
Lectures 1 and 2: Fundamental Interactions in Colloid Science

Revision Time: 9/4/2023

1. Definitions of Colloids and Scope of Colloid Science

1.1 Definition

A colloid is a material that is intermediate between a single molecule and large objects that are **dominated by gravitational forces**. A Common definition of a colloid is that it is a **dispersed material in which one of its dimensions is in the range of 1-1000 nm**.

1.2 Dimensional Colloids

1D	Plates	Clays
2D	Needles	Asbestos
3D	Particles	Titania, latex

1.3 Nomenclature and Examples

Dispersed Phase	Dispersed Medium	Name	Examples
Gas	Liquid	Foam	Beer
Liquid	Liquid	Emulsion	Milk, Butter
Solid	Liquid	Dispersion	Paint, Ink
Gas	Solid	Solid foam	Pumice, Ice cream
Liquid	Solid	Solid Emulsion	Ice cream
Solid	Solid	Solid Dispersion	Opals
Liquid	Gas	Aerosol	Mist, Inhaler
Solid	Gas	Solid Aerosol	Smoke

1.4 Preparation of Colloids

Top-down	Breaking up a large lump of material by grinding milling	The average particle size of no smaller than around 1 micron
Bottom-up	Aggregation of small molecules	Hard to achieve and expensive to control Better products for advanced applications (no real limit on particle size)

1.5 Surface area

Colloids have a very high surface area, and it is the property of their surfaces rather than the bulk material that determines their properties.

2. Van der Waals attractions

2.1 Van der Waal gas law

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (1)$$

where b is to account for the finite size of the molecules and $\frac{a}{V^2}$ is to account for the attractive intermolecular forces.

2.2 Interparticle attraction

Keesom Interaction	permanent dipole --- permanent dipole
Debye Interaction	permanent dipole --- induced dipole
London Interaction	fluctuating dipole --- induced dipole (always present)

Features: long ranged, usually attractive (the only exception is the repulsive interaction between

different materials in a medium), can align molecules, influenced by the presence of other bodies nearby

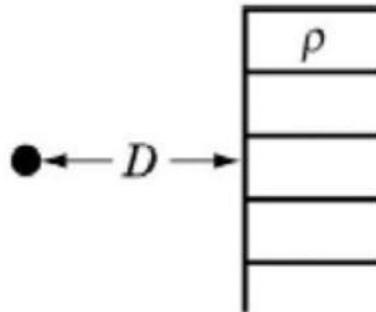
2.3 Van der Waals interactions between atoms

$$w(r) = \frac{-3\alpha_0^2 I}{4(4\pi\epsilon_0)^2 r^6} \quad (2)$$

where I is the ionization potential, α is the atomic polarizability and ϵ_0 is the permittivity of the free space.

2.4 Van der Waals interactions between macroscopic bodies: the interaction of a molecule with a surface is the sum of its interactions with all the molecules in the body

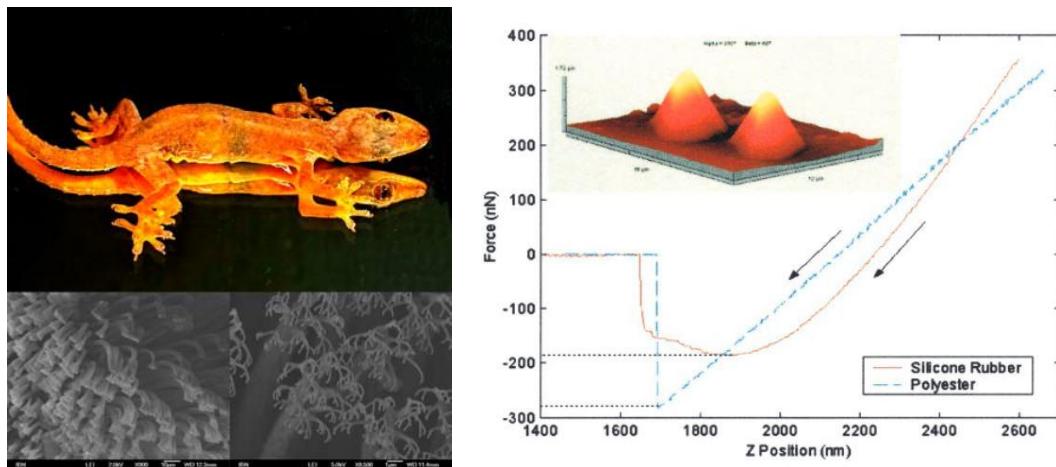
$$w(D) = \frac{-\pi C\rho}{6D^3} \quad (3)$$



