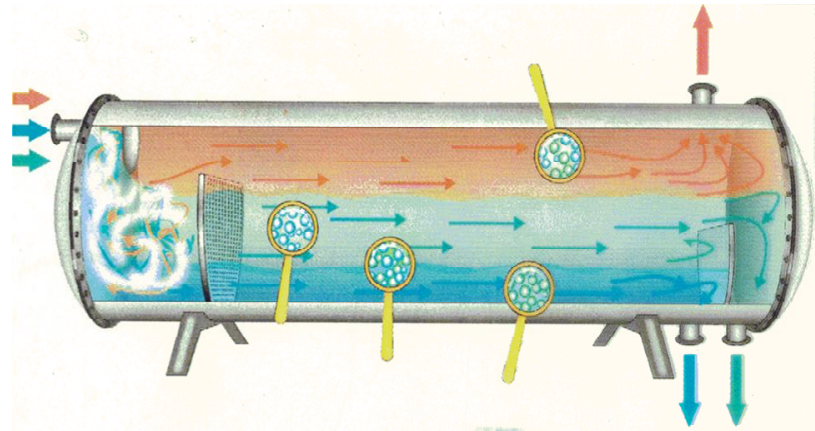
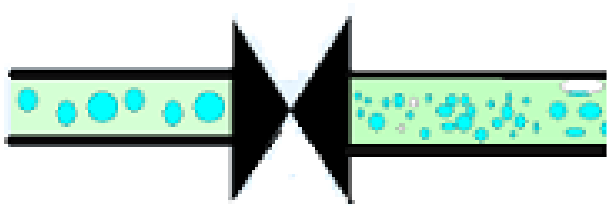
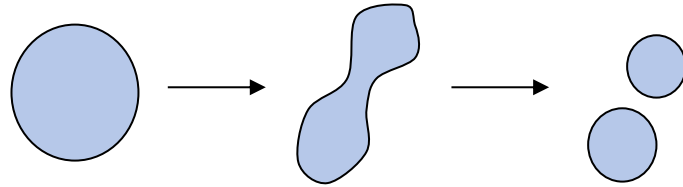
Polar permanent dipol

Hexadecan: $C_{16}H_{34}$

Non polar

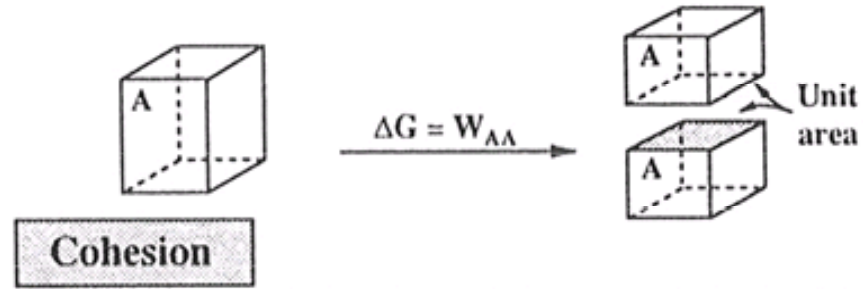
Interfacial tension

- formation of emulsions/aerosols/foam



Surface tension – work of cohesion

No surface → 2A surfaces

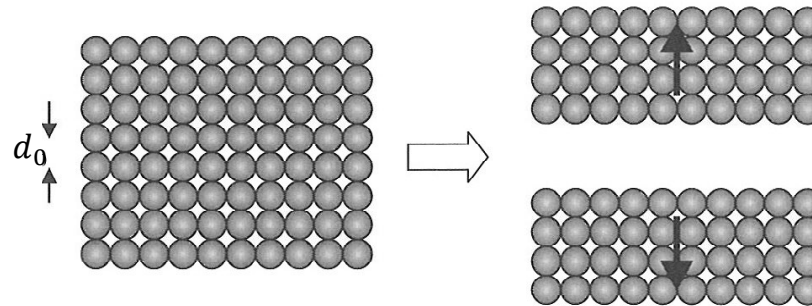


$$\Delta G = 2\gamma_A \text{ (work of cohesion - } W_{AA}\text{)}$$

– *measure of the attraction between molecules in the liquid*

Surface tension & Van der Waals forces

Surface energy and Hamaker constant:



d_0 : equilibrium spacing between molecules of the bulk material

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

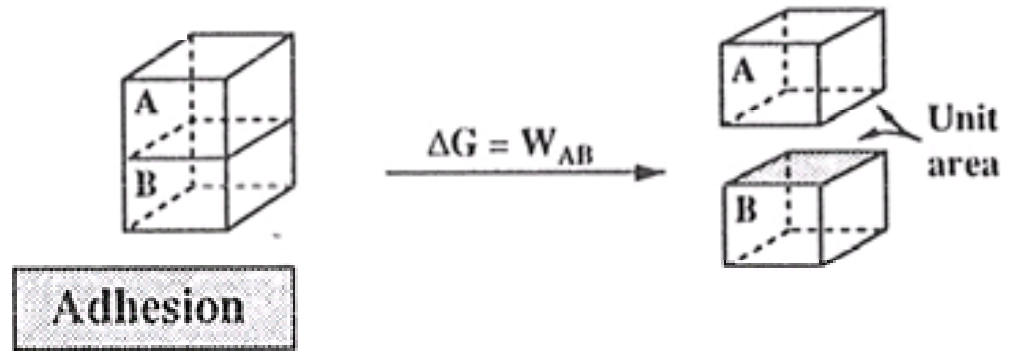
$w = 2\gamma$
Work of cohesion

$$V_A = -\frac{A}{12d^2\pi} \xrightarrow{\text{de delir seg}} \gamma = \frac{A}{24\pi d_0^2}$$

$$\Delta V = V_{\text{oo}} - V_A = 0 + \frac{A}{12d^2\pi} = 2\gamma \Rightarrow \gamma = \frac{A}{24\pi d_0^2}$$

Interfacial tension - work of adhesion

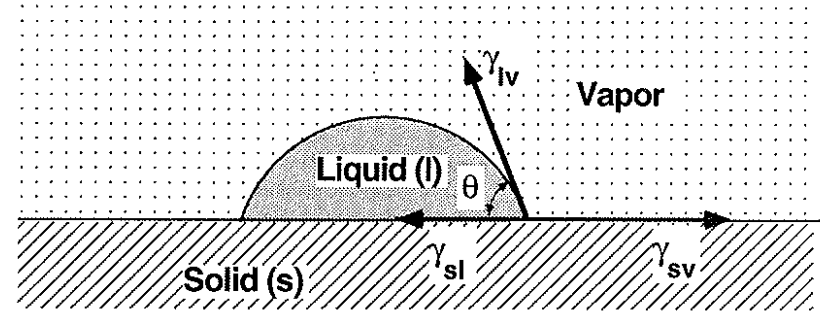
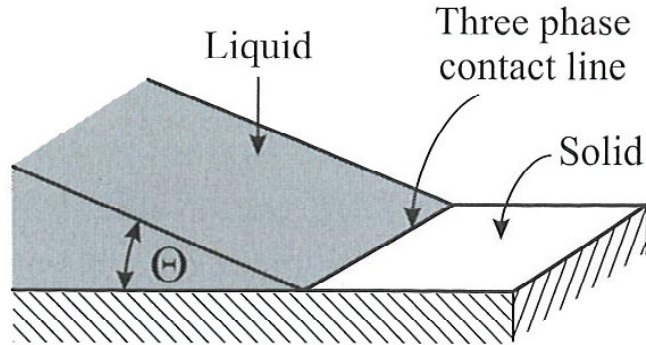
1AB surface $\rightarrow$ 1A og 1B surface



$$\Delta G = \gamma_A + \gamma_B - \gamma_{AB} \quad (\text{work of adhesion} - W_{AB})$$

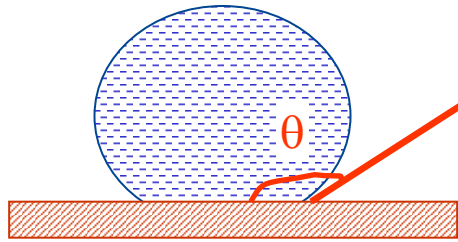
– *measure of attraction between two different phases*

Contact angle/wettability



$$\gamma_{sv} = \gamma_{lv} \cos(\theta) + \gamma_{sl} \quad \cos(\theta) = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad \text{Youngs}$$

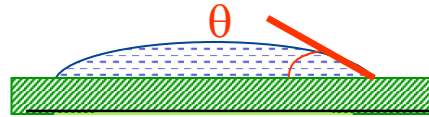
Contact angle/wettability



Wax

$\theta > 90^\circ$:

Non-wetting (drop)



Polymer

$\theta < 90^\circ$:

Wetting (lense)



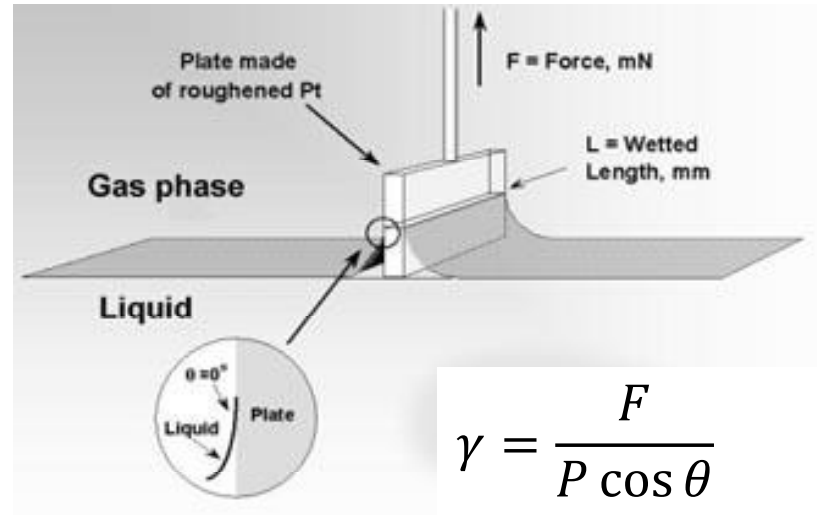
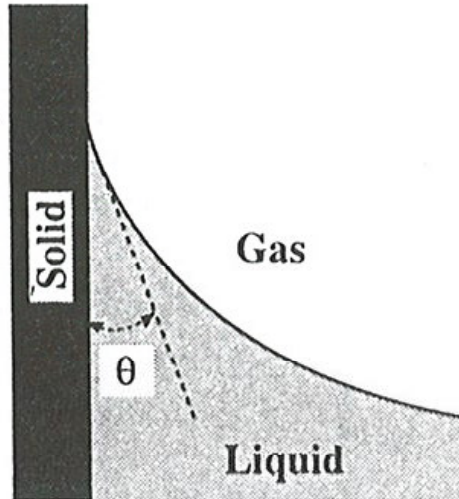
Glass

$\theta = 0$:

Complete wetting

Measuring surface tension/ contact angle

Force measurements: *Wilhelmy plate method*



$$\gamma = \frac{F}{P \cos \theta}$$

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	—	$\gamma_i + \gamma_j - 2\phi\sqrt{\gamma_i\gamma_j}$	$2\phi\sqrt{\gamma_i\gamma_j}$
Neumann	—	$\gamma_i + \gamma_j - 2\sqrt{\gamma_i\gamma_j}e^{-\beta(r_i - r_j)^2}$	$2\sqrt{\gamma_i\gamma_j}e^{-\beta(r_i - r_j)^2}$
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	$\gamma = \gamma^d + \gamma^{spec}$	$\gamma_i + \gamma_j - 2\sqrt{\gamma_i^d\gamma_j^d} - 2\sqrt{\gamma_i^{spec}\gamma_j^{spec}} =$ $\left(\sqrt{\gamma_i^d} - \sqrt{\gamma_j^d}\right)^2 + \left(\sqrt{\gamma_i^{spec}} - \sqrt{\gamma_j^{spec}}\right)^2$	$2\sqrt{\gamma_i^d\gamma_j^d} + 2\sqrt{\gamma_i^{spec}\gamma_j^{spec}}$
Hansen	$\gamma = \gamma^d + \gamma^p + \gamma^h$	$\gamma_i + \gamma_j - 2\sqrt{\gamma_i^d\gamma_j^d} - 2\sqrt{\gamma_i^p\gamma_j^p} - 2\sqrt{\gamma_i^h\gamma_j^h}$	$2\sqrt{\gamma_i^d\gamma_j^d} + 2\sqrt{\gamma_i^p\gamma_j^p} +$ $2\sqrt{\gamma_i^h\gamma_j^h}$
Van Oss et al.	$\gamma^{LW} + \gamma^{AB} =$ $\gamma^{LW} + 2\sqrt{\gamma^+\gamma^-}$	$\left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}}\right)^2 + 2\left(\sqrt{\gamma_i^+} - \sqrt{\gamma_j^+}\right)\left(\sqrt{\gamma_i^-} - \sqrt{\gamma_j^-}\right) =$ $\gamma_i + \gamma_j - 2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} - 2\sqrt{\gamma_i^+\gamma_j^-} - 2\sqrt{\gamma_i^-\gamma_j^+}$	$2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} +$ $2\sqrt{\gamma_i^+\gamma_j^-} + 2\sqrt{\gamma_i^-\gamma_j^+}$

Home experiment - floating paper clip



Materials:

- Paper clips
- A transparent glass bowl
- Clean water
- Tissue paper
- Pencil with eraser
- Dish soap

Procedure:

1. Take a clean and transparent glass bowl on your experiment table and fill it with fresh water almost up to the top of the bowl.
2. Take a tissue paper and cut it in the shape of a square, make sure the square is larger than the paper clip
3. Gently place the tissue paper square on the water surface, so that it floats on the top of the surface.
4. Immediately place the paper clip on the top of the tissue paper.
5. Sink the tissue paper, using the eraser part of the pencil, without touching the paper clip.
6. The paper clip should float by this point.
7. Add dish soap at the surface.
8. Observe and explain what happens.

Recording procedure:

1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no



<http://web.mit.edu/nnf/education/wettability/blade.wmv>

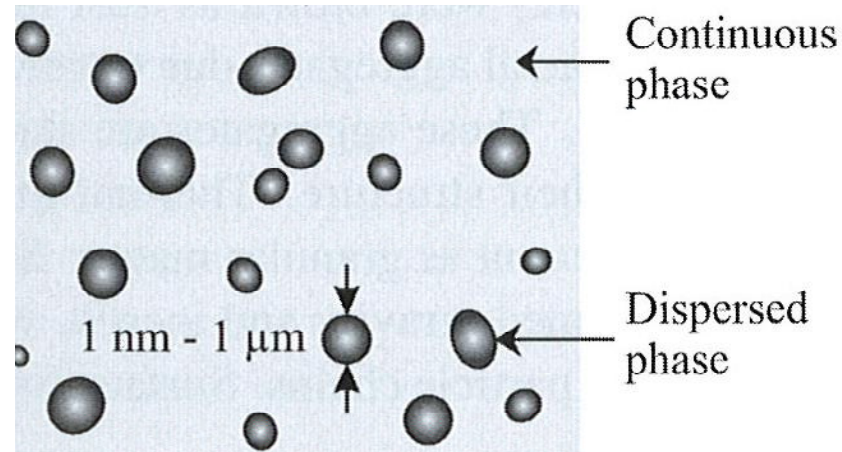
Fundamental equations in Colloid and Surface Science

- Young-Laplace equation
- Kelvin equation
- Young equation
- Gibbs adsorption equation

Curved interfaces

Dispersed phase in colloidal systems: drops, bubbles or solid particles

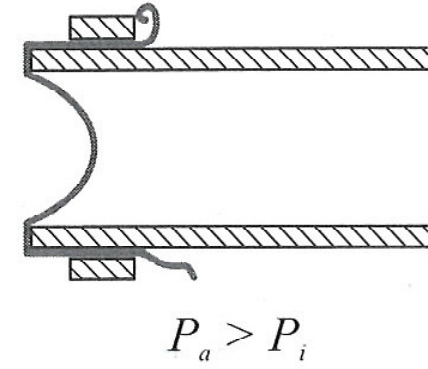
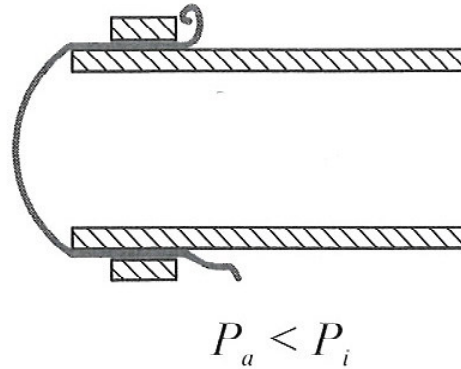
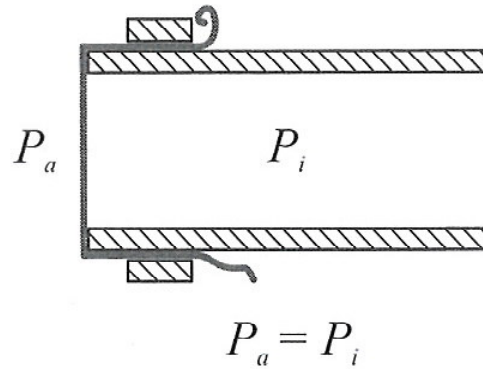
Common: ***curved interfaces***



Always a pressure difference across curved interfaces

Curved interfaces

Macroscopic illustration:



capillary pressure

Young-Laplace Equation

Difference between inside and outside of bubble

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

The pressure difference is dependent on:

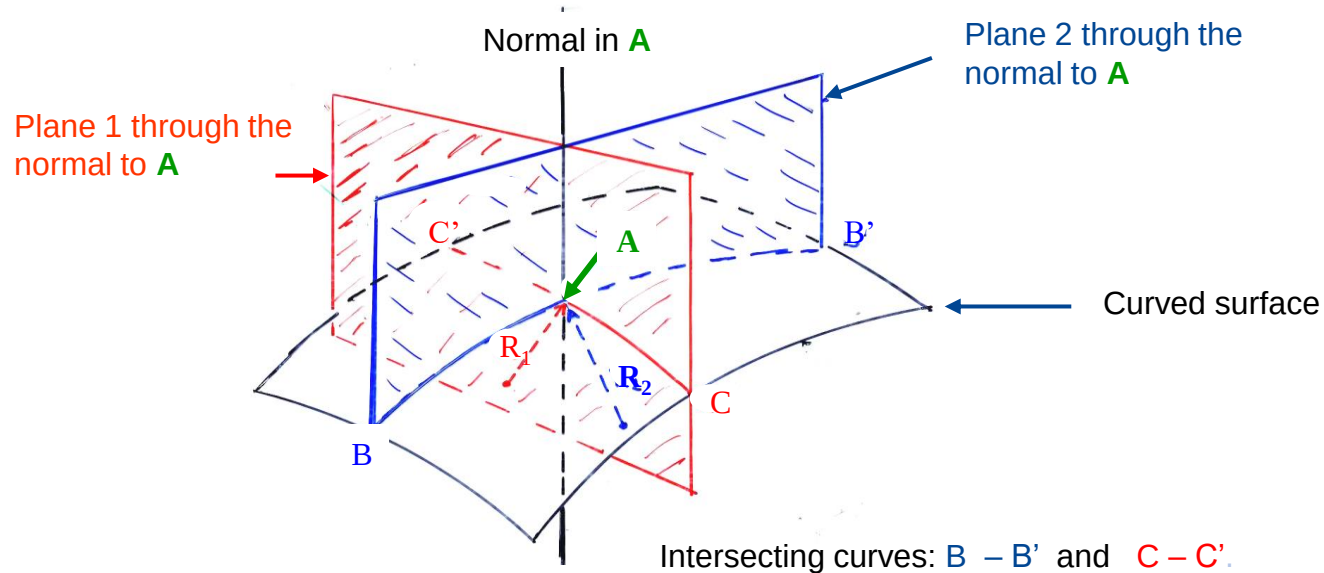
- surface tension
- curvature (i.e. particle shape)

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 described by R_1 and R_2

Young-Laplace Equation

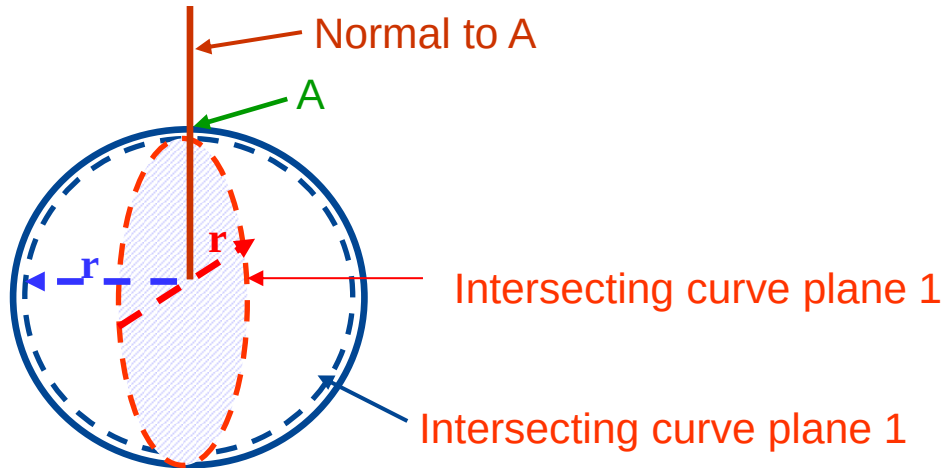


Radii of curvature in point **A**: R_1 (for **C-C'**) and R_2 (for **B-B'**)

- R_1 and R_2 : radii of curvature for the intersecting curves of two perpendicular planes normal to a point at a surface

Young-Laplace equation – special cases

Spherical surface:



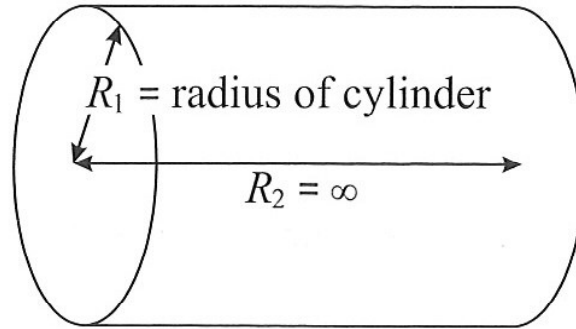
$$R_1 = R_2 = R_s$$

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

<https://www.youtube.com/watch?v=ZRVxr4-gls8>

Young-Laplace equation – special cases

Cylindrical surface:



$$R_2 \rightarrow \infty$$

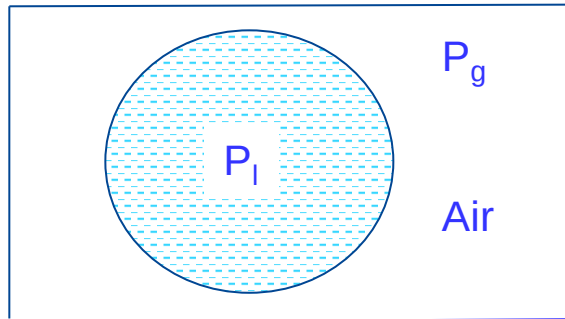
$$\Delta P = \frac{\gamma}{R_1}$$

Planar surface: $R_1 = R_2 \rightarrow \infty$ $\Delta P = 0$

Young-Laplace equation – application

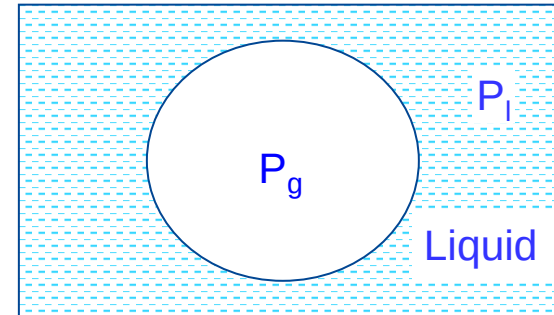
Largest pressure is *a*lways on the concave side of interface

Drop in air



$$P_l > P_g$$

Bubble in liquid

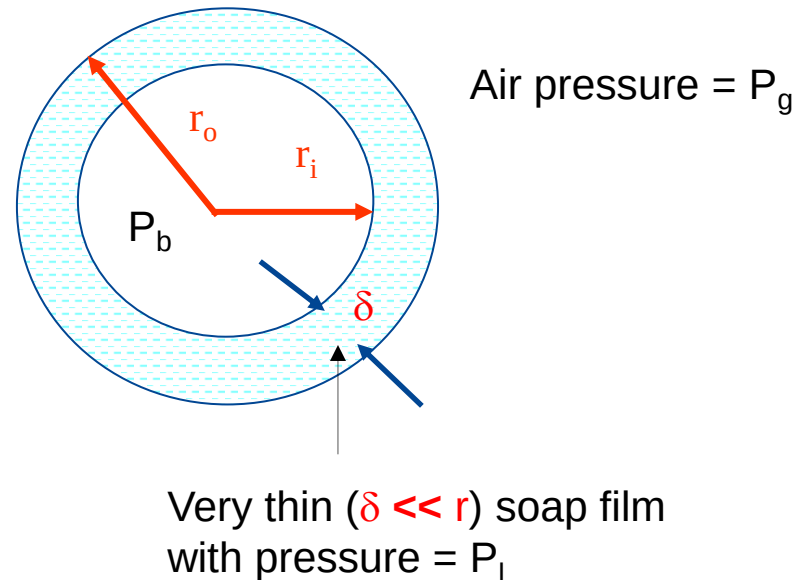


$$P_l < P_g$$

Def!
 $\Delta P = P_l - P_g$

Young-Laplace equation - example

What is the pressure difference across a soap bubble?



Outer interface:

$$\Delta P_o = P_i - P_g = \frac{2\gamma}{r_o}$$

$$P_g = P_i - \frac{2\gamma}{r_o}$$

Inner interface

$$\Delta P_i = P_i - P_b = -\frac{2\gamma}{r_i}$$

$$P_o = P_i + \frac{2\gamma}{r_i}$$

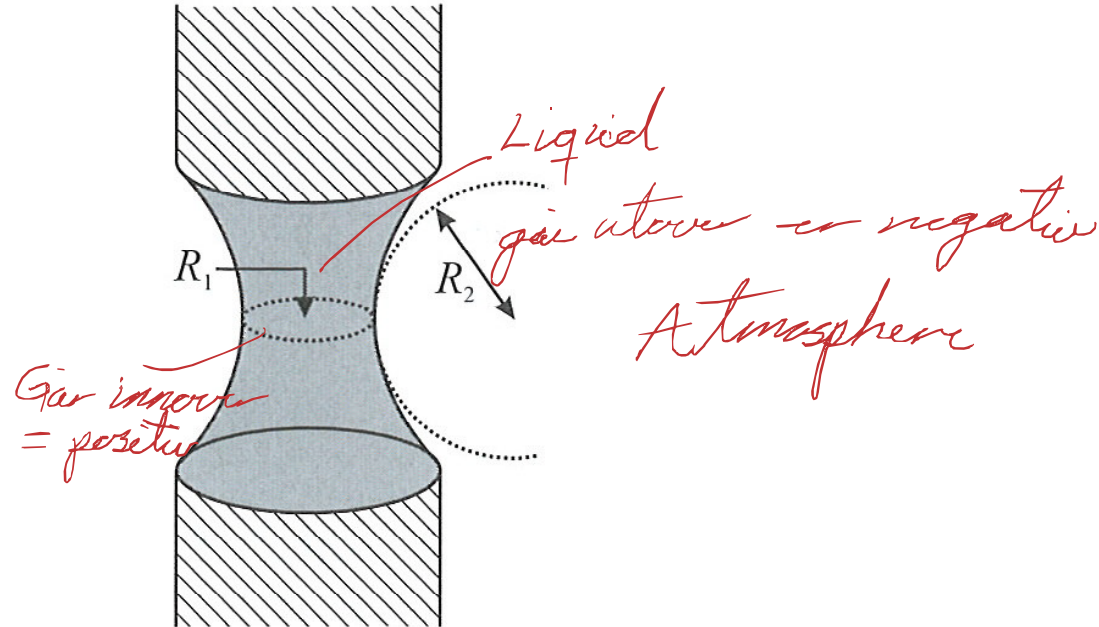
$$\begin{aligned} \Delta P_o - \Delta P_i &= P_o - P_g = P_i + \frac{2\gamma}{r_i} - P_i + \frac{2\gamma}{r_o} \\ &= 2\gamma \left(\frac{1}{r_i} + \frac{1}{r_o} \right) \end{aligned}$$

$\delta \ll r \Rightarrow r_o \approx r_i \rightarrow \frac{4\gamma}{r}$

Young-Laplace equation - example

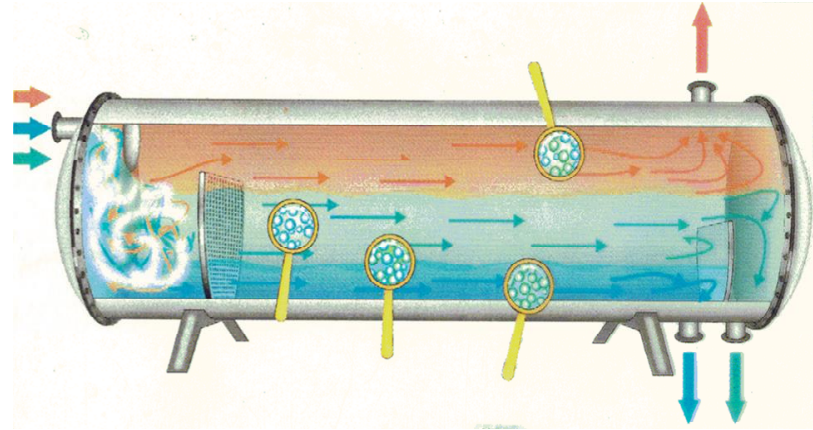
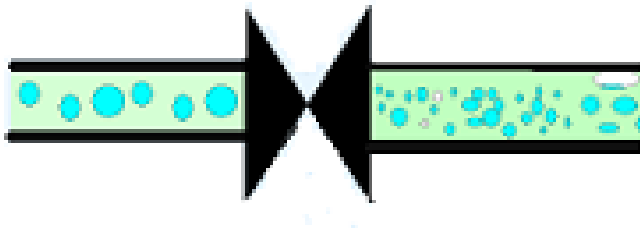
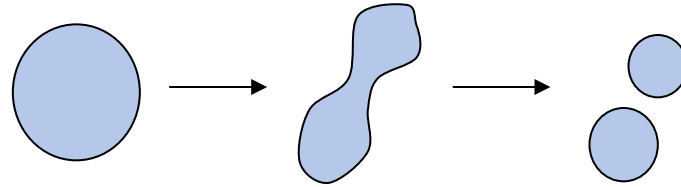
$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

$$\Delta P = \gamma \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$



Interfacial tension

- formation of emulsions/aerosols/foam





Home experiment - connecting balloons

Materials:

- 2 balloons
- Tube open at both ends with diameter necessary to fit the balloon ends (e.g. a straw)

Procedure:

1. Inflate both balloons so that one of them is significantly smaller in volume than the other (50% of the other should work well)
2. Attach both of the balloons at each end of the tube/straw and immediately hold and press the ends of the straw so that there is no air flow
3. Stop pressing and holding the ends of the straw
4. Observe and explain what happens

Recording procedure:

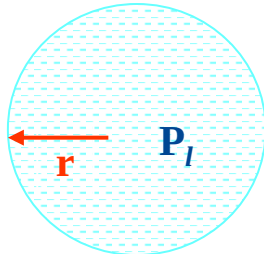
1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no



Kelvin Equation

Phase equilibria are affected by ΔP across curved interfaces

Vapour-Liquid Equilibria:



$\Delta P = 0$ across a planar surface
(normal vapour pressure, P^{sat})

Curved interfaces: equilibrium vapour pressure change

- drop: vapour pressure higher than flat surface
- bubble: vapour pressure lower than flat surface

Kelvin Equation

Quantitative change in vapour pressure: *of a curved interface*

$$RT \ln \left(\frac{P}{P^{sat}} \right) = \gamma V^l \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad \text{(Kelvin Equation)}$$

Normal vapour pressure

Molar volume liquid

Spherical droplet with radius R_S :

$$RT \ln \left(\frac{P}{P^{sat}} \right) = \frac{2\gamma V^l}{R_S} = \frac{2M\gamma}{\rho R_S} \quad \text{(Kelvin Equation)}$$

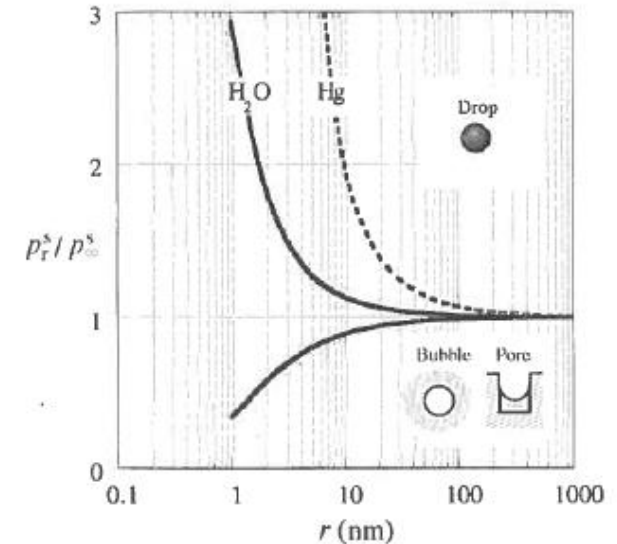
Vap pressure will decrease exponentially

Kelvin Equation

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

Vapour pressure.

$R_s(\text{m})$	(water droplets, 20°C)	(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

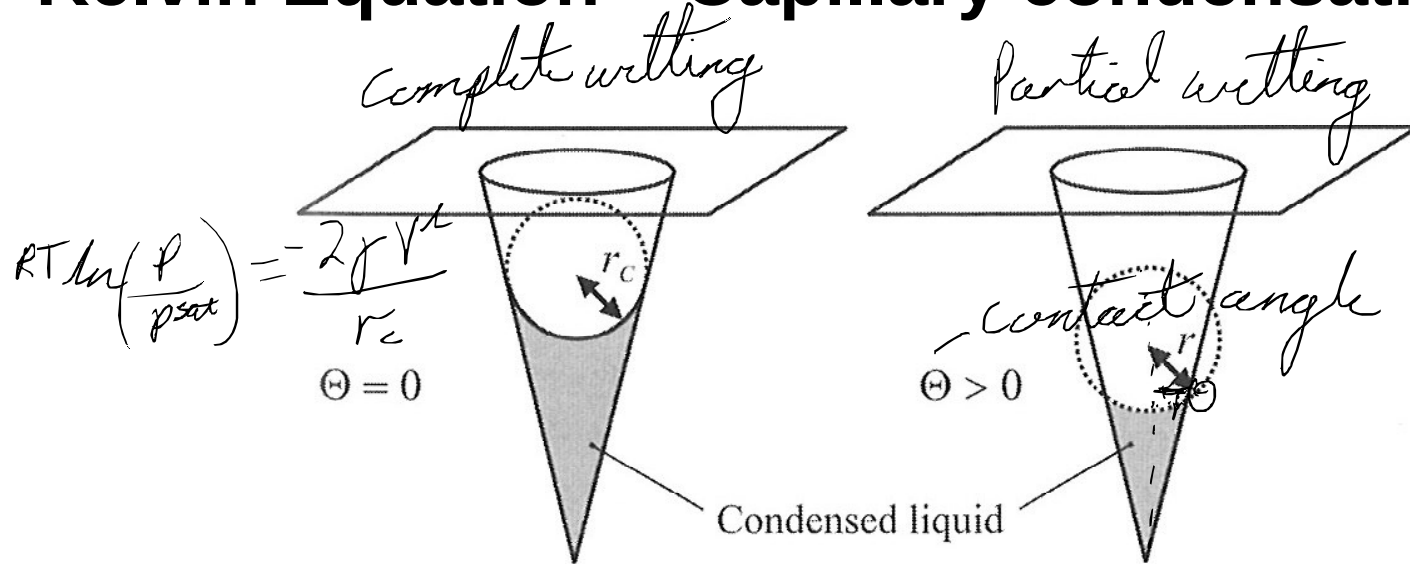


Oswald ripening



Large droplet expands at the cost of the small ones.

Kelvin Equation – Capillary condensation

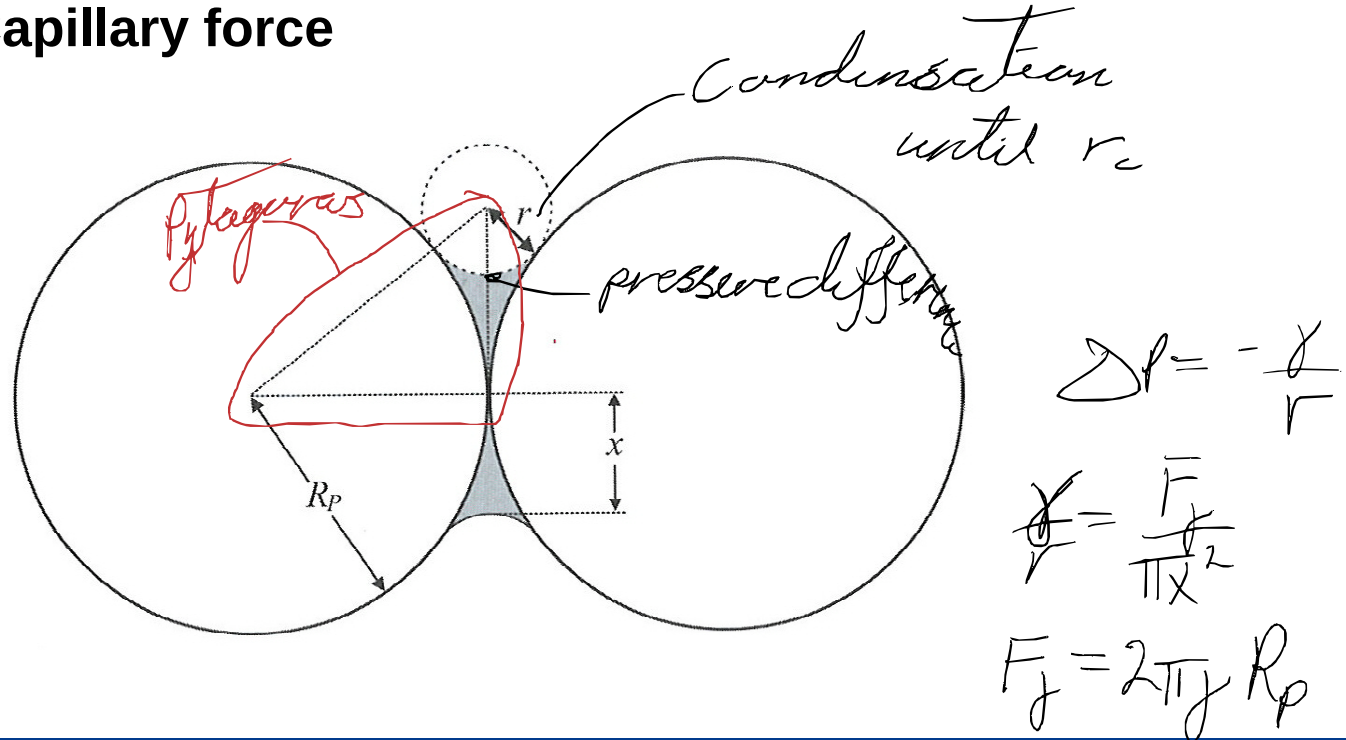


$$RT \ln\left(\frac{P}{P_{sat}}\right) = \gamma V^l \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

Condensation of vapour at a curved interface (etc pores) occurring at lower vapour pressure than P_{sat} until critical size r_c

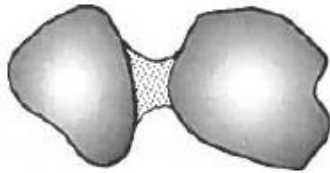
Kelvin Equation – Capillary condensation

Consequence: **Capillary force**

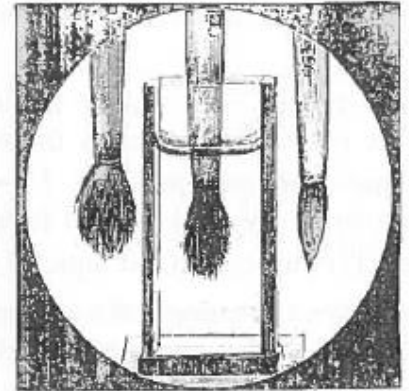
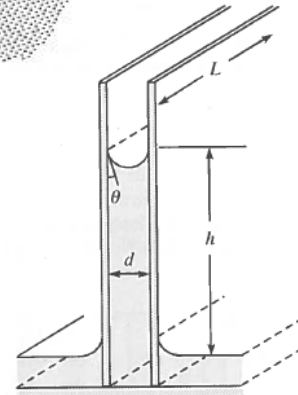
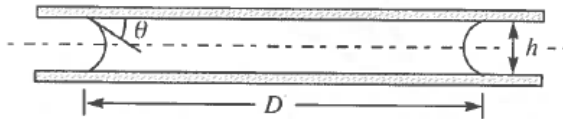
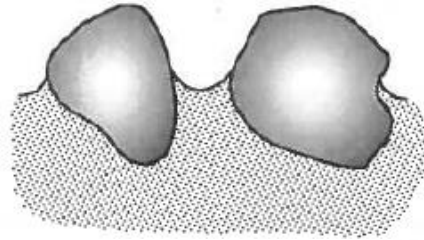


Capillary interactions

Liquid bridge



Shared meniscus



Kelvin equation – solubility

$$\ln \left(\frac{S(r)}{S(r \rightarrow \infty)} \right) = \frac{V_s}{RT} \frac{2\gamma}{R_s}$$

Relates solubility of flat surface and spherical surface

Small particles will have larger solubility in solution than larger particles

This will lead to Ostwald ripening

Nucleation in oil and gas processing

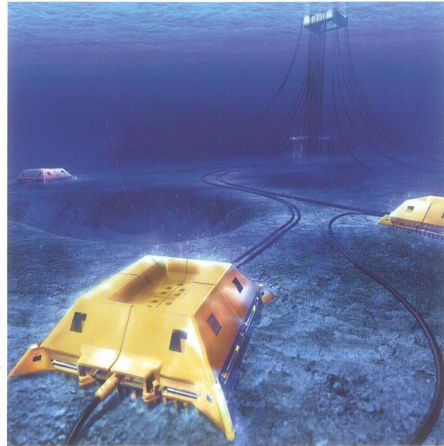
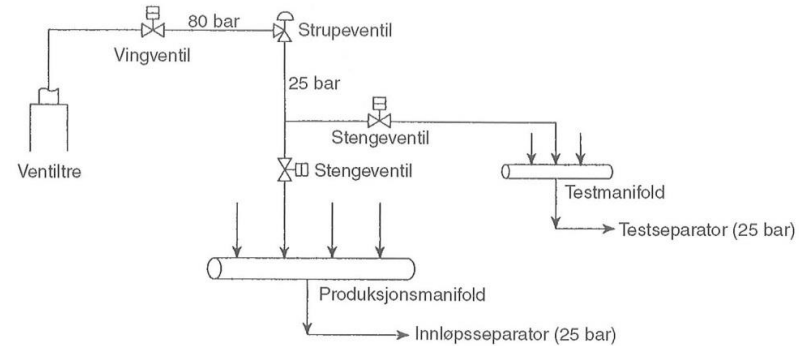


Foto: Arctic Petroleum AS © Norsk Hydro AS&A

Illustrasjon av brønnhode og prosessutstyr på havbunnen (Troll Pilot)



Figur 2.4 Strupeventilens plass i prosessen. Trykkfallet over ventilen er her vist som 55 bar (80–25), men det vil variere fra brønn til brønn. At det i dette tilfellet er 25 bar er bestemt av prosessanleggets nedstrøms ventiler

Scale formation

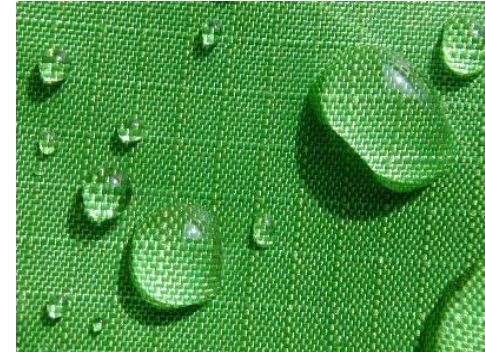
Release of gas

Young equation

Relates surface tension and contact angle

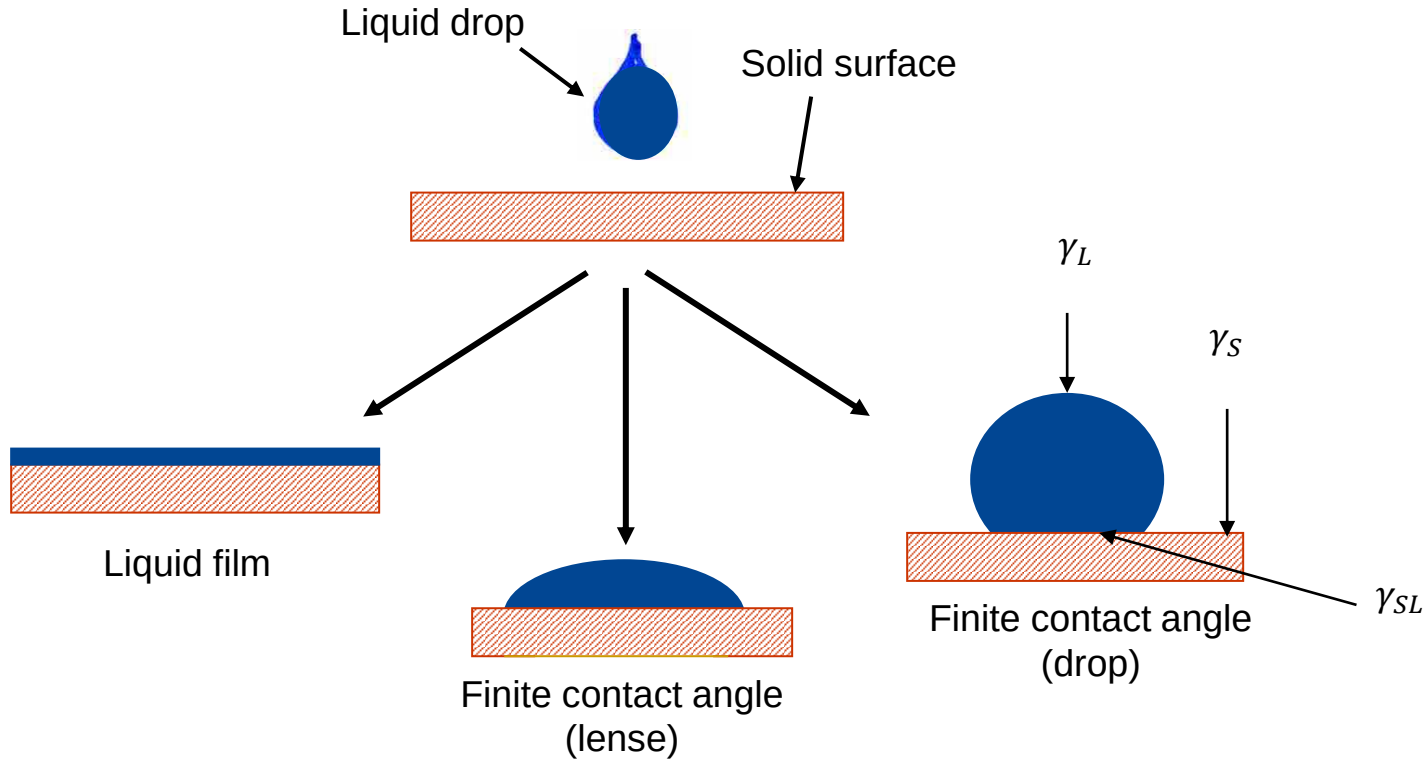
Solid surfaces are much more complex than liquids:

- Roughness
- Chemical heterogeneity
- Impurities



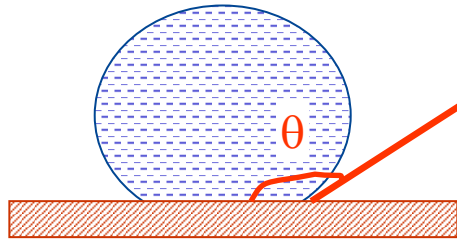
Contact angles are important for understanding solid surfaces

Contact angle



Equilibrium:
condition
with largest
reduction of
surface free
energy

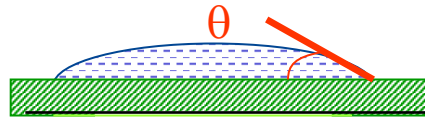
Contact angle/wettability



Wax

$$\theta > 90^\circ:$$

Non-wetting (drop)



Polymer

$$\theta < 90^\circ:$$

Wetting (lense)