$$w = -\pi C\rho / 6D^3$$

Sphere with a flat surface	$w(D) = \frac{-AR}{6D}$ (4)
Two equally sized spheres	$w(D) = \frac{-AR}{12D}$ (5)
Two parallel surfaces	$w(D) = \frac{-A}{12D^2}$ (6)
For derivations	forze-tra-oggetti.pdf (infn.it)

2.5 Short-range forces have long-range (macroscopic effects)



Scientists have proposed a van der Waals mechanism in gecko setae, suggesting that the remarkable adhesive properties are merely a result of the size and shape of the tip, and are not strongly affected by its surface chemistry.

Reference:

Evidence for van Der Waals Adhesion in Gecko Setae. *Nature* **2002**.
<https://doi.org/10.1038/news020826-2>.

Sun, W.; Neuzil, P.; Kustandi, T. S.; Oh, S.; Samper, V. D. The Nature of the Gecko Lizard Adhesive Force. *Biophysical Journal* **2005**, 89 (2), L14–L17.
<https://doi.org/10.1529/biophysj.105.065268>.

2.5 Problems with Hamaker Approach

Lifshitz theory (quantum chemistry based) treats matter as a continuum, which is often considered to be more accurate.

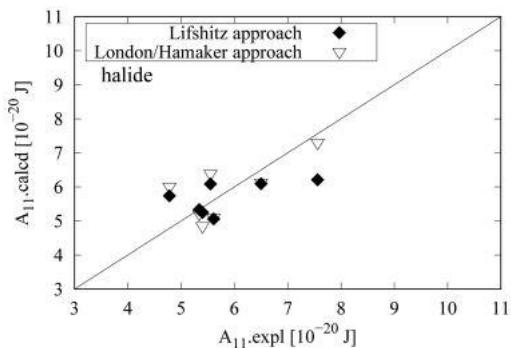
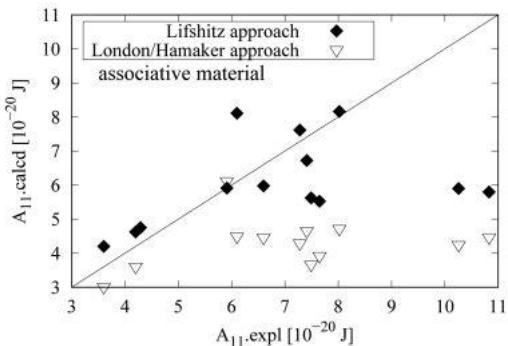
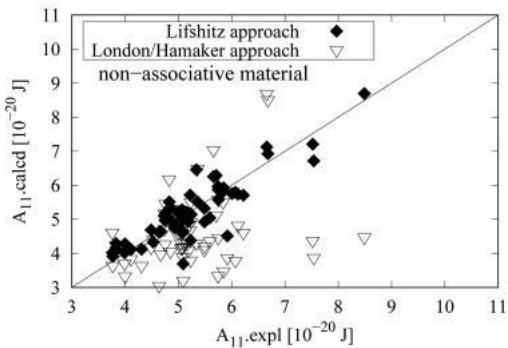
$$A_{132} = \frac{3}{4} k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3h}{4\pi} \int_{v_1}^{\infty} \left(\frac{\epsilon_1(iv) - \epsilon_3(iv)}{\epsilon_1(iv) + \epsilon_3(iv)} \right) \left(\frac{\epsilon_2(iv) - \epsilon_3(iv)}{\epsilon_2(iv) + \epsilon_3(iv)} \right) dv \quad (7)$$

London/Hamaker Approach

$$A_{11} = \pi^2 C_6 \rho^2 \quad (8)$$

$$C_6 = \frac{3}{4\alpha^2 I} \quad (9)$$

Comparison between approaches: Assumption for London approach is interaction between fluctuating dipoles is instantaneous. OK is atoms are close but not when further away



 Reference:

Takagishi, H.; Masuda, T.; Shimoda, T.; Maezono, R.; Hongo, K. Method for the Calculation of the Hamaker Constants of Organic Materials by the Lifshitz Macroscopic Approach with Density Functional Theory. *The Journal of Physical Chemistry A* **2019**, *123* (40), 8726–8733.
<https://doi.org/10.1021/acs.jpca.9b06433>.

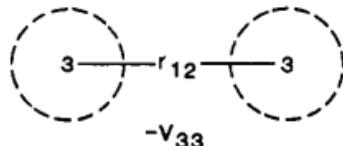
2.6 Solvent Effect

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (10)$$

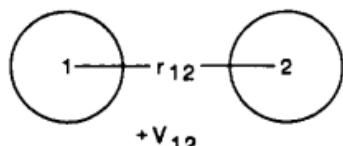
1. Break 1-3 and 2-3 interactions, with the 1-2 pairs at infinite separation.



2. Break 3-3 interaction at r_{12} separation.



3. Form 1-2 interaction at r_{12} separation.



4. Form 3-3 and 3-3 interactions at separation r_{12} , with pairs at infinite separation.



Figure 2. Energy changes accompanying the process of bringing spherical molecules 1 and 2 of equal size (solid circles) from infinite separation to separation r_{12} in solvent 3. Dashed circles are volumes of solvent equivalent in volume to molecules 1 and 2.

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

We get $A_{132} = \left(A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}} \right) \left(A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}} \right)$ (12)

It is noticed that, only when the solvent Hamaker constant is intermediate to those of the particles, A_{132} is negative, suggesting repulsive interactions.

If the particles are identical $A_{131} = (A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})^2$ (13), which is always attractive

Reference:

Vilker, V. L.; Uyeno, G. P.; McMillan, W. G. Solvent Effect on the Dispersion (Hamaker-London) Coefficient from Third-Order Perturbation Theory. *The Journal of Physical Chemistry* **1981**, *85* (14), 2013–2021. <https://doi.org/10.1021/j150614a012>.