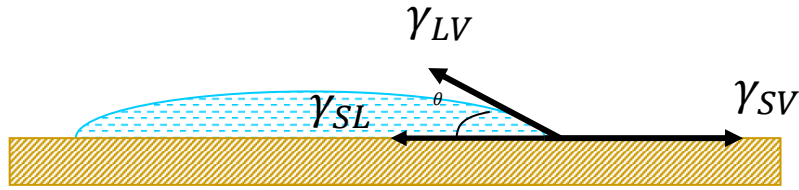
Glass

$$\theta = 0:$$

Complete wetting

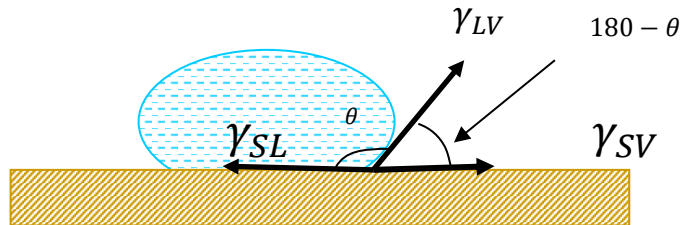
Young equation

Equilibrium condition: $\Sigma \gamma_{horizontal} = 0$



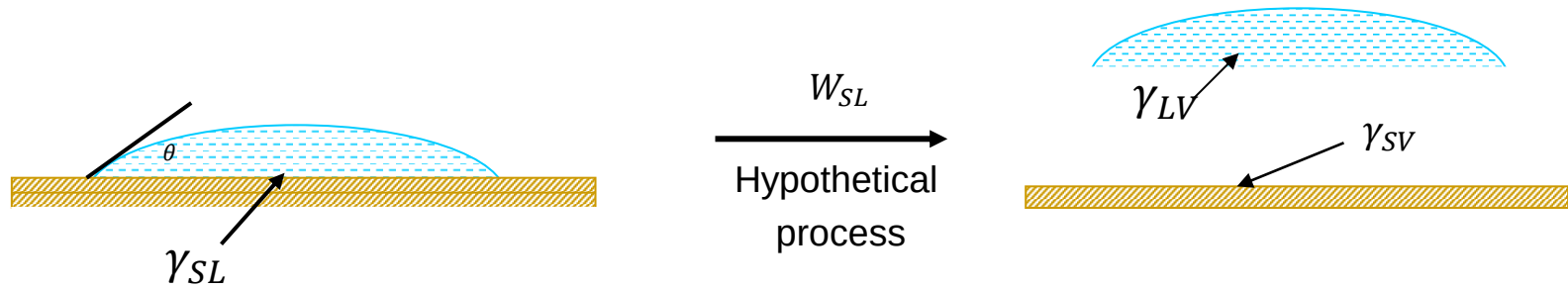
$\theta < 90^\circ$

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



$\theta > 90^\circ$

Work of adhesion

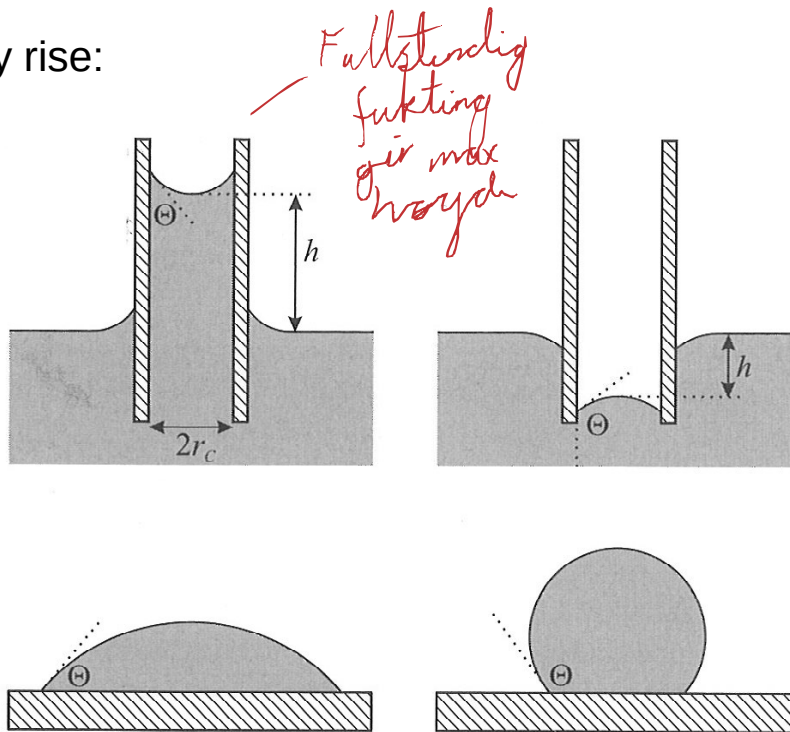


$$W_{SL} = \gamma_{LV}(1 + \cos\theta)$$

(Young-Dupre equation)

Wetting geometries

Capillary rise:



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

Vertikal komponenten av γ_{LV} : $\gamma_{LV} \cos(\theta)$

Total kapillær kraft

$$F_g = \gamma_{LV} \cos(\theta) 2\pi R_c$$

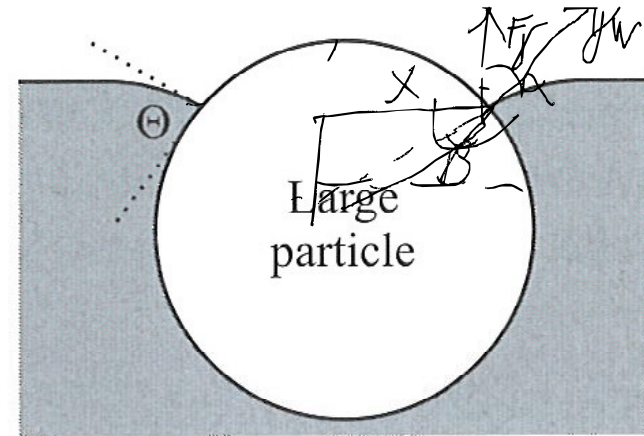
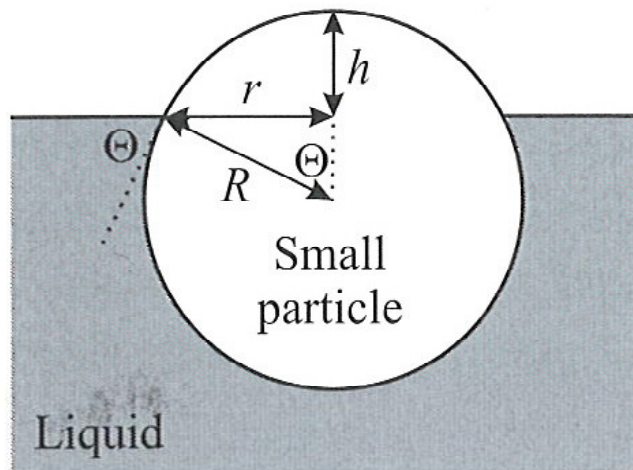
$$F_g = mg = V \rho g = h R_c^2 \pi \rho g$$

$$F_g = F_g \Rightarrow h R_c^2 \pi \rho g = \gamma_{LV} \cos(\theta) 2\pi R_c$$

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

Wetting geometries

Particles at liquid-gas (or liquid-liquid) interfaces:



$$A \cdot L = \text{"Volume under water"} \\ = \left[\pi \frac{90 + \beta}{180} + 2 \sin \beta \cos \beta \right] r^2 \cdot L$$

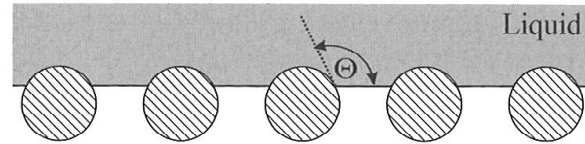
$$F_b = S_w (A \cdot L) g \\ F_g = \pi r^2 L S_c g$$

$$F_y = \gamma_w \cos(\alpha) (4x + 2L)$$

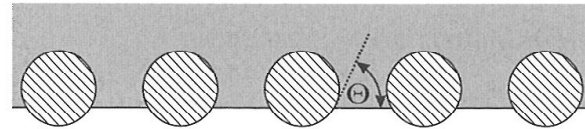
Wetting geometries

Network of cylinders:

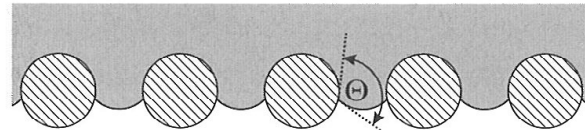
$$\Theta > 90^\circ$$



$$\Theta < 90^\circ$$

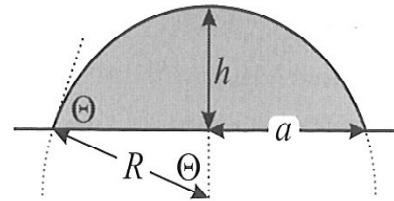
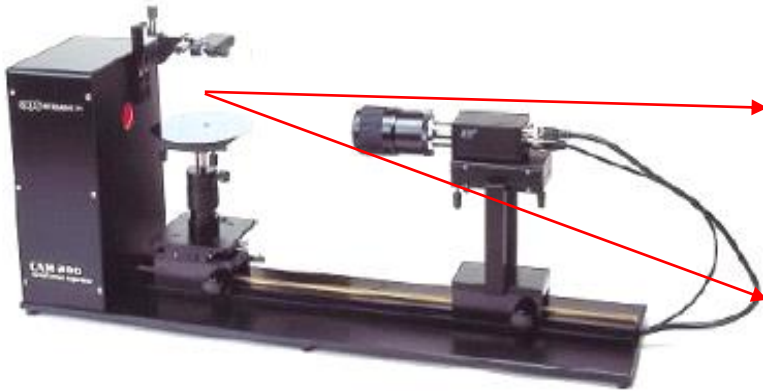


$$\Theta > 90^\circ \text{ with pressure}$$

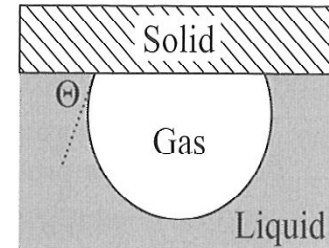


Measuring contact angles

Sessile drop/bubble method:



Sessile drop

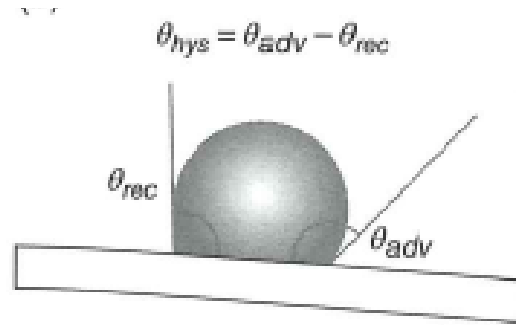


Sessile bubble

<https://www.youtube.com/watch?v=CtF8ZgW2AOQ>

Hysteresis

Tilted plate: contact angle is different at different contact points



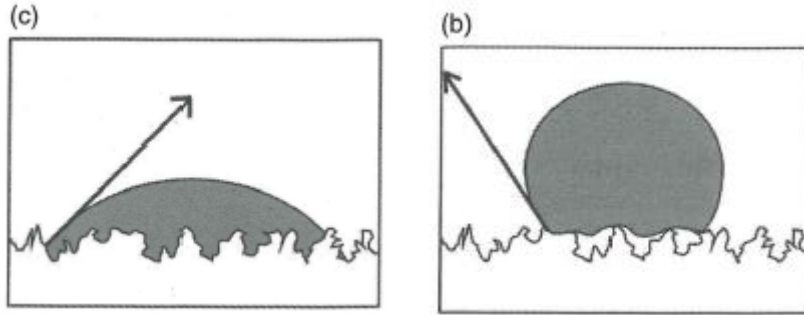
θ_{adv} : Advancing contact angle

θ_{rec} : Receding contact angle

Reasons for hysteresis:

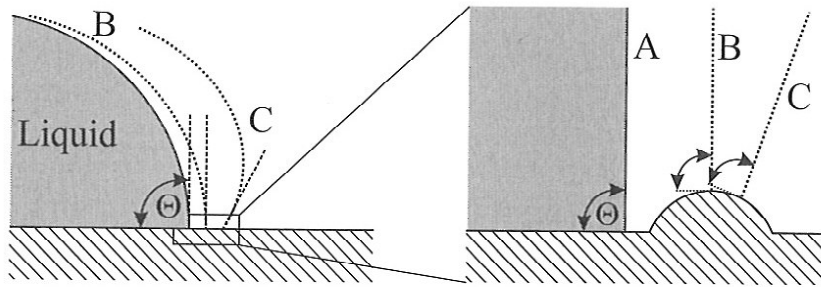
- Surface roughness
- Equilibrium not reached
- Surface contamination
- Surface undergo changes during contact with liquid
- Spreading coefficient may be significant for low contact angles

Surface roughness

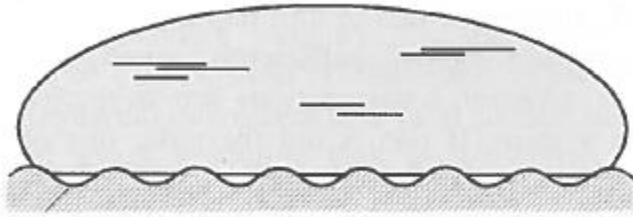


$$\cos \theta_{app} = R_{rough} \cos \theta$$

(Wenzel equation)

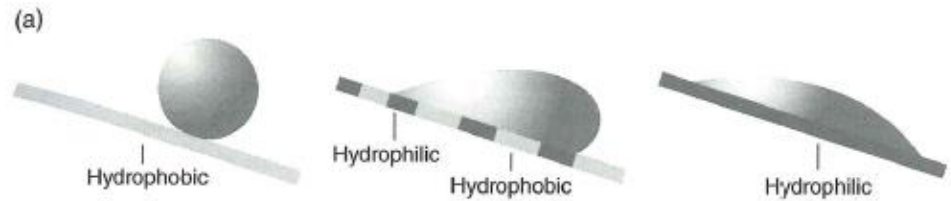
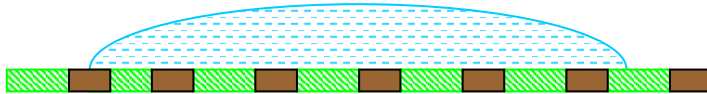


Lotus effect



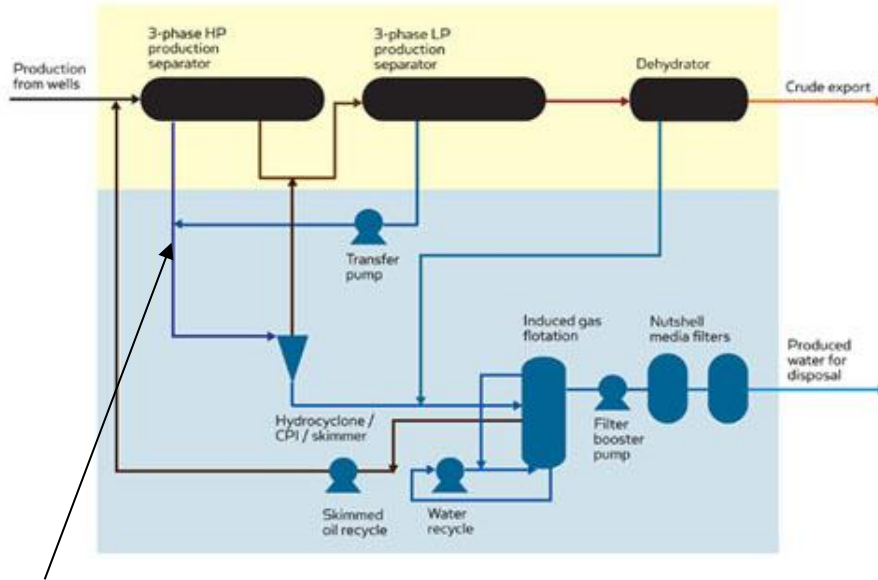
Chemical heterogeneity

Surface divided into fractions of chemical types 1 and 2:



$$\cos \theta_{app} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (\text{Cassie-Baxter equation})$$

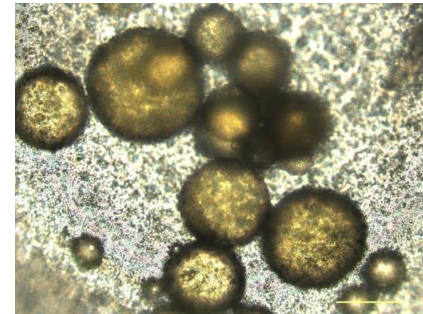
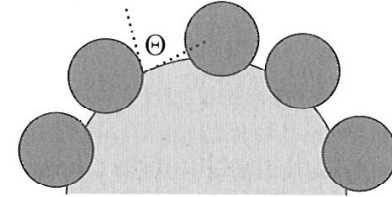
Wettability in produced water treatment



Dispersed solids

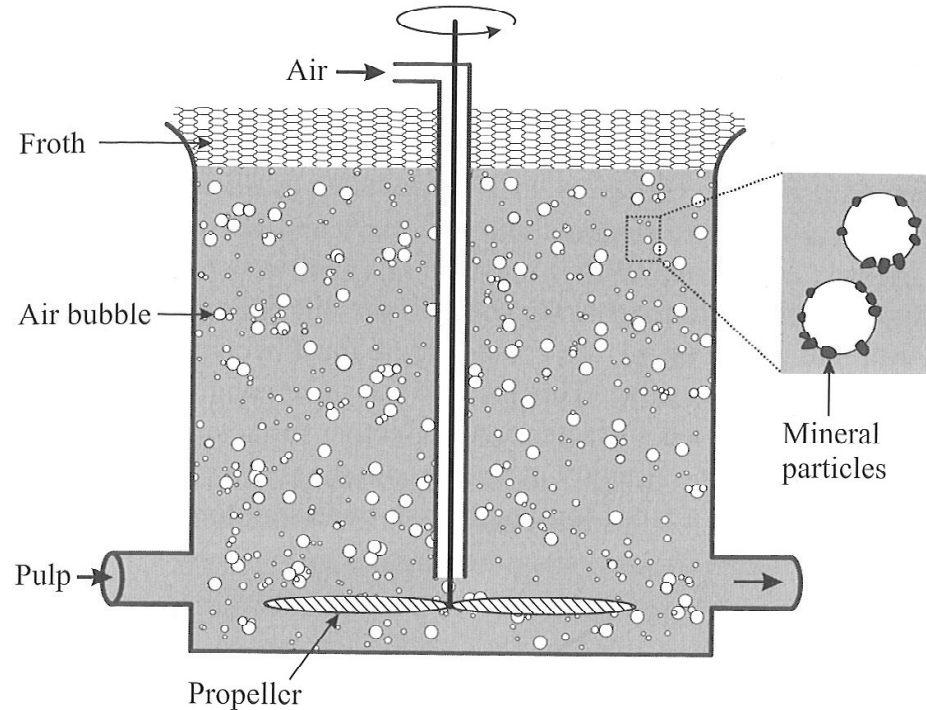
Dispersed oil (o/w emulsions)

Dissolved gas and organics

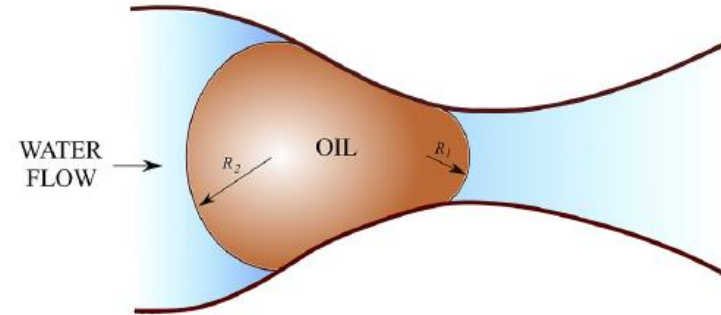
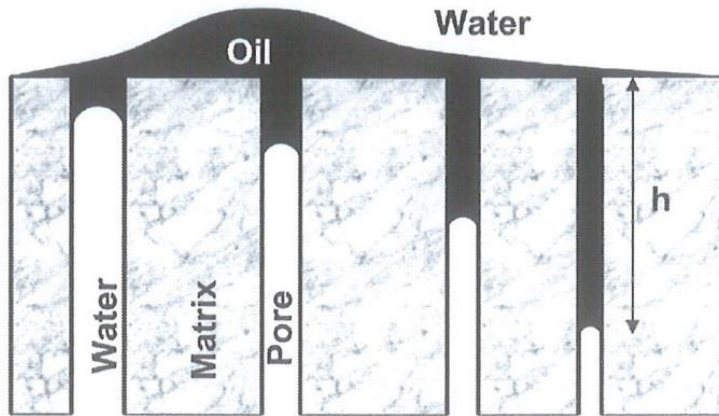


Wettability in mining

Flotation:



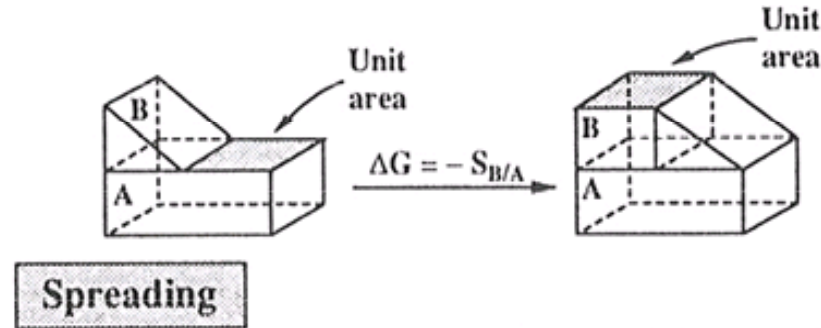
Wettability and capillary forces in enhanced oil recovery



Hirasaki et al, SPE Journal 80988

Spreading (B on A)

1A surface $\rightarrow$ 1AB + 1B surface



Difference between final and initial process of spreading B over A (B/A):

$$\Delta G_{B/A} = \gamma_{AB} + \gamma_B - \gamma_A$$

$$S_{B/A} = -\Delta G_{B/A} = \gamma_A - \gamma_B - \gamma_{AB} \quad (\text{spreading coefficient})$$

Spreading and solubility

Liquid spreading on liquid: $S_{O/W} = \gamma_{WA} - \gamma_{OA} - \gamma_{OW} = W_{adhesion,OW} - W_{cohesion,O}$

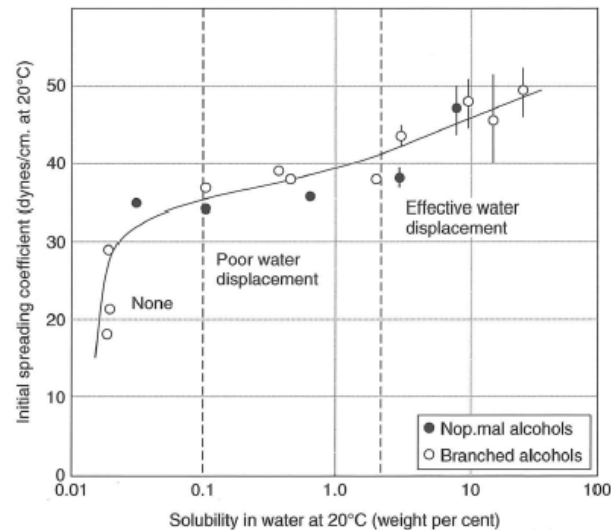
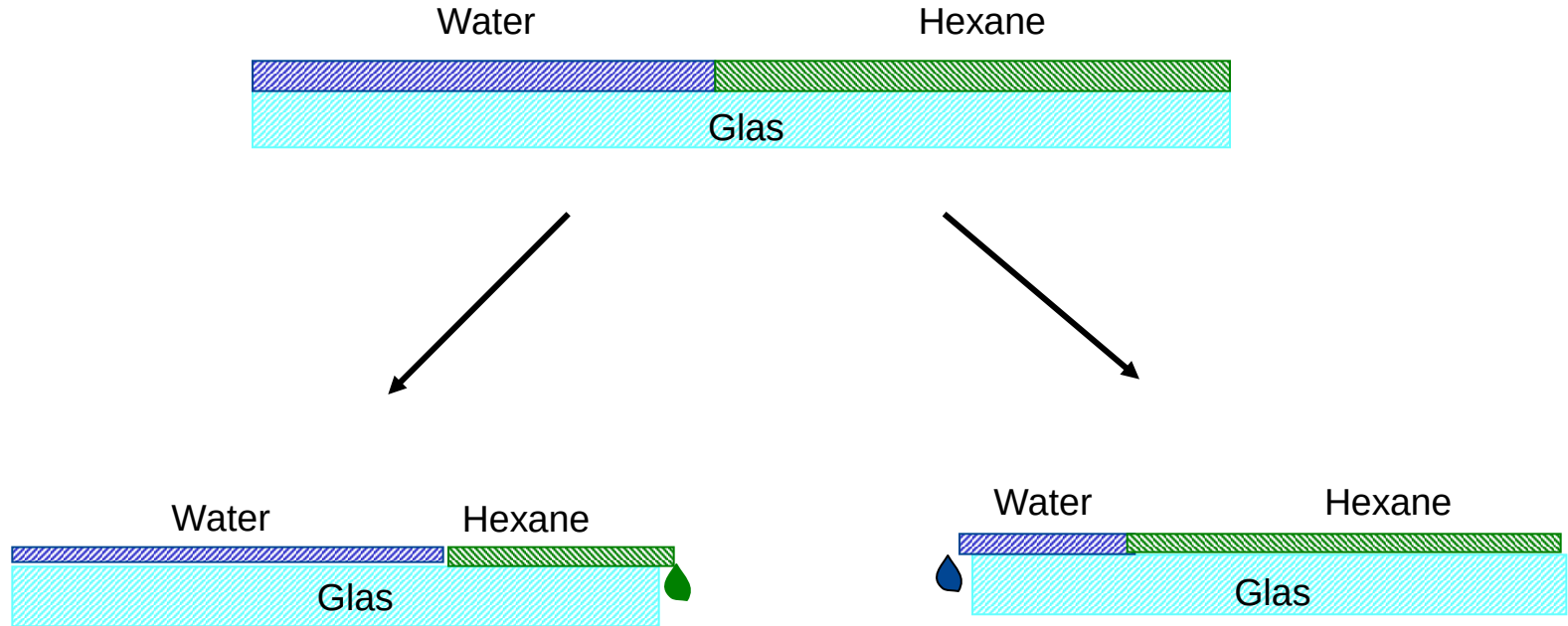


Figure 3.15 Relationship of water solubility to the initial spreading coefficient and the water displacing ability of simple alcohols. The vertical lines through points in the region of strong displacement are proportional in length to the areas of a 2-mm water film displaced by the respective alcohols. Reprinted from Baker et al. (1967), with permission from American Chemical Society

Example:



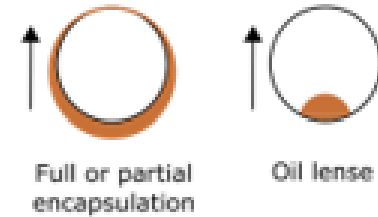
Spreading in produced water treatment



Flotation:



Flotation (bubble-drop interactions):



Gibbs adsorption equation

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln c} \right)_T$$

Relates interfacial tension and surface excess solute

Gibbs (soluble) monolayers

- Adsorption onto liquid-liquid interfaces (Gibbs adsorption isotherm)
- Adsorption onto solid-liquid interfaces (Langmuir adsorption isotherm – chapter 7)

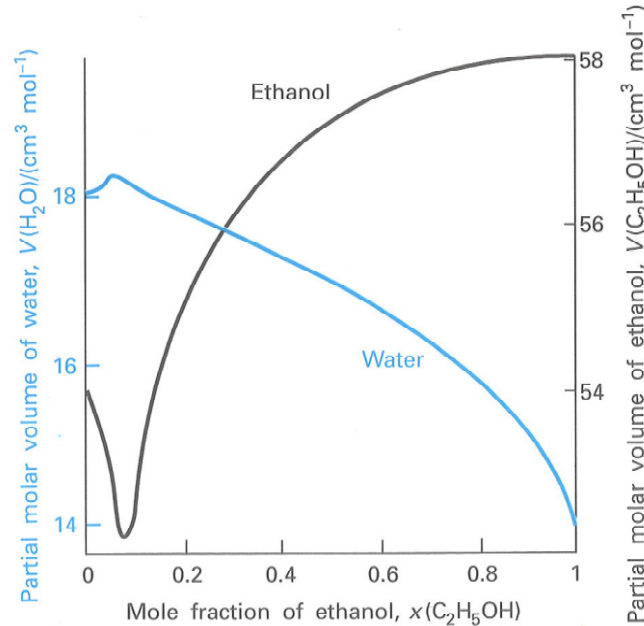
Langmuir (insoluble) monolayers

<http://tv.nrk.no/serie/oeyeblikket/DMPV73050115/sesong-1/episode-1>

Partial molar quantities

Describes the contribution of one component to the total property

Example: volume

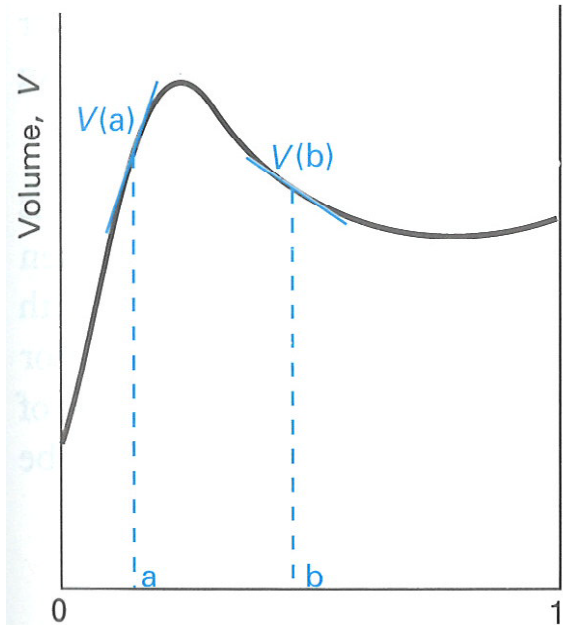


$$V_i = \left(\frac{\partial V}{\partial n_i} \right)_{p, T, n_{j \neq i}}$$

n_i : amount of component i

$n_{j \neq i}$: all other components kept constant

Partial molar quantities



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



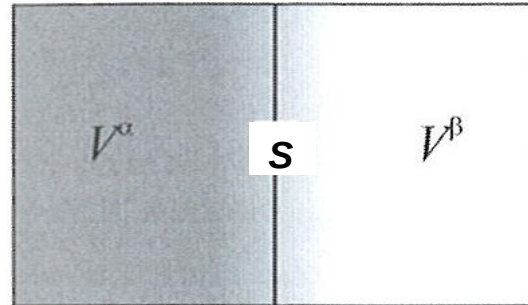
Partial molar quantities

Chemical potential (partial molar Gibbs free energy): $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_{j \neq i}}$

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

$$dG = \sum \mu_i dn_i \quad (\text{constant } T \text{ and } p)$$

Defining an interface



Gibbs ideal interface

All extensive parameters of a system are affected by an interface

$$dG = dG^{\alpha} + dG^{\beta} + dG^{\sigma}$$

t surface excess

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{p, T}$$



Gibbs adsorption isotherm

$$\sum_i n_i^\sigma d\mu_i + A d\gamma = 0$$

Relates surface tension to the number of moles and chemical potential of the components at the interface

2-component system:

Component 1: solvent (løsemiddel)

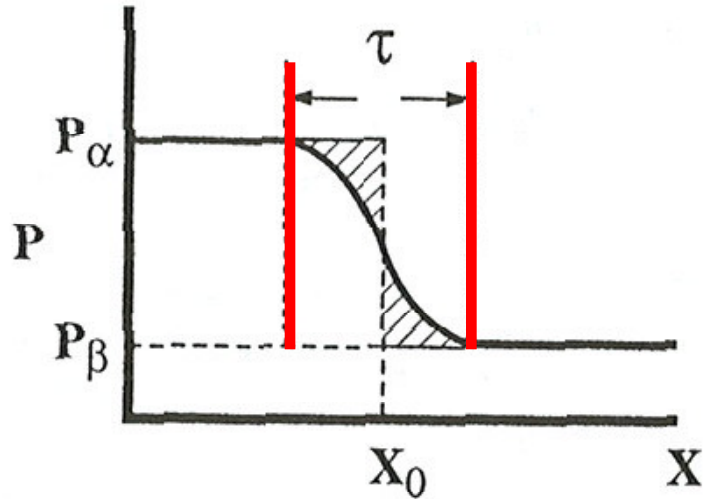
Component 2: solute (løst komponent)

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

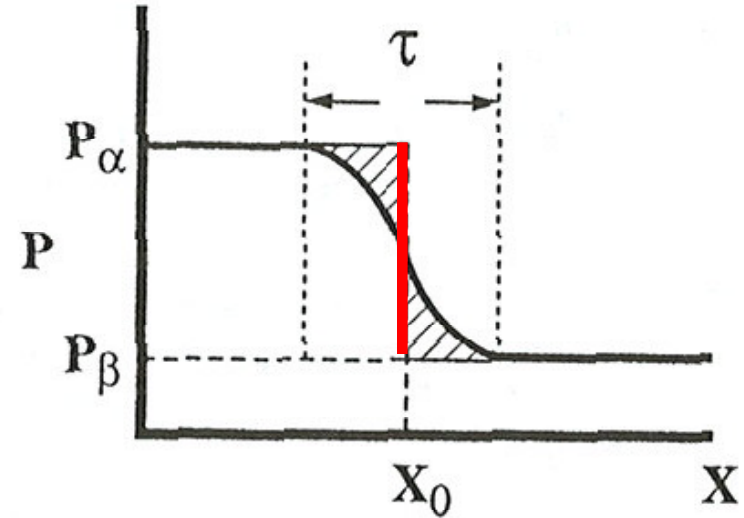
$$\Gamma_i = \frac{n_i^\sigma}{A} \quad \text{- surface excess of component i}$$

Location of ideal surface

Real situation:

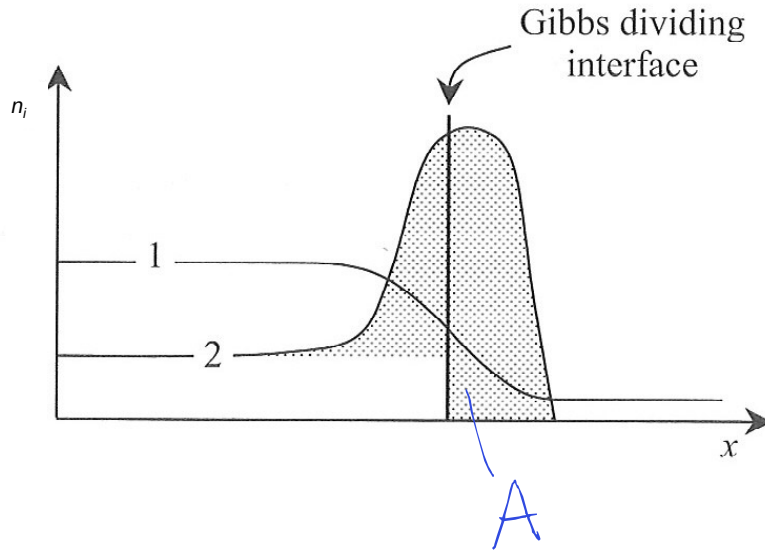


Ideal situation:



Location of ideal surface

Different properties have different profiles across interface



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

$$d\gamma = -\Gamma_2 d\mu_2$$

$\uparrow$
 $= \frac{n_2}{A}$

Gibbs adsorption isotherm

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln c} \right)_T$$

*Relates interfacial tension
and surface excess solute*

Applicable since γ and c are measurable:

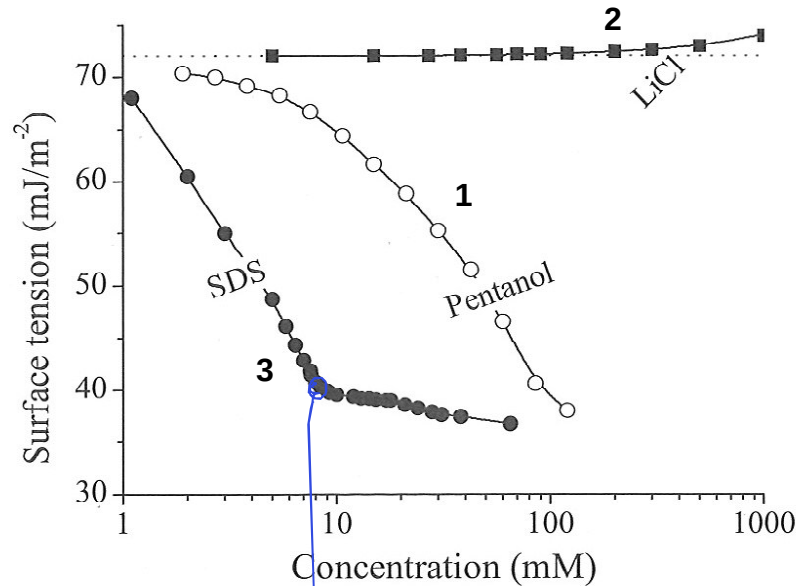
Slope of γ plotted against $\ln c$ gives Γ_2

Applications

- Determine surface excess (surface tension – concentration measurements)
- Calculate molecular area (from surface excess)
- Use surface pressure to calculate molecular weights

Gibbs adsorption isotherm

γ plotted against $\ln c$ can result in 3 general curve shapes:



1 and 3: $\left(\frac{d\gamma}{d \ln c} \right) < 0 \Rightarrow \Gamma_2$ positive

adsorption of solute at surface

2: $\left(\frac{d\gamma}{d \ln c} \right) > 0 \Rightarrow \Gamma_2$ negative

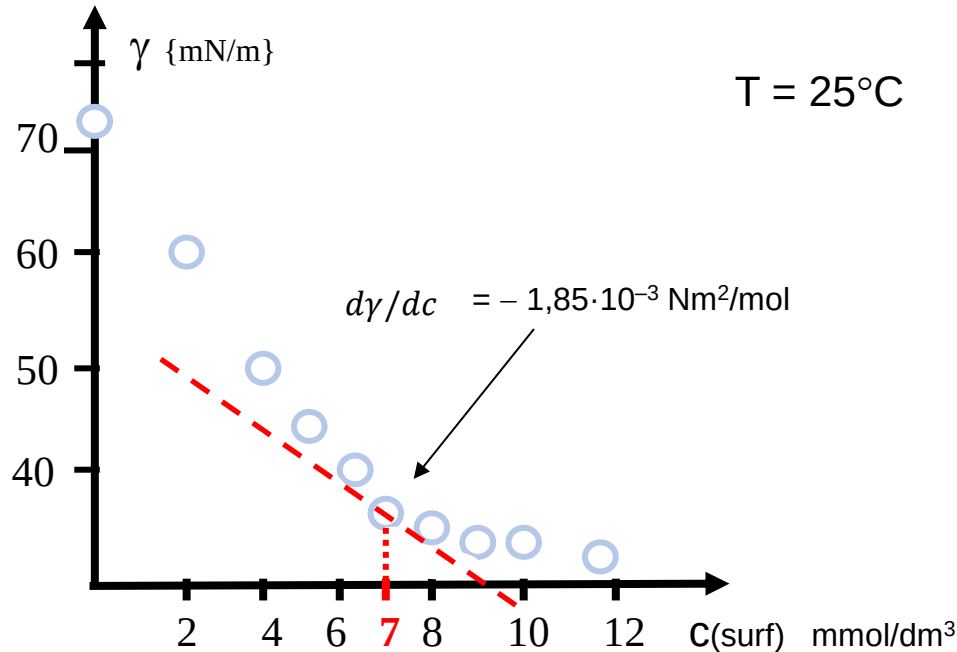
depletion of solute from surface

Kritisk micelle concentration

Gibbs adsorption isotherm

Example: Surface tension at different concentrations of a nonionic surfactant

$T = 25^\circ\text{C}$



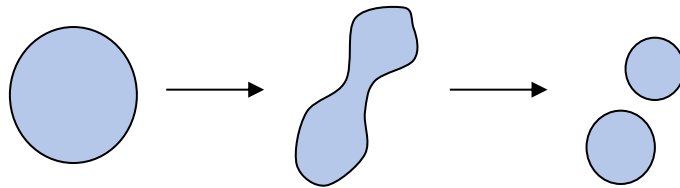
$$\Gamma_2 = -\frac{1}{nRT} \left(\frac{d\gamma}{d \ln c} \right)_T$$

When the bulk concentration of surfactant is 7 mmol/dm³ calculate:

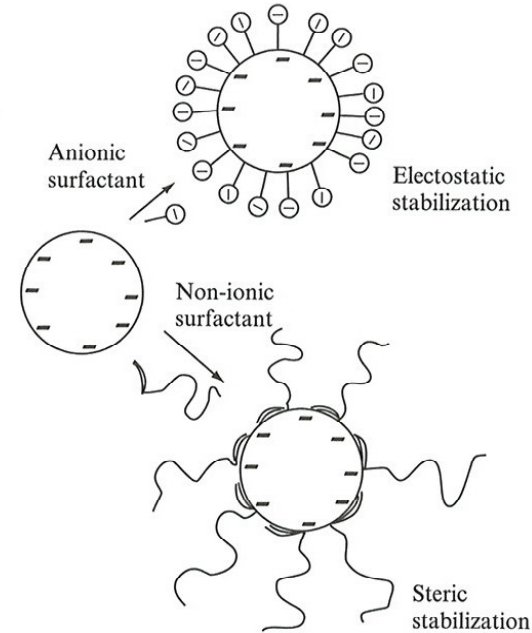
- the surface excess of surfactant
- The area per surfactant molecule

Adsorption at liquid-liquid interfaces – emulsion formation and stability

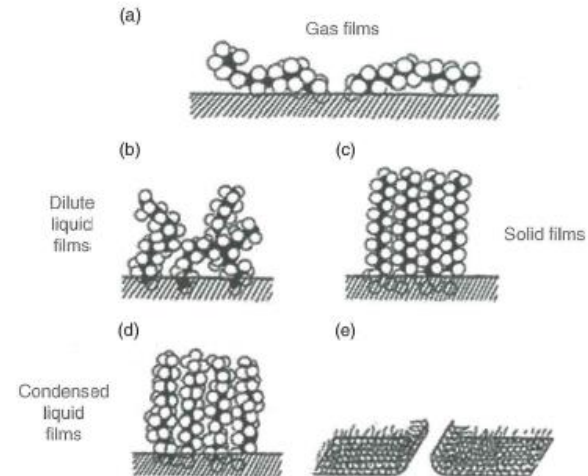
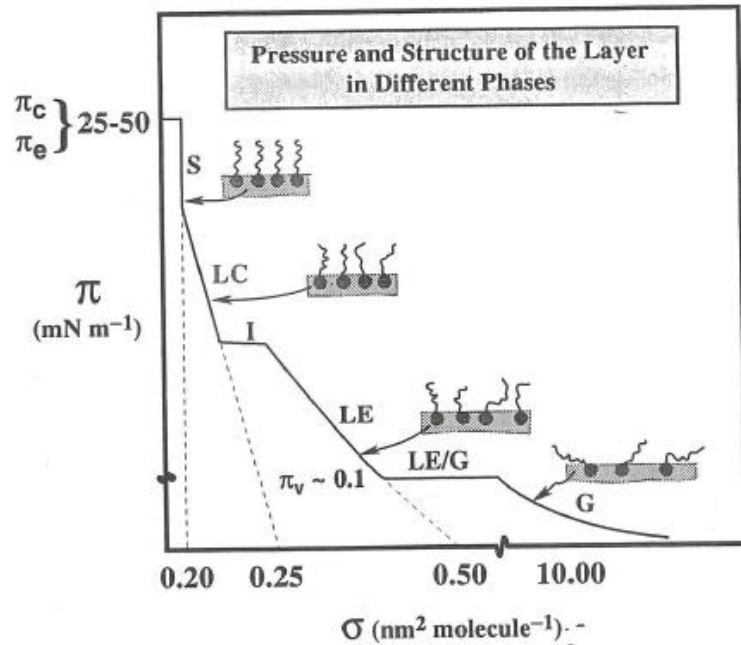
- Deformation of droplets
- Diffusion of surfactants
- Breakup of droplets/coalescence?