3. Electrical Interactions

3.1 Charged Surfaces and Electrical Double Layer

3.1.1 Origination of Charged Surface

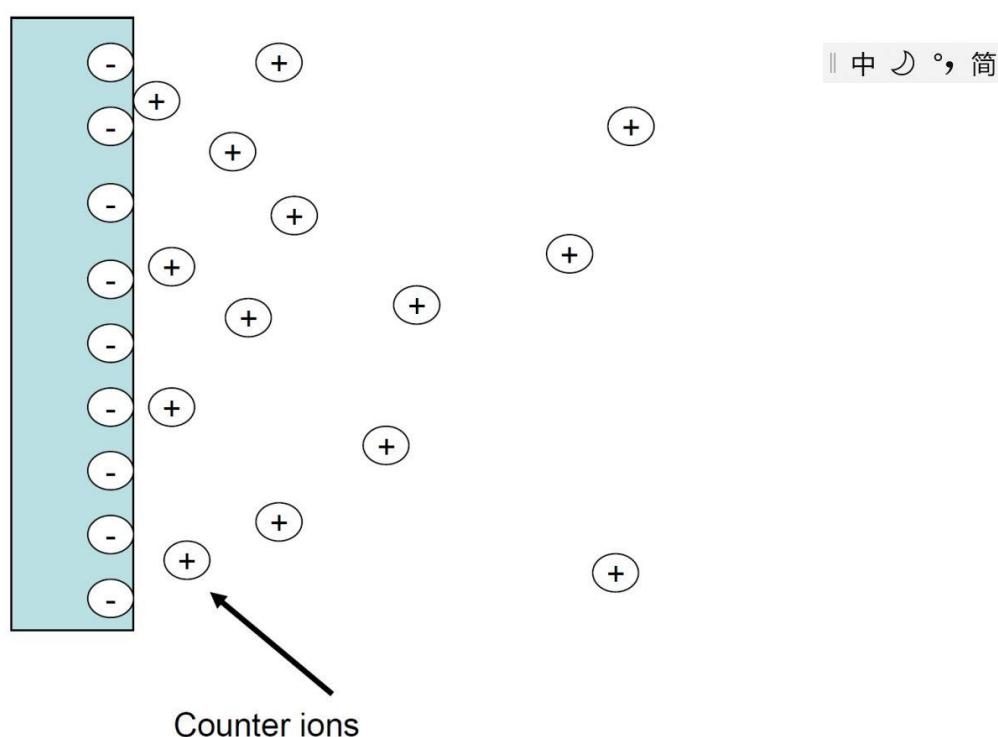
Charges can originate from 3 different sources:

- Dissolution of soluble ions, mainly metal ions, such as in clays
- Adsorption of ions to surfaces, generally anions, such as iodide in silver iodide
- Adsorption of surfactants or polyelectrolyte

3.1.2 Electrical Double Layer

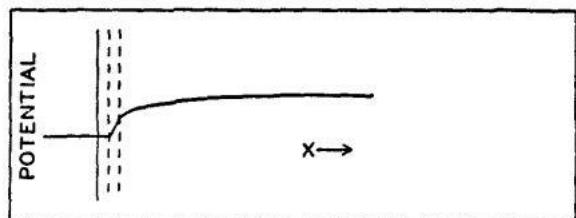
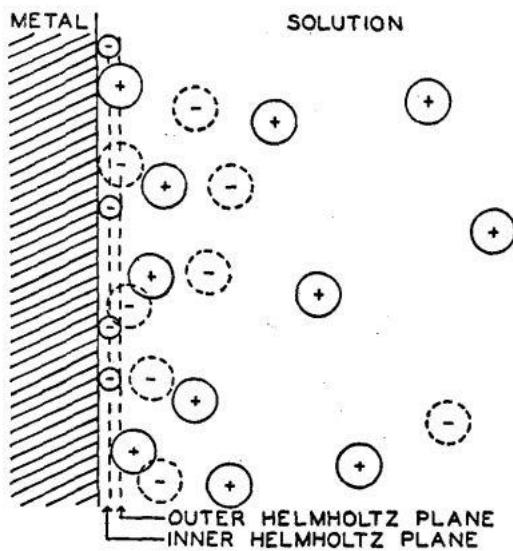
Enthalpic point of view: ions closed to the charged surface