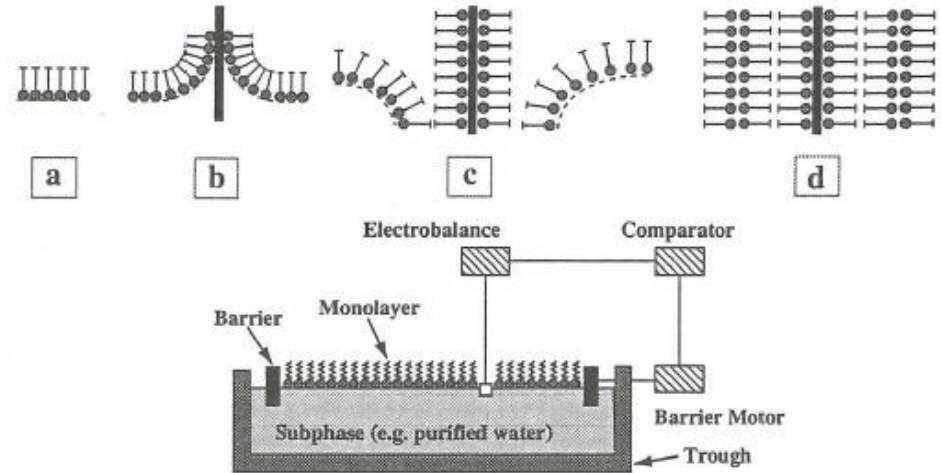
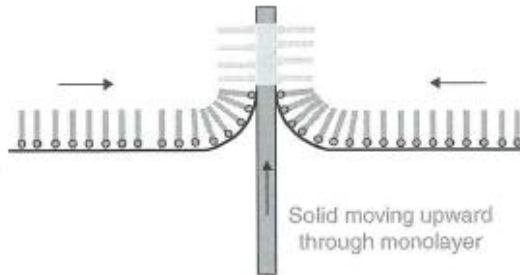
$$\Delta p = \frac{2\gamma}{R_s}$$



Langmuir monolayers



Langmuir-Blodgett films



Surfactants and Self-assembly

Surfactants



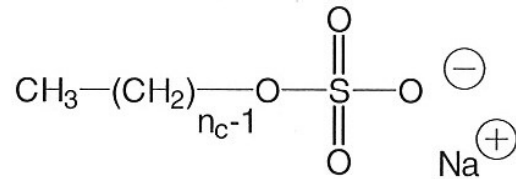
Surfactants (amphiphiles, tensids, emulgators):
Classified according to their head group

Surfactants

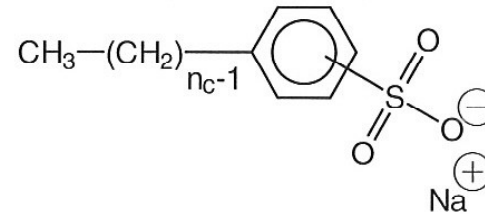


Anionic surfactants:

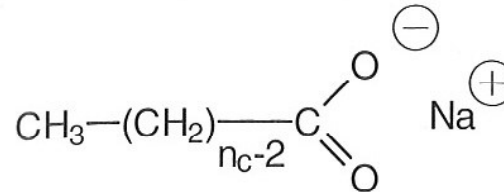
Sodium alkylsulfate



Sodium alkylbenzenesulfonate



Sodium alkylcarboxylate

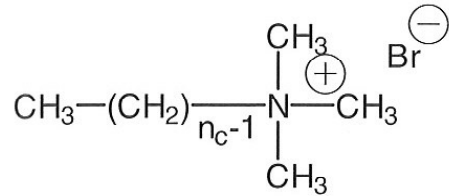


Surfactants

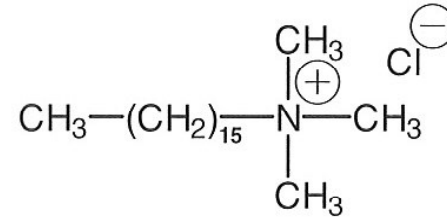


Cationic surfactants:

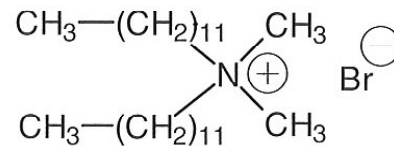
Alkyltrimethylammonium bromide



Alkyltrimethylammonium chloride



Dialkyldimethylammonium bromide



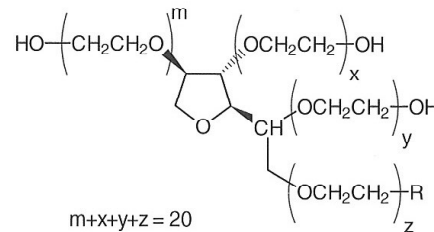
Surfactants

Nonionic surfactants:

Alkylethylene glycol

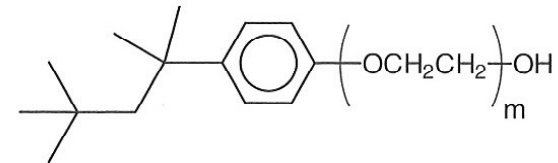


Poly(ethylene oxide)
sorbitan monoalkanoate



Poly(ethylene oxide)

iso-octylphenyl ether

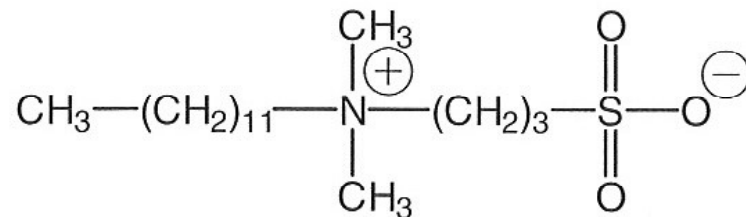


Surfactants



Zwitterionic surfactants:

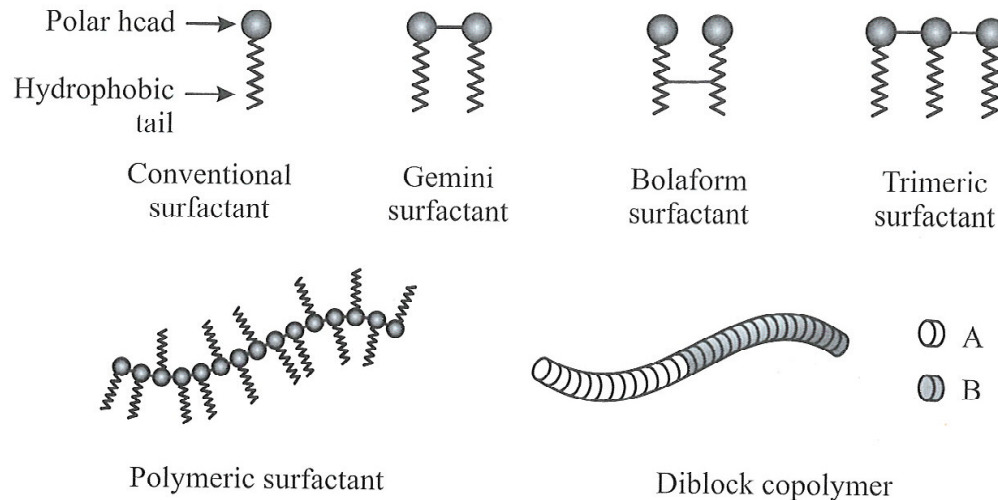
Alkyldimethylpropanesultaine



Surfactants

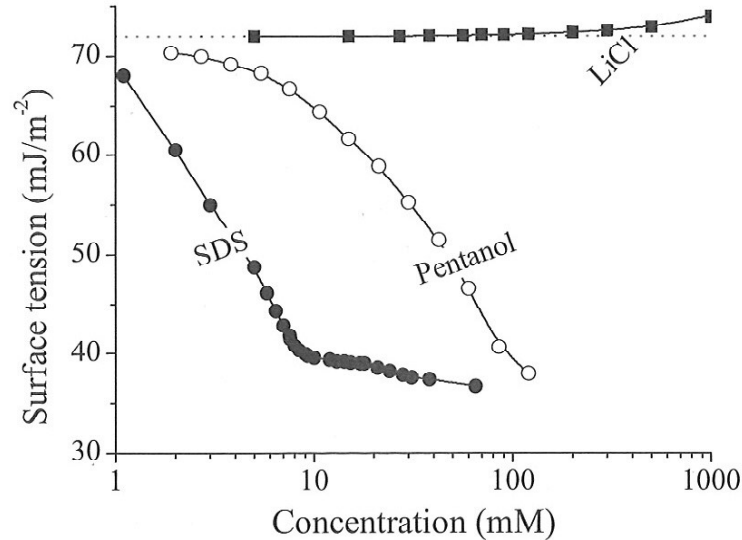
Hydrophobic part

- Alkyl chain (single, double, triple): $\text{CH}_3(\text{CH}_2)_n -$
- Aromatic moieties within the chain: $\text{CH}_3(\text{CH}_2)_n - \text{Ph} -$
- Fluoronated hydrocarbon chain: $\text{CF}_3(\text{CF}_2)_n -$

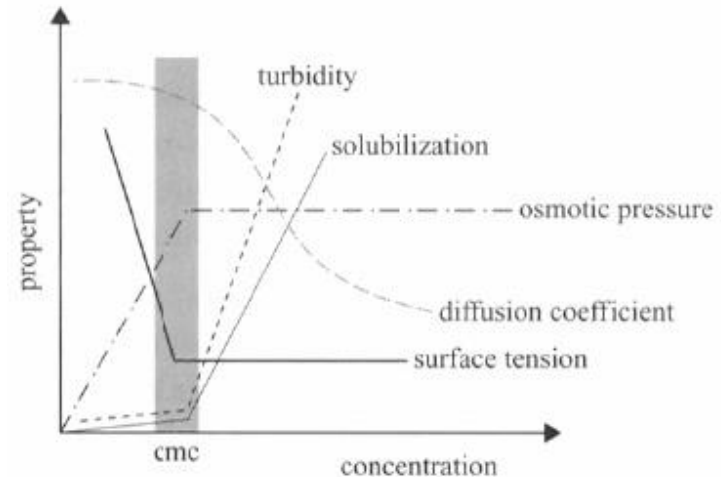


Surfactants in solution

Sharp break in surface tension when bulk concentration increases:

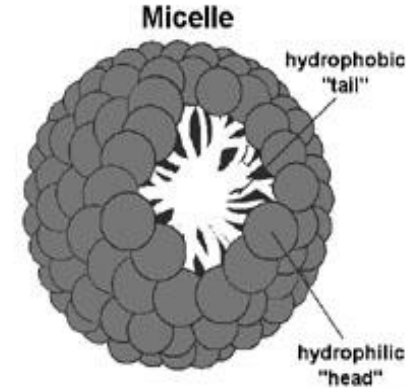
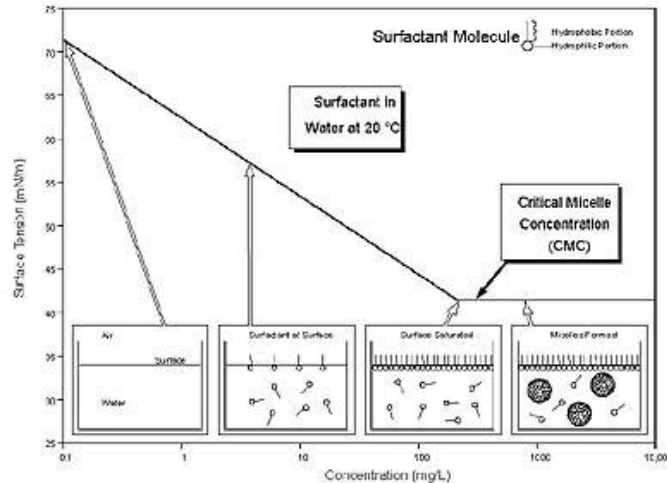


Threshold for many properties at the same concentration:



Break point: CMC – critical micelle concentration

Surfactants in solution

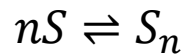


- 1: Pure water-air interface
- 2: Decrease in interfacial tension as surfactants are added
- 3: Interface covered by surfactants (CMC)
- 4: More surfactants: no change in interfacial tension, micelles form in the bulk

Surfactants in solution



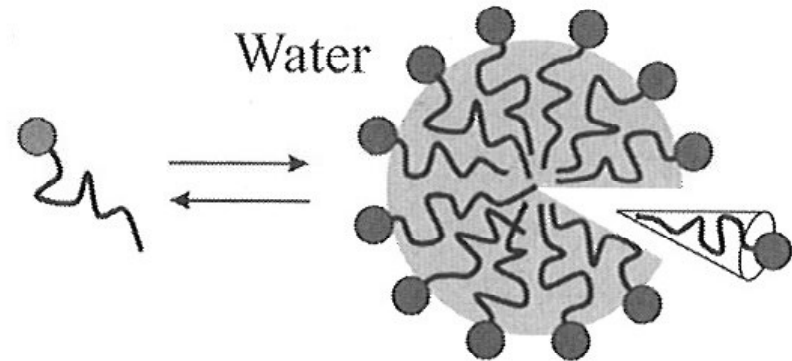
Single surfactants (monomers) in solution $\rightleftharpoons$ micelles (aggregates of surfactants)



S – surfactant monomer

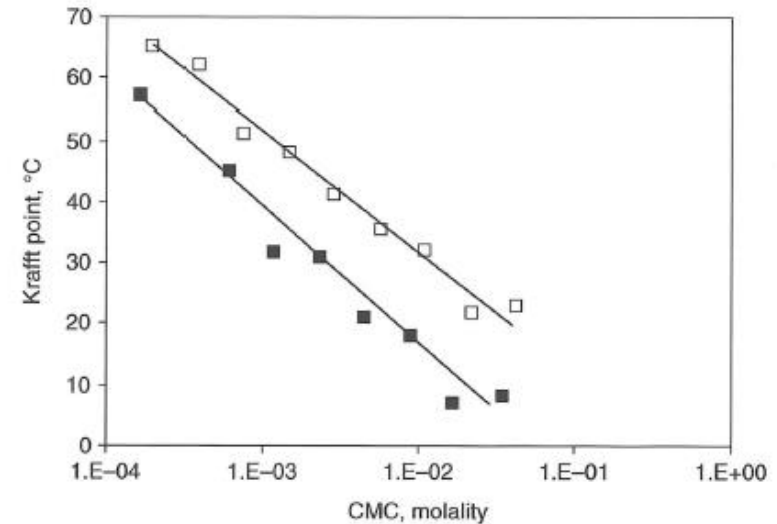
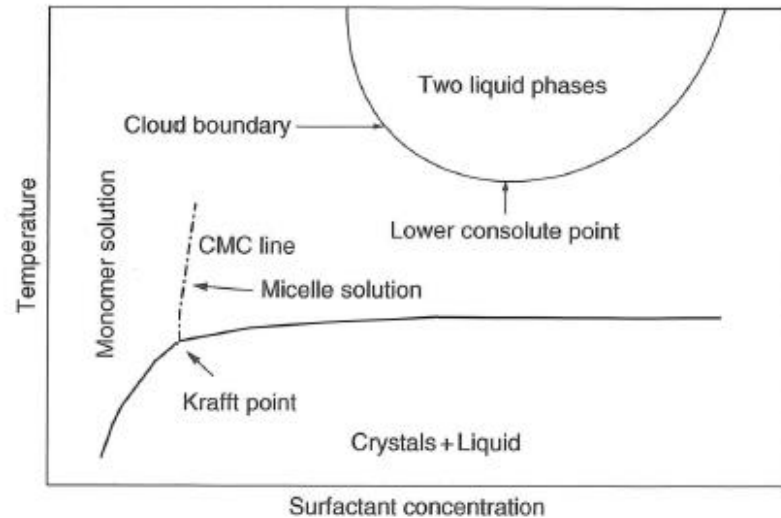
n – number of surfactants

S_n – micelle with a degree of aggregation

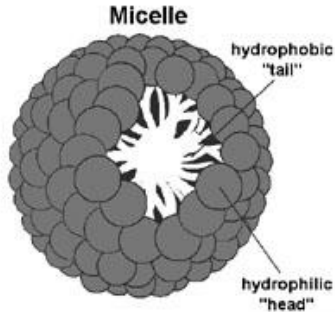


Krafft point

Temperature above which micelles are created



Structure of micelles



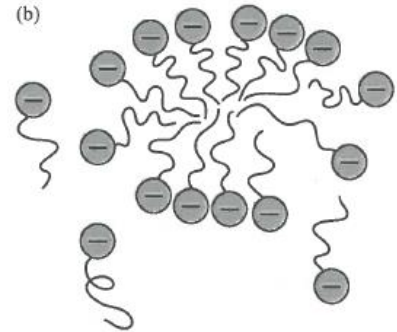
Hydrocarbon chains: Central core.

Polar headgroups: Interface against water

Micelles are *highly dynamic systems*:

- Surfactant exchange between micelles: 10 μ s
- Formation and disintegration of micelles: ms

Micelle interfaces are turbulent at the molecular level



Micellization

Micelle formation is driven by increase in entropy:

Surfactant	Gibbs energy change of micellization (kJ mol^{-1})	Enthalpy change of micellization (kJ mol^{-1})	Entropy change of micellization ($\text{J K}^{-1} \text{mol}^{-1}$)
SDS	-21.9	+2.51	+81.9
C_{12}E_6	-33.0	+16.3	+49.3
Dodecyl pyridinium bromide	-21.0	-4.06	+56.9
<i>N,N</i> -Dimethyl-dodecylamine oxide	-25.4	+7.11	+109.0
<i>N</i> -Dodecyl- <i>N,N</i> -dimethyl glycine	-25.6	-5.86	+64.9



Micellization

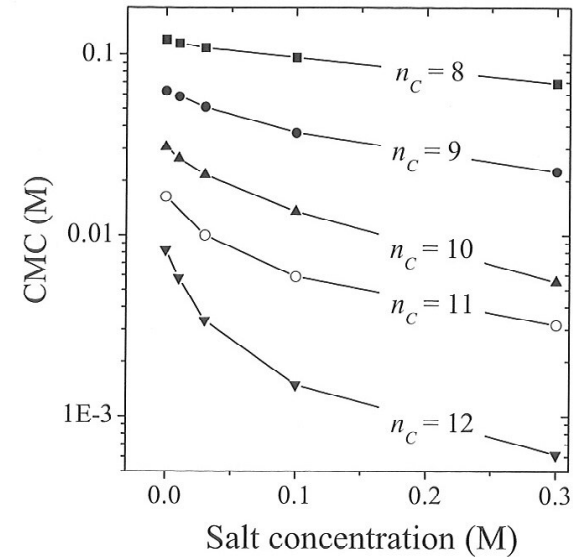
Micelle formation is a balance between two opposing forces:

- 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 (hydrophilic groups are often hydrated)
 - *tend to increase effective headgroup area*

Effective headgroup area: balance between a) and b)

Factors influencing CMC

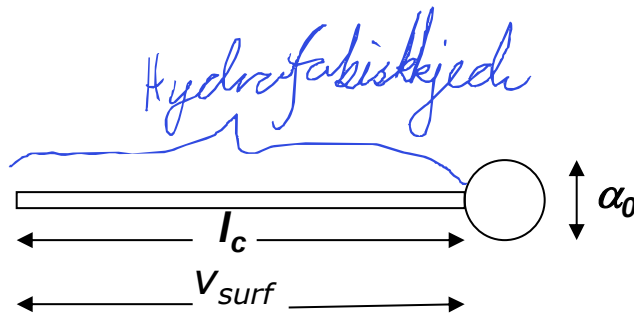
- Hydrophobic chain length
- Type of head group (ionic or nonionic)
- Electrolytes (ionic surfactants)
- Temperature (nonionic surfactants)
- Organic additives (solubilisation)



Critical Packing Parameter

Relates surfactant structure to structure of aggregates

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



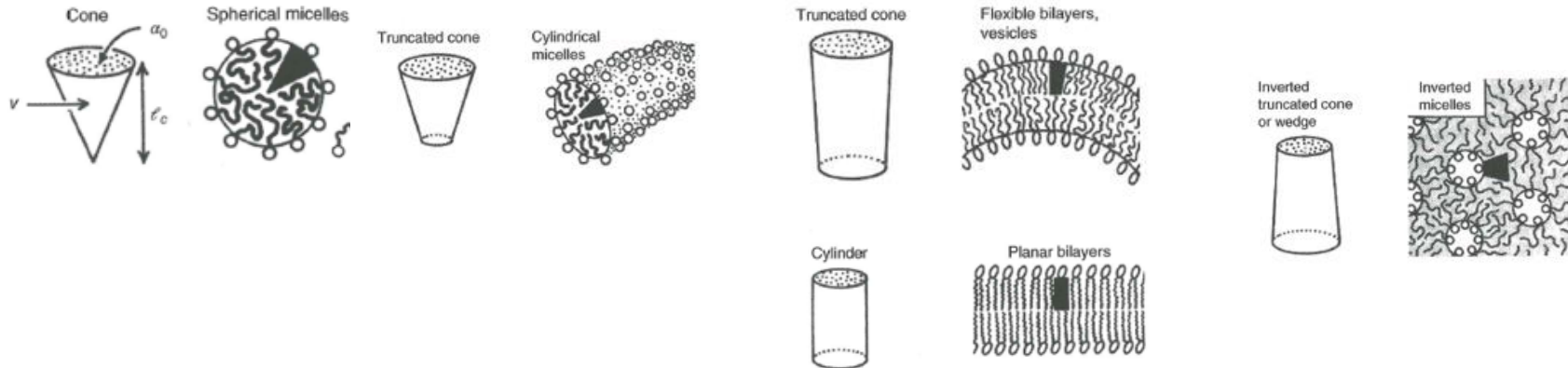
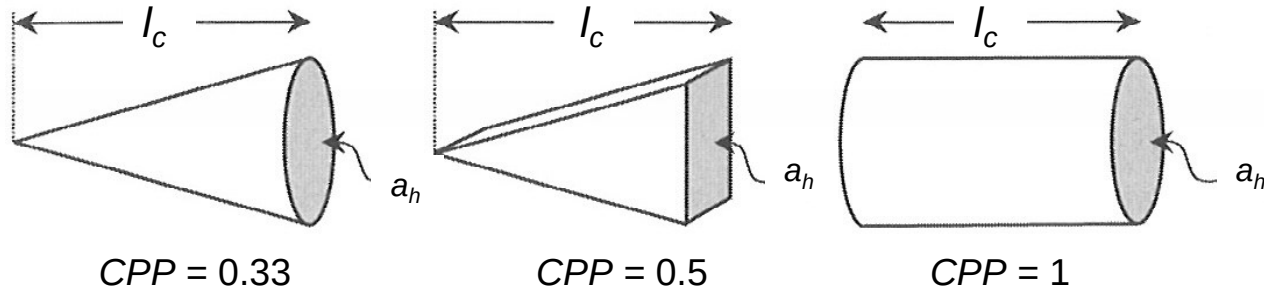
α_0 – optimal head group area

l_c – chain length

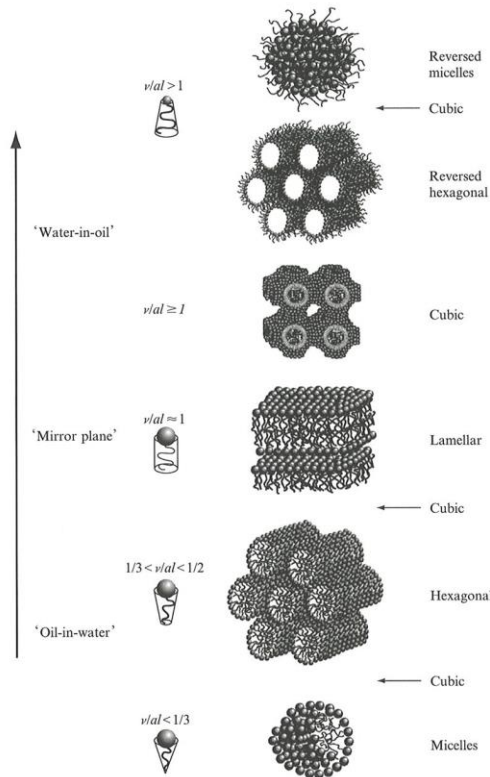
V_{surf} – volume of the chain

CPP Tar ikke hensyn til lateralkjæder eller forgreining.

Critical Packing Parameter



Critical Packing Parameter



Double chain surfactants with small headgroups

Double chain surfactants with large headgroup areas

Single chain surfactants small headgroup areas
(SDS/CTAB in high salt)

Single chain surfactants large headgroup areas
(SDS in low salt)

$$n_{agg} = \frac{V_{mic}}{V_c} = \frac{\frac{3}{4}\pi R_{mic}^3}{V_c}$$

$$n_{agg} = \frac{S_{area}}{\alpha_o} = \frac{4\pi R_{mic}^2}{\alpha_o}$$

$$\frac{V_c}{\alpha_o} = \frac{1}{3} \text{ eller mindre} \Rightarrow \text{sforisk.}$$



Critical Packing Parameter

Rule of thumbs for micelle structures/changes in aggregate structures:

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:

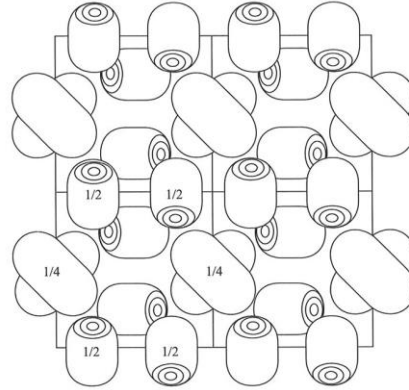
- Increasing chain length
- Increasing number of chains
- Introduce branching in chains
- Unsaturated hydrocarbon chains

Liquid Crystalline Phases:



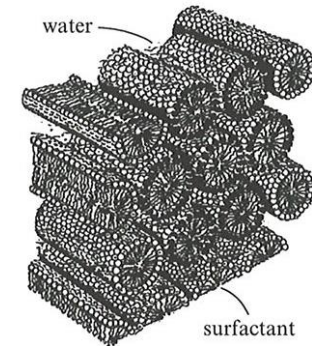
Micellar cubic phase (I_1):

Regular packing of micelles



Hexagonal Phase (E):

Long cylindrical micelles arranged in a hexagonal pattern

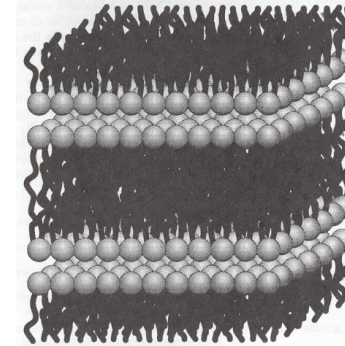


Liquid Crystalline Phases:



Lamellar Phase (D):

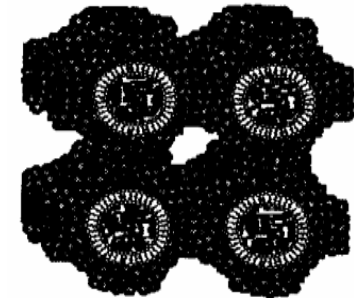
Bilayers of surfactants alternating with water layers



Bicontinuous phases (I_1 , V_1):

Several different structures forming 3-D connected structures

- Connecting rod-like/branched micelles
- Bilayer structures

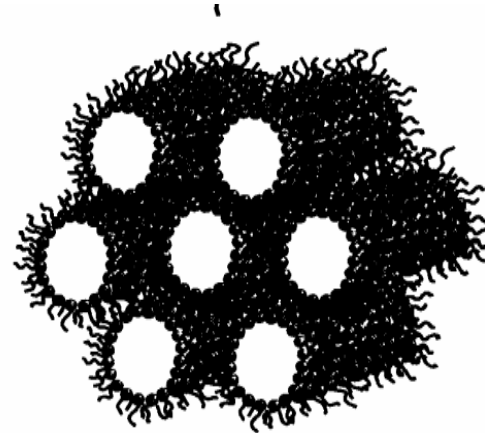
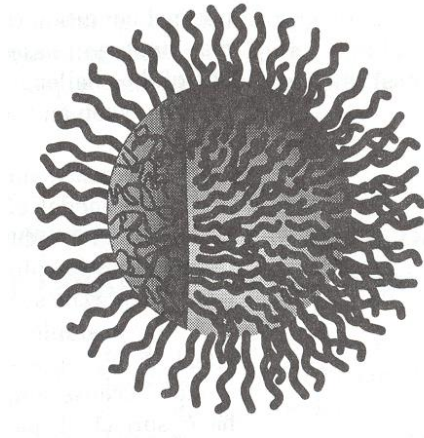


Reversed Phases:

Reverse structures:

Water droplets (L_2)

Hexagonally packed water cylinders (F)



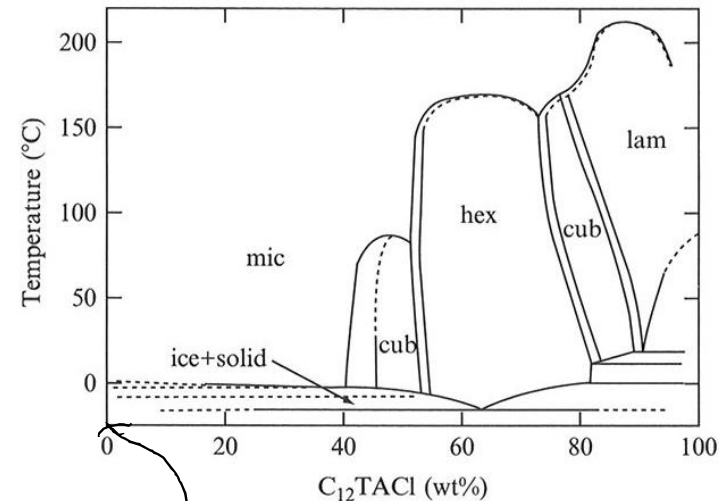
Phase Diagrams

Determined experimentally and contains information about:

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

Binary phase diagram :

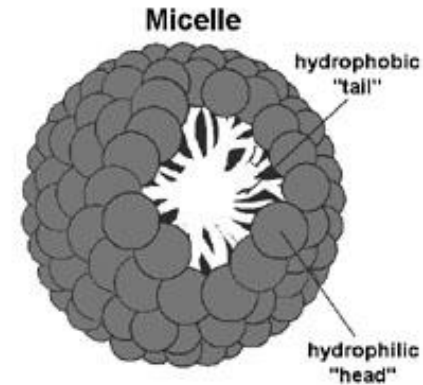
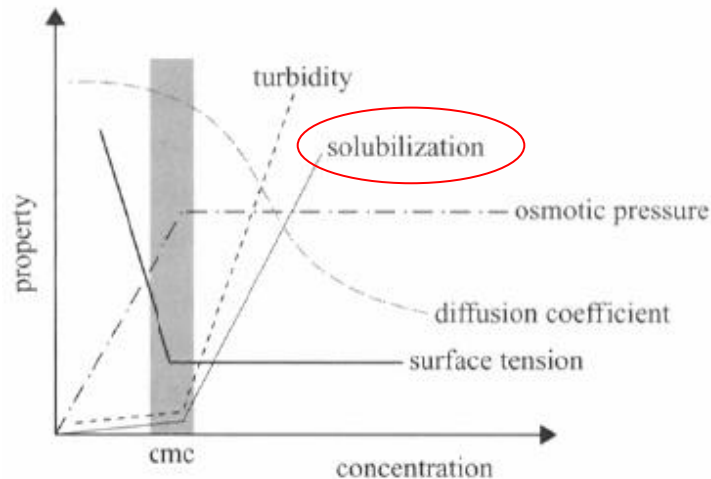
- Micellar solution up to high surfactant concentration (~40 wt%)
- Cubic phase of globular micelles
- Packing restrictions $\Rightarrow$ deformation of micelles and transition into hexagonally phase
- Second cubic phase, bicontinuous
- Lamellar phase
- Solid hydrated surfactant



$CMC \sim 10^{-3} M$

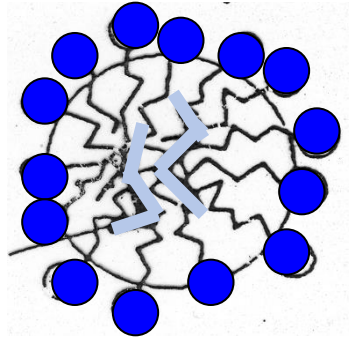
Solubilisation

Non-polar or semi-polar compounds can dissolve extensively in surfactant solutions above CMC - ***solubilisation***

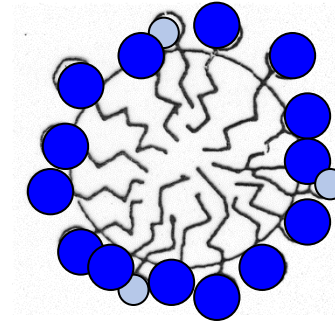


Solubilisation

The polarity of the solubilisate determines its location in the micelles



Hydrocarbons

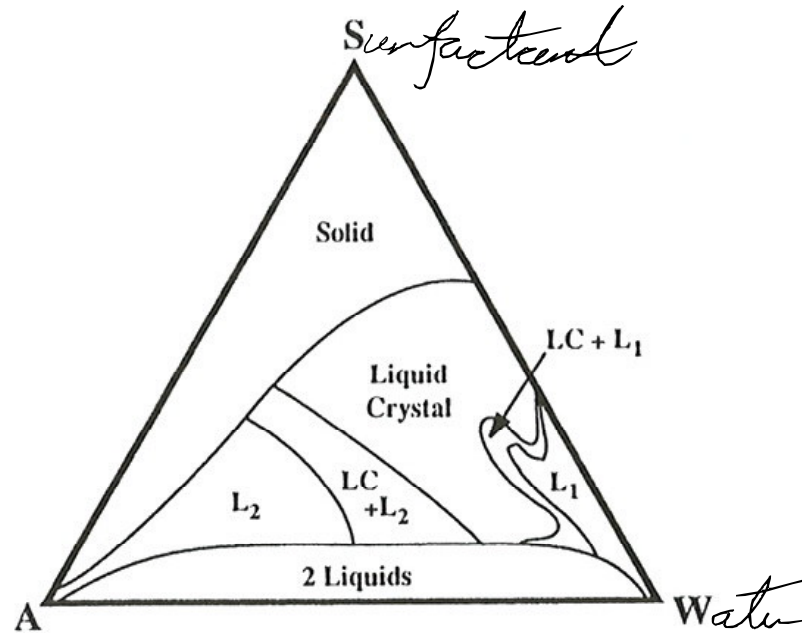


Polar compounds
(Alcohol)

Upper limit for the amount of solubilisation into micelle solutions

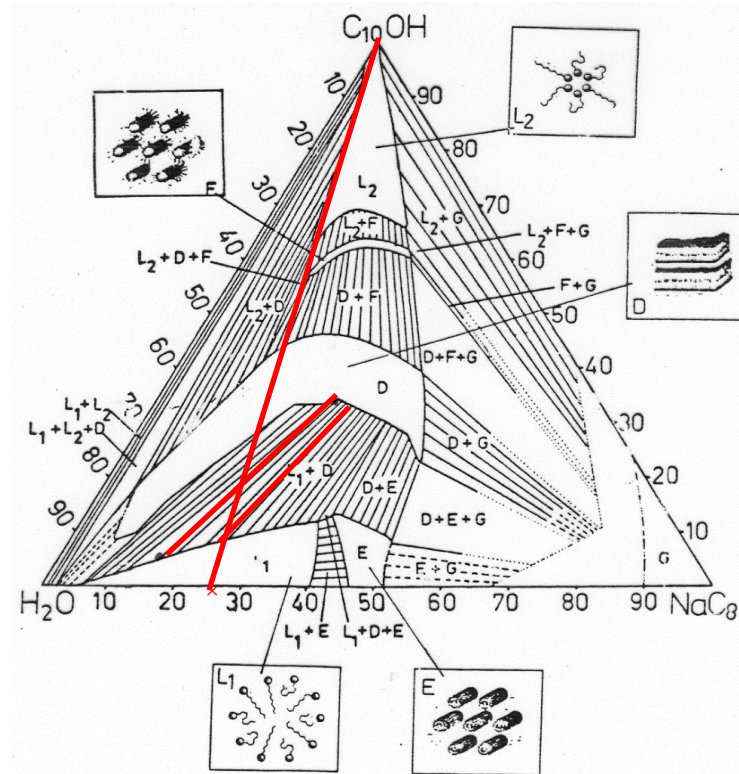
Ternary phase diagrams

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



Asphatic = oil

Ternary phase diagrams



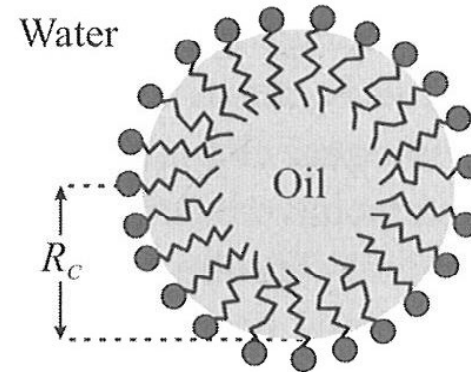
Microemulsions

Formed in 3-component systems (oil, water and surfactant)

Often a 4th component is present as well (*co-surfactant*)

General properties:

- *Thermodynamically stable*, i.e. 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





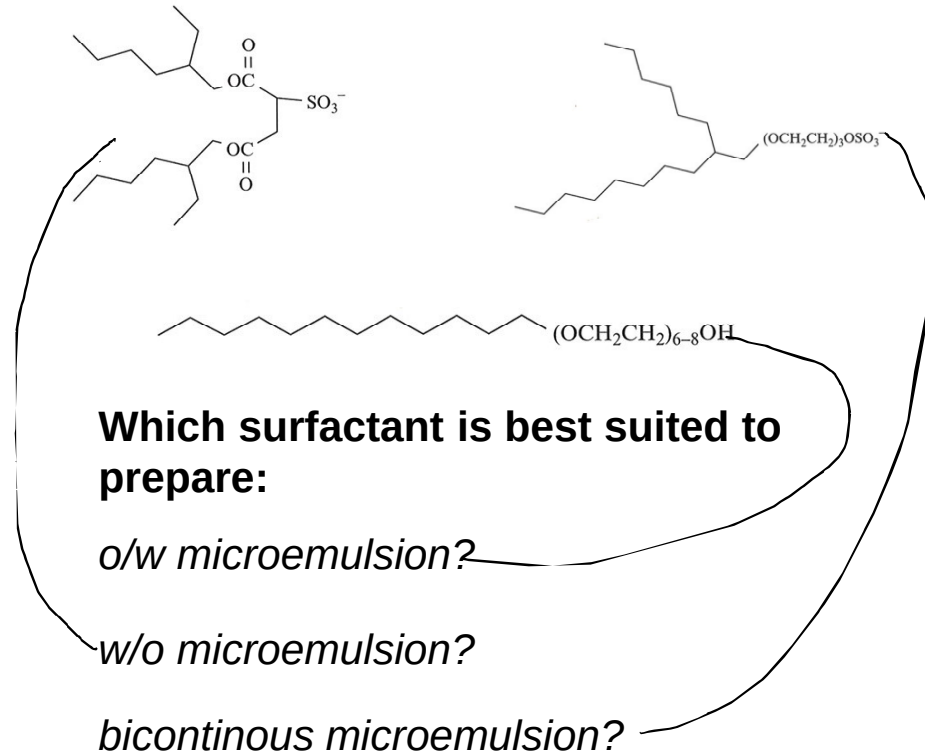
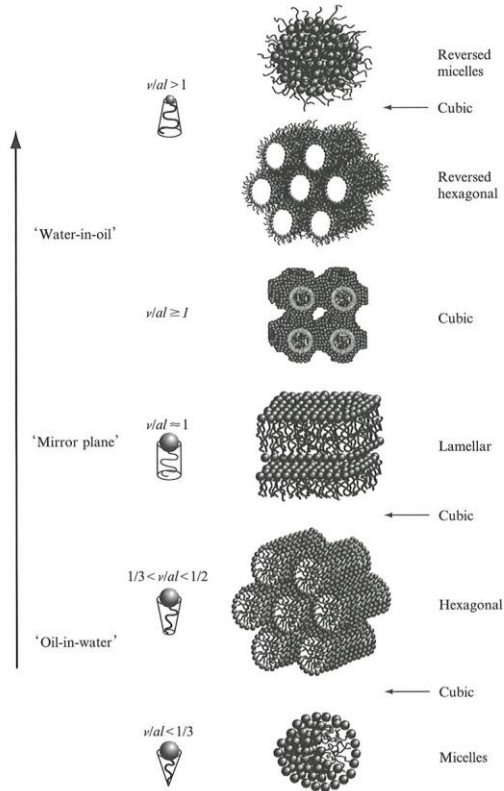
Microemulsions

Microemulsions can be considered as swollen micelles - similar curvature:

- Highly curved towards oil – o/w microemulsion (micelle)
- Highly curved towards water – w/o microemulsion (inverted micelle)
- Zero mean curvature – bicontinuous microemulsions

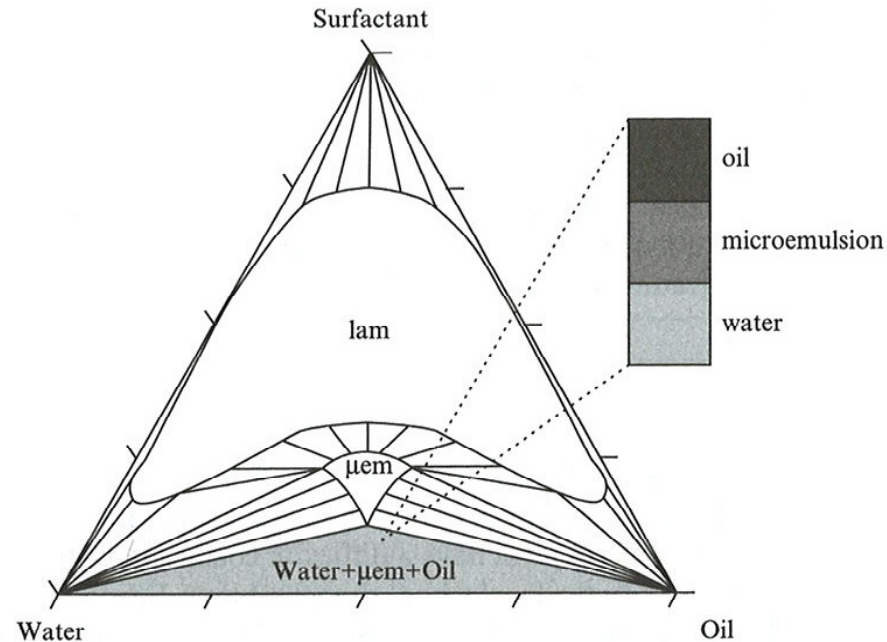
Packing Parameter concept is useful for microemulsions as well

Microemulsions



Microemulsions

Ternary phase diagrams is effectively representing the phase behaviour of microemulsions



Detergency - removal of oily drop

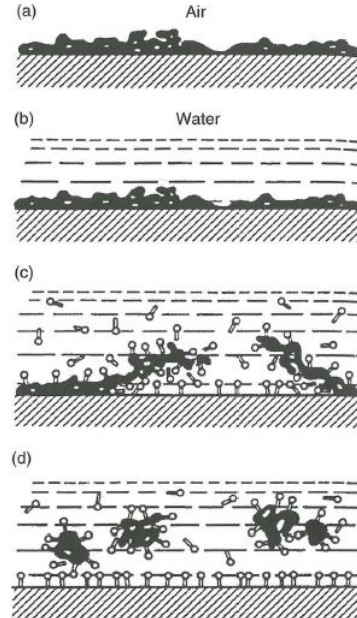
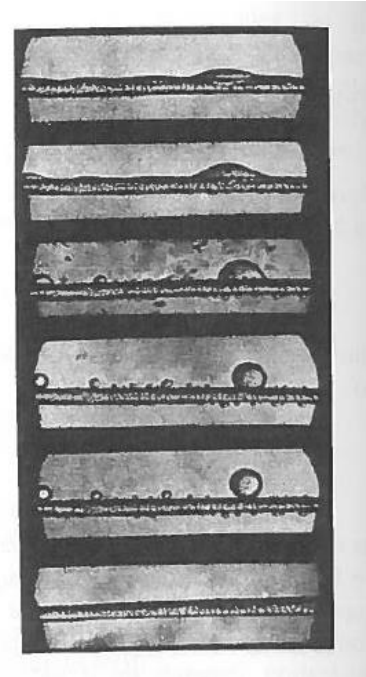
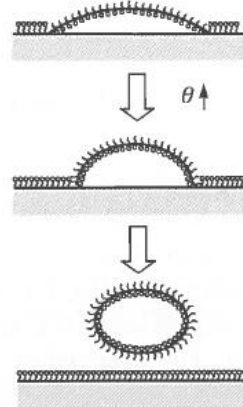


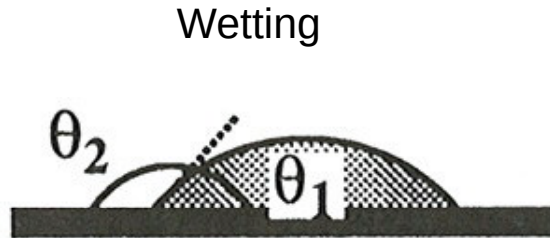
Figure 5.13 The three major mechanisms in the cleaning of surfaces via surfactants: (a) The solid substrate with the dirt prior to adding water and surfactants, (b) wetting with water alone, (c) decrease of adhesion with the presence of surfactants and (d) solubilization inside micelles. Shaw (1992). Reproduced with permission from Elsevier

Add surfactant: $\cos \theta = \frac{\sigma_{SW} - \sigma_{SD}}{\sigma_{DW}}$



Detergency - removal of oily drop

Spreading of oily drop on surface:

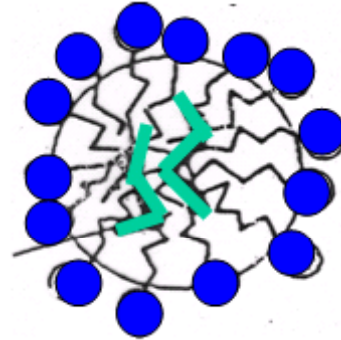


- Efficient for polar textiles (cotton)
- Less efficient for non-polar textiles (polyester)

Detergency - removal of oily drop

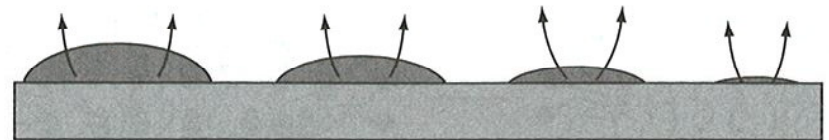
When dirty spot is removed from surface it is important to prevent redeposition

Solubilisation of oily material into micelles:



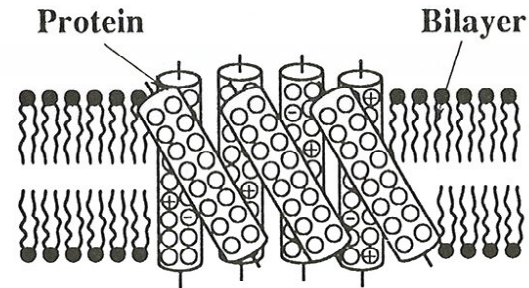
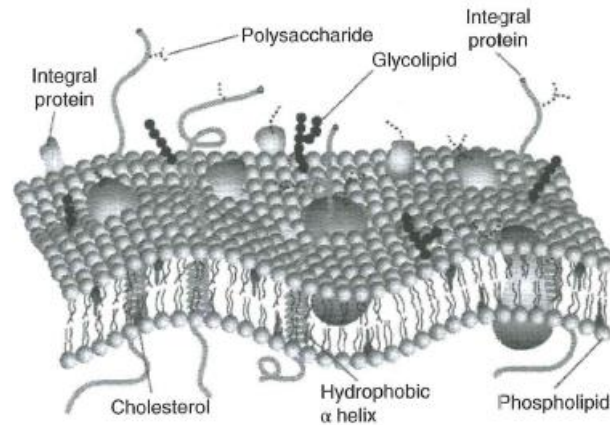
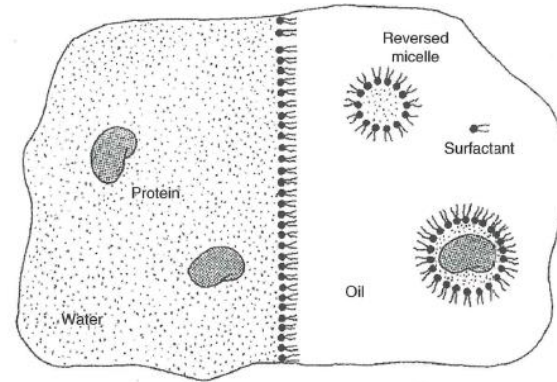
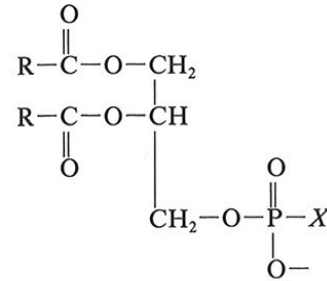
Oily drop is solubilised into micelles and microemulsions formed *in situ*

Solubilisation will occur independent of surface



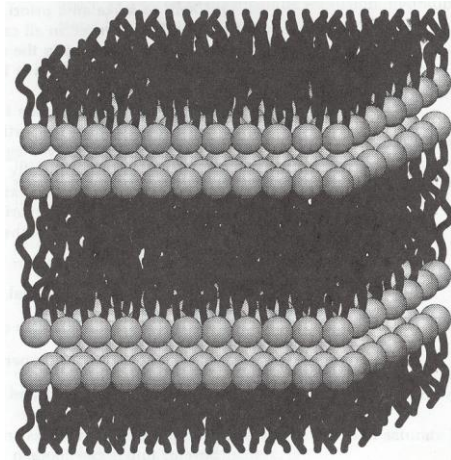
Biological membranes

Phospholipids:

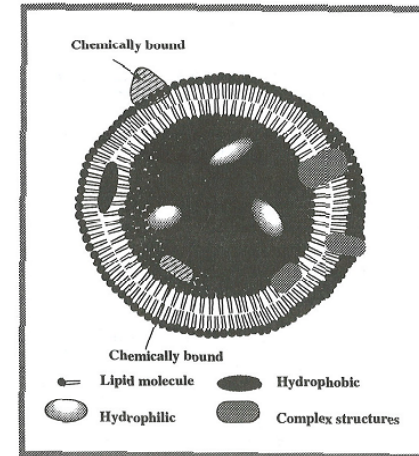


Vesicles (liposomes)

Formed by dispersion of a lamellar liquid crystalline phase

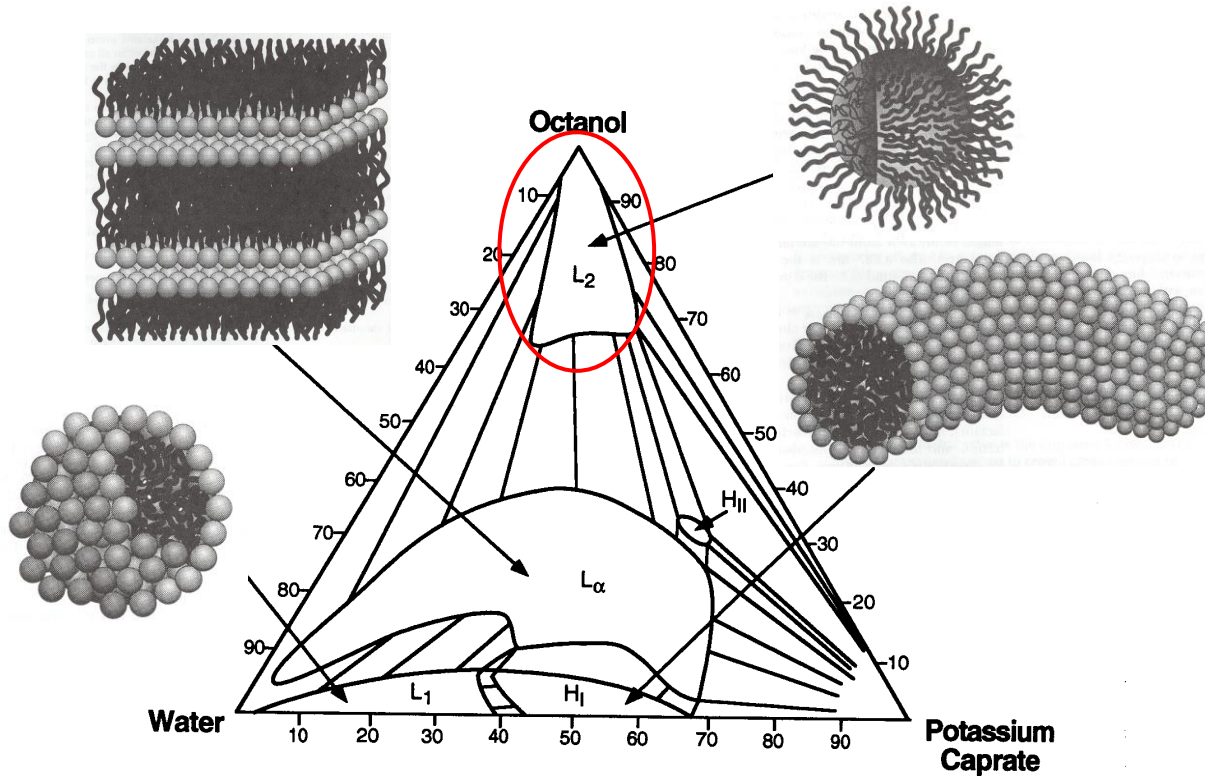


Folding of sheets

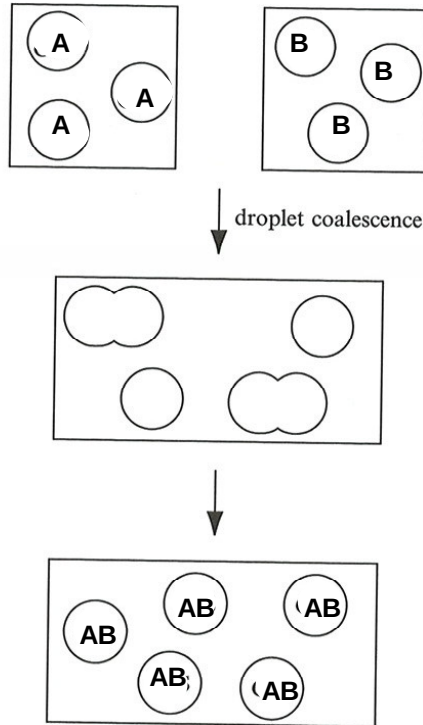


Molecules can be solubilised in different parts, depending on chemical nature
(medicine carriers)

Nanostructures using self-assembly systems



Nanoparticles - synthesis

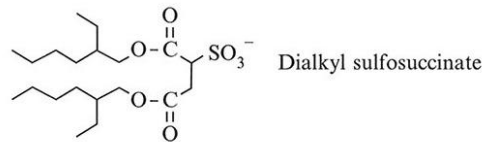


A and B solubilised in 2 inverted micellar systems

The two systems are mixed and exchange processes ensure that A and B come in contact

Depending on the precursors (A and B) nanosized semiconductors, metals or oxides can be formed.

Typical surfactant:



Typical precursors:

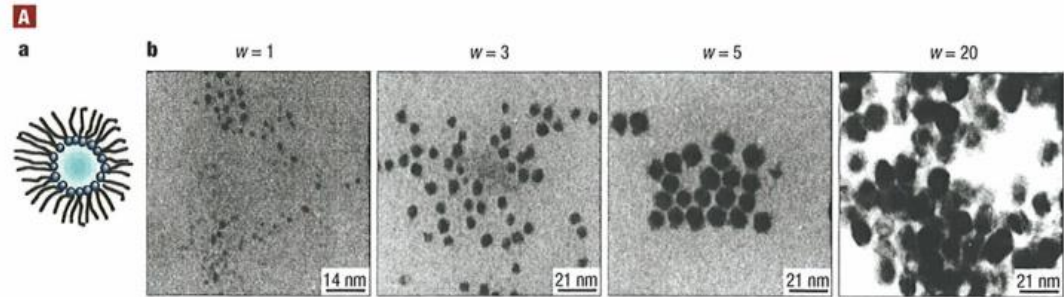
Metal ions

Reducing agent (N_2H_4)

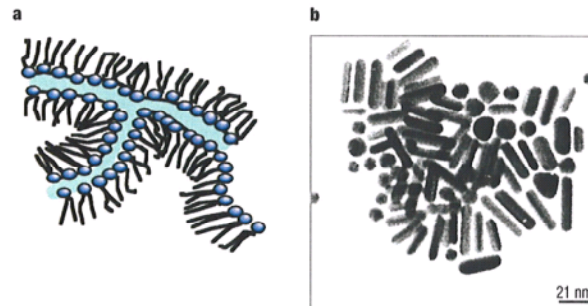
Nanoparticles - size and shape

Copper nanocrystals.

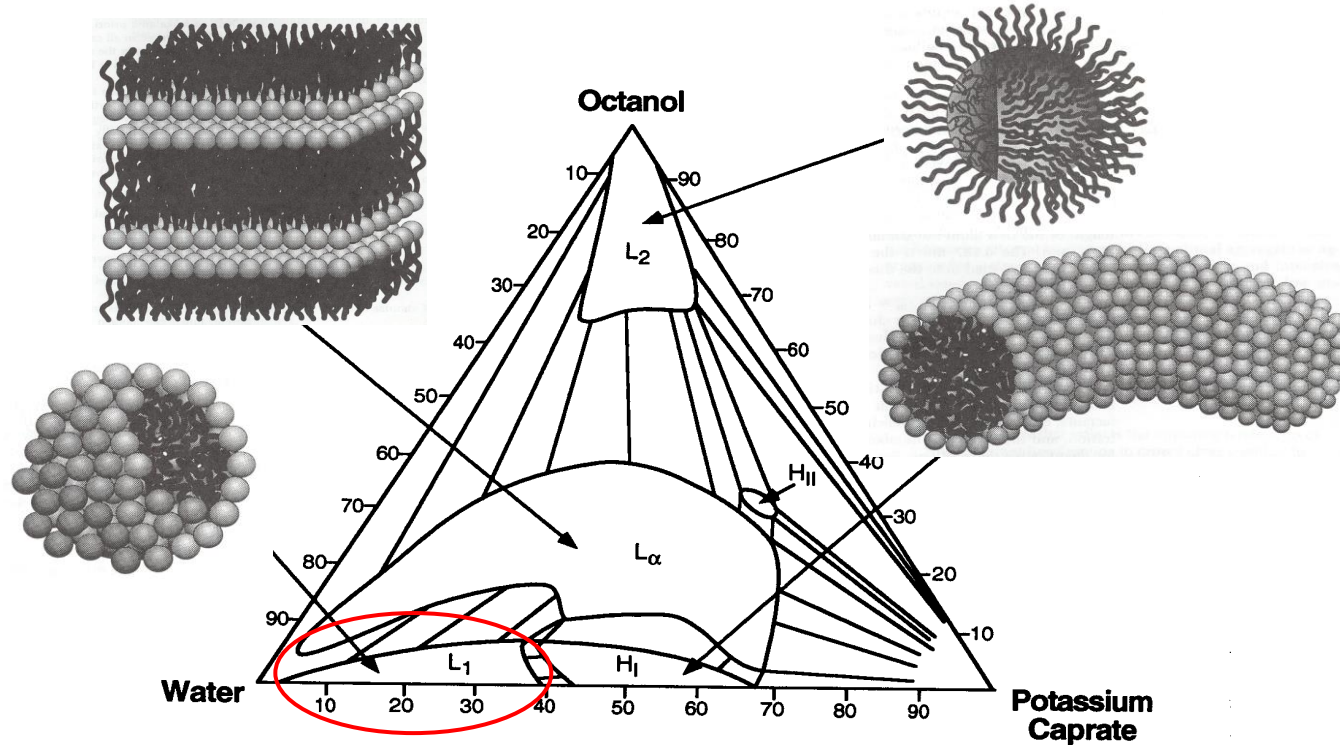
Size controlled by water content:



Copper cylindrical nanocrystals:

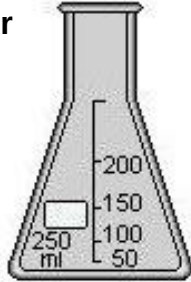


Nanostructured materials using self-assembly systems



Porous materials - synthesis

Silica
precursor



Micelle solution

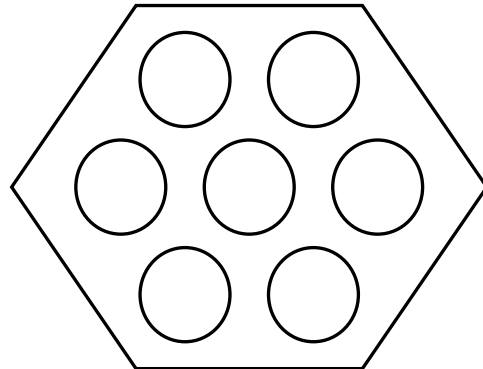
Sol-gel route:

Hydrolysis: $\equiv\text{Si-OR} + \text{H}_2\text{O} \leftrightarrow \equiv\text{Si-OH} + \text{ROH}$

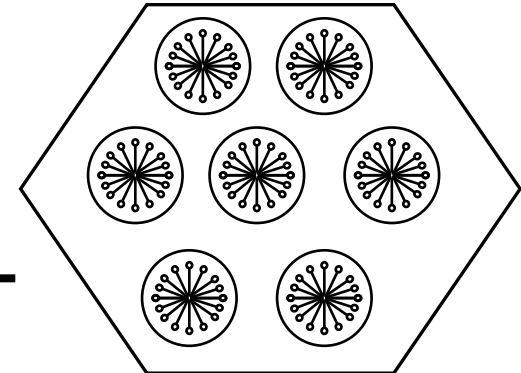
Water condensation: $\equiv\text{Si-OH} + \equiv\text{Si-OH} \leftrightarrow \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O}$

Alcohol condensation: $\equiv\text{Si-OR} + \equiv\text{Si-OH} \leftrightarrow \equiv\text{Si-O-Si}\equiv + \text{ROH}$

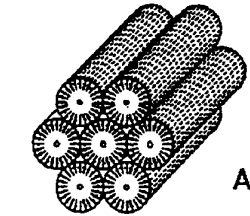
Self-assembly and
Charge Density Matching



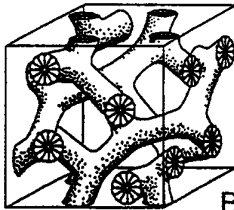
Calcination or Extraction



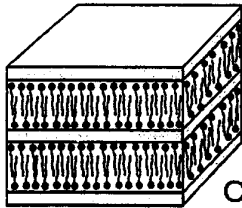
Porous materials - structure



A



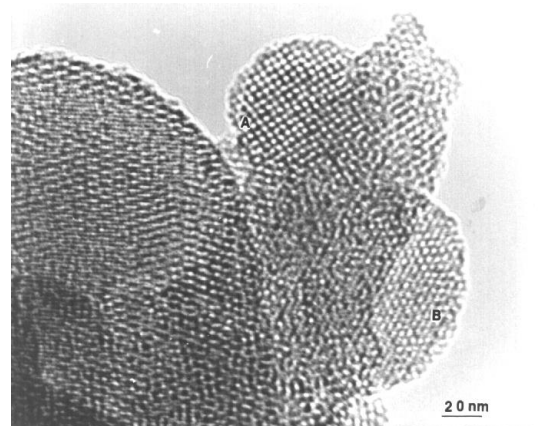
B



C

Advantages of using self-assembling “templates”:

- Regular pore ordering
- Narrow pore size distribution
- Tuneable pore size (20-500Å)
- Large surface areas (700-1200 m²/g)



Adsorption in colloid and surface science

Adsorption onto solids

- from gas phase (Langmuir and BET isotherms)
- from solution (Langmuir isotherm)

Models to *predict* how surface coverage varies with P/c

Important applications

- Stabilization
- Cleaning
- Heterogeneous catalysis
- Surface modification
- ...

Amount of adsorbed gas as a function of pressure can also be used to determine:

- Specific surface area of solid (A_{sp})
- Porous solids: pore sizes and pore volume

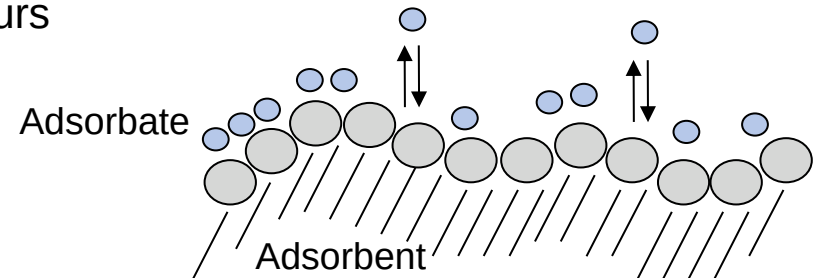
Gas adsorbed on solids

- Chemisorption – formation of chemical bonds, irreversible
- *Physisorption* – van der Waals interactions, reversible

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 ($<10 \text{ kcal mol}^{-1}$)	High heat of adsorption ($5\text{--}100 \text{ kcal mol}^{-1}$)

Adsorbent: solid surface where adsorption occurs

Adsorbate: specie adsorbed at the adsorbent

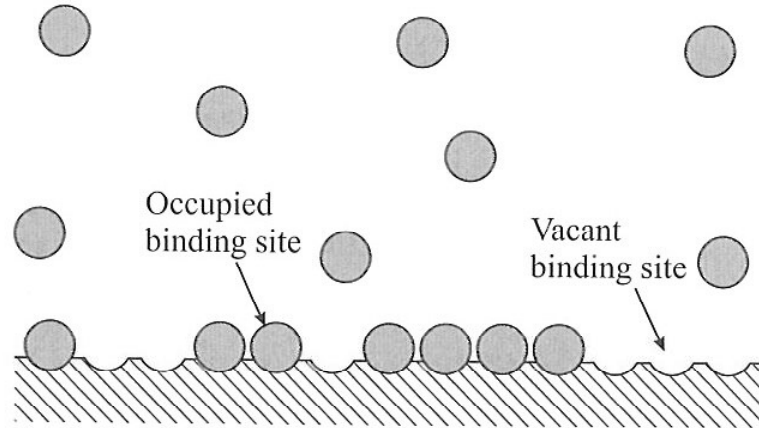


Gas adsorbed on solids

Langmuir adsorption isotherm:

$$\Theta = \frac{V}{V_m} = \frac{BP}{1 + BP}$$

Volume adsorbate (pointing to V)
pressure (pointing to P)
konstant (pointing to B)
Volume monolayer (pointing to V_m)

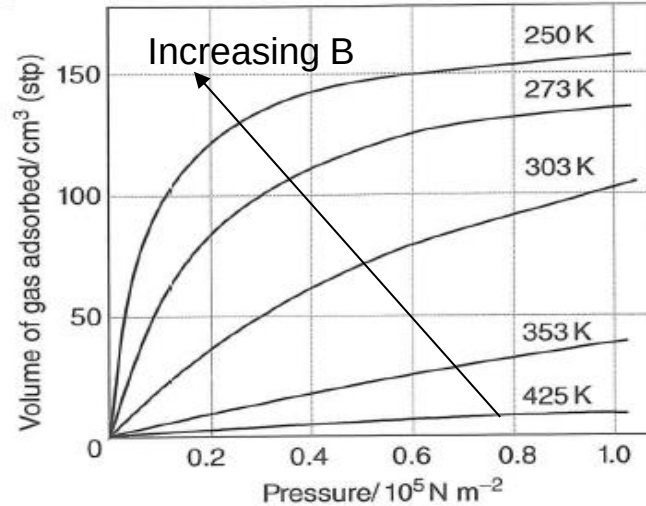


Langmuir isotherm

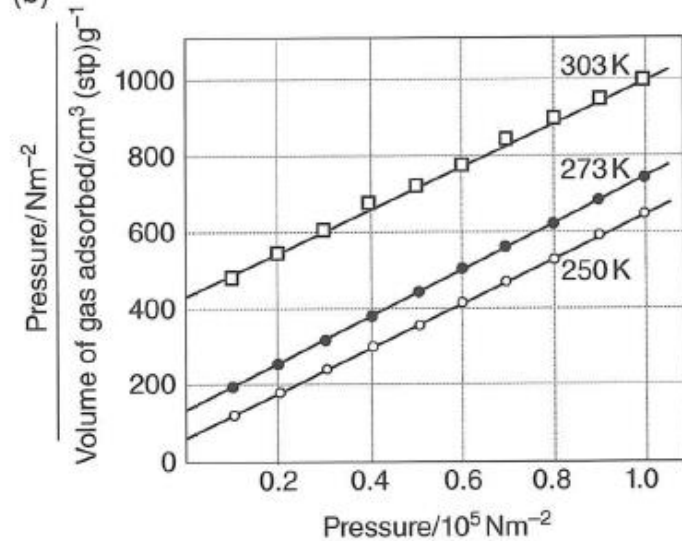
$$\Theta = \frac{V}{V_m} = \frac{BP}{1 + BP}$$

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

(a)

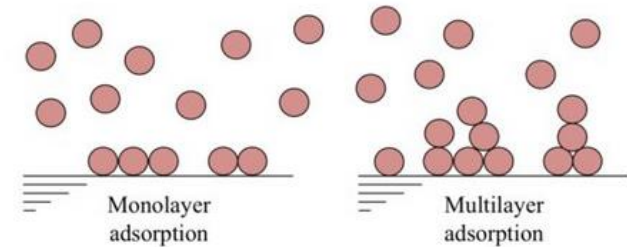


(b)



Gas adsorbed on solids

Difference between monolayer and multilayer adsorption:

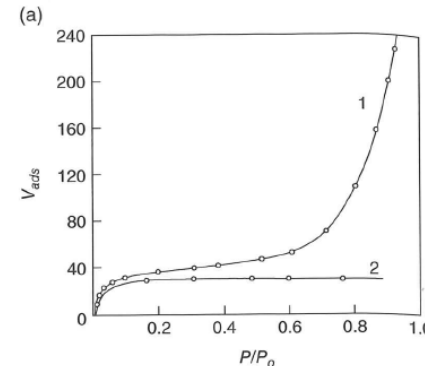


θ defined as the fraction of filled sites

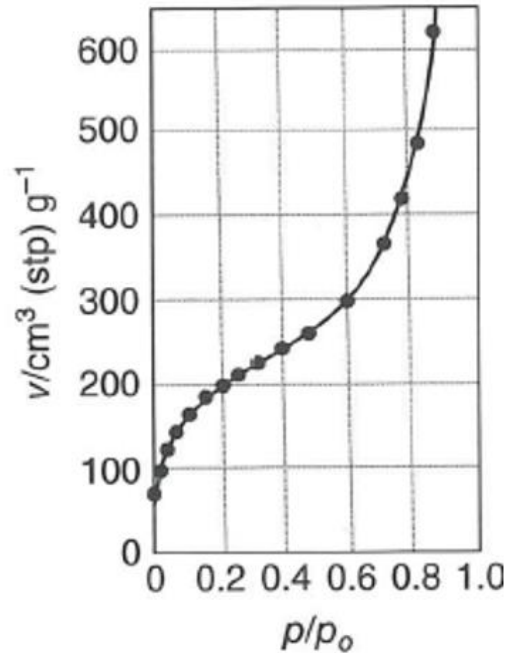
$\theta = 1$: Monolayer coverage

$\theta < 1$: Submonolayer

$\theta > 1$: Multilayer



BET isotherm



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

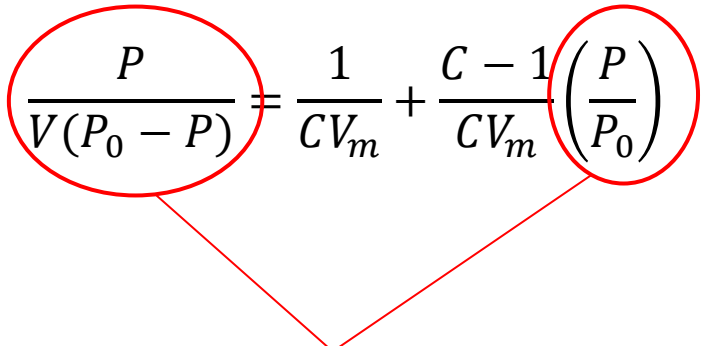
V : total volume of adsorbed gas

V_m : volume of adsorbed gas at monolayer

C : temperature dependent constant

BET isotherm

Linearised BET equation – practical form:

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


Measured in experiment

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

$$\text{Intercept} = \frac{1}{CV_m}$$



Gas adsorbed on solids

Determine A_{sp}

Determine volume of adsorbed gas that would saturate the surface if adsorption were limited to a monolayer (V_m)

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

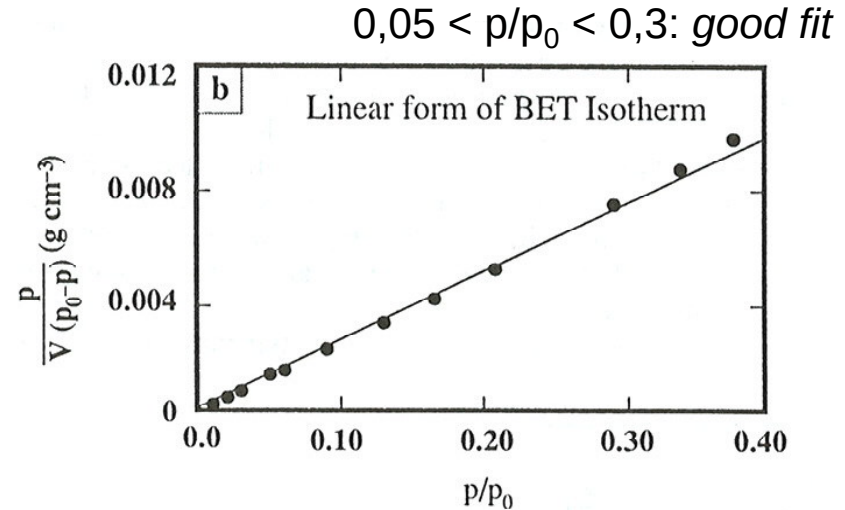
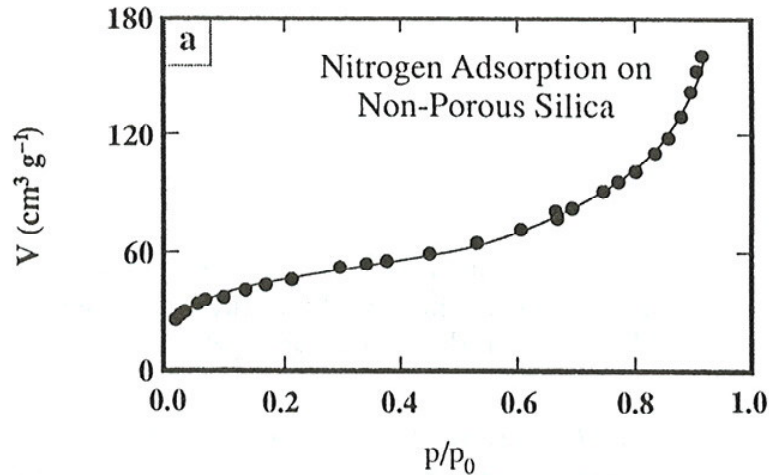
$V_g = 22,414 L/mol$: Gas volume at standard temperature and pressure

A_0 : Area occupied by one gas molecule

Gas adsorbed on solids



Example: Adsorbate: N₂ Adsorbent: Silica T = 77K (liquid nitrogen)



$$\text{Slope} = \frac{C - 1}{CV_m} = 0,0257 \text{ g/cm}^3 \text{ (STP)}$$

$$\text{Intercept} = \frac{1}{CV_m} = 2,85 \cdot 10^{-4} \text{ g/cm}^3 \text{ (STP)}$$



Adsorption from solution

Measured indirectly:

A solution is put in contact with a solid surface.

The solute adsorb at the solid-liquid interface.

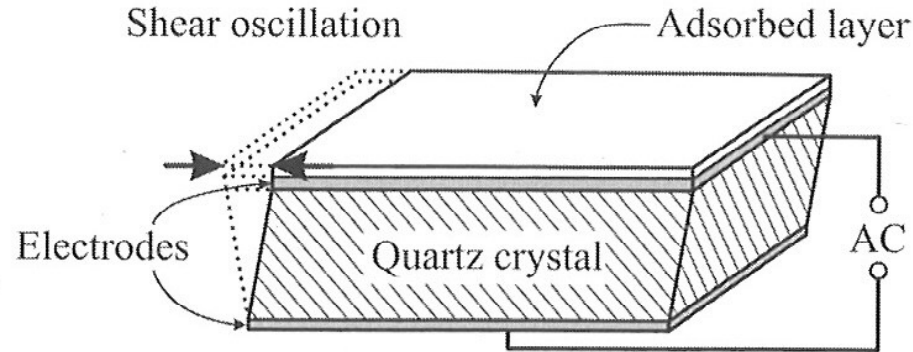
The concentration of solute in the bulk solution will be reduced.

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).

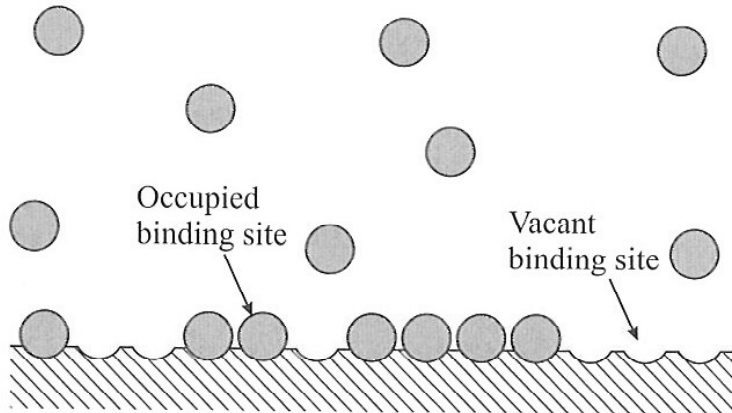
Adsorption from solution

Direct measurement – quartz crystal microbalance (QCM)



Adsorption from solution

Langmuir adsorption isotherm:
$$\Theta = \frac{\Gamma}{\Gamma_{\max}} = \frac{kC}{1 + kC}$$

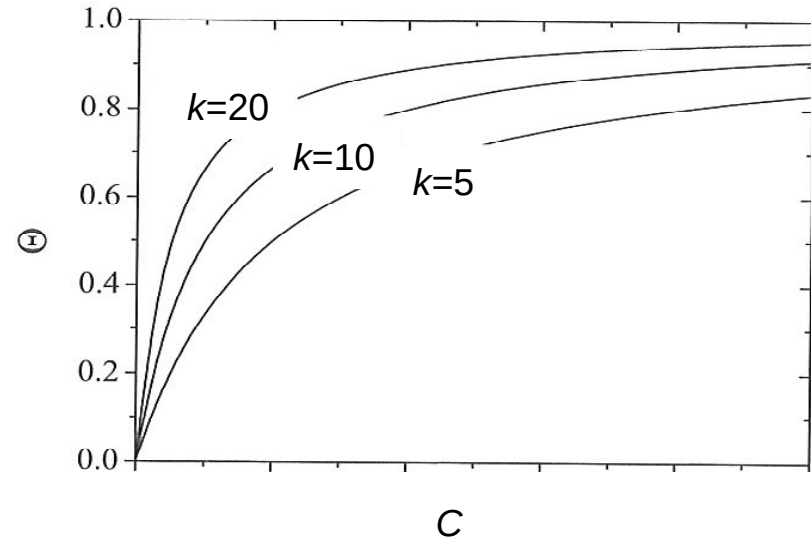
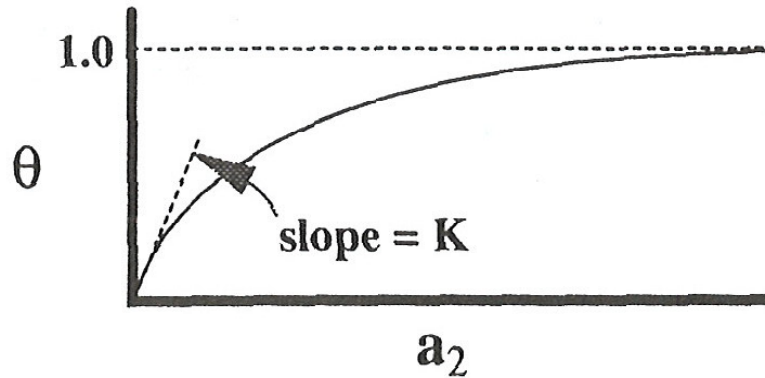


Assumptions:

- Homogeneous surface
- Only monolayer adsorption possible
- No solute-solvent or solute-solute interactions

Adsorption from solution

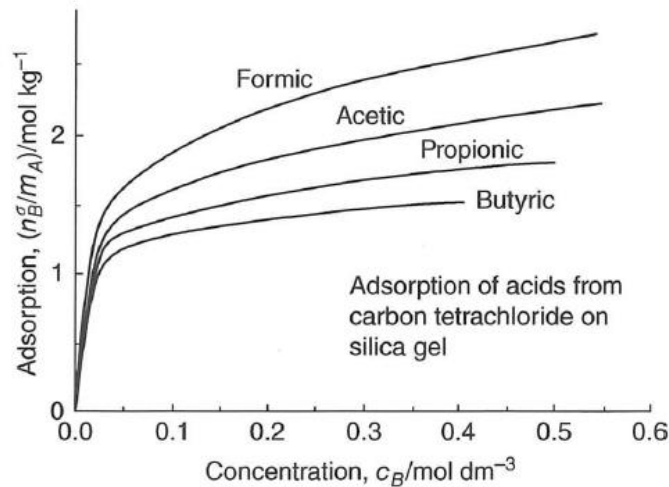
Linearized Langmuir isotherm: $\frac{C}{\Gamma} = \frac{C}{\Gamma_{\max}} + \frac{1}{k\Gamma_{\max}}$ $A_{sp} = \Gamma_{\max} N_A A_0$



Adsorption from solution

The solvent makes adsorption from solution more complex than adsorption of gases

Solvent

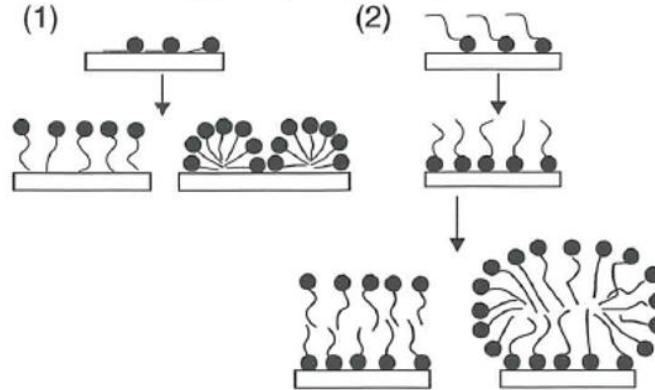


Adsorption of surfactants from solution



Depends on surface properties and interactions between surfactants

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



Non-polar surfaces: adsorption is related to CCP

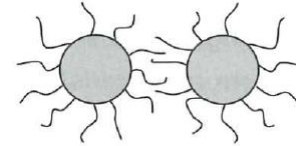
Polar surfaces: adsorption requires interactions between head group and surface

Adsorption of surfactants from solution



Important in many applications:

- Stabilisation of colloidal dispersions – steric stabilisation (paint, food, cosmetics, pharmaceuticals,...)



Best if...

- Thick and dense layers
- Extended conformations – good solvent
- Strong adsorption – poor solvent
- Complete particle coverage

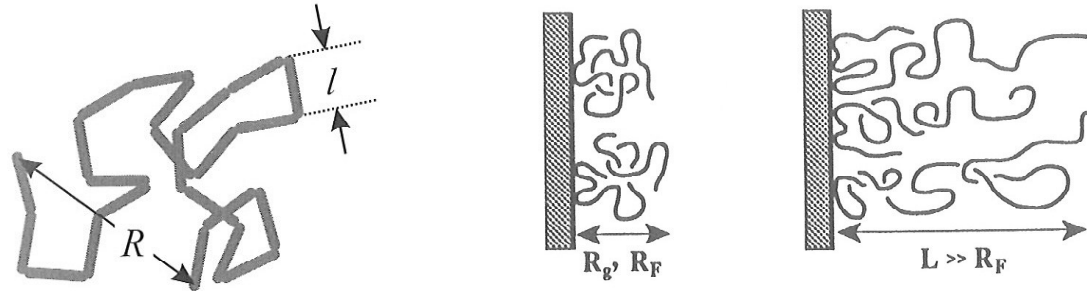
- Promote destabilisation – flocculation (water treatment, mineral processing,...)



- Surface modification (food processing, bioapplications,...)
- Surface functionalisation (bio-tech applications,...)
- Changing properties (rheology, foaming,...)

Adsorption of polymers

Role of solvent:



"Ideal" solvent: Interactions between monomer subunits equal to interactions with solvent

"Good" solvent: Repulsive force acts between monomers, polymer swells

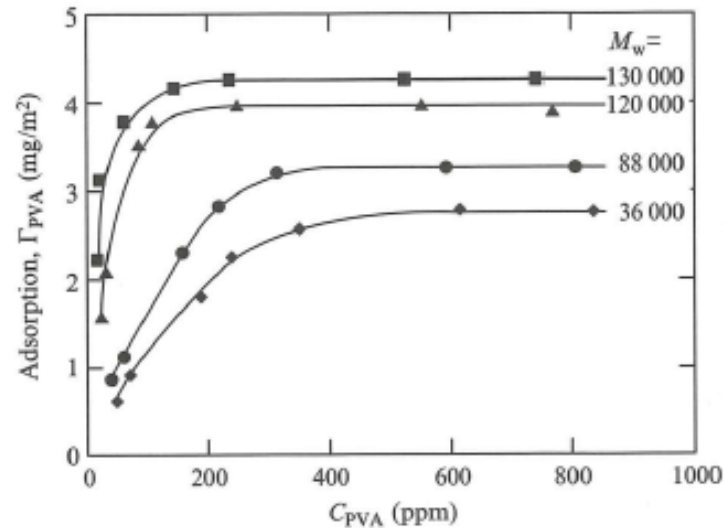
"Bad" solvent: Monomers attract each other, polymer shrink

Temperature dependent transition between "good" and "bad" solvent

- ideal polymer behaviour at a given temperature

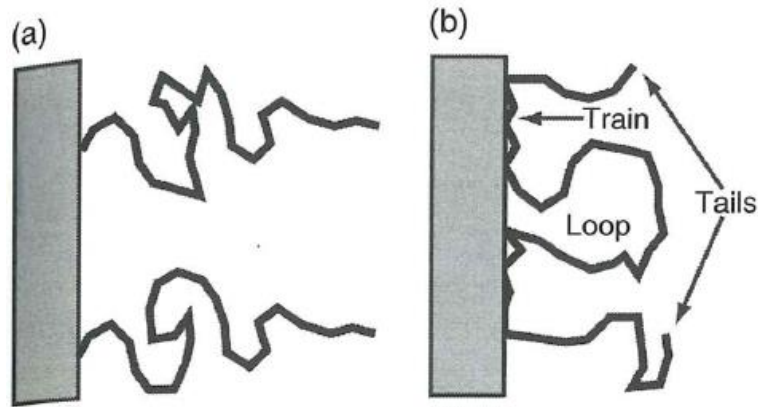
Adsorption of polymers

Influence of molecular weight:



Adsorption of polymers

Configuration upon adsorption:



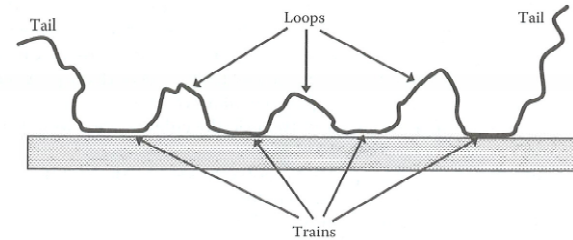
Diblock copolymer
(good stabilisers)

Adsorption of polymers

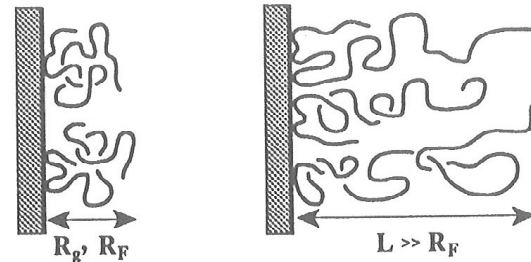
Interactions during steric stabilisation are – influenced by two main factors:

1. Type of solvent

- "Good solvent" – polymer swells
- "Bad solvent" – polymer shrinks



2. How much polymer at interface



Home experiment - sailing with soap fuel

Materials:

- Tub of water
- Paper/Construction paper/Cardboard
- Dishsoap
- A plate/A bigger bowl
- Q tips/Any similar object that can be dipped and covered with soap

Procedure:

1. Create a paper boat, using one of the materials indicated (paper/construction paper/cardboard).
2. Fill the plate or the bowl with at least 2cm of water or more in case the paper boat is bigger.
3. Place the paper boat on water and make sure it floats.
4. Dip the Q tip into dish soap and make sure it is covered in soap.
5. Dip the soap Q tip into water just near the boat.
6. Observe and explain what happens

Recording procedure:

1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no



Home experiment - milk painting

Materials:

- Whole milk
- Waterproof plate or shallow bowl
- Food coloring
- Liquid dish soap
- Cotton swabs

Recording procedure:

1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no

Procedure:

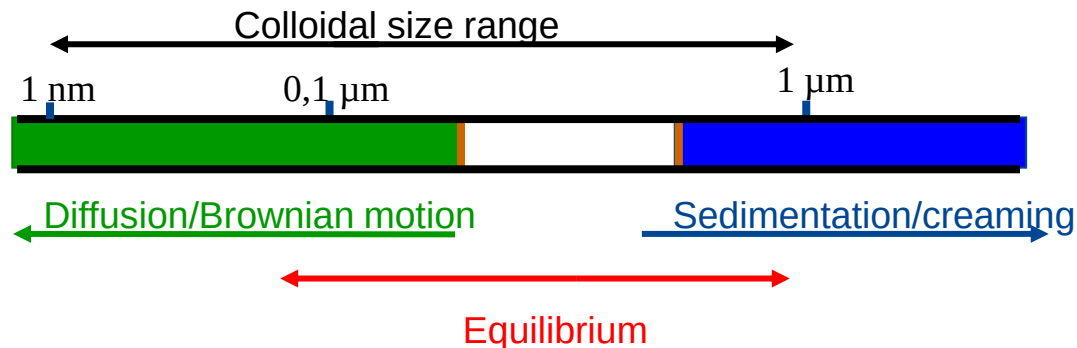
1. Fill the plate with whole milk, and let the milk settle for a minute
2. Add several drops of different food coloring close together, but separate, in the center of the plate of milk. For better visually looking results, use different colors.
3. Dip a cotton swab in the liquid dish soap, and then touch the tip of the cotton swab to the milk's surface near the drops of food coloring. Observe the reaction.
4. Then, move the swab to different areas of the plate to initiate more reactions.
5. Observe and explain what happens



Kinetic Properties and Rheology

Motion of dispersed phase

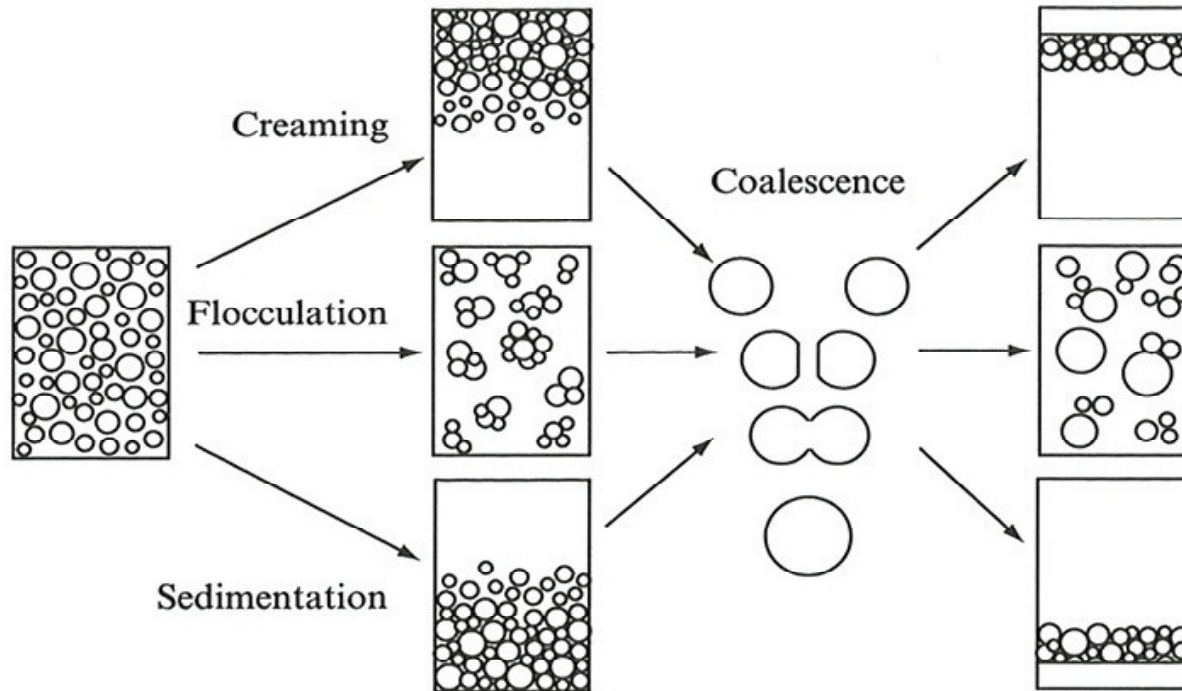
- gravitational field
- centrifugal field
- Brownian motion (thermal forces)



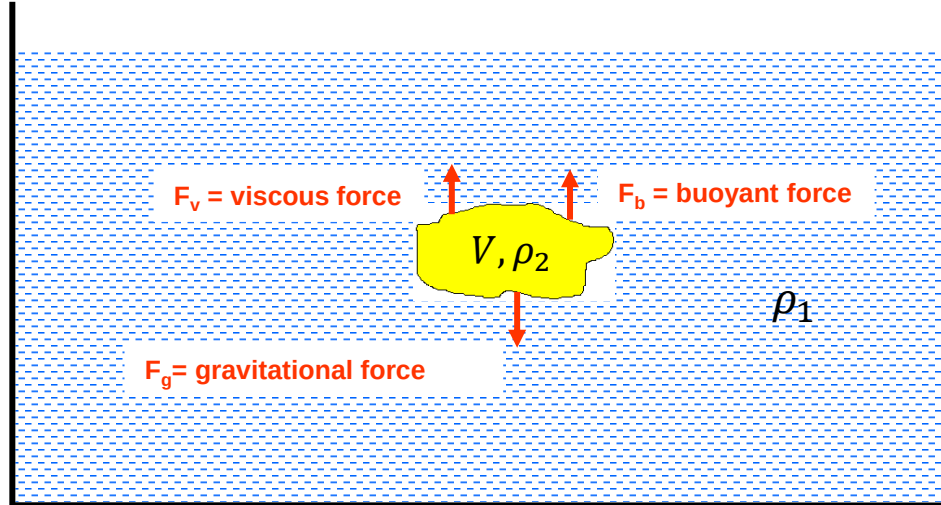
Osmotic pressure and rheology

Sedimentation and Brownian motion

– importance for colloidal systems



Gravitational sedimentation



Direction of particle movement: $\rho_2 > \rho_1$: Downwards - ***Sedimentation***

$\rho_1 > \rho_2$: Upwards - ***Creaming***



Gravitational sedimentation

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

$\frac{m}{f}$: mass-to-friction-factor

Two ways of evaluating f :

1. assume spherical particles
2. evaluate f in combination with diffusion studies



Gravitational sedimentation

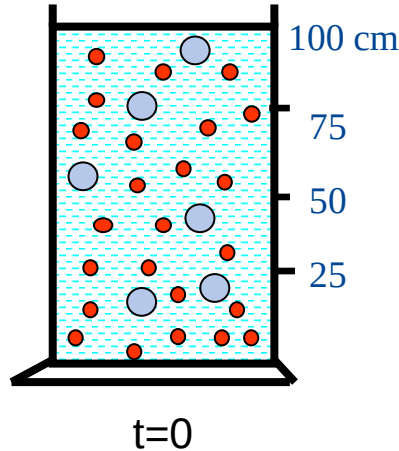
Stoke's Law: $F_v = 6\pi\eta R_s u$

Stokes (sedimentation) equation:

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

Gravitational sedimentation

Example:

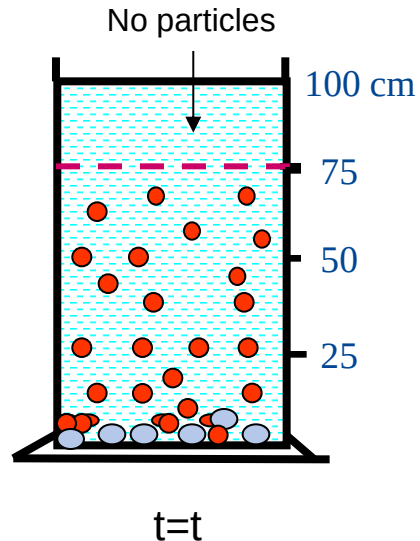


- = 20 μm diameter particles
- = 10 μm diameter particles

(same composition)

How many % of 10 μm particles are still in the dispersion at the point where all 20 μm particles have reached the bottom?

Gravitational sedimentation

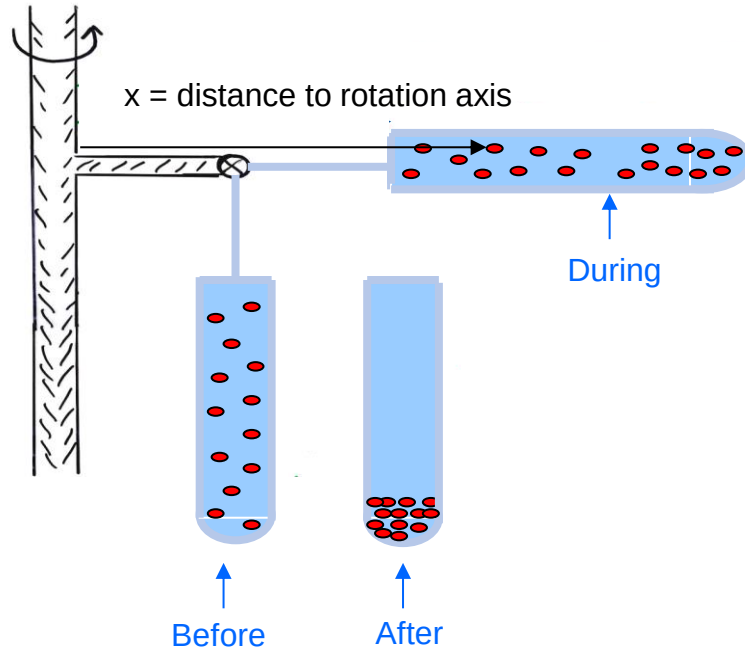


Sedimentation:

- Fractionation
- Phase separation

Centrifugal sedimentation

Centrifugal acceleration > gravitational acceleration - *ultracentrifuges*



Sedimentation coefficient:

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

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



Centrifugal sedimentation

Example:

Spherical particles with radii of $R_1 = 100 \text{ nm}$ and $R_2 = 900 \text{ nm}$ are dispersed in water

The largest particles are removed by centrifugation (5 minutes, $\text{rps} = 46,1 \text{ s}^{-1}$)

The centrifuge tube is filled to a height of 8 cm dispersion.

The surface of the liquid is situated 7 cm from the axis of rotation during centrifugation

How many percent of the smallest particles are removed?

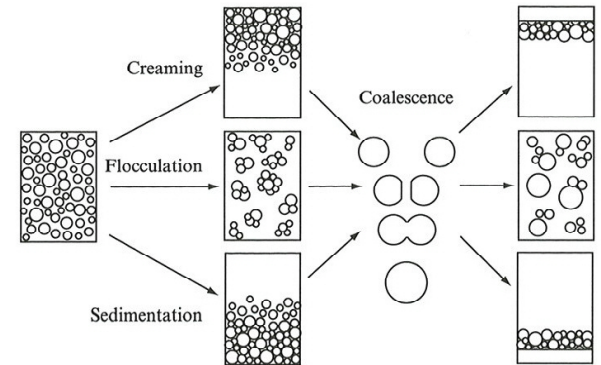
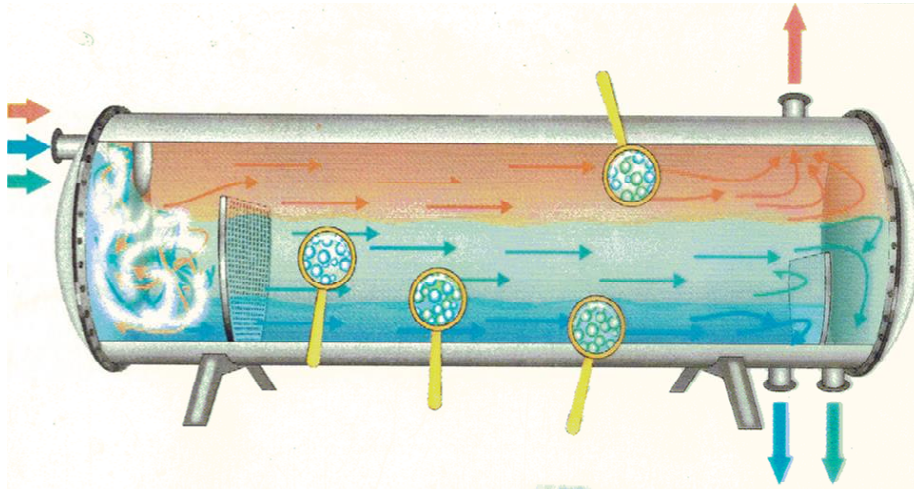
$$\rho_P = 1,15 \text{ g/cm}^3$$

$$\rho_W = 1,0 \text{ g/cm}^3$$

$$\eta_W = 8,9 \times 10^{-4} \text{ kg/m} \cdot \text{s}$$

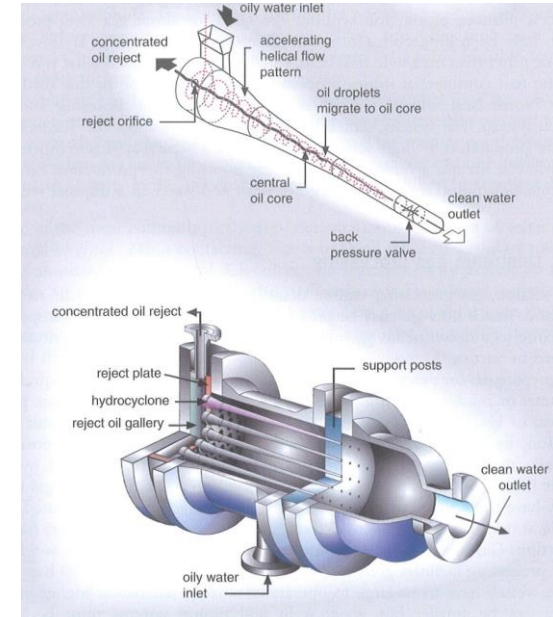
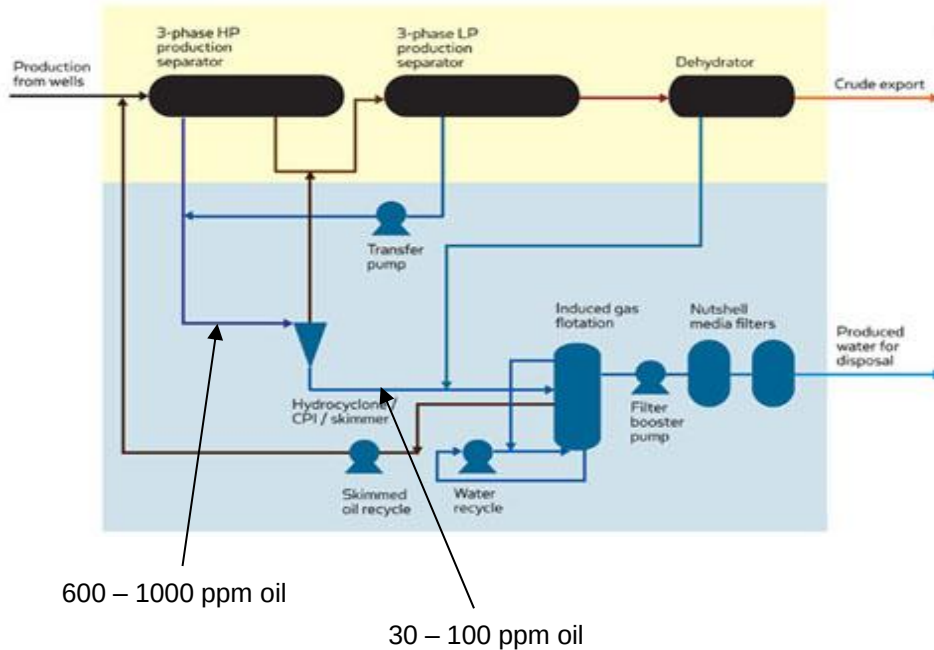
Oil and gas processing

Separators – gravitational separation:



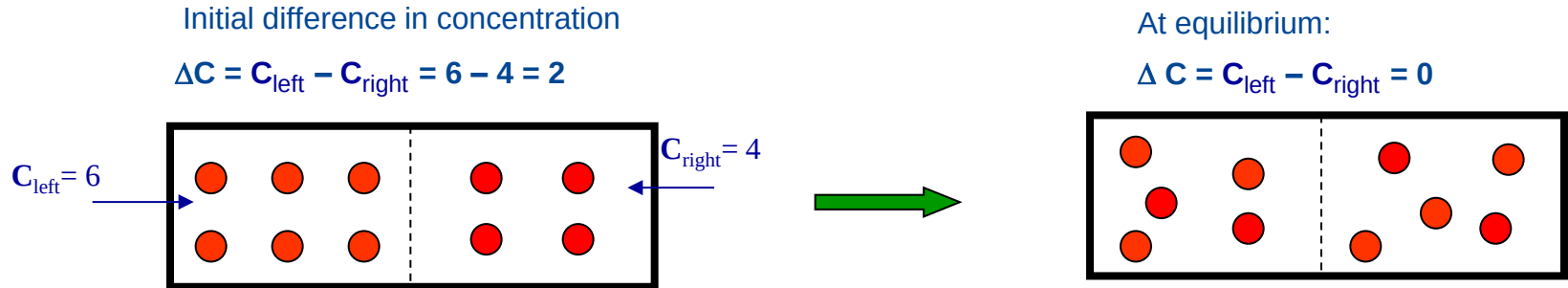
Petroleum processing

Hydrocyclones – centrifugal separation:



Diffusion

Particles with non-uniform distribution experience a force to obtain uniform distribution:



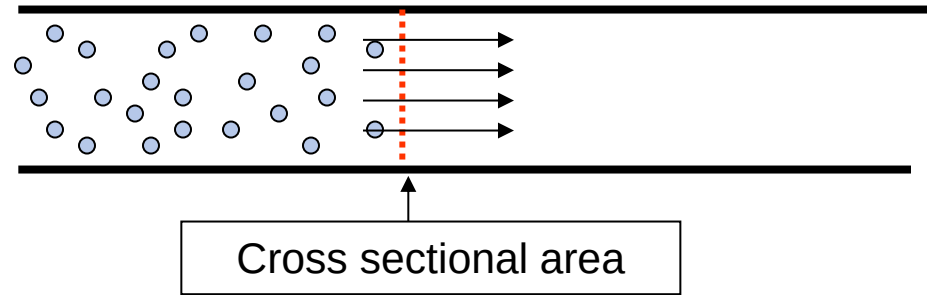
Macroscopically: uniform system

Molecular level: local fluctuations
(Brownian motion)

Transportation of matter: *Diffusion*

Fick's Laws of diffusion

Quantitative description of diffusion

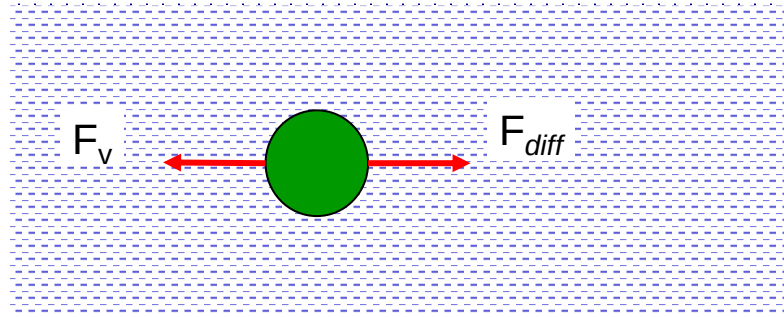


Fick's first law: $J = -D \frac{\partial c}{\partial x}$

Fick's second law: $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$

D : Diffusion coefficient (m^2/s)

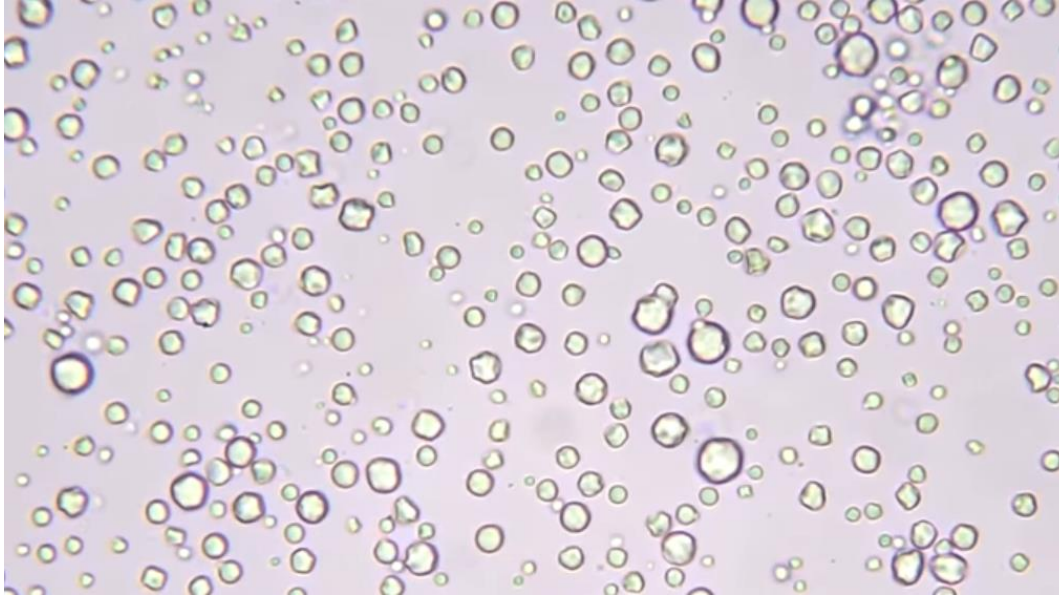
Diffusion Coefficient and Friction Factor



Einstein's diffusion law:
$$D = \frac{k_B T}{f}$$

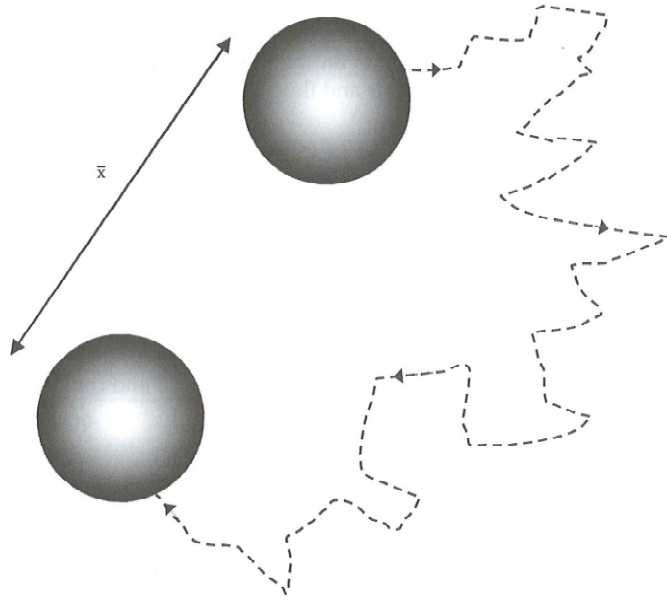
Stokes-Einstein relationship:
$$R_s = \frac{k_B T}{6\pi\eta D} \quad (\text{spherical particles})$$

Brownian motion



<https://youtu.be/NSe3TFLYcO8>

Brownian motion



$$\bar{x} = \sqrt{2Dt}$$

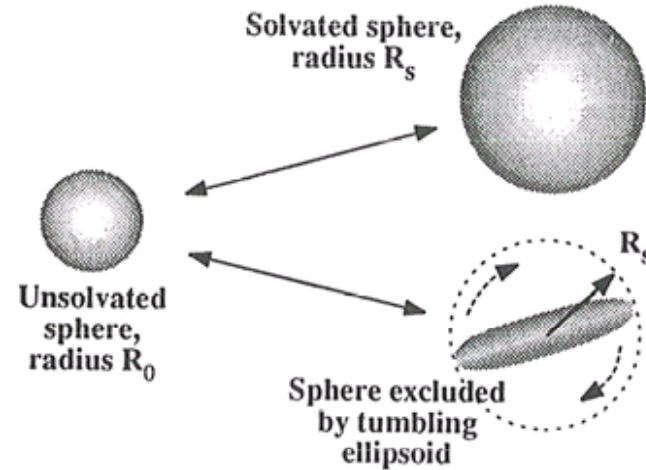
$\bar{x}$: "root mean square" displacement

Effects of solvation and asymmetry



Deviations from Stoke's model:

- Solvated (hydrated) particles
- Non-spherical particles:



$\frac{f}{f_0}$ - *measure of deviation from unsolvated sphere*

Effects of solvation and asymmetry



Example: Human hemoglobin in water

$$D = 6,9 \times 10^{-11} m^2 s^{-1}$$

$$s = 4,48 \cdot 10^{-13} s$$

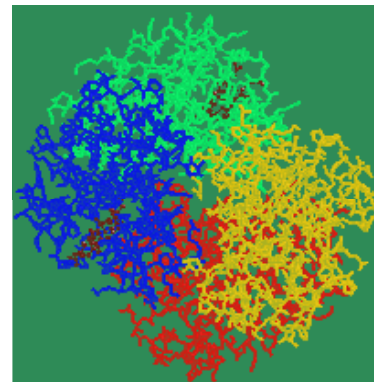
$$\rho(water) = 1 g/cm^3$$

$$\eta_{water} = 10^{-3} kg/m \cdot s$$

$$\rho(hem) = 1,34 g/cm^3$$

$$k_B = 1,38 \cdot 10^{-23} J/K$$

$$T = 20^\circ C = 293 K$$

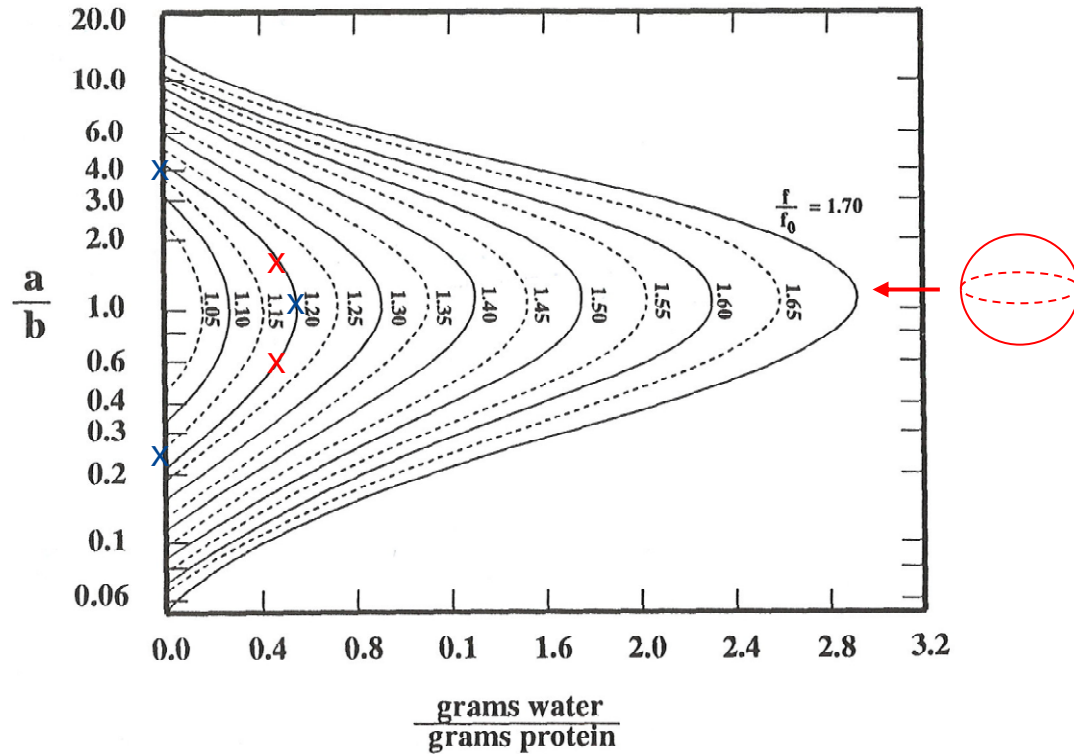


A. Determine the friction coefficient (f)

B. Evaluate f/f_0

C. Suggest possible states of solvation and asymmetry using $\frac{f}{f_0}$

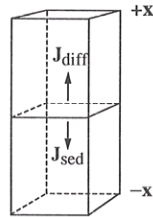
Effects of solvation and asymmetry



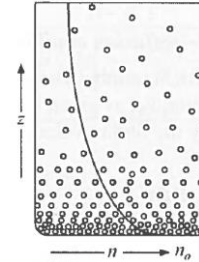
Sedimentation and Diffusion in equilibrium



Sedimentation and diffusion in equilibrium: *no macroscopic changes*

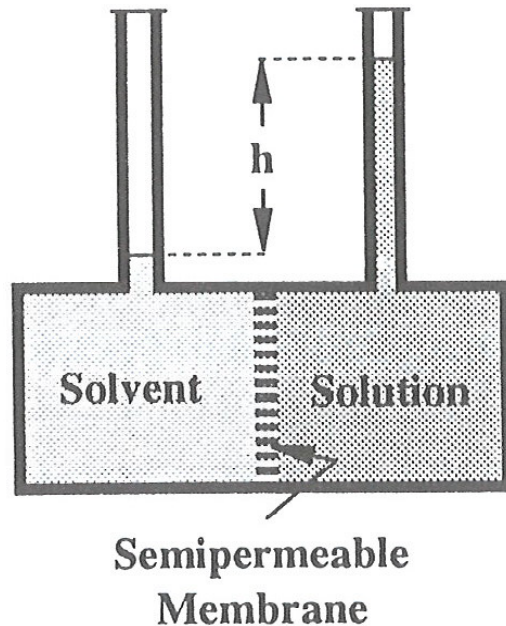


$$J_{\text{sed}} = J_{\text{diff}}$$



Radius (nm)	Sedimentation rate x 10 ⁷ m/s (u)			Diffusion rate x 10 ⁷ m/s ($\bar{v} = \bar{x}/t$)
	Polystyrene (1,1 g/cm ³)	Quartz (2,65 g/cm ³)	Gold (19,3 g/cm ³)	(t = 1 min)
10	0.014	0.24	2.6	9.0
50	0.36	6.0	66	4.0
100	1.4	24	260	2.9
500	36	600	6600	1.3

Osmotic pressure



Solvent (løsningsmiddel)

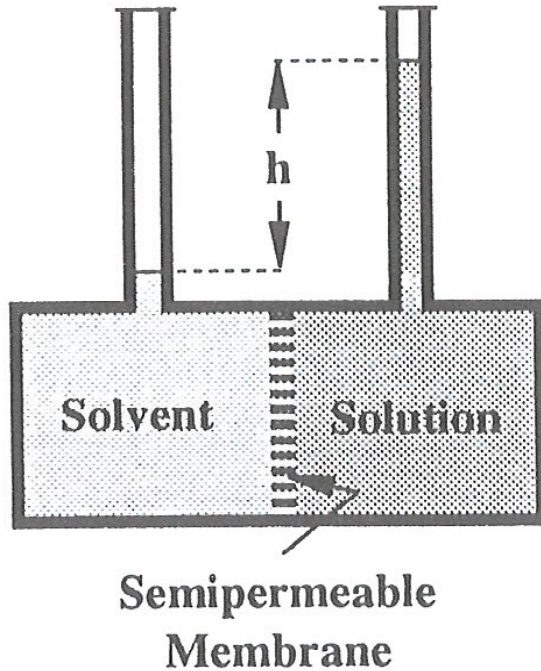
Solution (løsning): solute (løst stoff) + solvent

Semipermeable membrane: only permeable for solvent

Solvent will flow through the semipermeable membrane to try to equalise the concentration difference

Osmotic pressure: pressure needed to stop the flow

Osmotic pressure



Concentration difference created by semipermeable membrane represents difference in the chemical potential

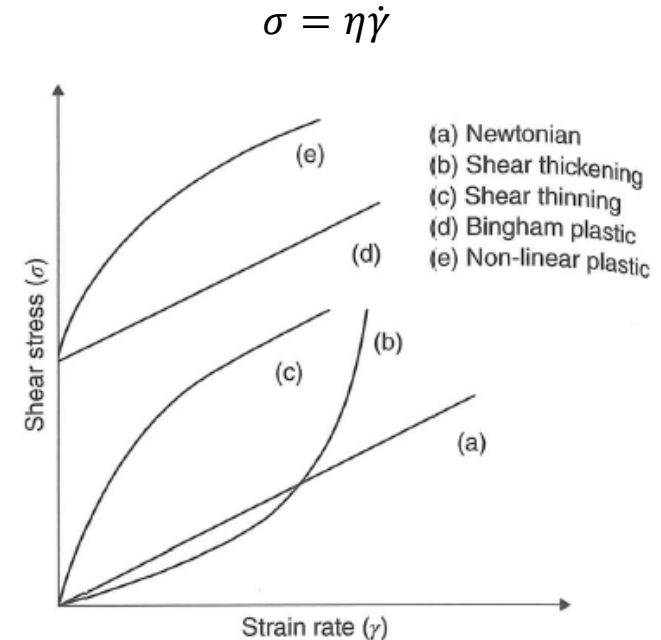
Osmotic pressure:

Counteracts difference in chemical potential between compartments

Rheology of colloidal dispersions

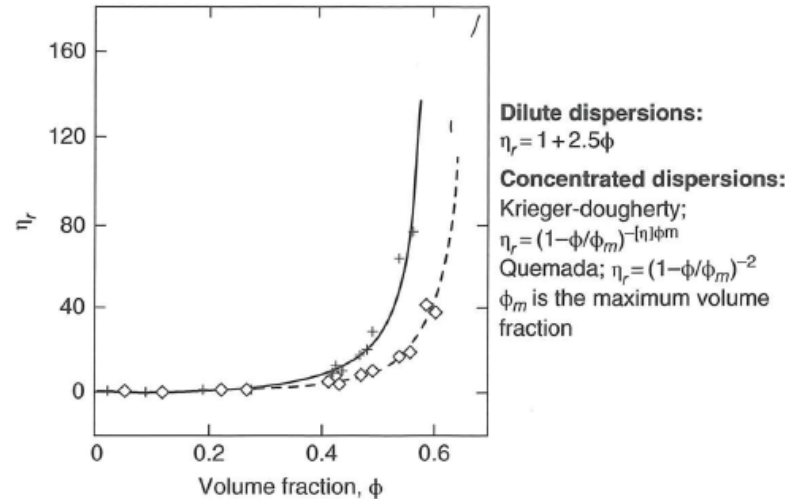
Characteristics for rheology of dispersions:

- Huge difference between dilute and concentrated dispersions
- Depends on continuous phase viscosity, 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

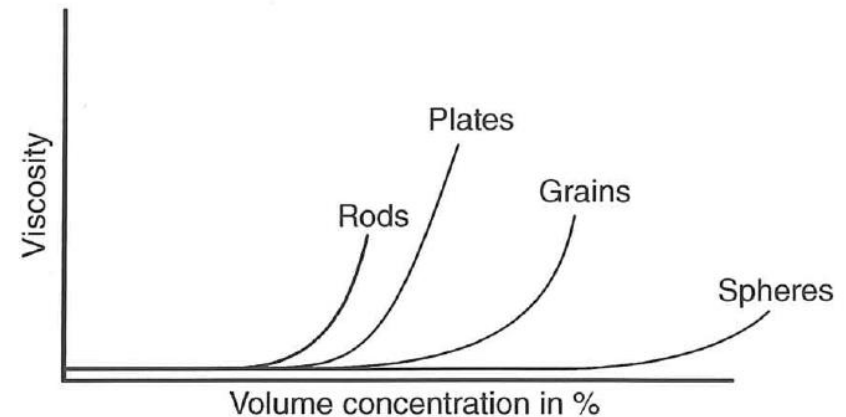


Rheology of colloidal dispersions

Particle concentration



Particle shape



Home experiment - diffusion of inks

Materials:

- 2 glasses
- Very cold and very hot water
- Ink or food coloring

Procedure:

1. Fill one glass with cold water and the other with hot water
2. Drop the same amount of ink or food coloring into each of the glasses
3. Observe and explain the differences.

Recording procedure:

1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no

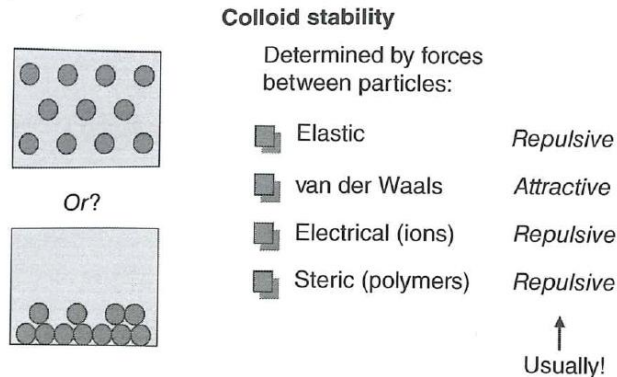


Colloidal Stability - van der Waals and Electrical forces

- Potential energy curves
- Electrical double layer, electrostatic stability
- Zeta potential

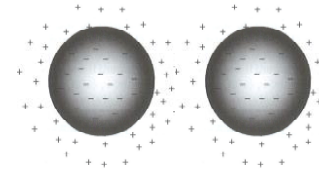
Colloidal stability

Colloidal stability – Balance between attractive and repulsive forces

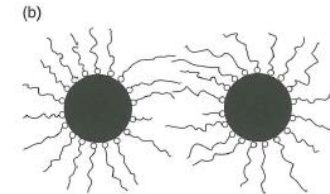


Also:
hydrophobic forces (attractive)
hydration forces (repulsive)

Electrostatic stabilisation

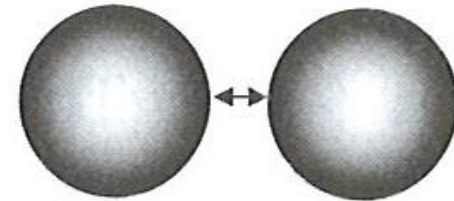
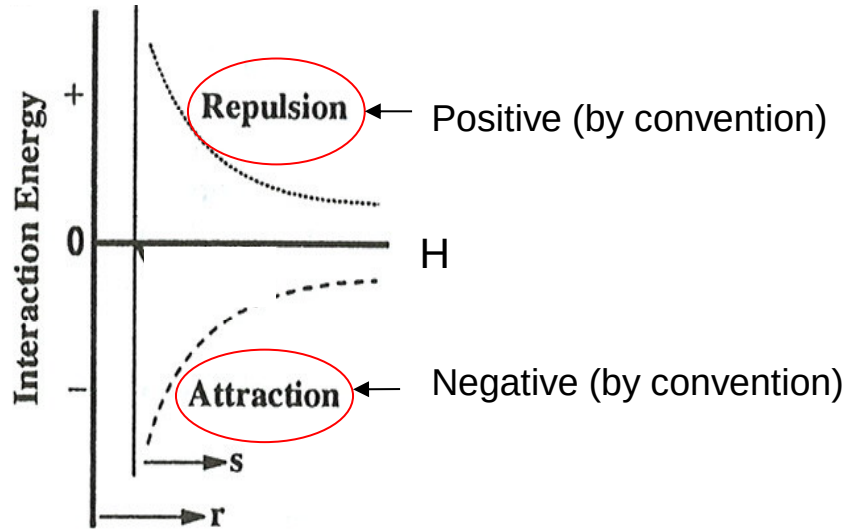


Polymer induced/steric stabilisation



Potential energy curves

Describe the interaction between two particles as a function of distance:



The curve describes a *kinetically stable system*



Potential energy curves

Net interaction energy = attractive + repulsive interaction energies

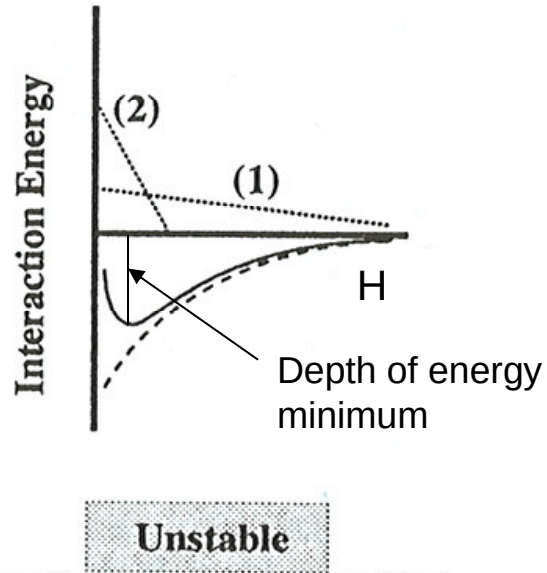
DLVO theory - repulsive part only due to electrostatic stabilization
(overlapping electrical double layers):

$$V = V_R + V_A = 2\pi R\epsilon\epsilon_0\psi_0^2 \exp(-\kappa H) - \frac{AR}{12H}$$

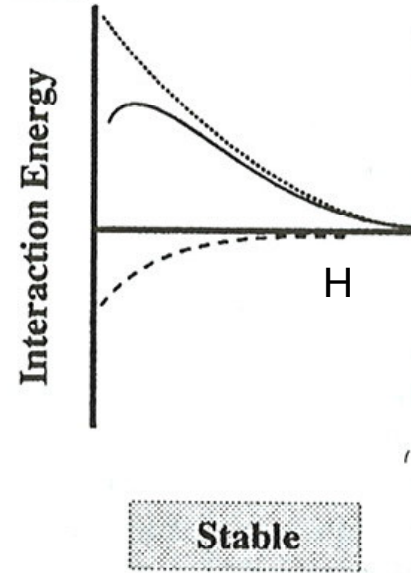
(two equal-sized spherical particles)

Potential energy curves

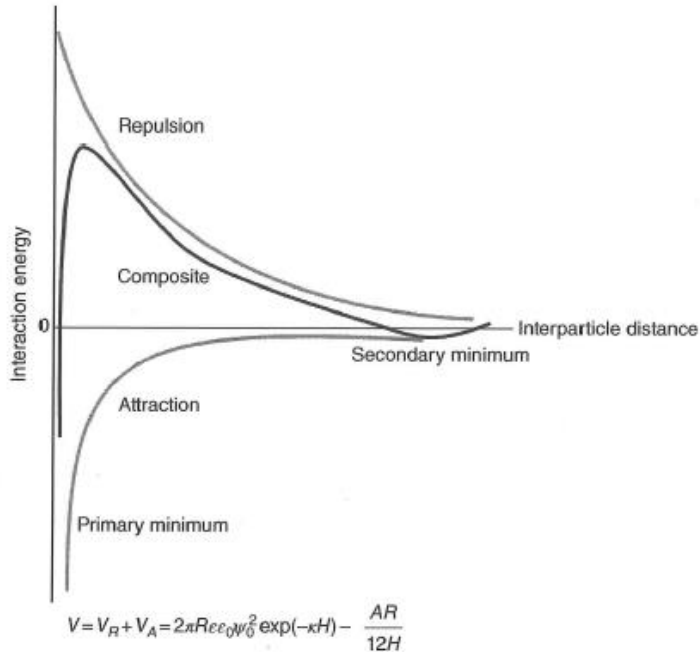
Attraction >> repulsion



Repulsion >> attraction



Potential energy curves



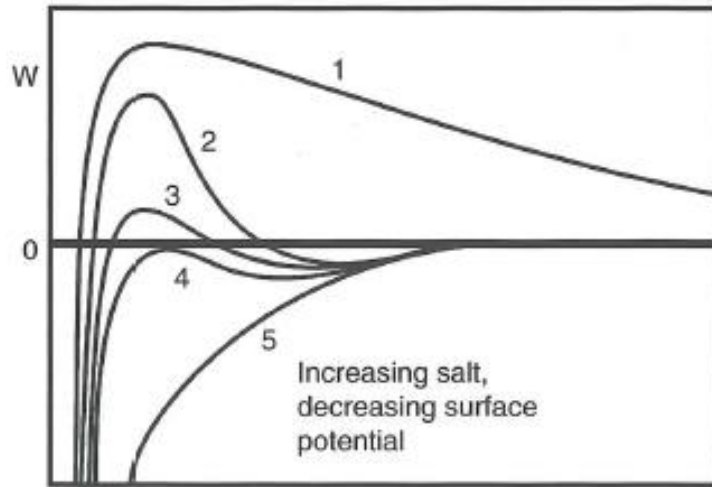
Attraction and repulsion dominate in different regions

Secondary minimum: Flocculation (reversible)

Primary minimum: Coagulation (irreversible)

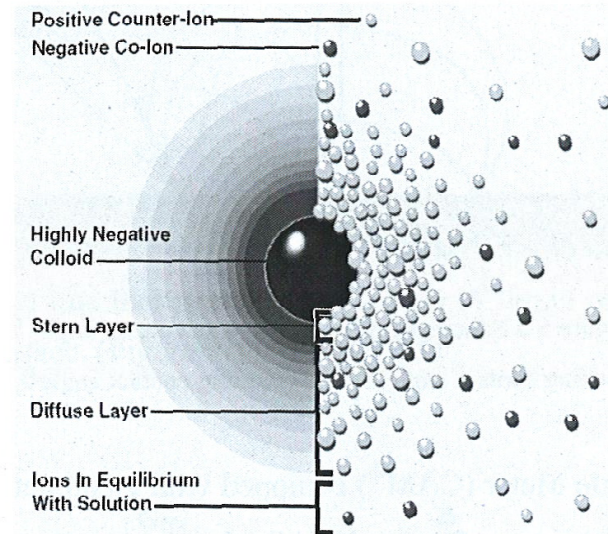
Energy barrier: Obstacle to coagulation

Potential energy curves



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

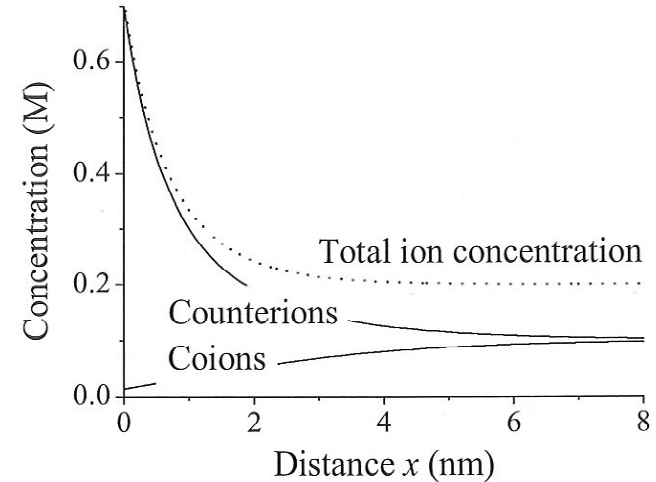
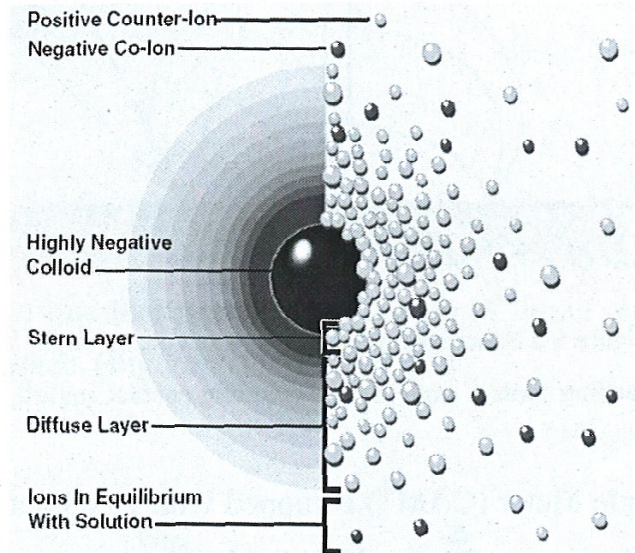
The Electrical Double Layer



- Origin of surface charges
- Structure of the electrical double layer (models)
- Overlapping electrical double layers – repulsive interactions

The Electrical Double Layer

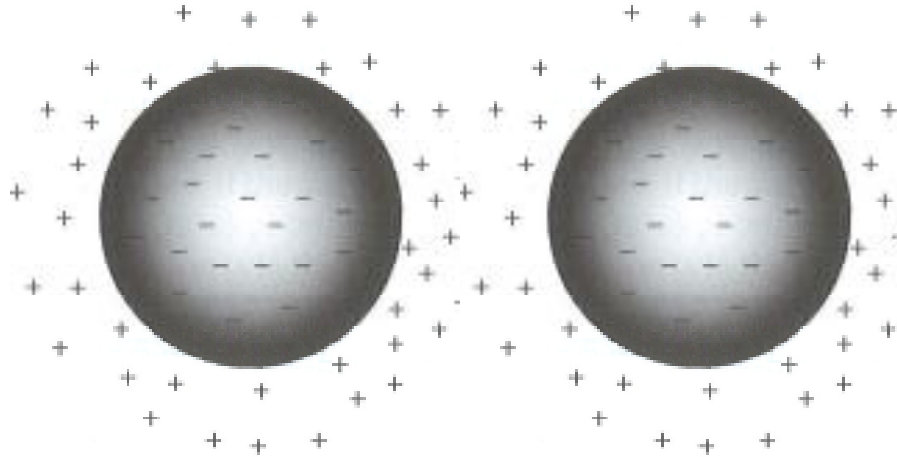
Electrical field originating from the surface charge: - Attract *counterions*
- Repel *co-ions*



Layer of surface charges and counter ions – ***electrical double layer***

The Electrical Double Layer

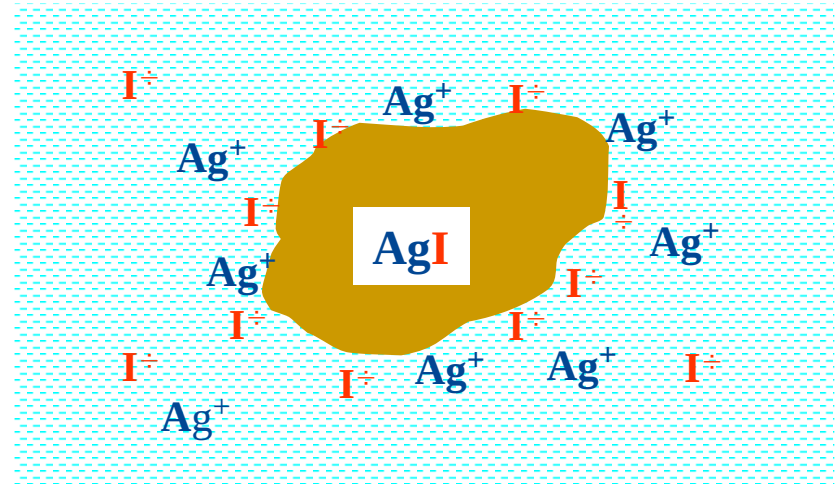
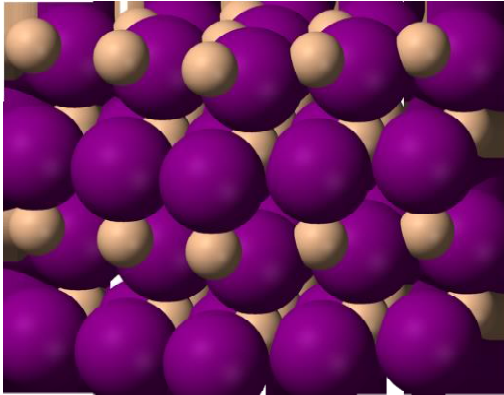
Overlapping electrical double layers give rise to repulsive interactions



Charging mechanisms

Silver iodide (and most solids consisting of ionic lattices):

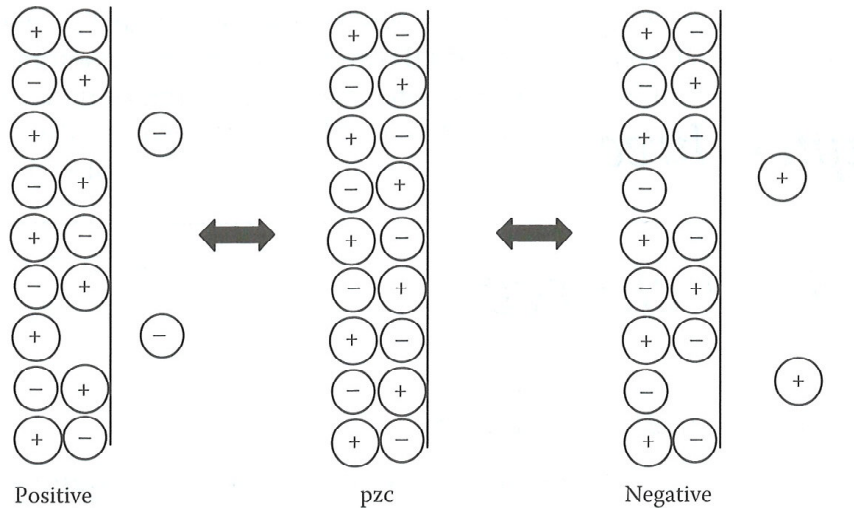
Differential loss of ions from ion lattice



Charging mechanisms



Silver iodide (and most solids consisting of ionic lattices):



Potential determining ions: change charge of surface

Indifferent ions: do not change charge of surface



Charging mechanisms

Relation between ψ_0 and concentration of potential determining ions

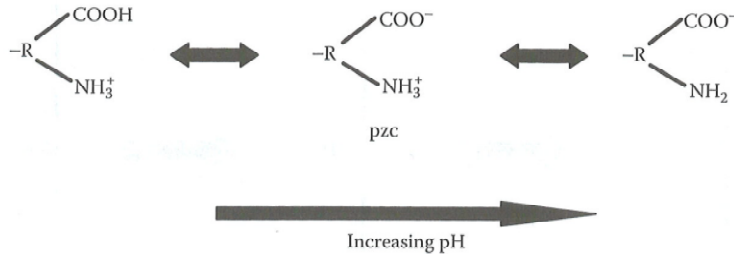
Nernst equation:
$$\psi_0 = \frac{2,303RT}{F} \log \frac{c(Ag^+)}{c^{pzc}(Ag^+)}$$

Charging mechanisms

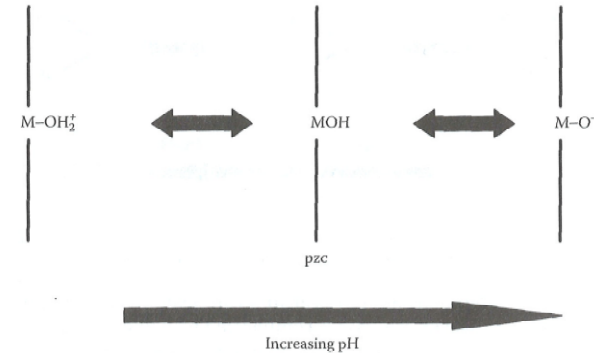
Oxides, proteins, water soluble polymers:

Amphoteric surfaces – take up or release proton depending on pH

Proteins:



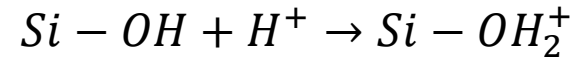
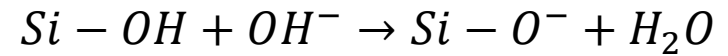
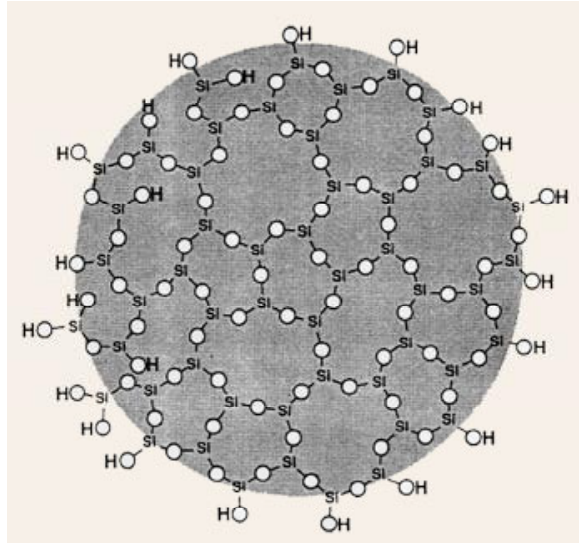
Oxides:



Potential determining ions: H^+ and OH^-

Charging mechanisms

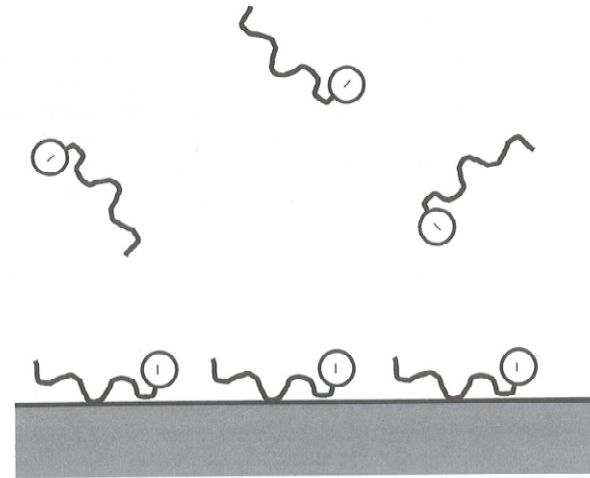
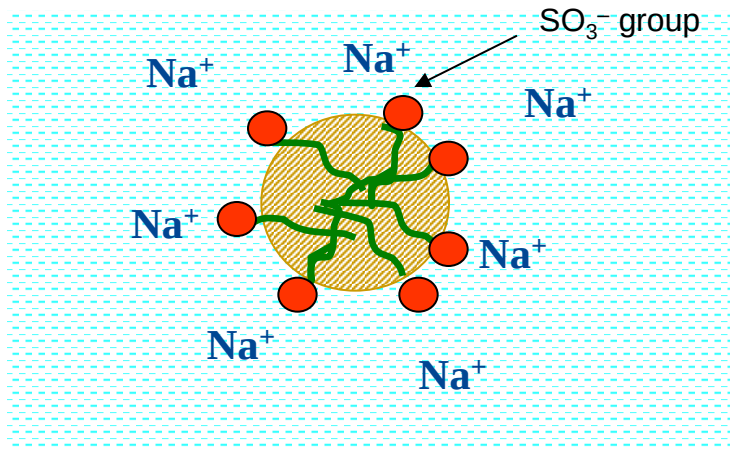
Silica:



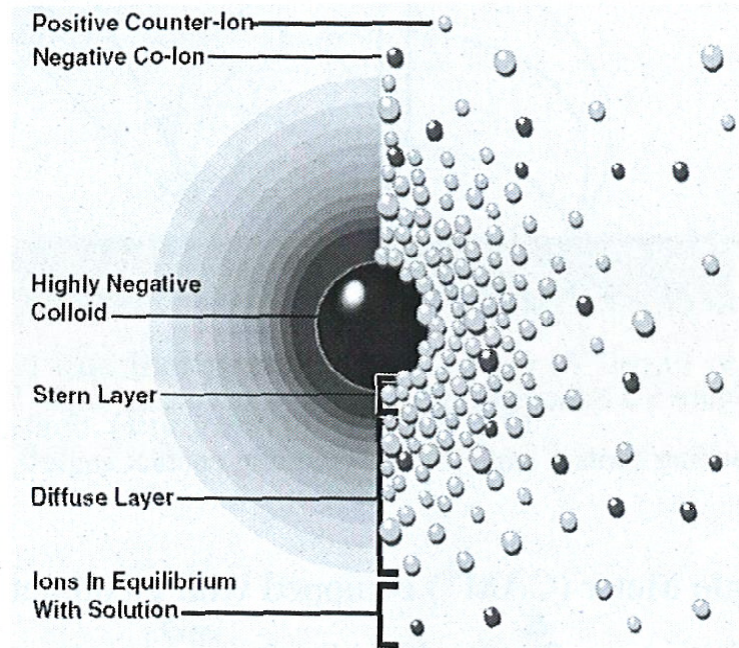
Charging mechanisms

Hydrophobic particles and emulsion droplets:

Adsorption of ionic surfactants



Electrical Double Layer (EDL)

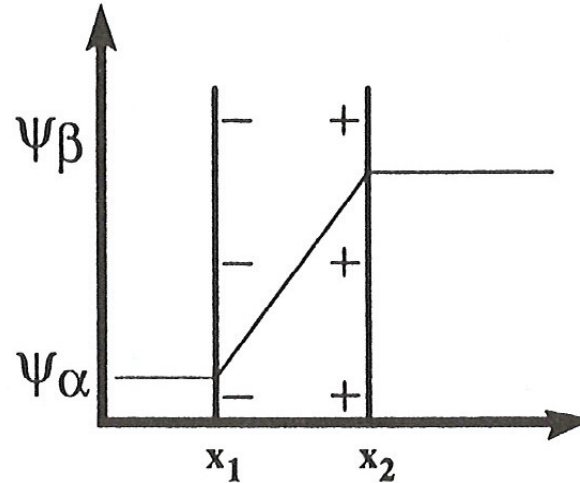
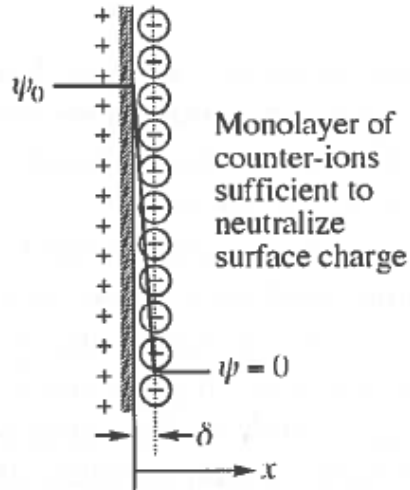


Variation in ion density near a charged interface

Goal: Describe how the electrical potential (i.e. ion distribution) vary near a charged surface

EDL - Capacitor model

Simplest model – only electrostatic interactions

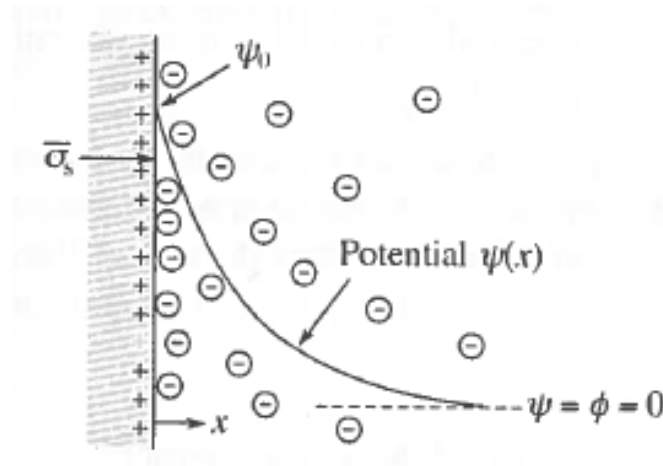


$$\Delta\psi = \frac{\sigma_0}{\epsilon_r \epsilon_0} \delta$$

Poor model for the entire electrical double layer - temperature effects on ions are not considered

EDL – Gouy-Chapman model

- Account for thermal motion of ions
- Charge density vary with distance from interface



Goal: describe how electrical potential varies with distance from interface



EDL – Gouy-Chapman model

Description of variation of potential with distance from a charged surface - *Poisson equation*:

$$\left(\frac{\partial^2 \psi}{\partial x^2}\right) + \left(\frac{\partial^2 \psi}{\partial y^2}\right) + \left(\frac{\partial^2 \psi}{\partial z^2}\right) = \nabla^2 \psi = -\frac{\rho^*}{\varepsilon}$$

$\varepsilon = \varepsilon_r \varepsilon_0$ (account for effect of medium)

ρ^* : charge density (function of x, y, z)

Planar surface: $\left(\frac{d^2 \psi}{dx^2}\right) = -\frac{\rho^*}{\varepsilon}$ (describe electrostatic effects)

Potential distribution can be calculated if exact charge distribution is known

EDL – Gouy-Chapman model

Description of spatial distribution of charge – *Boltzmann equation*

$$\rho^* = \sum_i z_i e n_{i\infty} \exp\left(\frac{-z_i e \psi}{k_B T}\right)$$

$n_{i\infty}$: concentration of i ions far from surface (bulk concentration)

z_i : valence number of ions

NB: ion concentrations given as number of ions/m³

*Gives the probability of finding an ion a certain distance from the interface
– charge density as a function of potential*



EDL – Gouy-Chapman model

Poisson-Boltzmann equation for potential distribution near a planar surface:

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

For planar surface:

- *General solution*
- *Solution when assuming low potentials (Debye-Hückel approximation)*

EDL – Gouy-Chapman model

Debye-Hückel approximation: Assuming low potentials, i.e. $z_i e \psi < k_B T$

$$\left(\frac{d^2\psi}{dx^2}\right) = \kappa^2\psi$$

$$\kappa^2 = \left[\left(\frac{e^2}{\epsilon k_B T}\right) \sum_i z_i^2 n_{i\infty}\right]$$

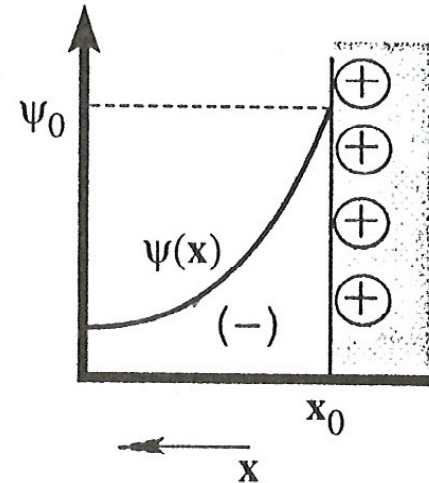
Conditions for solving equation: $\psi \rightarrow \psi_0$ as $x \rightarrow 0$

$\psi \rightarrow 0$ as $x \rightarrow \infty$

EDL – Gouy-Chapman model

Solution of P-B equation for planar surface (Debye-Hückel approximation):

$$\psi = \psi_0 \exp(-\kappa x)$$



EDL – Gouy-Chapman model

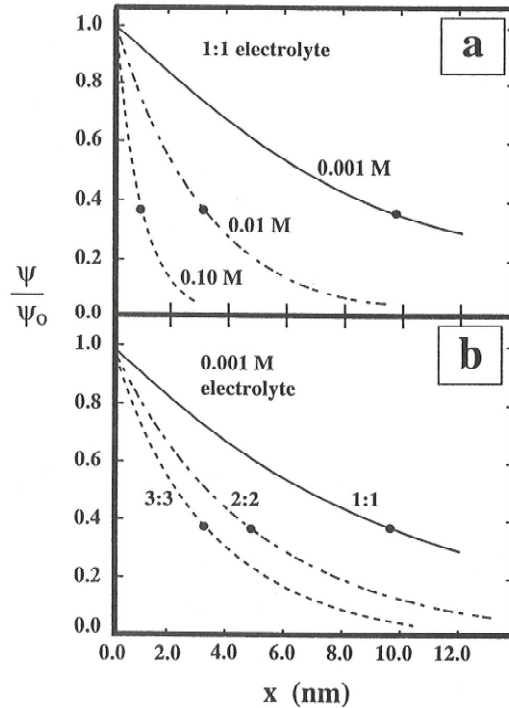
Debye-Hückel parameter: $\kappa = \sqrt{\frac{e^2}{\epsilon k_B T} \sum_i z_i^2 n_{i\infty}} = \sqrt{\frac{1000 e^2 N_A}{\epsilon \epsilon_0 k_B T} \sum_i z_i^2 C_i}$

(ions/m³) (mol/l)

Debye length: $\frac{1}{\kappa}$ (length units, extension of double layer)

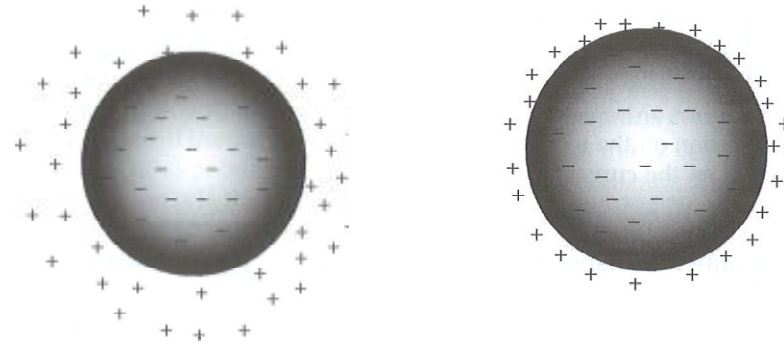
Varies with T and electrolyte concentration and valency in solution

EDL – Gouy-Chapman model



Diffuse layer extension:

- Decrease with increased electrolyte concentration
- Decrease with increased valency of ions



EDL – Gouy-Chapman model

Solution of P-B equation for planar surface *without* assuming low potential:

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

(Variation in potential with distance from surface)



EDL – Gouy-Chapman model

Potential near a charged surface will depend on the number of charged groups at the surface

Grahame equation: relates surface charge (σ_0) and surface potential (ψ_0)

Planar surface (Debye-Hückel approximation): $\sigma_0 = \varepsilon \varepsilon_0 \psi_0 \kappa$



EDL – Gouy-Chapman model

Solution of P-B equation for spherical surface (D-H approximation):

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

R_s – particle radius

r – distance of any point in the double layer from *center* of sphere

Grahame equation (D-H approximation):

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



Stern adsorption

Electrolytes:

- Potential determining ions: influence surface potential
- Indifferent ions: Do not influence surface potential (but influence extension of double layer)

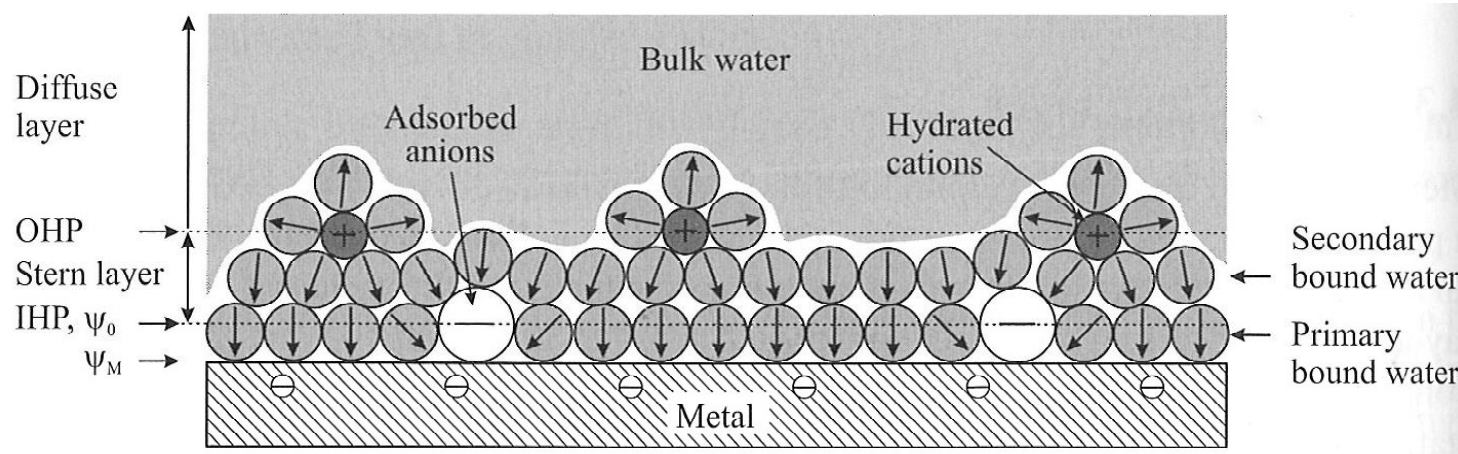
Gouy-Chapman model: mobile ions

Experimentally: Some indifferent ions can be directly adsorbed at surface – immobile

Stern model - divides the electrical double layer into two parts:

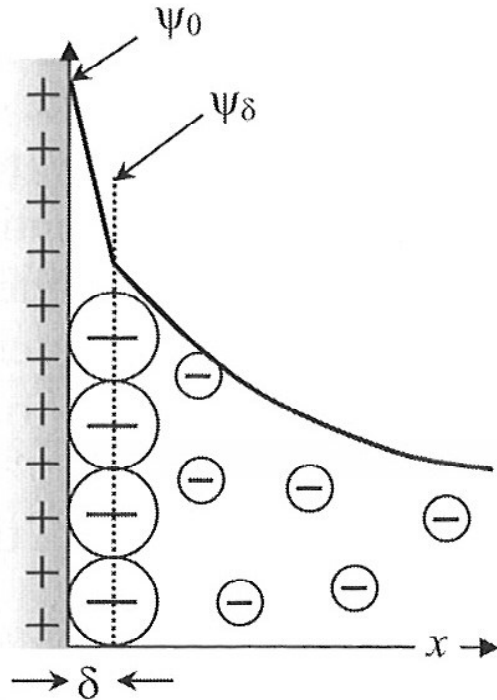
- Inner part (immobile ions – specific adsorption) – Stern layer
- Outer/diffuse part (mobile ions) – Gouy-Chapman layer

Stern adsorption



"Indifferent" ions adsorb directly at surface
 – specific adsorption (**Stern adsorption**)

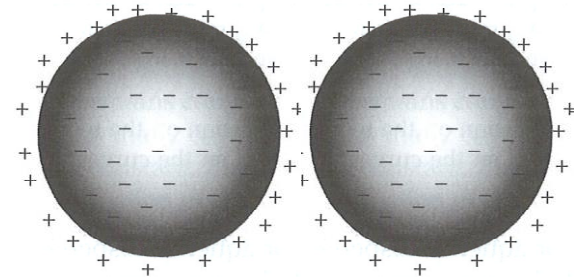
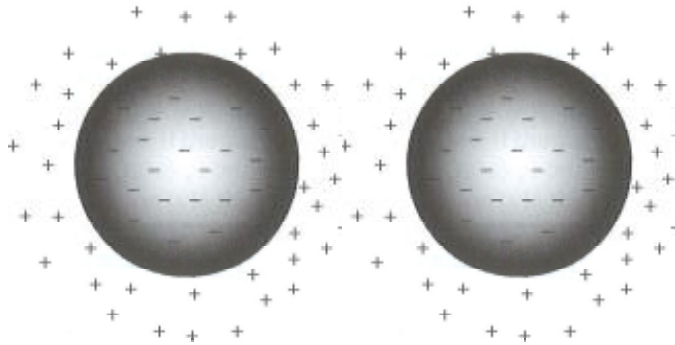
Inner layer



Due to size and hydration there is limit in how close ions can approach the solid surface – ***indifferent ions***

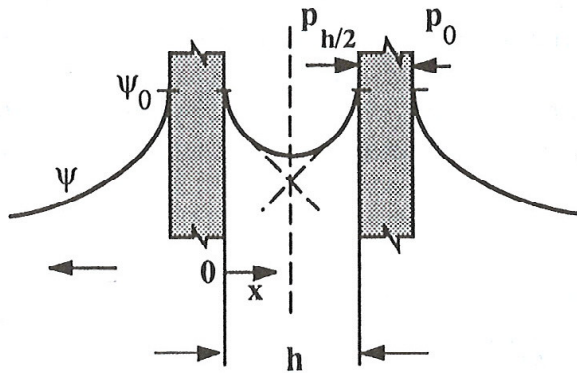
Overlapping double layers

Origin of repulsive forces between surfaces



Overlapping double layers

Repulsion between planar double layers:

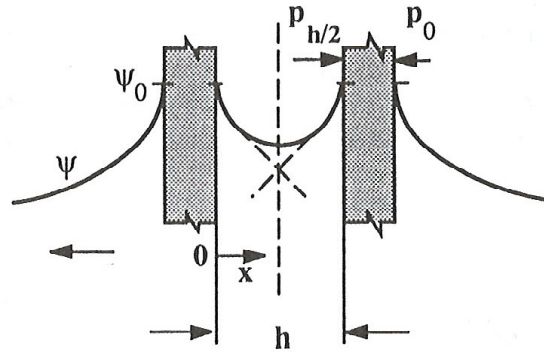


Two plates with planar faces are separated a distance h

The plates are immersed in infinite reservoir of electrolyte, bulk concentration n_∞

Surface potential: ψ_0

Overlapping double layers



At equilibrium: all forces (osmotic and electrostatic) on any volume element x must balance

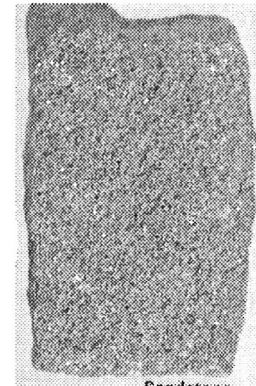
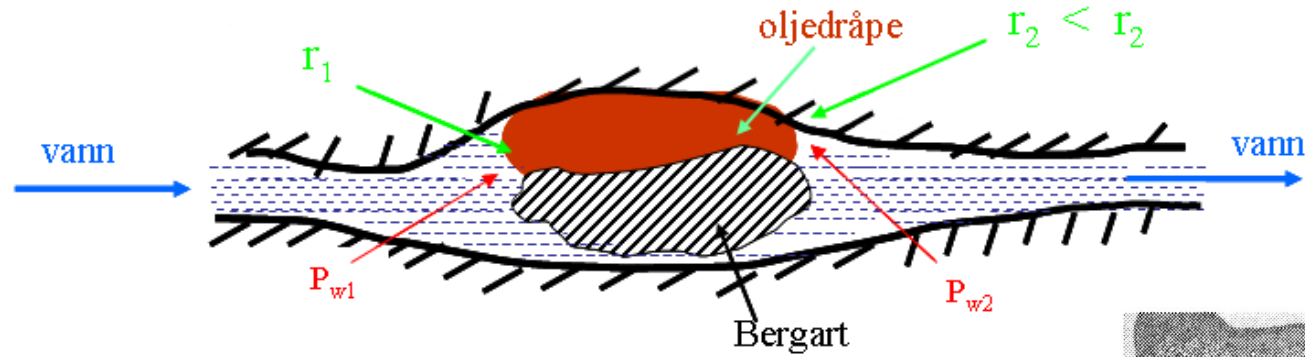
Repulsive force: $F_R \approx 64k_B T n_\infty T_0^2 \exp(-h\kappa)$

Repulsive interaction energy: $V_R = 64k_B T n_\infty \kappa^{-1} T_0^2 \exp(-h\kappa)$

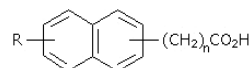
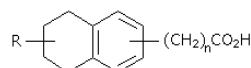
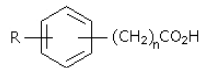
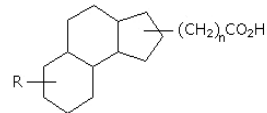
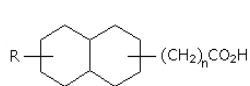
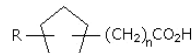
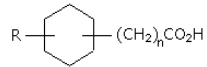
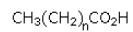
Overlapping double layers

Geometry	Expression for the potential energy $V_R (H)$
Two equal-sized spherical particles at close distances ($H \ll R$) and low potential. $\kappa R < 5$. Debye-Hückel approximation must hold: $\frac{ z\psi_0 e}{2k_B T} \ll 1$	$V_R = 2\pi\epsilon\epsilon_0 R \psi_0^2 e^{-\kappa H}$
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 . Case 2. Constant surface charge (e.g. isomorphous substitution in a lattice). Should be used with caution, especially at close approach (Goodwin, 2009).	$V_R = 2\pi\epsilon\epsilon_0 R \psi_0^2 \ln(1 + e^{-\kappa H})$ $V_R = -2\pi\epsilon\epsilon_0 R \psi_0^2 \ln(1 - e^{-\kappa H})$
Unequal-sized spheres with different (or same) surface potential in a single electrolyte and $H \ll R_1, R_2$ (Reerink-Overbeek expression).	$V_R = \left(\frac{64\pi\epsilon\epsilon_0 R_1 R_2 k_B^2 T^2 \gamma_1 \gamma_2}{(R_1 + R_2) e^2 z^2} \right) e^{-\kappa H}$
Reduces to the first equation in this table for equal-sized spheres and when the Debye-Hückel approximation holds.	$\gamma_i = \frac{e^{\frac{z\psi_{0i}}{2k_B T}} - 1}{e^{\frac{z\psi_{0i}}{2k_B T}} + 1}, \quad i = 1, 2$
Two similar flat surfaces (low potential, i.e. Debye-Hückel approximation). For high potentials see Goodwin (2009).	$V_R = 2\epsilon\epsilon_0 \kappa \psi_0^2 e^{-\kappa H}$
Sphere-plate with same surface potential ($H \ll R$): 1. weak double-layer overlap ($\kappa R < 5$); 2. close approach and large κR .	$V_R = 4\pi\epsilon\epsilon_0 R \psi_0^2 e^{-\kappa H}$ $V_R = 4\pi\epsilon\epsilon_0 R \psi_0^2 \ln(1 + e^{-\kappa H})$

EDL in enhanced oil recovery



Sandstone



Electrophoresis

Some definitions:

Electrokinetics: Combined effects of motion and charge
(colloidal particles: motion affected by electrical double layer phenomena)

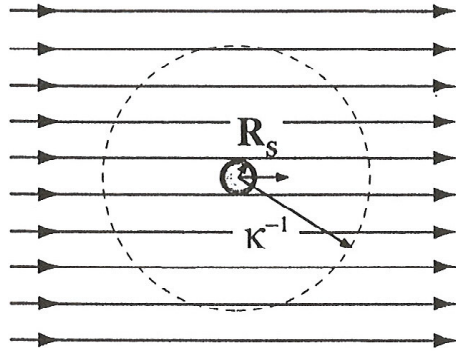
Outcome of electrokinetic measurements: **Zeta potential**

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**)

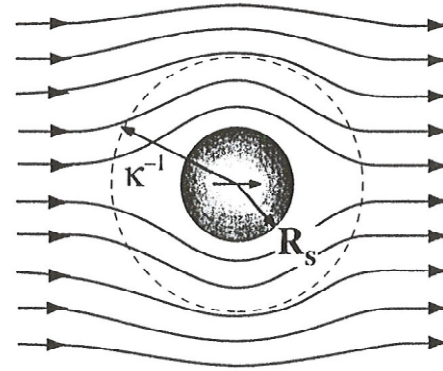
Electrophoretic mobility of colloids

Two extreme cases of spherical particles:



Particle size is *small* compared to
"thickness" of double layer

$$\kappa R_s < 0,1$$



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

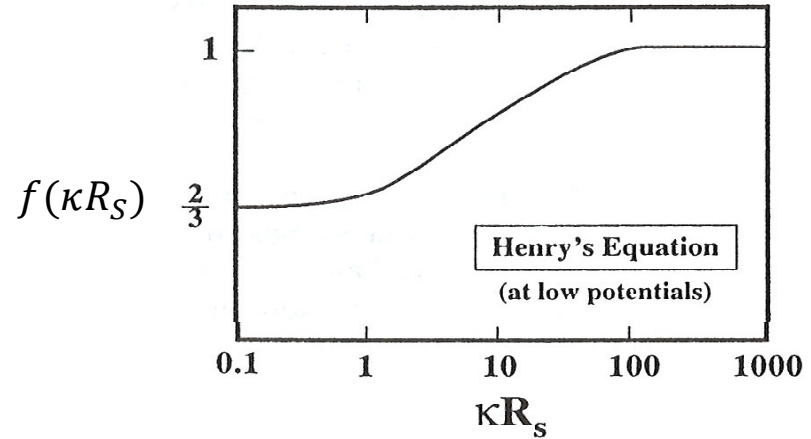
$$\kappa R_s > 100$$

Electrophoretic mobility of colloids

General relationship between electrophoretic mobility and zeta potential:

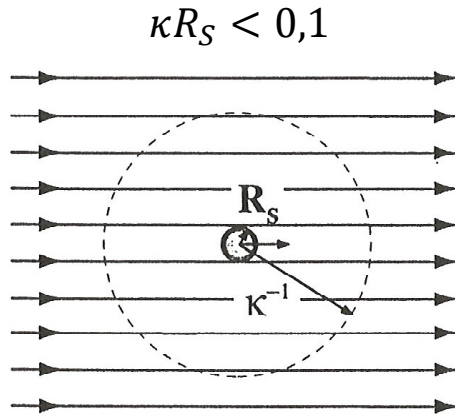
$$\mu = \frac{\varepsilon \zeta}{\eta} f(\kappa R_s)$$

(Henry's equation)

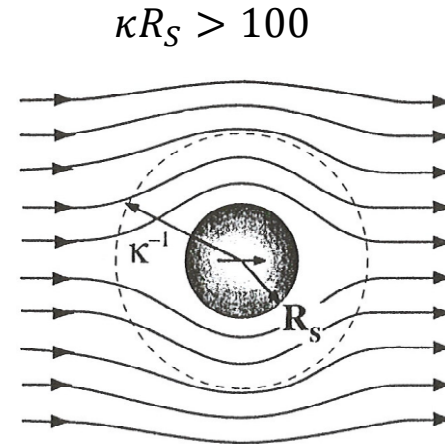


Electrophoretic mobility of colloids

Two extreme cases of spherical particles:



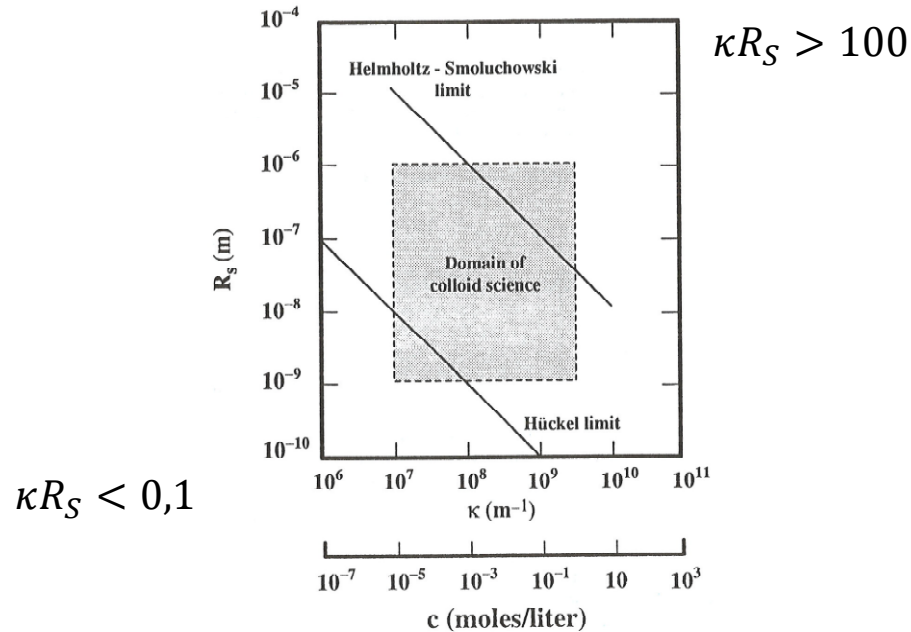
$$\mu = \frac{2}{3} \frac{\epsilon \zeta}{\eta} \quad (\text{Hückel equation})$$



$$\mu = \frac{\epsilon \zeta}{\eta} \quad (\text{Smoluchowski equation})$$

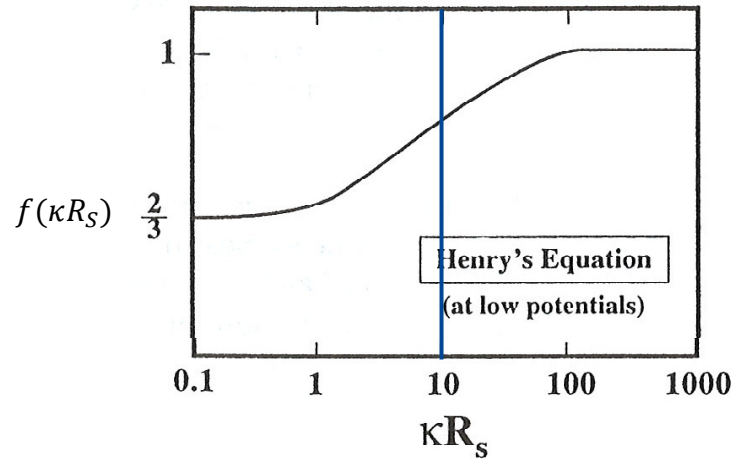
Electrophoretic mobility of colloids

Many colloidal systems fall outside the limiting cases:



Electrophoretic mobility of colloids

Practical approximations:



$$\kappa R_s < 10: \mu = \frac{2}{3} \frac{\varepsilon \zeta}{\eta}$$

(Hückel approximation)

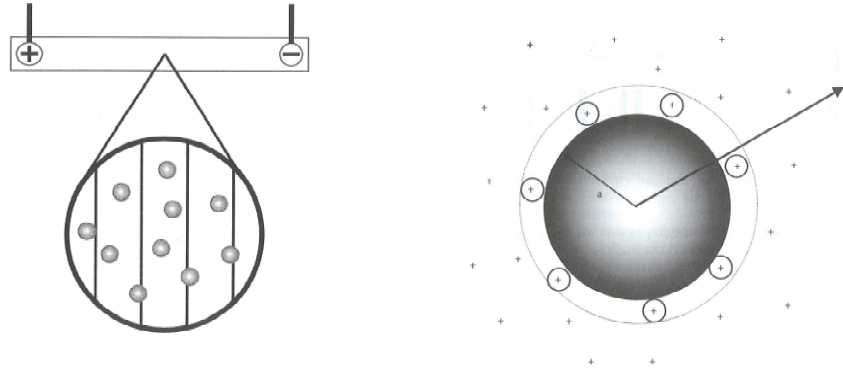
$$\kappa R_s > 10: \mu = \frac{\varepsilon \zeta}{\eta}$$

(Smoluchowski approximation)

Electrophoretic mobility – zeta potential



Electrophoresis – motion of charged colloids in an electrical field:



Surface of shear

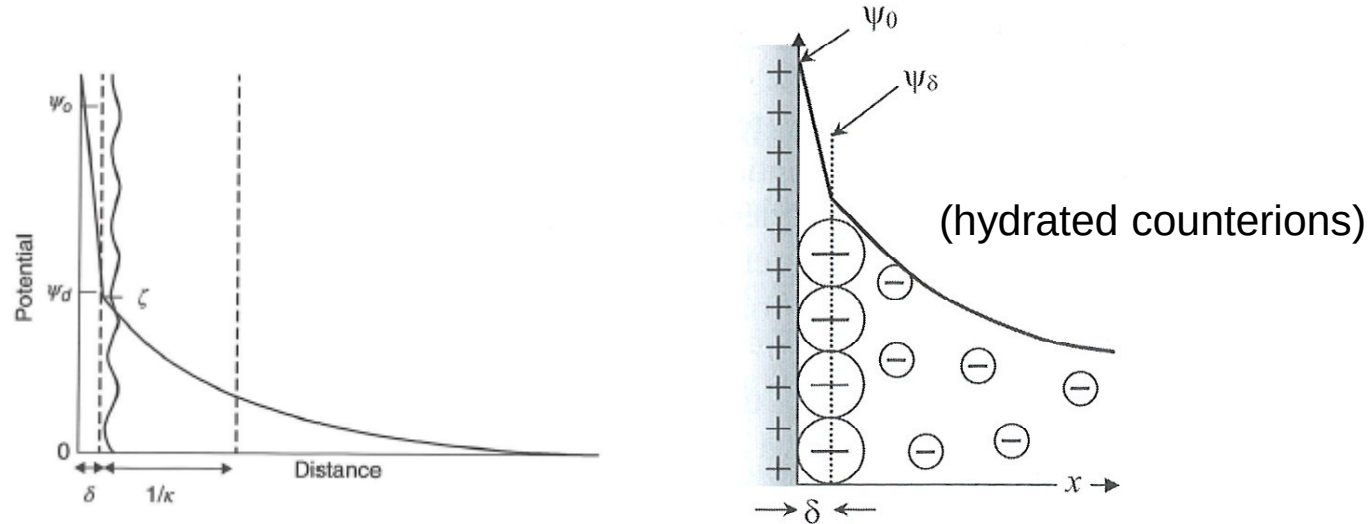
- Inside boundary: no motion of solution relative to surface
- Outside boundary: solution moves with velocity relative to surface

Potential at surface of shear – ***Zeta potential***

Electrophoretic mobility – zeta potential



Where in the double layer is the zeta potential?



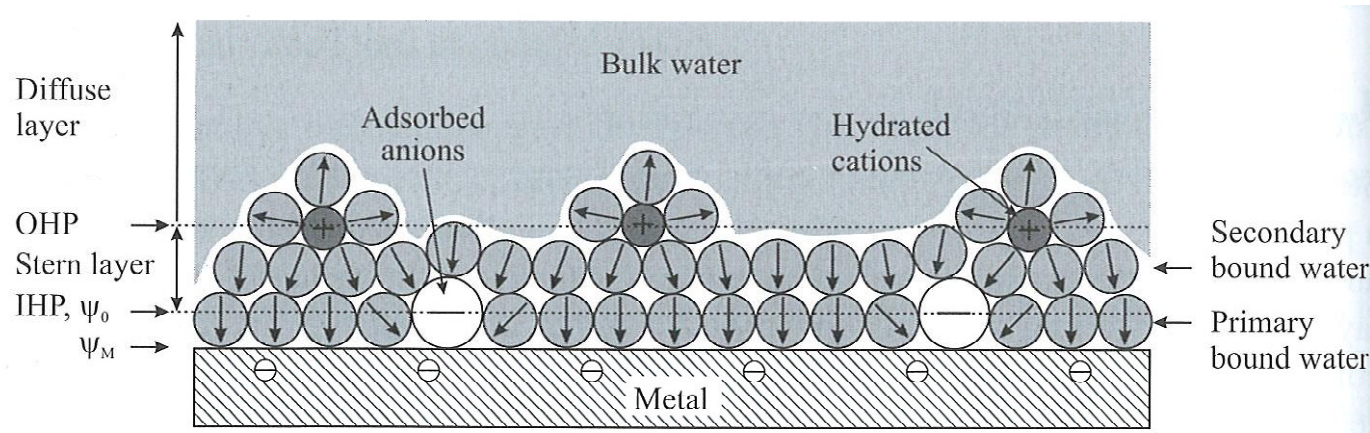
Potential near a charged surface – commonly $\psi_\delta \approx \zeta$

Electrophoretic mobility – zeta potential



Where in the double layer is the zeta potential?

(hydrated counterions and specific adsorption)



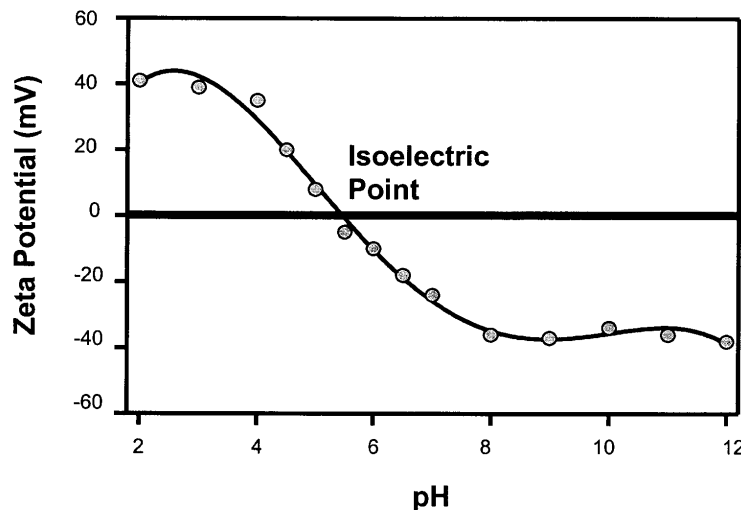
Potential near a charged surface – commonly $\psi_\delta \approx \zeta$

Electrophoretic mobility – zeta potential



Factor affecting Zeta Potential:

- potential determining ions
- Ionic strength (indifferent ions)
- specific adsorption



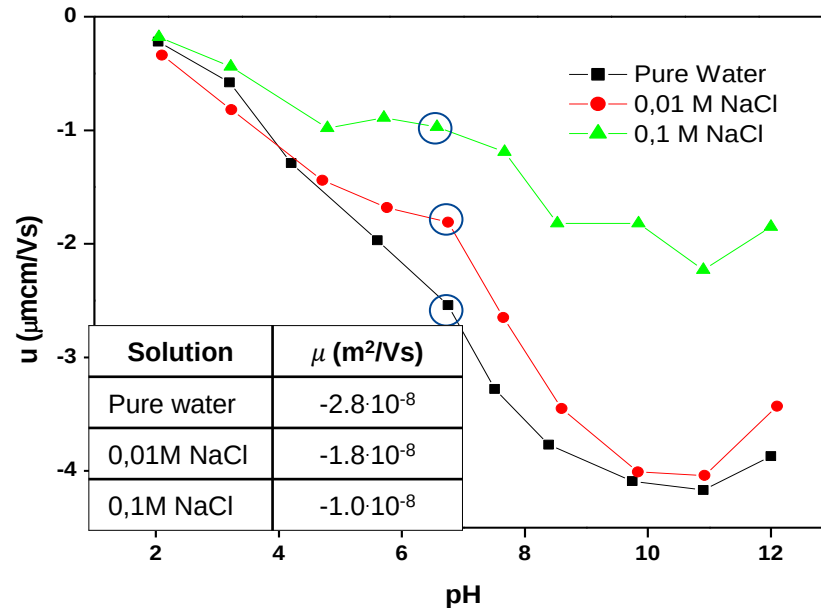
Isoelectric point (IEP): $\zeta = 0$ (hydrodynamic interface)

Point of zero charge (PZC): $\psi_0 = 0$ (solid-liquid interface)

EDL of silica

Example:

Electrophoretic measurements of silica dispersed in 3 aqueous solutions (pure water, 0,01M NaCl, 0,1M NaCl) have been carried out



$$R_s = 89nm$$

$$T = 25^\circ C$$

$$\eta = 8,9 \times 10^{-4} Ns/m^2$$

$$\varepsilon = 6,95 \times 10^{-10} F/m$$

Evaluate the extension of the electrical double layer in the 3 dispersions at pH 6.5

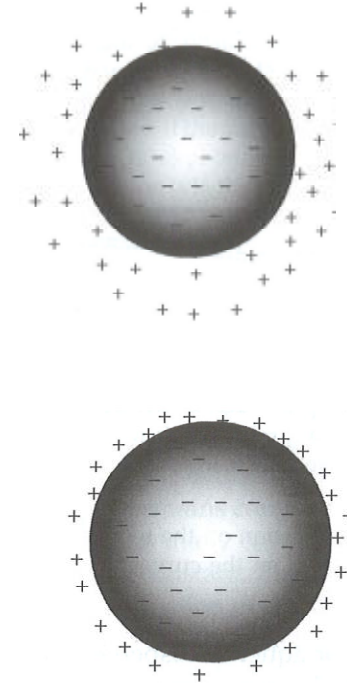
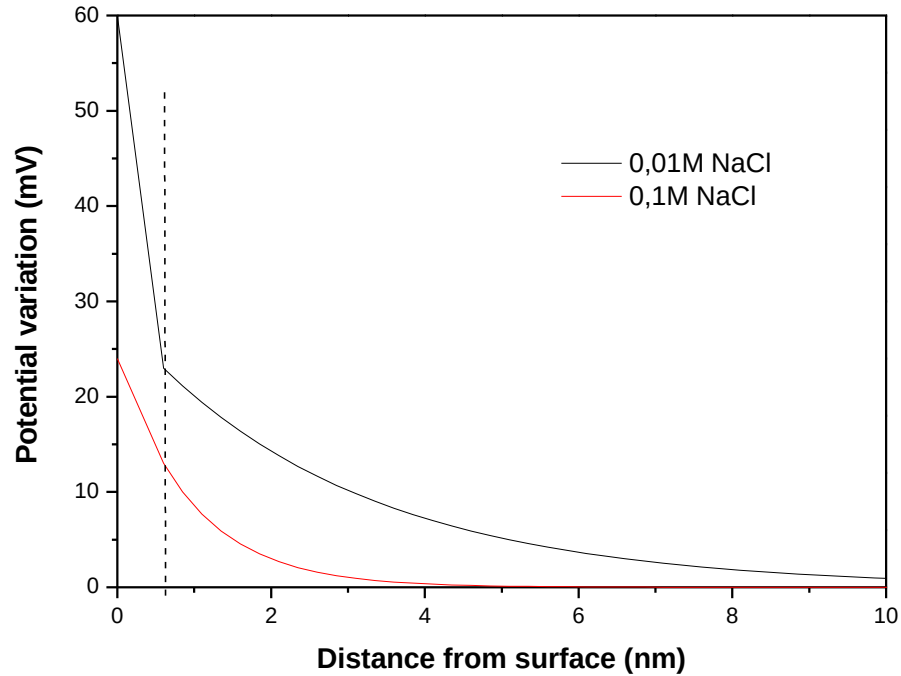
EDL of silica



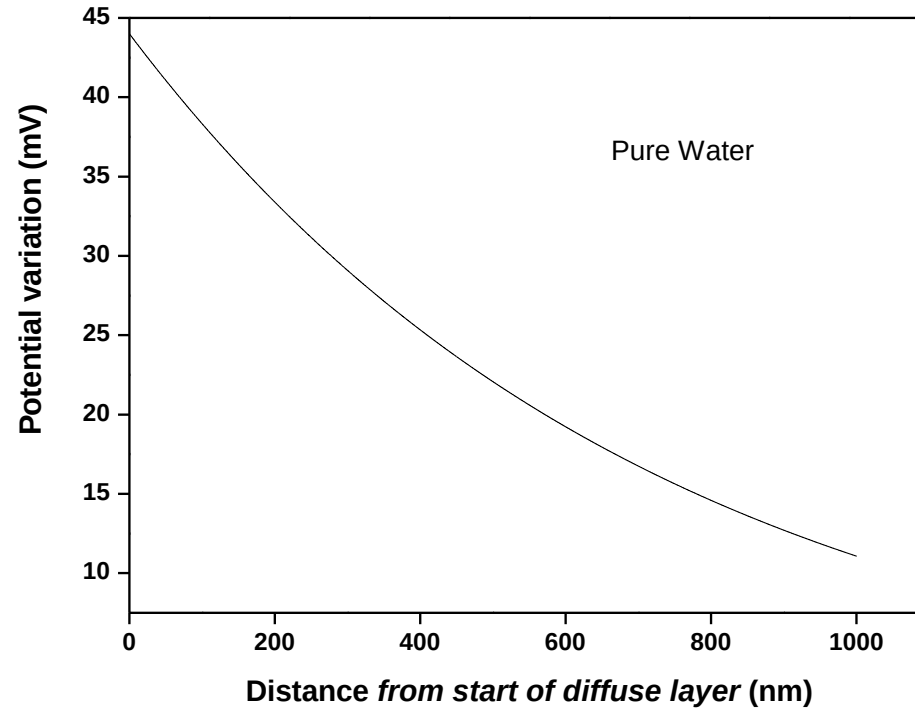
Comparing surface and zeta potentials (pH 6.5)

Solution	Surface potential (mV)	Zeta potential (mV)
Pure water	NA	-48
0,01M NaCl	-60	-23
0,1M NaCl	-24	-13

EDL of silica



EDL of silica



Colloidal Stability

DLVO theory – Kinetics of aggregation

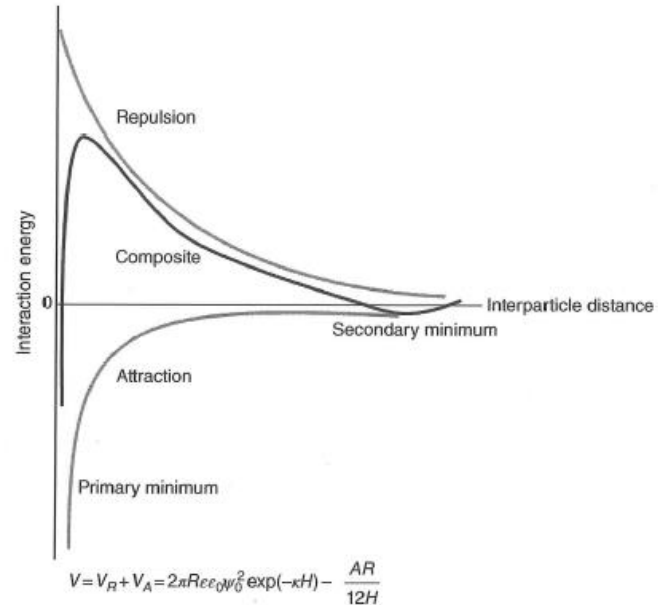
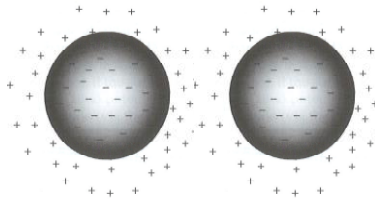
- Electrostatic stability (DLVO theory)
- Coagulation theory

DLVO theory

Net interaction energy = attractive + repulsive interaction energies

$$V = V_R + V_A$$

Electrostatic stabilisation



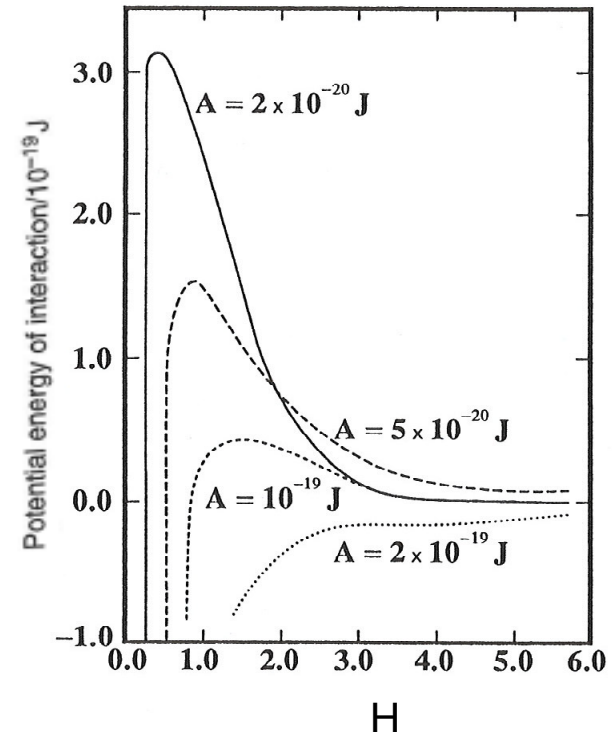
DLVO theory

Effect of Hamaker constant:

A can be controlled by choice of solvent
and composition of dispersed phase:

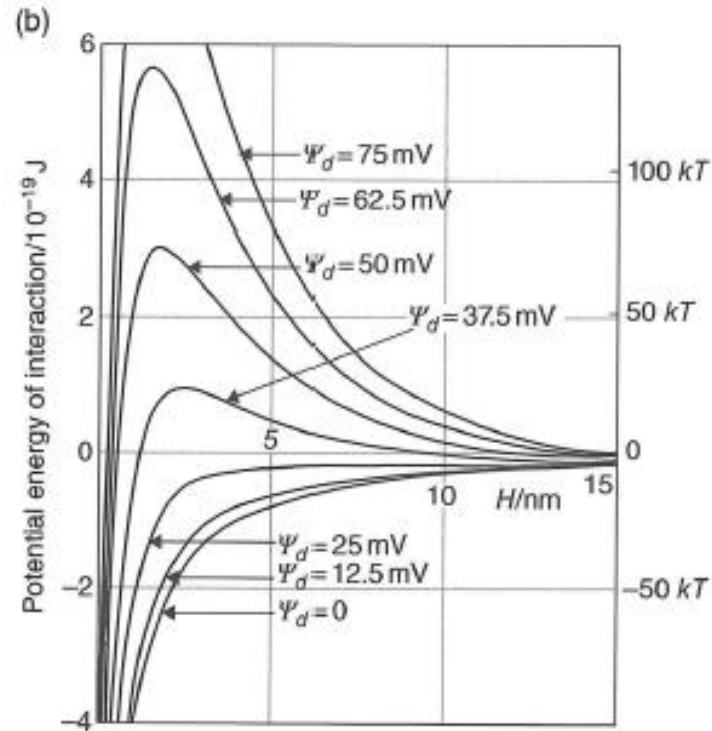
$$A_{121} = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

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



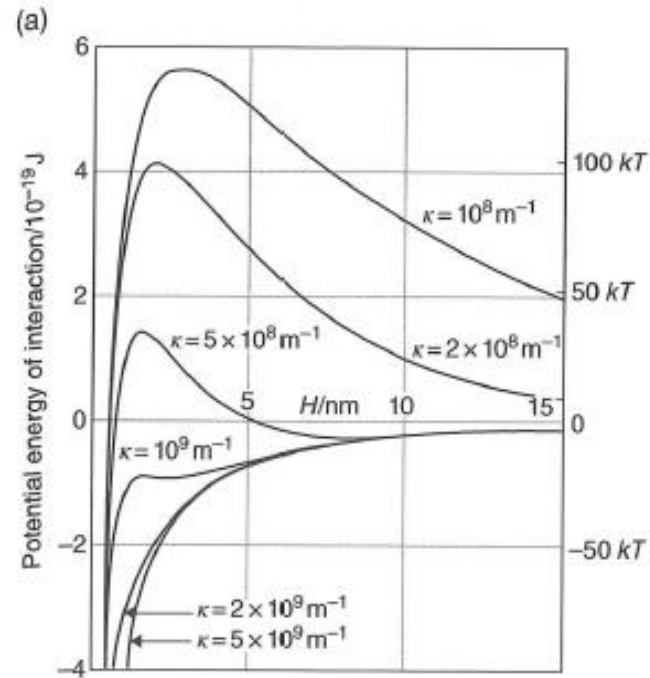
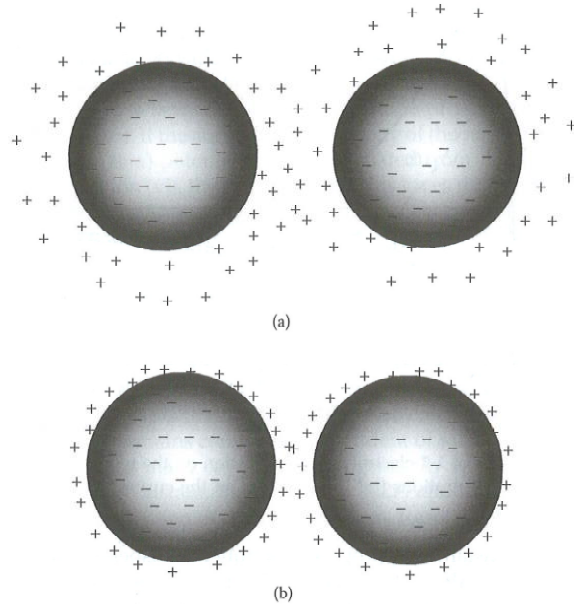
DLVO theory

Effect of surface/ zeta potential:



DLVO theory

Effect of ionic strength:





DLVO theory

Summary:

1. High surface/zeta potential:
Large repulsion between particles
2. Low electrolyte concentration:
Repulsion between particles at long distances (large double layer extension)
3. Large Hamaker constant:
Large attraction between particles

Generally: Trends of interest – not parameters themselves

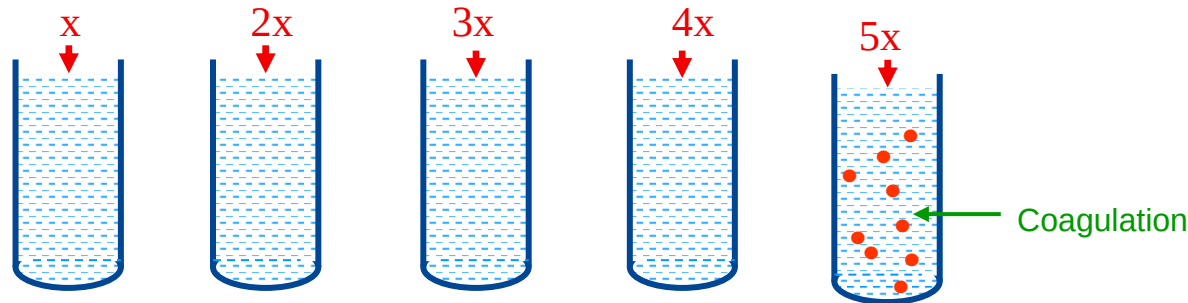
Critical coagulation concentration (CCC)

Experimental determination of colloidal stability:

A defined electrolyte concentration is needed to induce coagulation – CCC

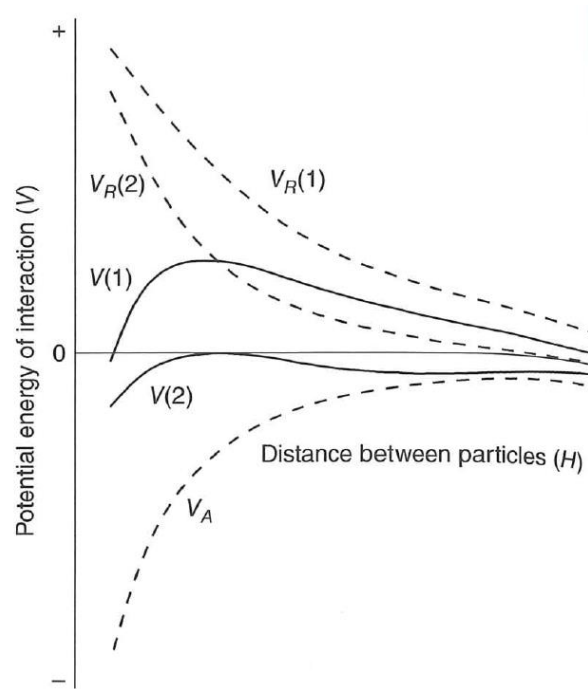
Determination of CCC:

1. Make a series of test tubes containing same amount of dispersed phase, but different electrolyte concentration
2. Measure size of dispersed phase a given time after preparation





Critical coagulation concentration (CCC)



$$\text{Schulze-Hardy rule: } \text{CCC} = \frac{1}{z^6}$$

**Lyotropic (hofmeister) series
effectiveness of coagulation**

$\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ (monovalent)

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

$\text{CNS}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^- > \text{NO}_3^- > \text{ClO}_4^-$

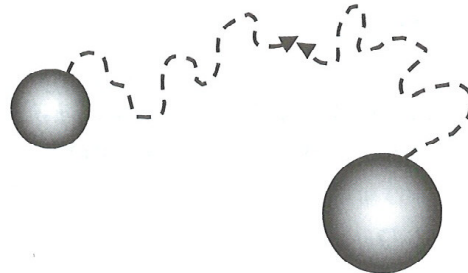
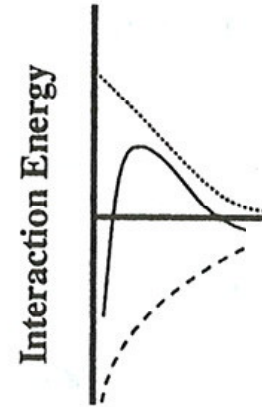
Coagulation in dilute dispersions

All kinetically stabilised systems are unstable over time

Stability determined by rate of coagulation (or coalescence)

Rate of coagulation determined by:

1. Particle collision frequency
2. Probability that particles stick together upon collision



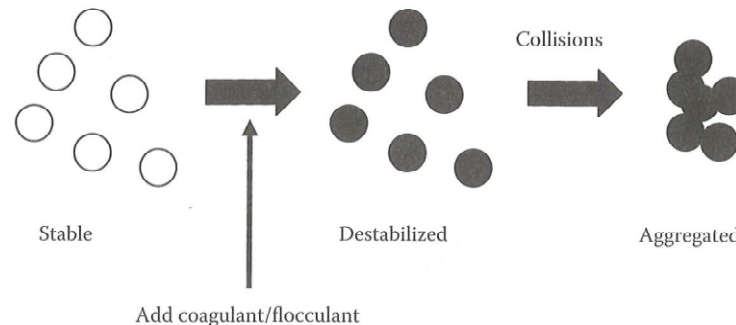
Coagulation in dilute dispersions

Fuchs' stability ratio : $W = \frac{k_2^0}{k_2}$

k_2^0 : rate constant for rapid coagulation (no repulsive interactions – diffusion controlled)

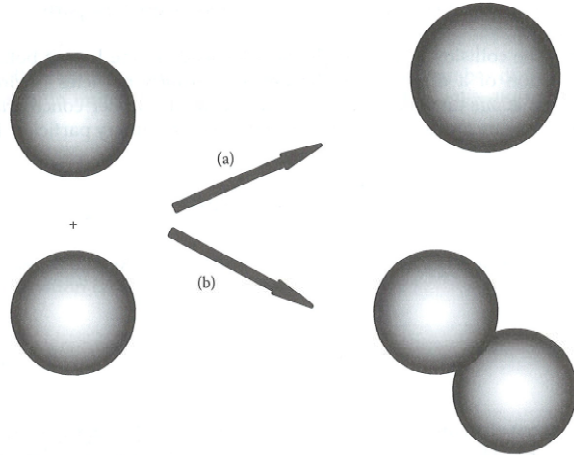
k_2 : rate constant for slow coagulation (interaction controlled collisions)

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



Coagulation in dilute dispersions

Fast coagulation: *no repulsive barrier*

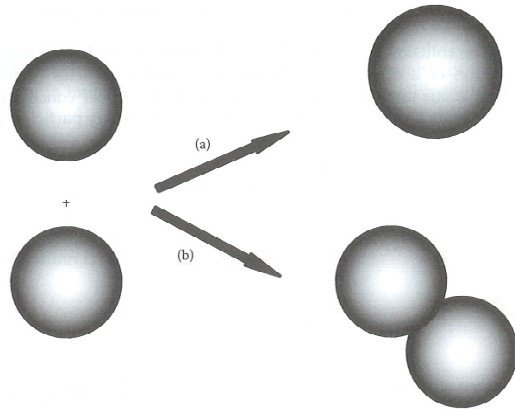


Collision frequency: $Z = 8\pi R_S D N$

Rate constant: $k_2^0 = \frac{4k_B T}{3\eta}$

Coagulation in dilute dispersions

Fast coagulation:



Particles adhere upon contact
– doublet formation/coalescence

Coagulation rate: $\frac{dN}{dt} = -k_2^0 N^2$



Coagulation in dilute dispersions

Example - rapid coagulation

Aqueous dispersion: 10^9 particles/cm³

$$T = 293K$$

$$\eta(\text{water}) = 10^{-3} \text{ kg/ms}$$

$$k_B = 1,38 \times 10^{-23} \text{ J/K}$$

$$k_2^0 = \frac{4k_B T}{3\eta}$$

What is the time required for the concentration of dispersed particles to drop to 90 % of the initial concentration?

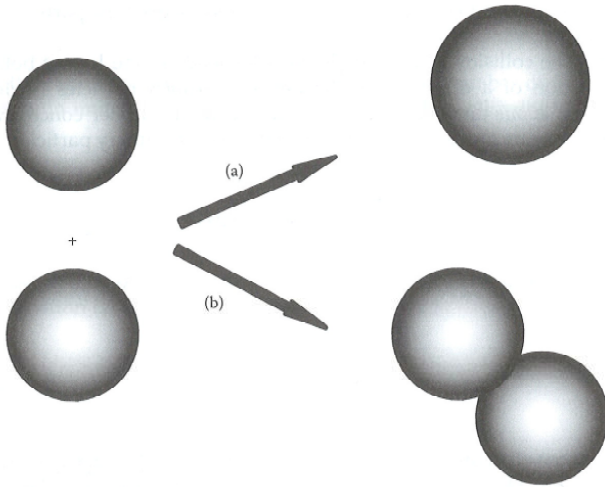
Coagulation in dilute dispersions

Slow coagulation: *energy barrier*

Collision frequency reduced by interaction potential:

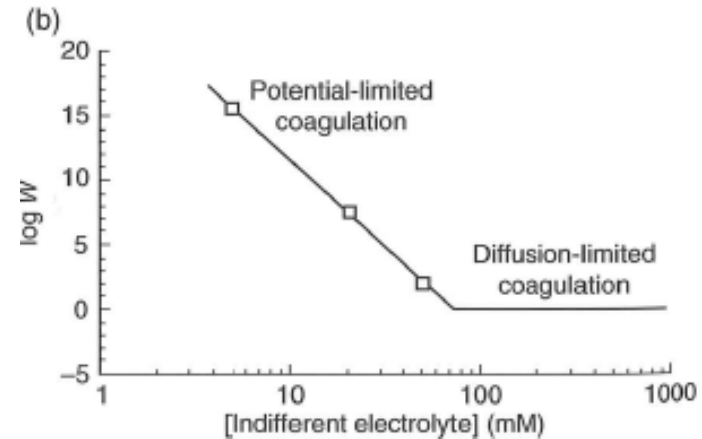
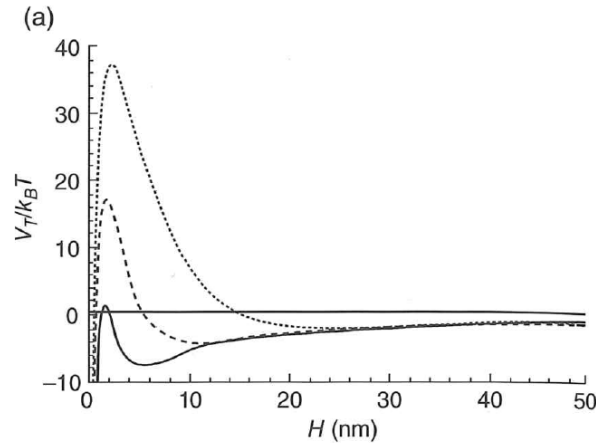
$$Z = \frac{8\pi DR_s N}{\int_s^\infty e^{\frac{\varphi(s)}{k_B T}} \frac{ds}{(s+2)^2}}$$

Coagulation rate: $\frac{dN}{dt} = -k_2 N^2$



Coagulation in dilute dispersions

Stability ratio and CCC:

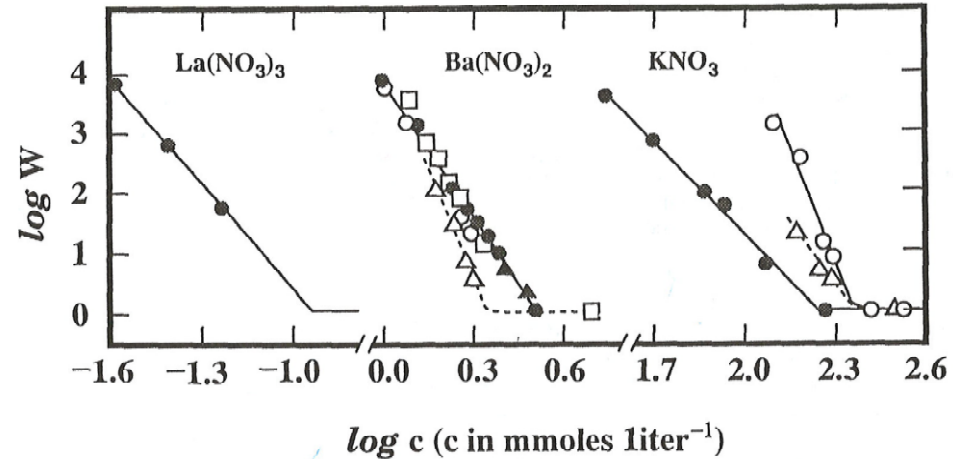


$$\log W = K_1 \log c + K_2$$

Coagulation in dilute dispersions

Stability ratio and CCC:

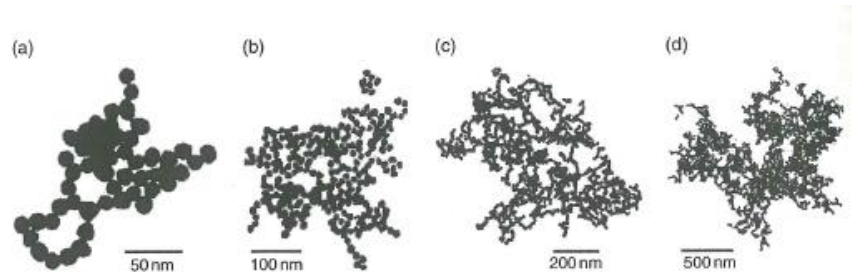
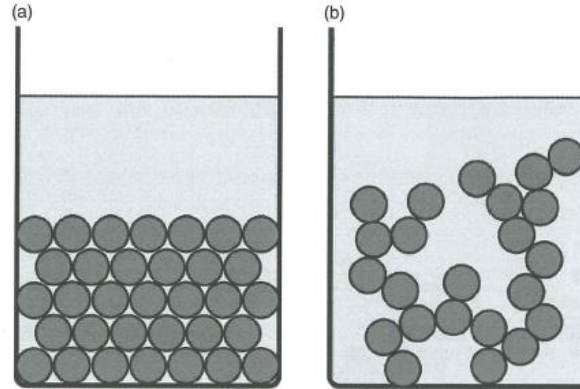
AgI dispersions:



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

Coagulation in dilute dispersions

Aggregate structures:



Home experiment - salt in beer

Materials:

- 1 glass
- 100-200 mL of beer
- A few grams of table salt

Procedure:

1. Fill the glass with beer
2. Add salt
3. Observe and explain what happens

Recording procedure:

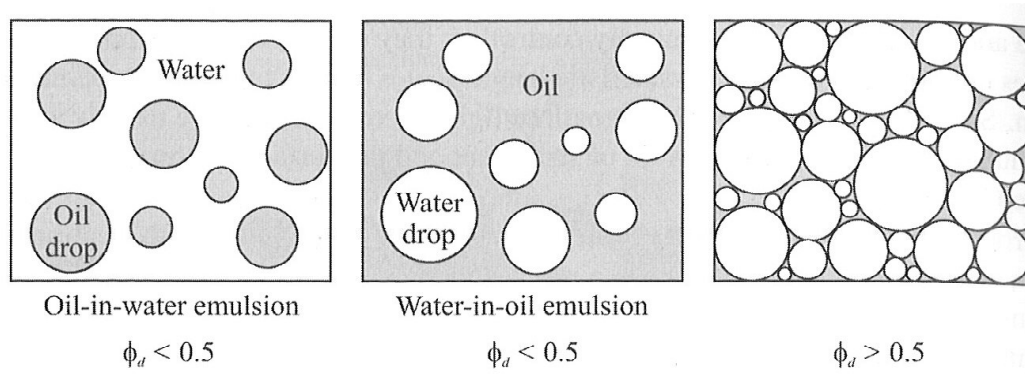
1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no

Emulsions

Applications, characterisation and stability

Emulsions

Mixture of two immiscible liquids - separates rapidly without stabilisation

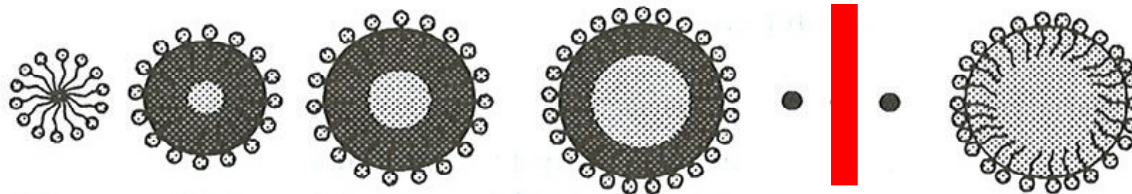


- 2-phase system - *kinetically stabilised* (energy required for formation)
- w/o or o/w emulsions
- can have high amounts of dispersed phase
- Polydisperse drops – average drop size:
- Surfactants adsorb on the o-w interface and orient as monolayers

Microemulsions and emulsions

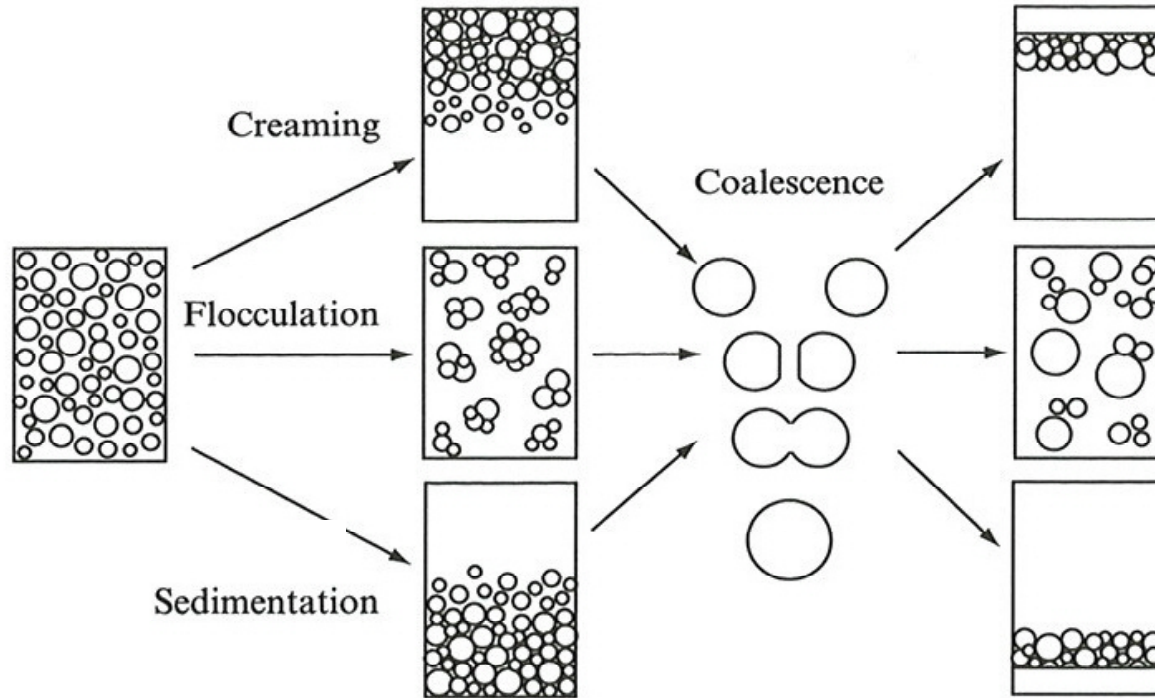
- Mostly microemulsions have droplets at least on order of magnitude lower than for emulsions
- Microemulsions are clear, emulsions are cloudy
- Microemulsions form spontaneously (thermodynamically stable), emulsions require energy input (kinetically stable)
- Microemulsions are highly dynamic systems, emulsions are relatively static systems (in terms of surfactants)

Important: main difference is *not* drop size
– *microemulsion can be a misleading term!*



No continuum from micelles/microemulsions to emulsions

Emulsions



Colloidal stability



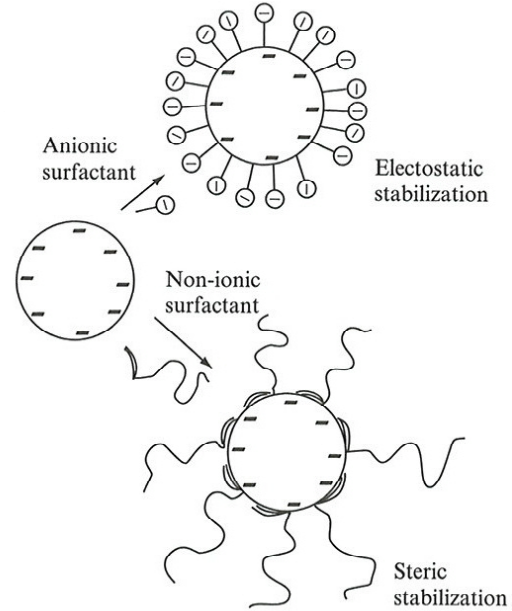
Interaction energy between dispersed particles/droplets:

- Attractive part: van der Waals interactions
 - long-ranged
 - strong at small distances
 - always present
- Repulsive part - provided in several ways:
 - Osmotic and electrostatic interactions (repulsion due to overlapping double layers)
 - electrostatic stabilisation
 - Polymer induced stability (masked van der Waals attraction)
 - steric stabilisation
 - Elastic interfacial films (particles, surfactants)

Emulsions

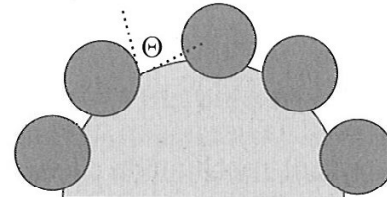
Stabilisation:

Electrostatic stabilisation:



Steric stabilisation:

Particle stabilisation:



Emulsions



Factors enhancing stability:

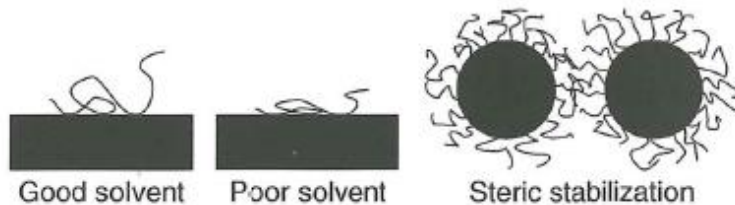
- Low interfacial tension
- A mechanically strong and elastic interfacial film
- Electrical double layer repulsions
- Relatively small volume of dispersed phase
- Narrow droplet size distribution

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

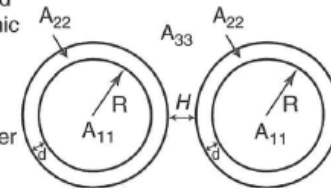
Steric stabilisation

Requirements for surfactants:

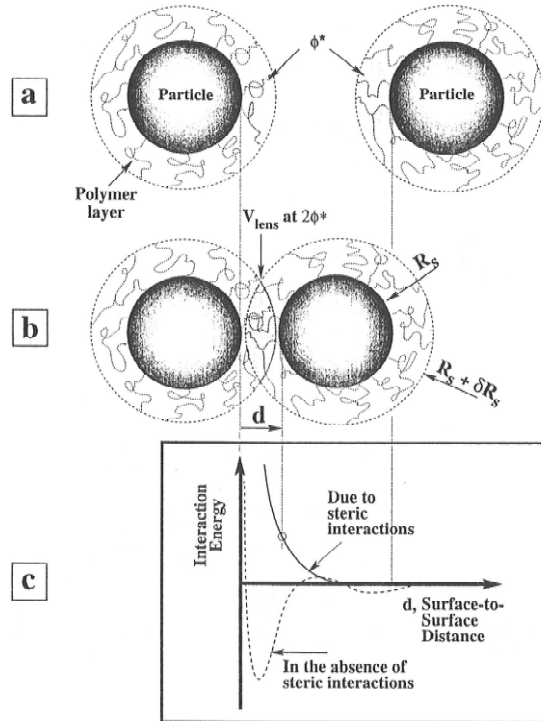
- Reduce the o-w interfacial tension
- Rapid diffusion to newly created interfaces
- Low molecular weight surfactants are superior when creating emulsions
- High molecular weight polymers, particles, proteins and liquid crystals diffuse slowly to the interface, may play a larger role in stabilisation



1. Enhanced double-layer repulsions for ionised stabilizers e.g. anionic surfactants
2. Reduced vdW interactions due to lowering the Hamaker constant
3. "Steric effects" (all the others...)

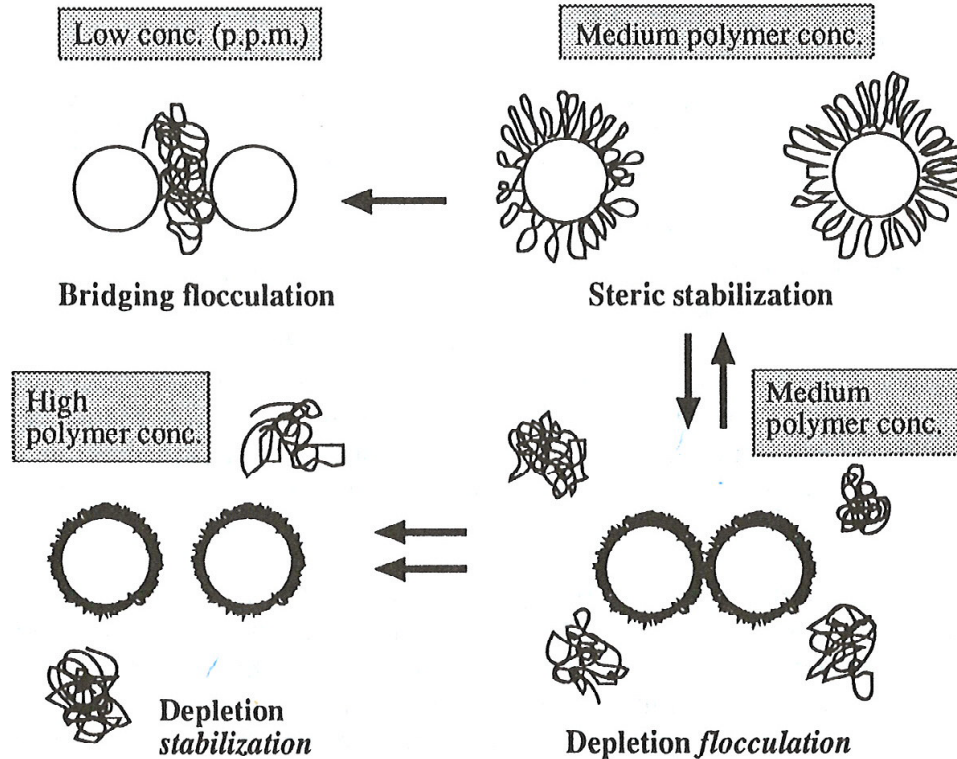


Steric stabilisation



$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

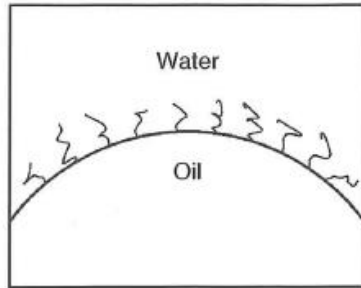
Steric and depletion interactions



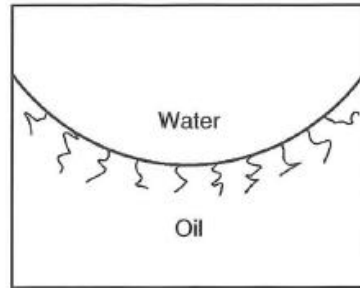
Emulsion design

Bancroft's 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)

HLB scale:

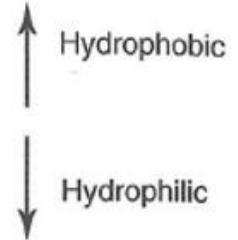
3–6 : w/o emulsions

7–9 : wetting agents

8–15 : o/w emulsions

13–15 : detergents

15–18 : solubilizers



HLB<8: w/o emulsions

HLB>8: o/w emulsions

Phase inversion temperature

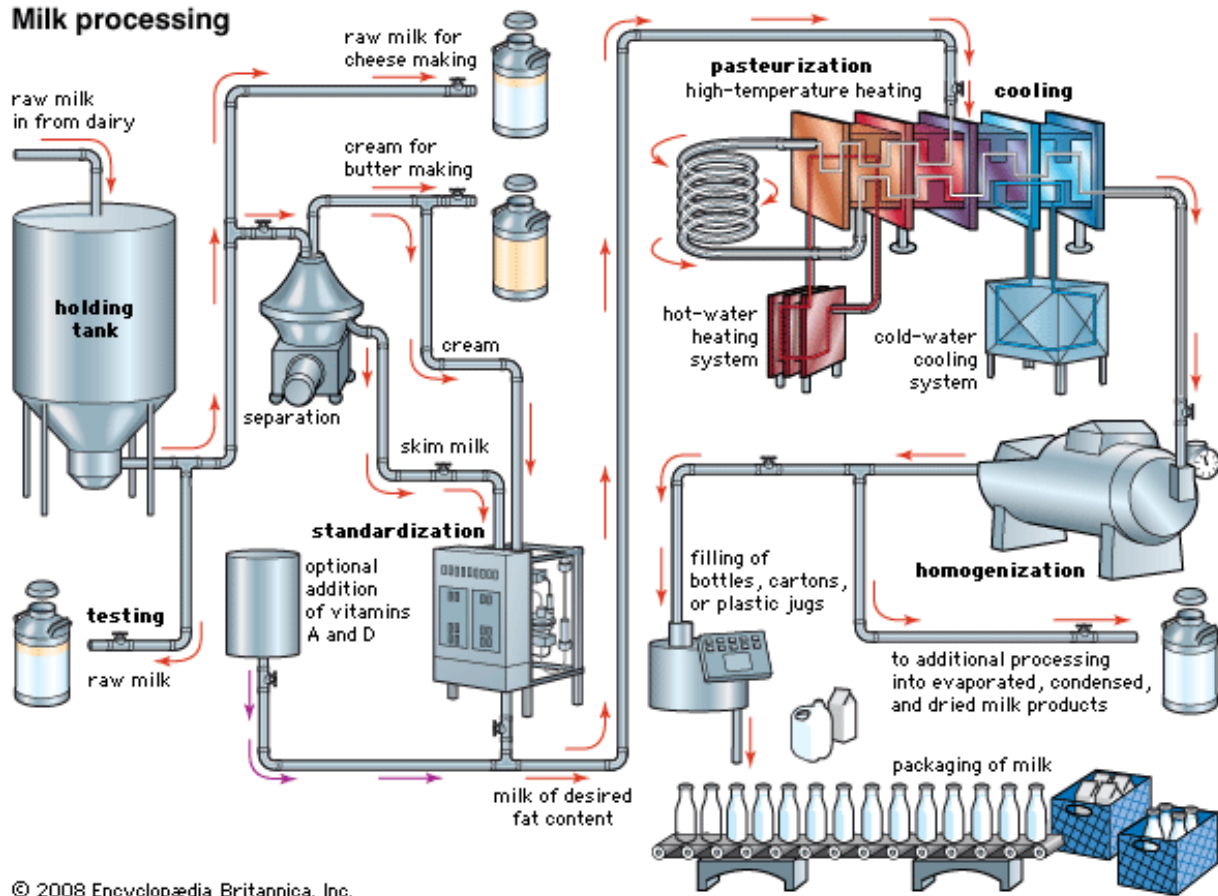
Food emulsions



Schroën and Berton-
Carabin, 2016

Milk processing

Milk processing

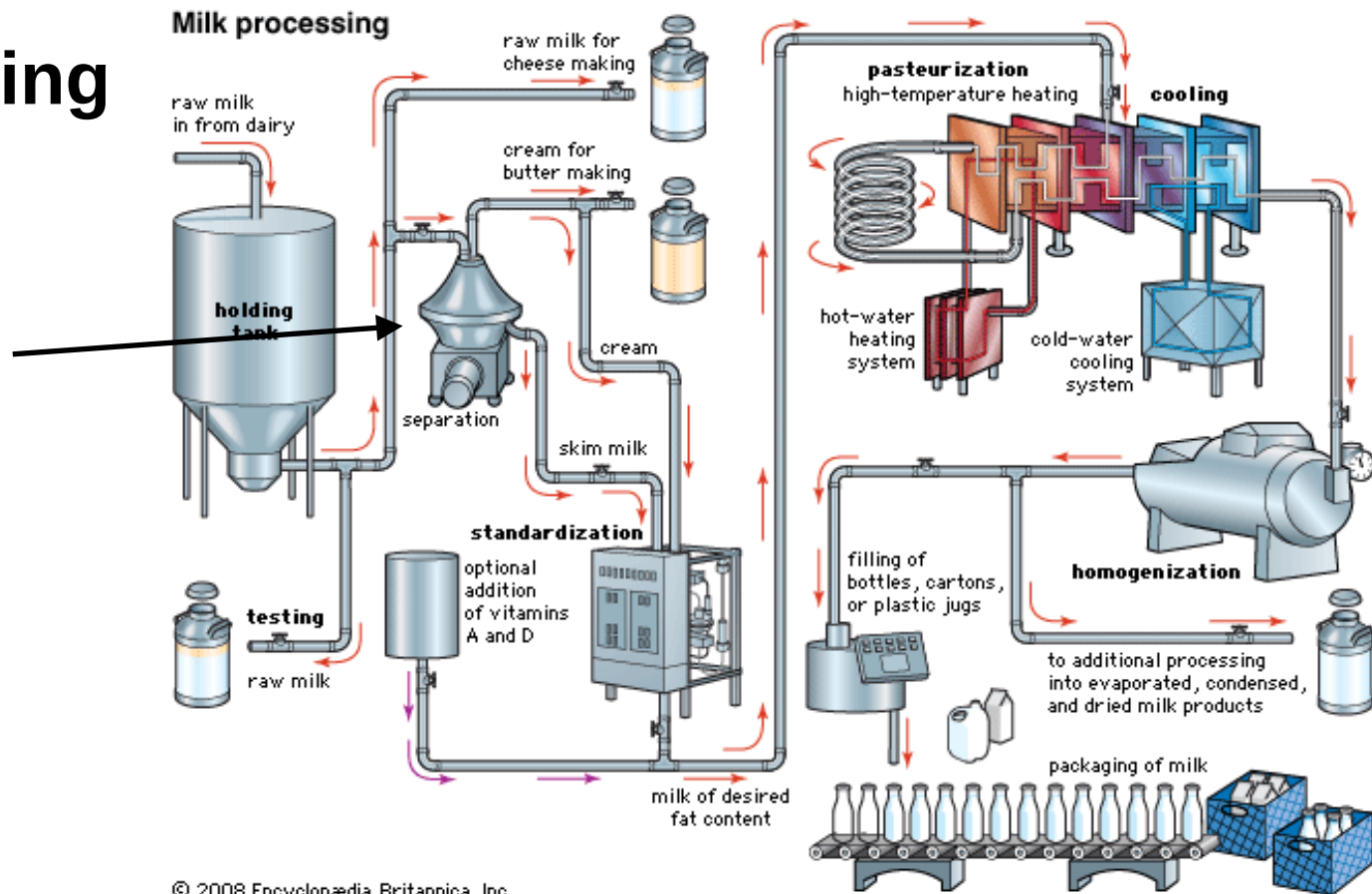


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<https://kids.britannica.com/students/article/dairy-industry/273899>

Milk processing

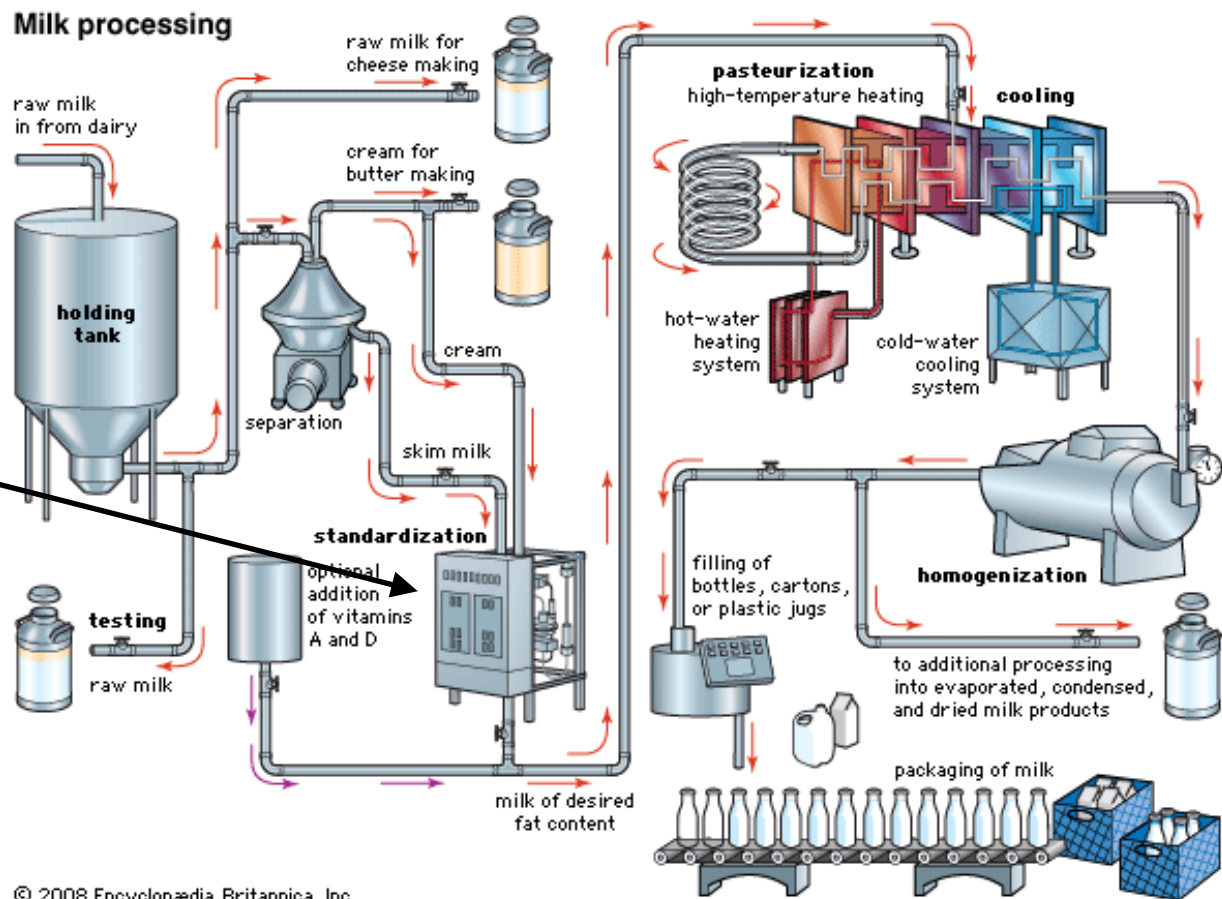
Centrifugation to separate the globular milk fat from the serum, the skim milk



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Milk processing

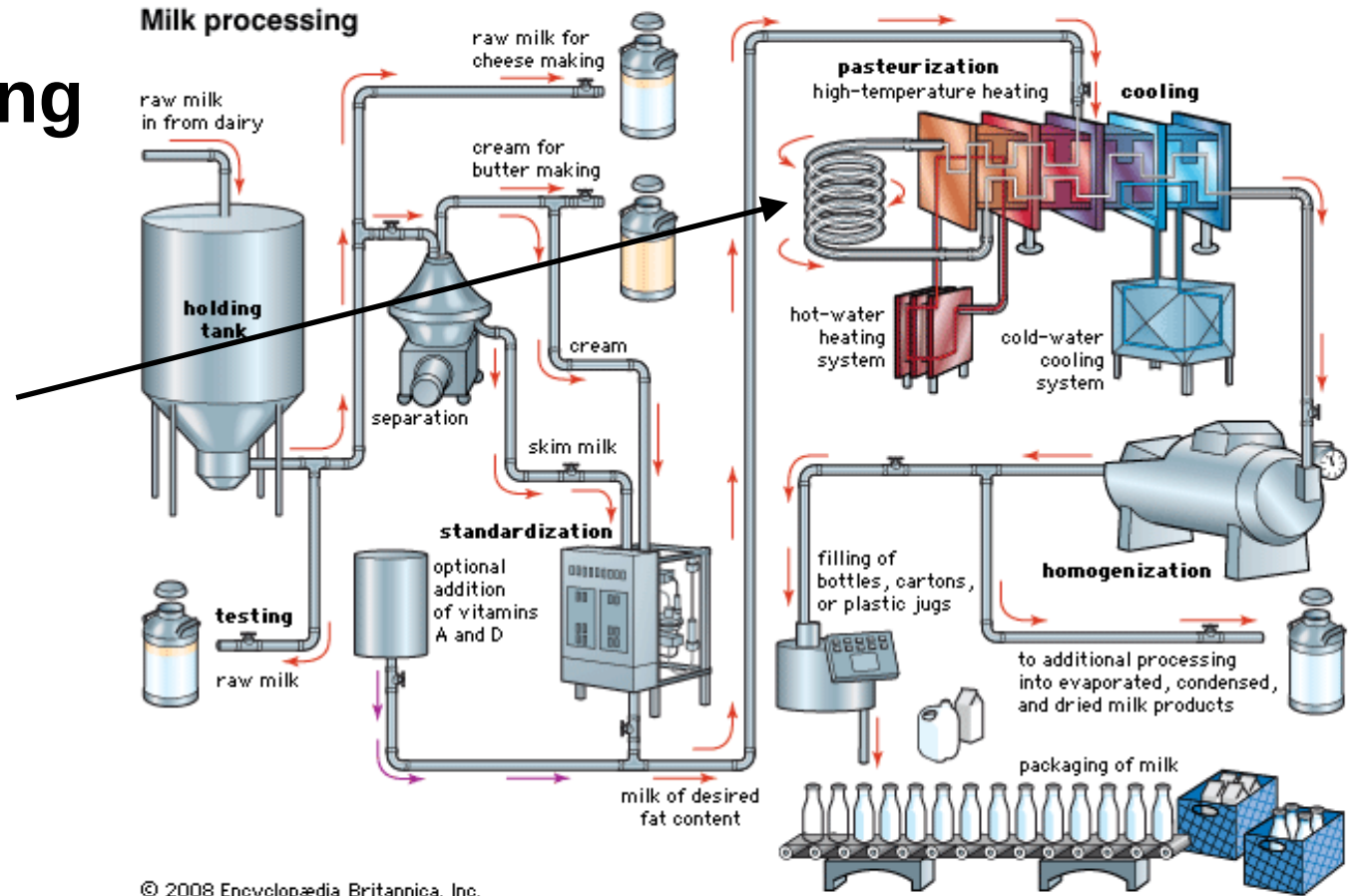
Standardization of milk is the alteration of fat and solids-not-fat (SNF) levels, i.e., raising or lowering of these levels. to create a uniform milk fat content in the final dairy product



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Milk processing

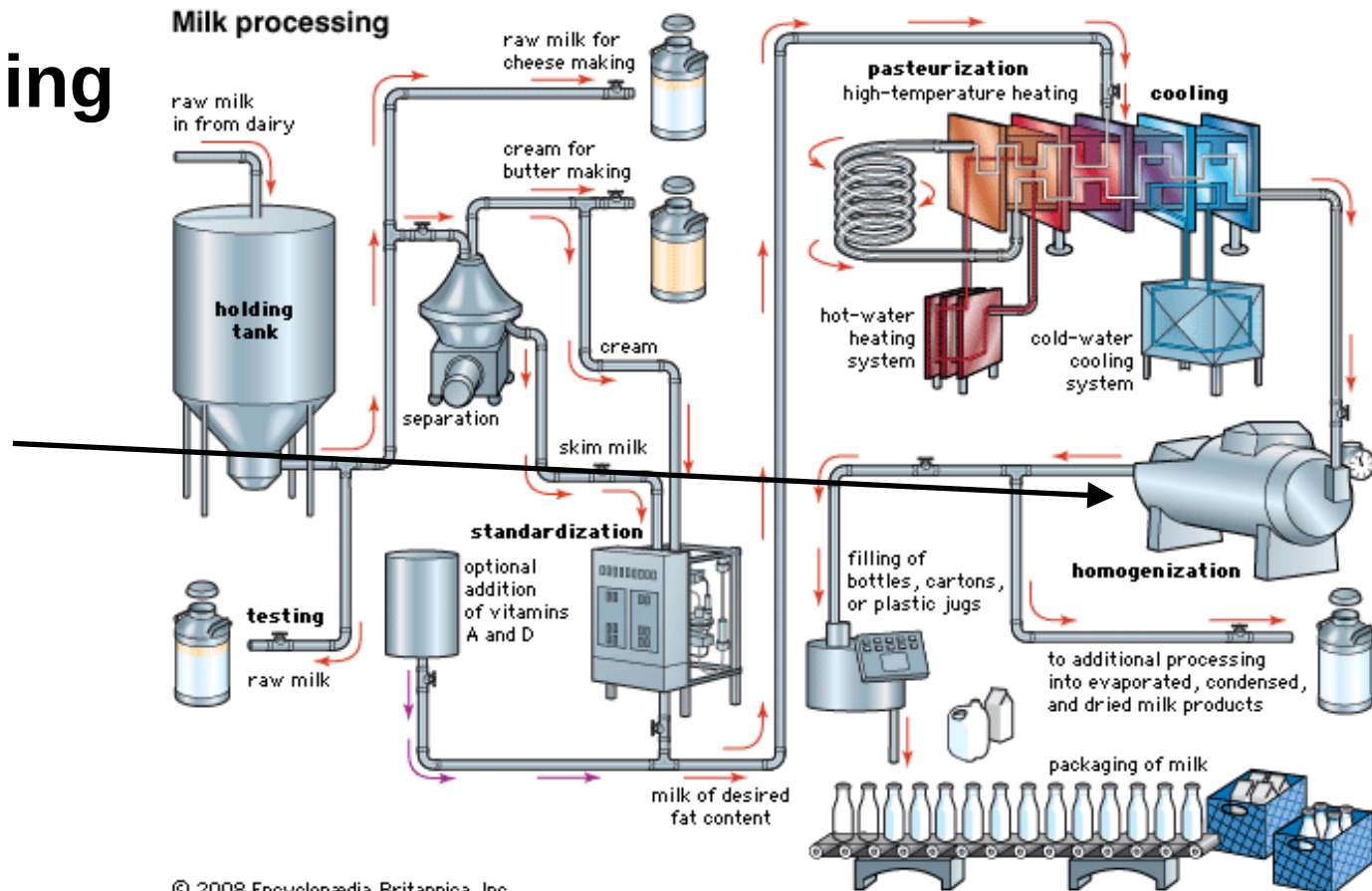
- HTST
pasteurization: 71-73°C for 15 s
- UHT sterilization:
130-150°C for 1-4 s



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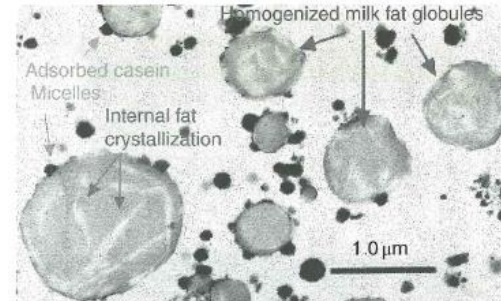
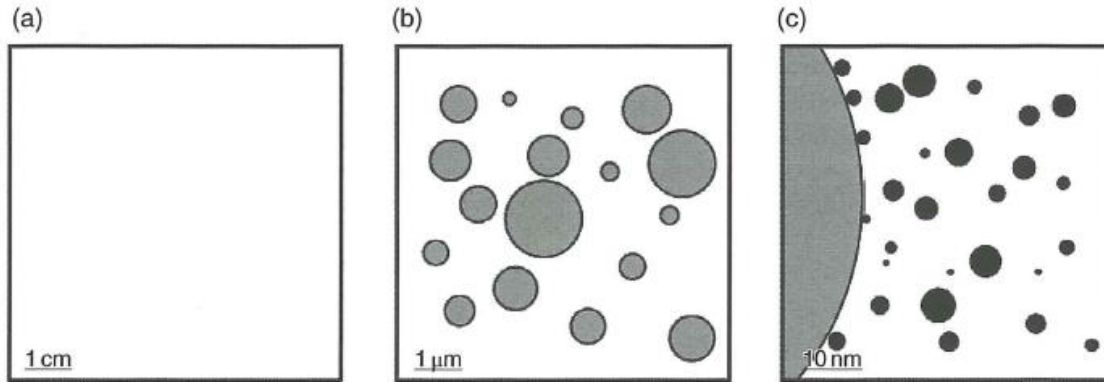
Milk processing

Homogenization:
decrease the fat
droplet size to
reduce creaming
Milk globules
passes through
tiny orifices at high
pressure

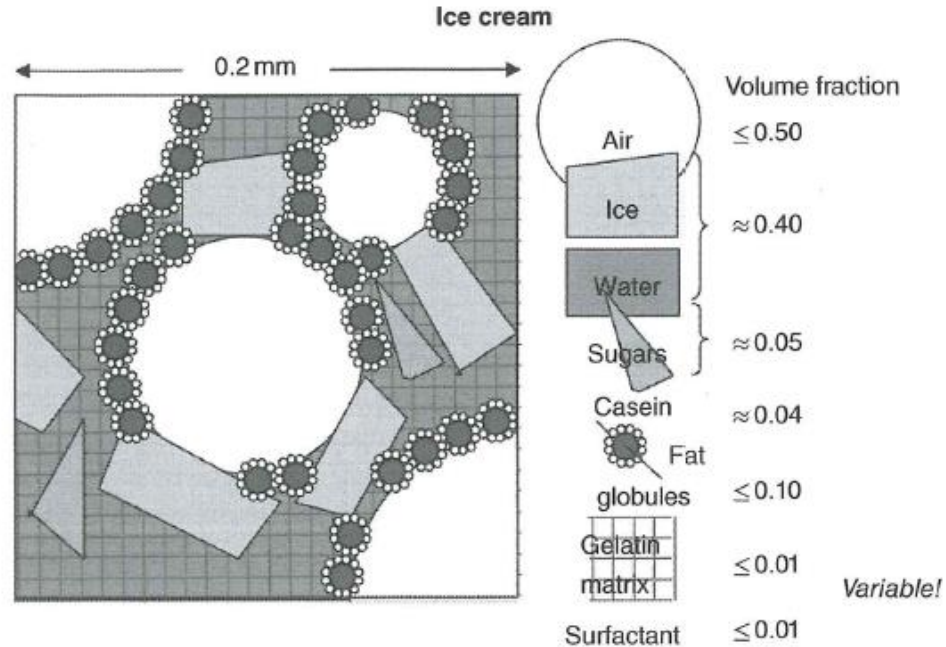


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Food emulsions

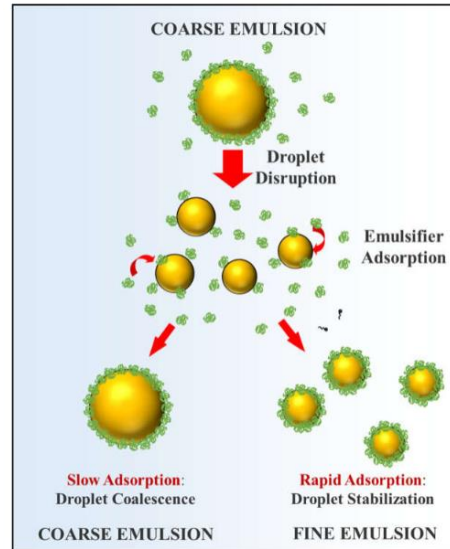
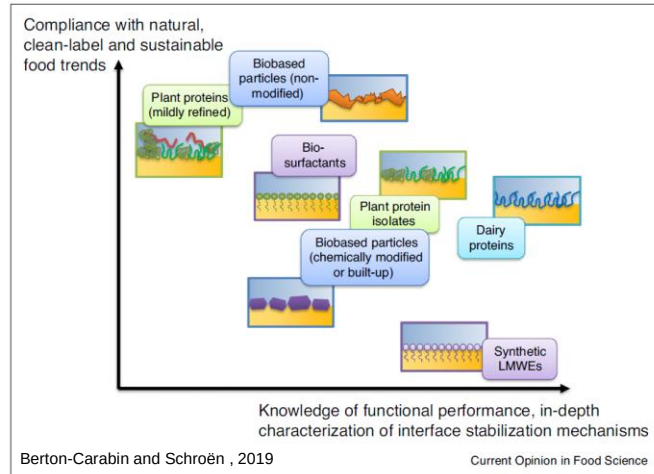


Food emulsions

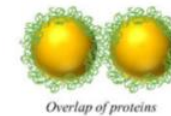
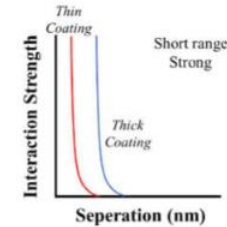


Trends in food emulsions

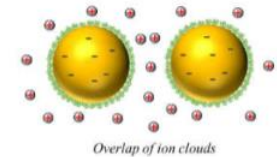
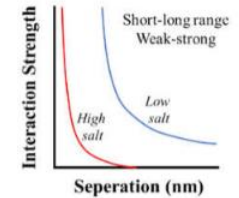
Replace proteins from animals with alternative proteins (plants, algae, microbes) as emulsifiers and stabilizers



Steric Repulsion



Electrostatic Repulsion

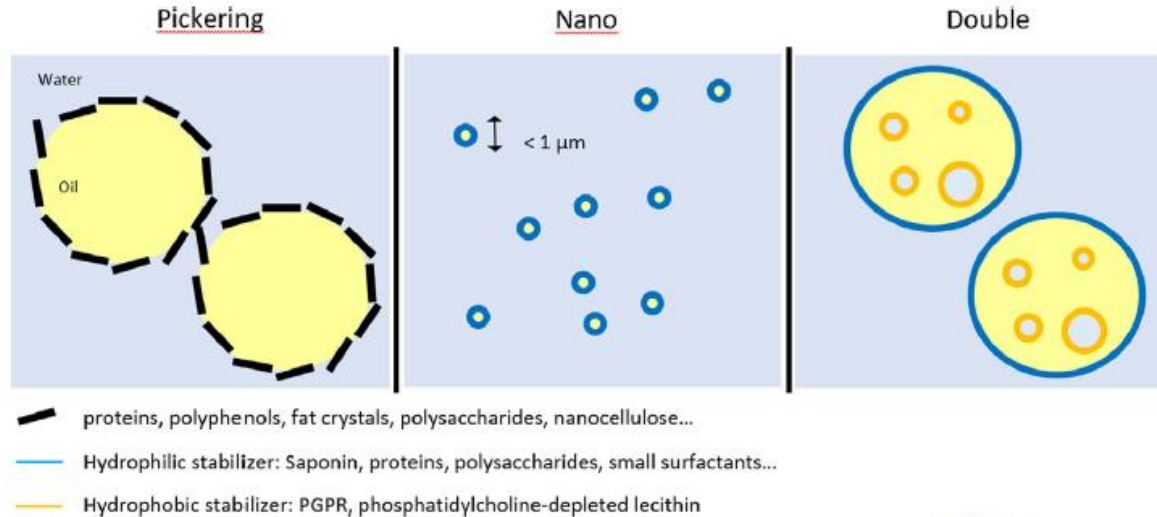


Challenge: Alternative proteins have very different molecular structures, i.e. different emulsifying properties, nutritional properties, and sensory properties

<https://doi.org/10.3390/colloids6020019>

Trends in food emulsions

Amore advanced emulsion systems



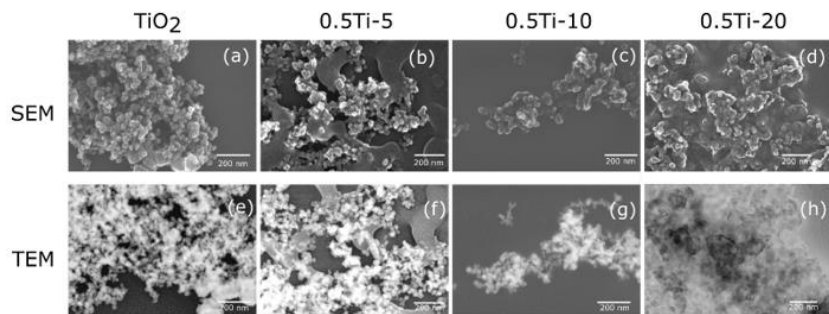
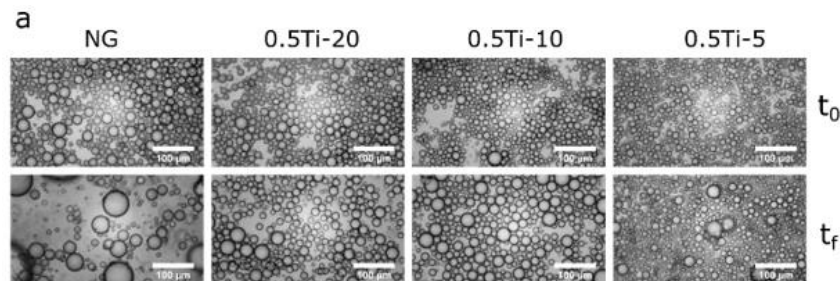
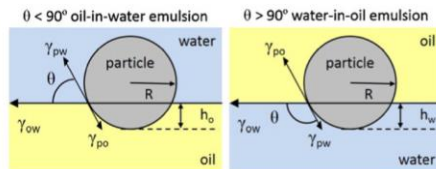
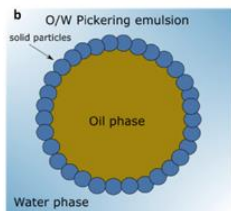
Current Opinion in Food Science

Pickering emulsions for water treatment

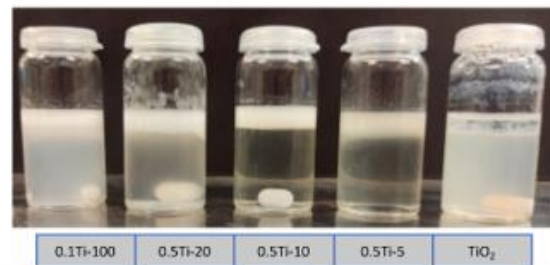


Use photocatalytic nanoparticles to stabilize emulsions

Dissolved organic pollutants will be composed by the photocatalyst



After photocatalysis



Droplet based microfluidics



Tool to produce and study emulsions

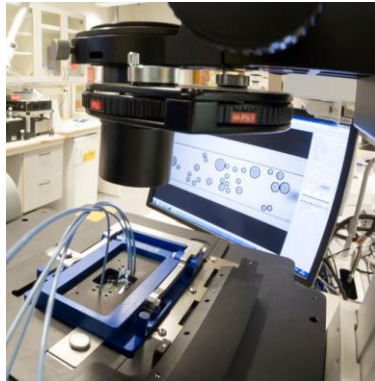
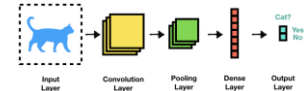
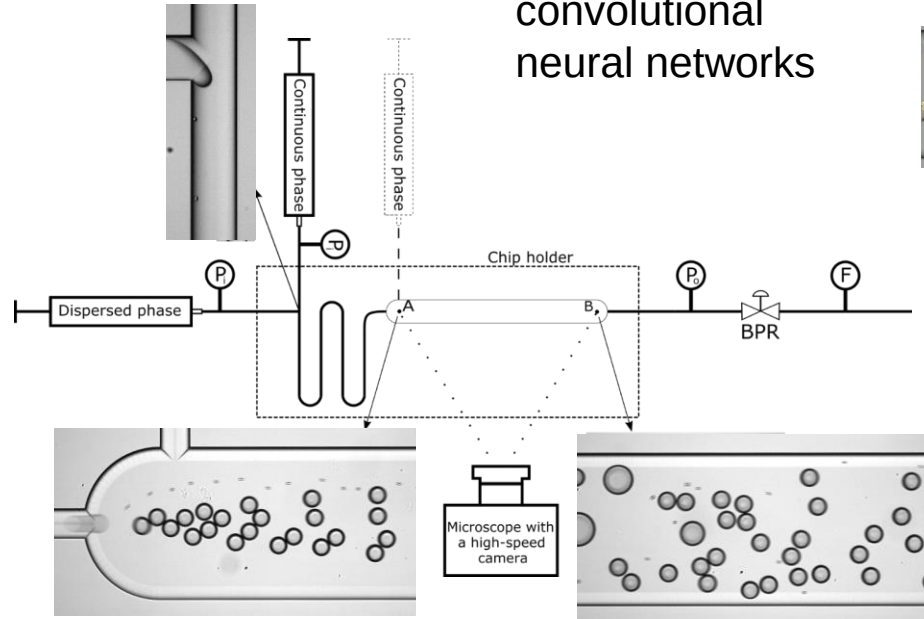
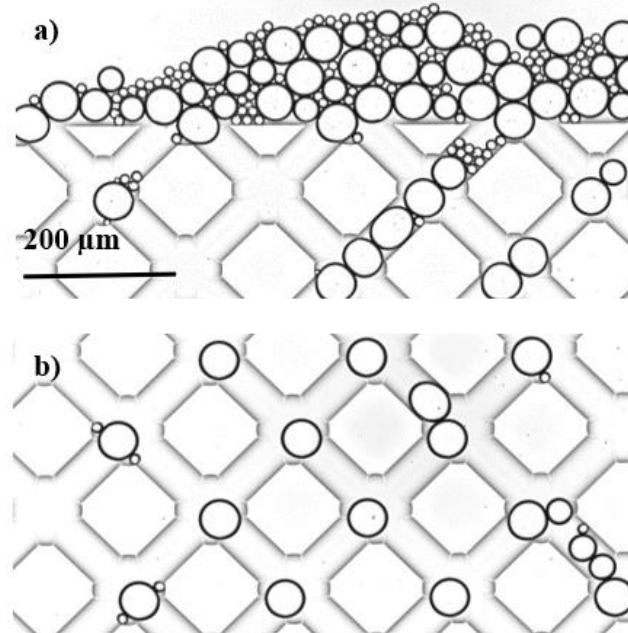
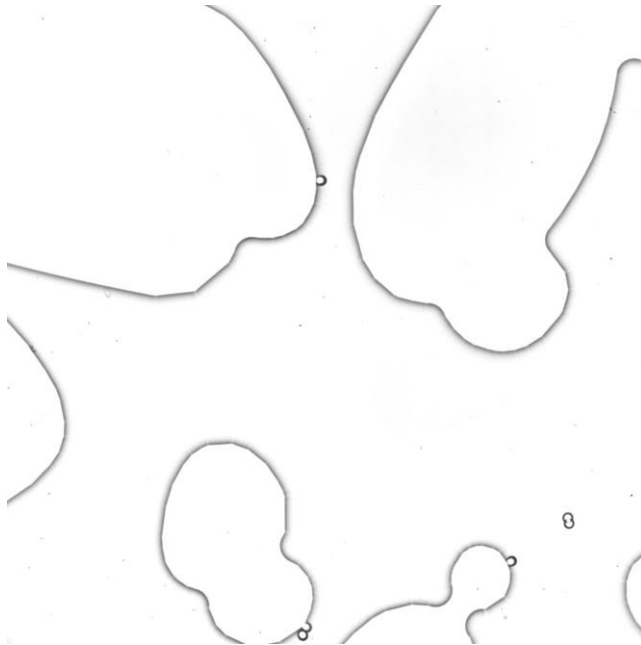


Image analysis by
convolutional
neural networks



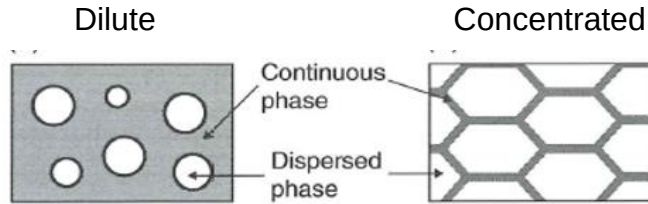
Emulsions in porous media



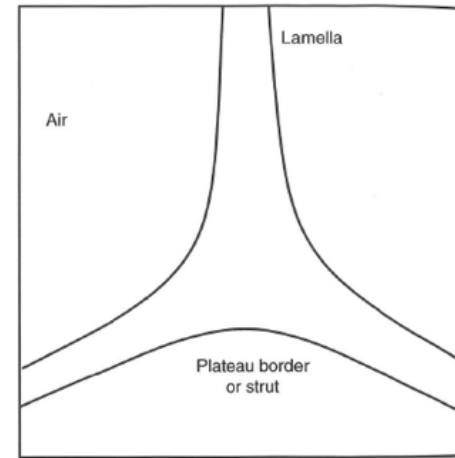
Foams

Applications, characterisation and stability

Definitions

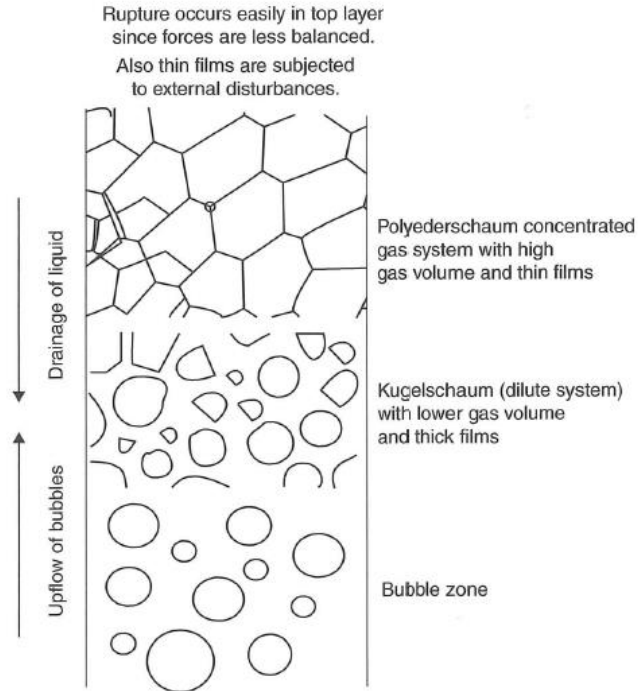


Volume fraction dispersed phase: 0.5-0.9
 Sizes: 1 mm – several cm (but also nm)



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

Characterisation

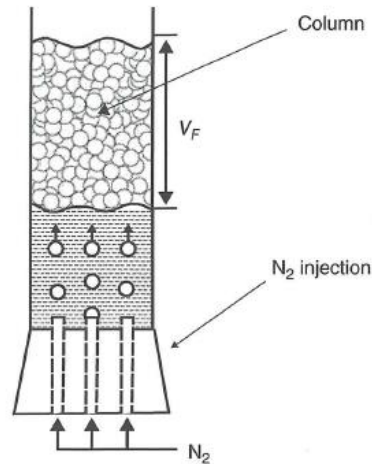


Foam number:
$$F = \frac{V_F}{V_L}$$

Preparation

Condensation of dissolved gas (pressure reduction of liquid supersaturated with gas)

Dispersion (injection) into liquid:



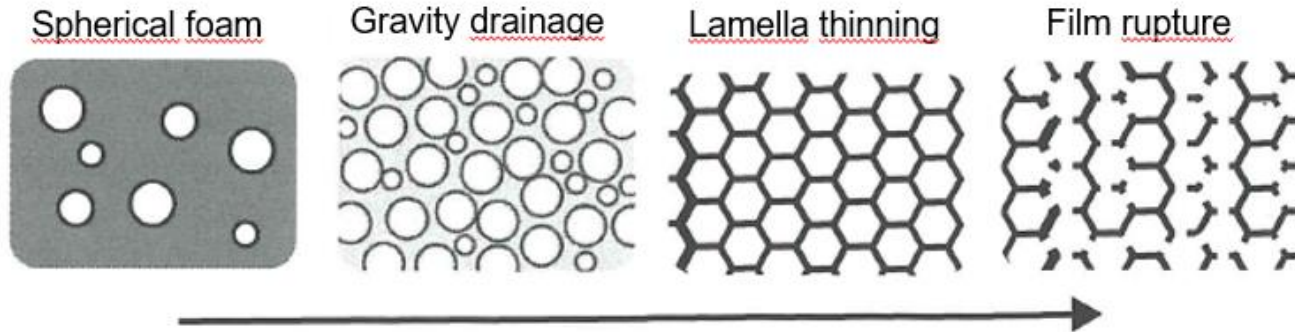
Bikerman column often used to characterise foams

Destabilisation mechanisms

Gas diffusion (Ostwald ripening)

Drainage

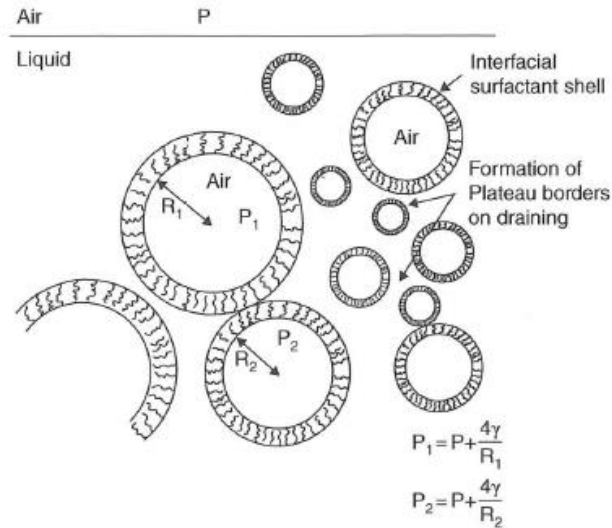
Coalescence



Destabilisation mechanisms



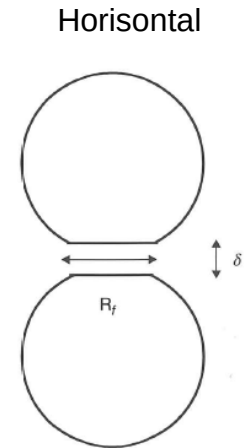
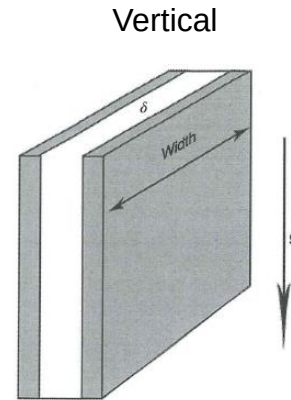
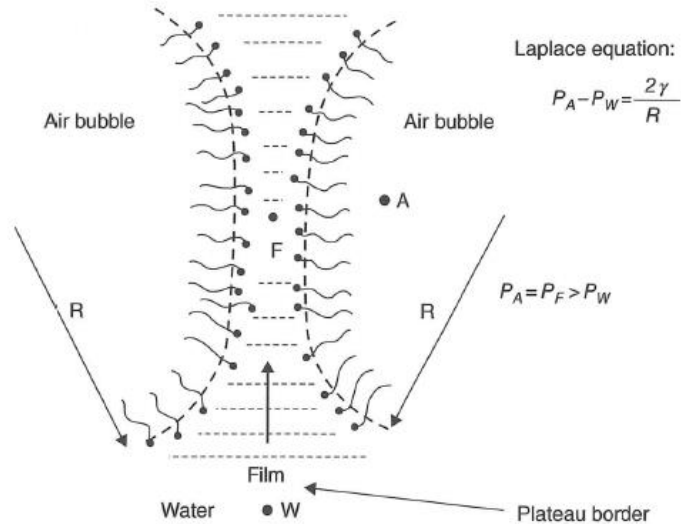
Gas diffusion (Ostwald ripening)



Destabilisation mechanisms

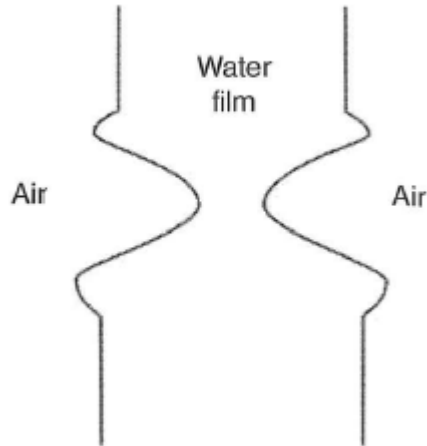


Drainage



Destabilisation mechanisms

Rupture and coalescence



Critical film thickness:

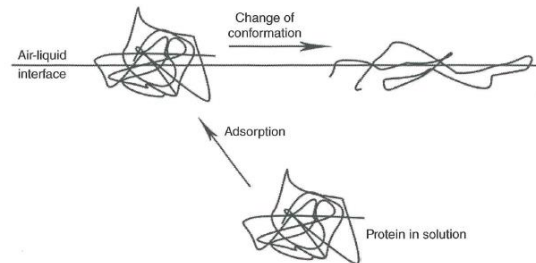
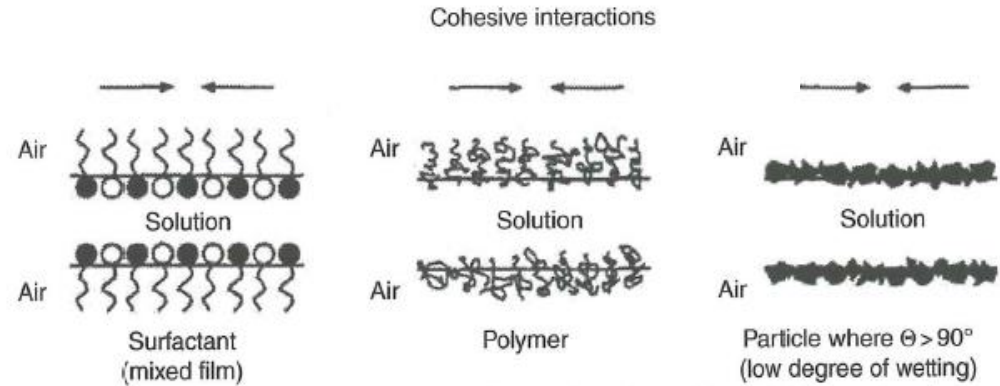
$$h_c = 0.207 \left(\frac{A_{121}^2 R_B^2}{\gamma_{AL} \Delta P} \right)^{\frac{1}{7}}$$

Pure water: 100-400 nm

Surfactant solutions: 5-15 nm

Stabilization

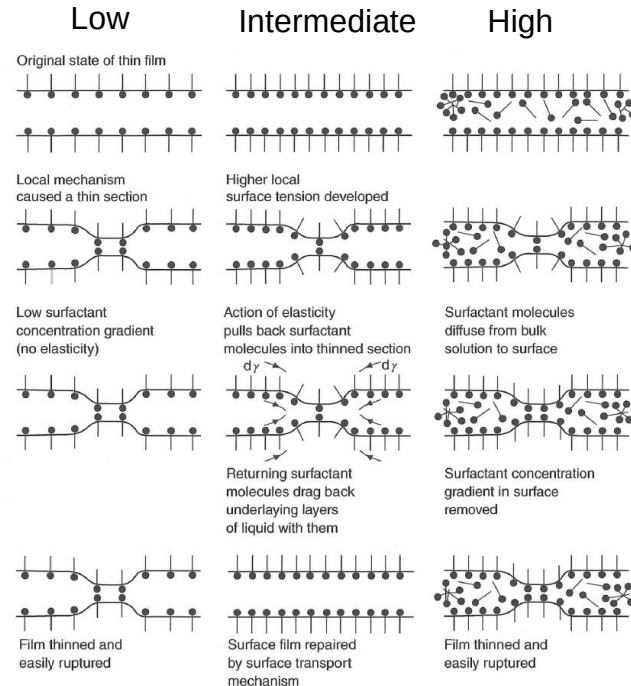
Increasing surface viscosity:



Stabilization

Surface elasticity (Gibbs-Marangoni effect):

Surfactant concentration:

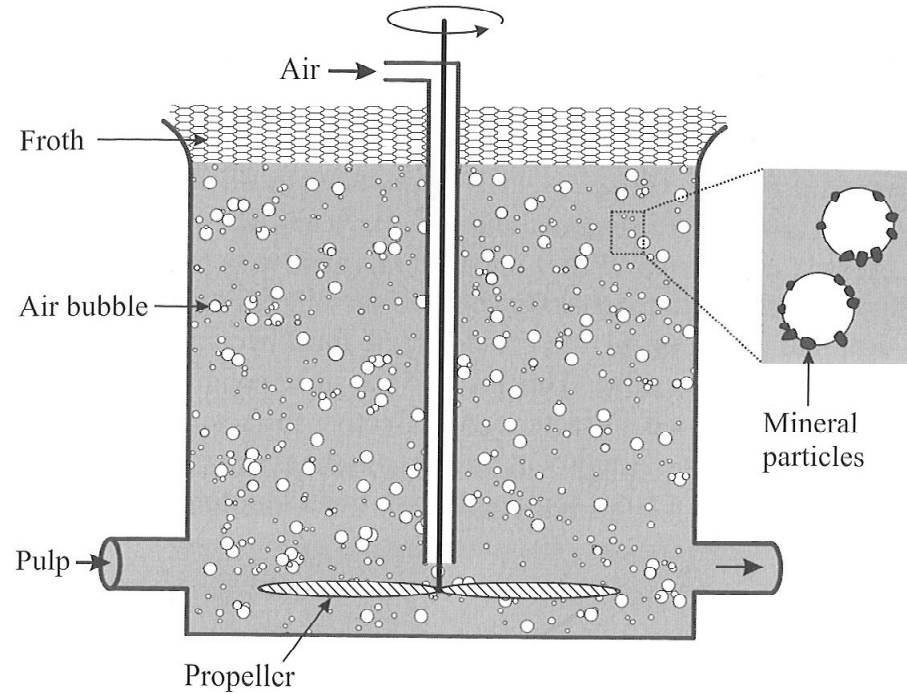


Applications



Froth flotation

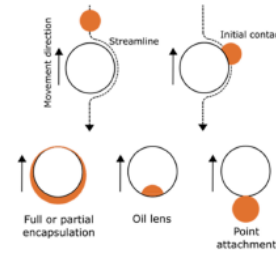
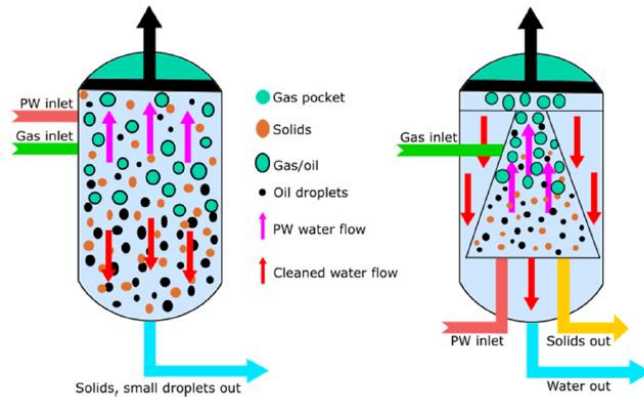
Mining:



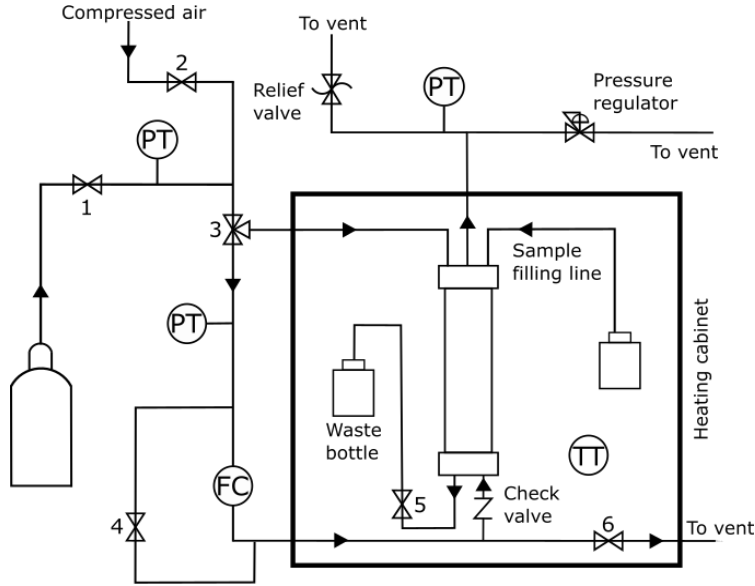
Gas flotation for water treatment



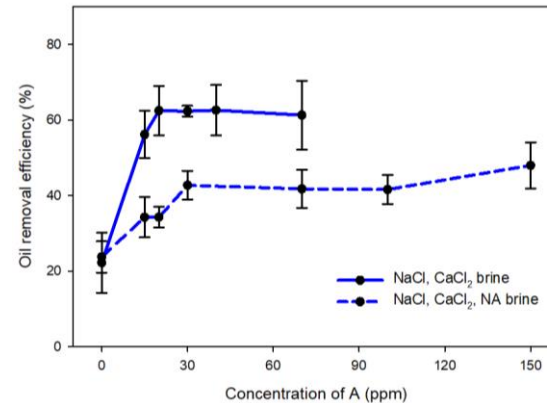
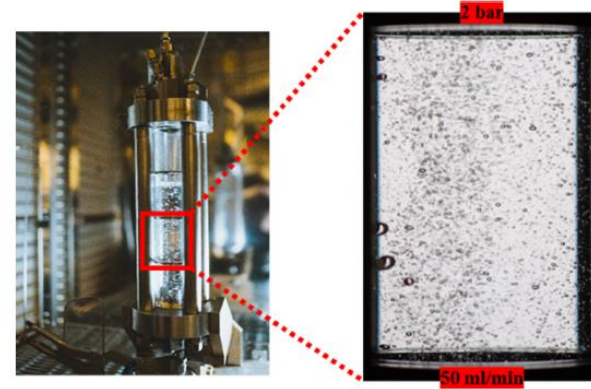
Removal of oil from water streams:



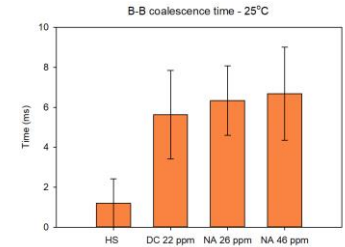
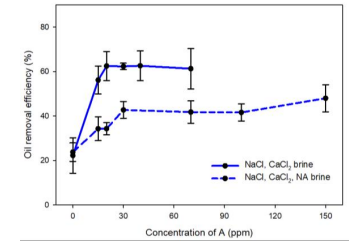
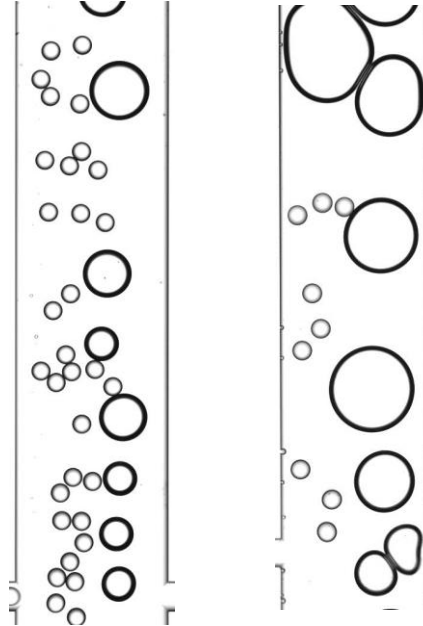
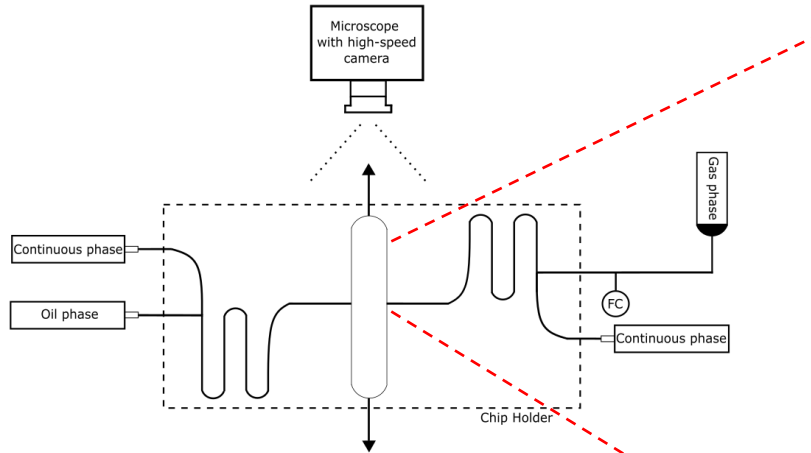
Gas flotation for water treatment



PT = pressure transmitter
TT = temperature transmitter
FC = flow controller

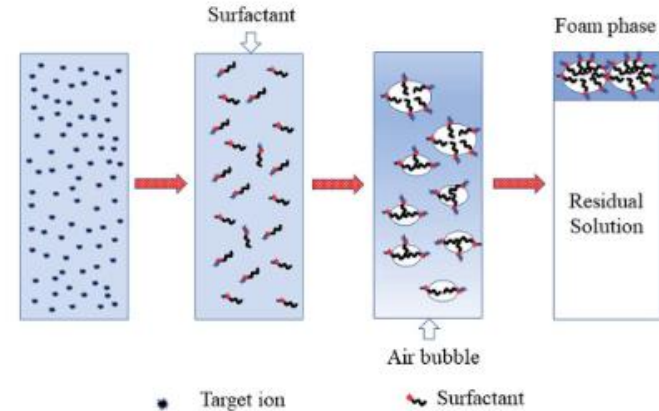
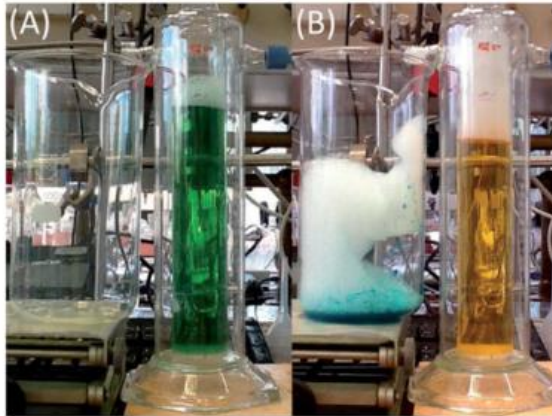


Gas flotation for water treatment



Ion flotation

Removal of heavy ions from water streams:



DOI: 10.1039/c9ra02905b

Home experiment - foam generation

Materials:

- Empty plastic bottle
- Dry yeast
- Warm water
- Liquid dish soap
- 3% hydrogen peroxide (can be acquired from the pharmacy)
- Cups
- Large tub or tray to catch the foam
- Location for the activity that can tolerate spills (of hydrogen peroxide as well as possibly food coloring), such as a kitchen or bathroom—or an outdoor location
- Liquid food coloring (optional)

Procedure:

1. Measure 1/2 cup of hydrogen peroxide, and carefully pour it into the bottle.
2. Add a significant amount of dish soap into the bottle (30-50mL), and swirl gently to mix.
3. If you want to make your foam a single color, add a few drops of food coloring directly into the hydrogen peroxide, and swirl the bottle gently to mix. If you want to give your foam stripes like some toothpastes, put the drops along the inside rim of the bottle's mouth. Let them drip down the inside of the bottle, but do not mix.
4. In a cup, mix together one tablespoon of yeast and three tablespoons of warm water. Stir for about 30 seconds.
5. Pour the yeast mixture into the bottle, then quickly step back, and watch the reaction happen
6. **Extra:** Try the activity without the dish soap
7. Observe and explain what happens.

Recording procedure:

1. Make a video of the experiment
2. Upload the video on wetransfer.com and generate a link (Get a link)
3. Send the link to gisle.oye@ntnu.no

1. Intro

Kolloidale systemer

- Minst 2 komponenter
 - Uniform på makroskala, ikke mikroskala
 - Partikkel/dråpe/boble av den ene fasen fordelt i den andre (matrix)
 - Interface: grenser mellom to faser
 - 5 typer:
 - solid-liquid
 - solid-gas
 - solid-solid
 - liquid-gas
 - liq-liq
 - Minst en linear dimensjon fra 1nm - 1µm (diamter, lengder, interfac)
- No gas-gas, gasses are not continuous $\Rightarrow$ solution.

Skille mellom kolloidale partikler og større partikler

- Mobilitet pga. termokinetisk energi
- Neglisjerbare trykkt effekt, men momentant svar til eksterne felt
- Neglisjerbare tyngdefelt
- Langdistanse intermolekylære interaksjoner
- Termodynamiske egenskaper er avhengig av størrelse
- Interaksjoner med elektromagnetisk stråling

Kolloidale systemer

1. Kolloidale dispersjoner
 - Lyfobisk system. Høy overflatefri energi $\rightarrow$ Termodynamisk ustabil
 - Irreversibel etter separasjon
2. Association colloids
 - Self-assembled surfaktanter. Micelle kolloid.
 - Termodynamisk stabil, lett reversibel.
3. Makromolekyl
 - Ekte løsninger, enkel lyofilske molekyler.
 - Termodynamisk stabil, reversibel.

Overflate

- Skille mellom to faser
- Lysnisk: A phase boundary with a thickness of molecular dimensions

Grensesnitt

- Det delende området mellom to faser
- Kolloidale dimensjoner ligger mellom atomer og bulk dimensjoner
- $\hookrightarrow$ Oppførselen til kolloidale systemer bestemmes mye av grensesnitt egenskapen. Høy overflate-volum ratio.

Spesifikt overflate areal (A_{sp})

- Arealet av partikler avhenger av # partikler

$$A_{sp} = \frac{A_{tot}}{m_{tot}} \leftarrow \text{areal}$$
$$\leftarrow \text{masse}$$

• Spesielt tilfeller

- Sfæriske: $A_{sp} = \frac{3}{r_s}$

- Tynn stave: $A_{sp} = \frac{2}{r_c}$

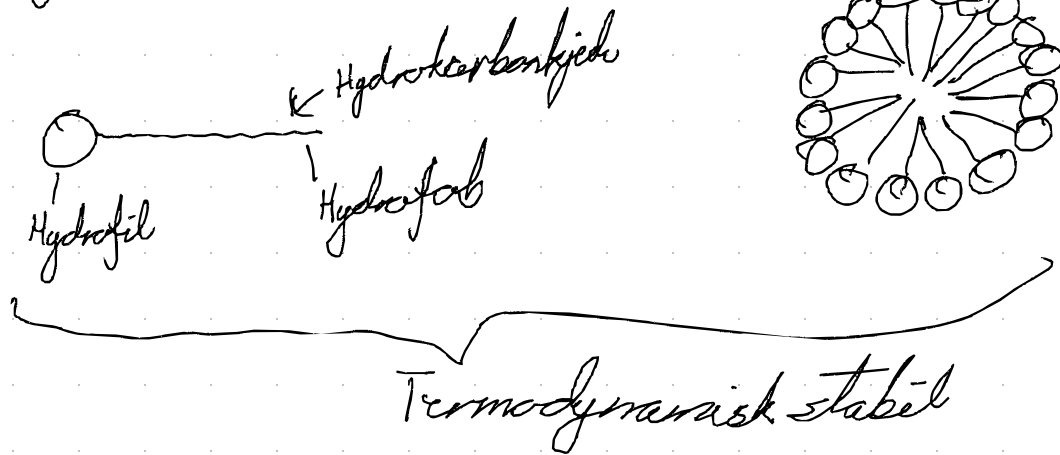
- Flat disk: $A_{sp} = \frac{3}{2 \cdot L}$

Kolloidale systemers stabilitet

- Termodynamisk eller kinetisk stabile

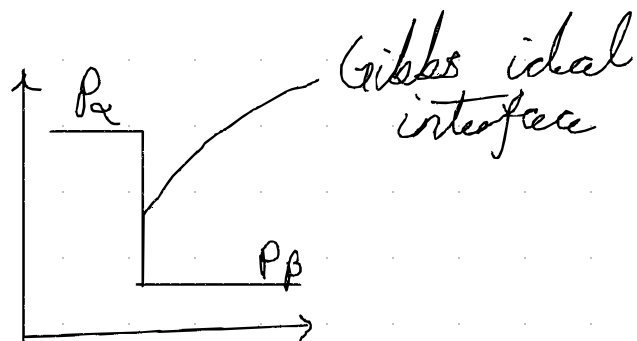
10. Jan

Emulsjon: Ser uniform et makra men ikke mikro
Surfaktanter



Tidser kinetisk stabil systemer bruker fordi de er skitt
avhenger av kinetikk.

Termodynamisk stabile systemer vil ikke skilles ved fase
og de vil formis spontant.



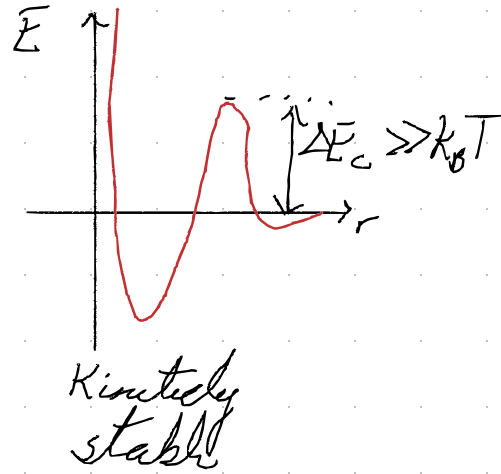
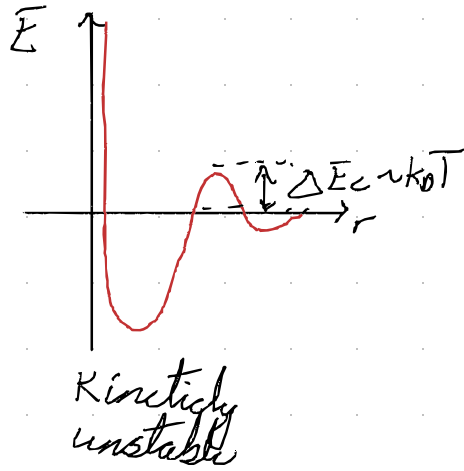
Spesifikt overflate areal

$$A_{sp} = \frac{A_{tot}}{m_{tot}}$$

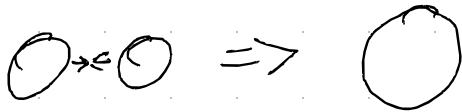
Brownisk beergelse:

Dråper som keng seg pga T.

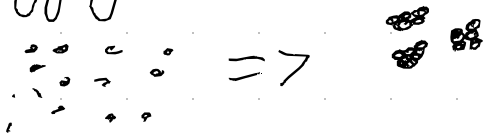
14. Jan



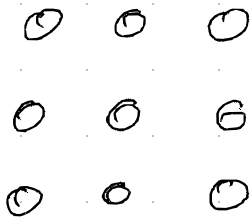
Coalescens



Aggregation (Koagulierung)



Monodispersed



Polydispersed



Particle size

Average diameter

$$\bar{d}_n = \frac{\sum n_i d_i}{\sum n_i} \quad \text{number average diameter}$$

Total area of spherical particles

$$A_{\text{tot}} = \sum n_i (\pi d_i^2)$$

Average area per particle

$$\bar{A} = \frac{\sum n_i (\pi d_i^2)}{\sum n_i}$$

$$= \pi \bar{d}_s^2 \quad \leftarrow \text{surface average diameter}$$

Volume

$$V_{\text{tot}} = \sum n_i \left(\frac{4}{3} \pi \left(\frac{d_i}{2} \right)^3 \right) = \bar{V} = \frac{\pi}{6} \frac{\sum n_i d_i^3}{\sum n_i}$$

$$\bar{d}_v = \left(\frac{6\bar{V}}{\pi} \right)^{1/3} = \left(\frac{\sum n_i d_i^3}{\sum n_i} \right)^{1/3}$$

$\begin{matrix} n \\ s \\ v \end{matrix} \left| \begin{matrix} \text{number} \\ \text{surface} \\ \text{volume} \end{matrix} \right. \left. \vphantom{\begin{matrix} n \\ s \\ v \end{matrix}} \right\} \text{if monodispersed} \\ \bar{d}_n = \bar{d}_v = \bar{d}_s$

2 Intermolekylære og interpartikkelkrefter

- Krefter mellom molekyler (i vakuum)
- Oppskallet til krefter mellom kolloidal partikler i vakuum
- Regn med løsemiddel

Intermolekylære krefter

Total energi hos molekyler:

- Kinetisk energi (proporsjonal med $k_B T$)
- Potensial energi (avhenger av posisjon og krefter)

Nyttig representasjon av intermolekylære krefter

$$F(r) = - \frac{dV(r)}{dr}$$

Tiltrukende

Potensial energi ($f(\text{avstand})$)

Forskjellige intermolekylære krefter:

Coulombiske krefter $100-600 \text{ kJ/mol}$

Hydrogenbindinger $10-40 \text{ kJ/mol}$

Van der Waals krefter $< 1 \text{ kJ/mol}$

Kovalente bindinger $150-900 \text{ kJ/mol}$

Van der Waals krefter - molekylært opphav

Tiltrukende krefter kommer fra induerte eller permanente dipoler i atomer/molekyl

3 bidrag

1.) **Polar** (Keesom) interaksjoner (permanent-permanent)

$$V_{12}^P = -\frac{1}{3} \left[\frac{\mu_1^2 \mu_2^2}{k_B T (4\pi\epsilon_0)^2} \right] r^{-6}$$

2.) **Indusert** (Debye) interaksjoner (permanent-indusert)

$$V_{12}^{ind} = - \left[\frac{\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2}{(4\pi\epsilon_0)^2} \right] r^{-6}$$

Den permanente dipolen i det ene molekylt inducerer en dipol i det andre molekylt

3.) **Dispersjons** (London) interaksjoner (indusert-indusert)

$$V_{12}^{disp} = - \left[\frac{3\alpha_1 \alpha_2}{2(4\pi\epsilon_0)^2} \right] \left[\frac{I_1 I_2}{I_1 + I_2} \right] r^{-6}$$

Ikke behov for permanente dipoler for at tiltrukning skal skje.

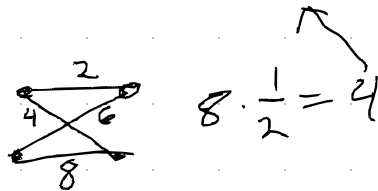
Dispersjons krefter er alltid tilstede.

Netto VdW interaksjoner

$$\begin{aligned} V_{12} &= V_{12}^P + V_{12}^{ind} + V_{12}^{disp} \\ &= -C_{12} r^{-6} \end{aligned}$$

21. Jan

$$dV_4(a) = - \underbrace{C r^{-6}}_{\text{Interactions per pair}} \underbrace{\left(\frac{1}{2} \left(\frac{8N_A}{M} \right)^2 d\mathbf{r}_1 d\mathbf{r}_2 \right)}_{\text{Number of pairwise interactions}}$$



$$\Delta V = V_{11} + V_{22} - 2V_{12}$$

Hamaker konstant A_{ijk} : interaksjoner mellom i og k i medium j

$$A_{12} \propto (A_{11} A_{22})^{1/2}$$

2 Intermolekylære og interpartikulære krefter

- Alle grovstatiske fenomener er påvirket av krefter som er fra interaksjoner på molekylært nivå

Intermolekylære krefter:

- Total energi til et molekyl

- Kinetisk: $\propto k_B T$
- Potensiell:

- Beskrivelse av intermolekylære/interpartikulære krefter

$$F(r) = -\frac{dV(r)}{dr}$$

- Coulombs lov

$$F = -\frac{q_1 q_2}{4\pi r^2 \epsilon_r \epsilon_0} = -\frac{dV}{dr} \Rightarrow V_{12} = \frac{q_1 q_2}{4\pi \epsilon_r \epsilon_0 r}$$

- Intermolekylære krefter

- Coulombie: 100-600 kJ/mol
- Hydrogenbinding: 10-40 kJ/mol
- VdW krefter: < 1 kJ/mol

Van der Waals krefter

[Formle 5.15]

- Hovedsakelig tiltrekkende krefter

- Indusert fra dipoler i atomer/molekyl

- Tre typer

- 1) Polar (Keesom), Permanent-Permanent

$$V_{12}^p = -\frac{1}{3} \left[\frac{\mu_1 \mu_2}{k_B T (4\pi \epsilon_0)^2 r^6} \right]$$

- 2) Induksjon (Debye), Permanent-Indusert

$$V_{12}^{ind} = -\frac{\epsilon_0 \mu_2^2 + \alpha_2 \mu_1^2}{(4\pi \epsilon_0)^2 r^6}$$

- 3) Dispersjon (London), Indusert-Indusert

$$V_{12}^{disp} = -\left[\frac{3\alpha_1 \alpha_2}{2(4\pi \epsilon_0)^2} \right] \left[\frac{I_1 I_2}{I_1 + I_2} \right] r^{-6}$$

- Alle molekyl: dipolmoment og polariserbarhet
- Alle 3 interaksjoner kan skje mellom et molekylpar.

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

$$f_D + f_H + f_L = 1$$

- London er størst i de fleste molekyl.

VdW-krefter for et utvalg geometrier

- Kuler med radius R_s

d : interpartikulæravstand

$$V_A = -\frac{AR_s}{12d} \quad R_s \gg d$$

- Kuler med radius R_1, R_2

$$V_A = -\frac{A}{6d} \frac{R_1 R_2}{R_1 + R_2} \quad R_1, R_2 \gg d$$

$$A = \left(\frac{8N_A \pi}{M} \right)^2 C$$

Hamaker konstanten.

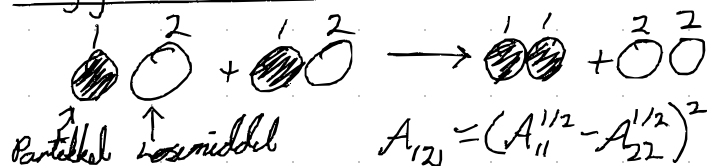
- Kule og plan

$$V_A = -\frac{AR_s}{6d}$$

VdW-krefter

- Normalt tiltrekkende
- Langdistanse
- Stark ved korte avstander.

Effekten av løsemiddel



3. Overflatespenning

Definisjoner

• Som en kraft