Entropic point of view: ions far away from the charged surface

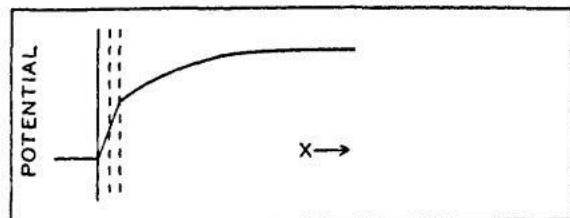
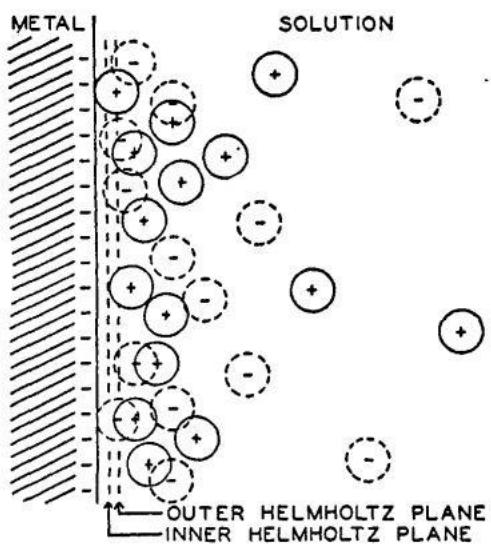


Different circumstances:

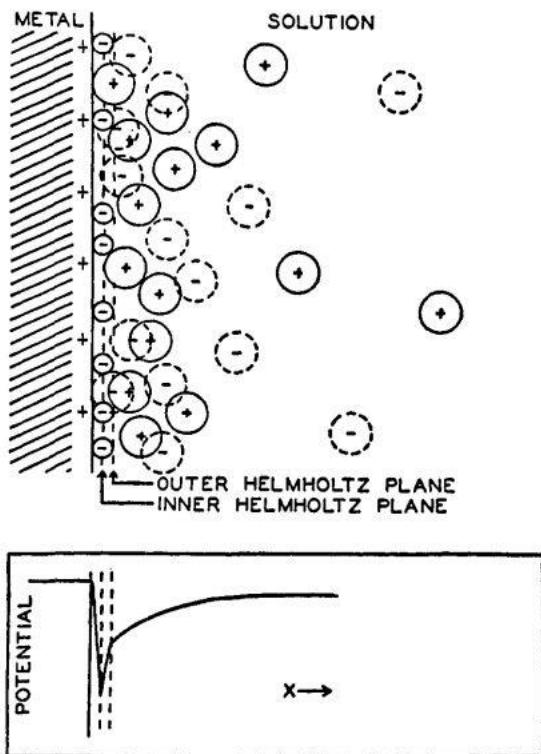
3.1.2.1 Electrical double layer at the potential of the electrocapillary maximum (*This potential, which corresponds to the maximum in the electrocapillary curve (i.e., to $\rho_s=0$), is referred to as the point of zero charge. The position of the point of zero charge is determined by the adsorption activity of ions present in solution and by the dipole moment of solvent molecules.*)



3.1.2.2 Electrical double layer with positive polarization



3.1.2.3 Electrical double layer with negative polarization



Reference:

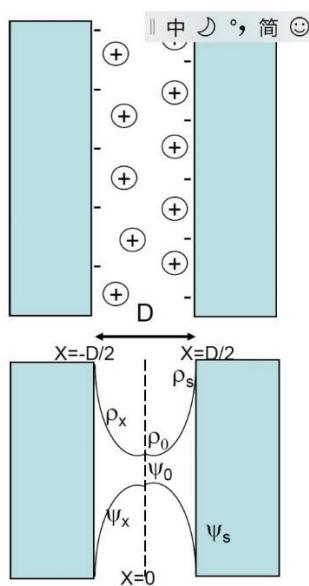
Grahame, D. C. The Electrical Double Layer and the Theory of Electrocapillarity. *Chemical Reviews* 1947, 41 (3), 441–501. <https://doi.org/10.1021/cr60130a002>.

3.1.3 Thermodynamics of Electrical Double Layer

3.1.3.1 A charged surface in water

$$\mu = ze\varphi = kT \log \rho \quad BC: \varphi_0 = 0, \frac{d\varphi}{dx} \Big|_0 = 0 \text{ when } x = 0 \quad (14)$$

where φ is the electrostatic potential, ρ is the number density of ions of valency z at any point x between two surfaces and e is the charge on an electron.



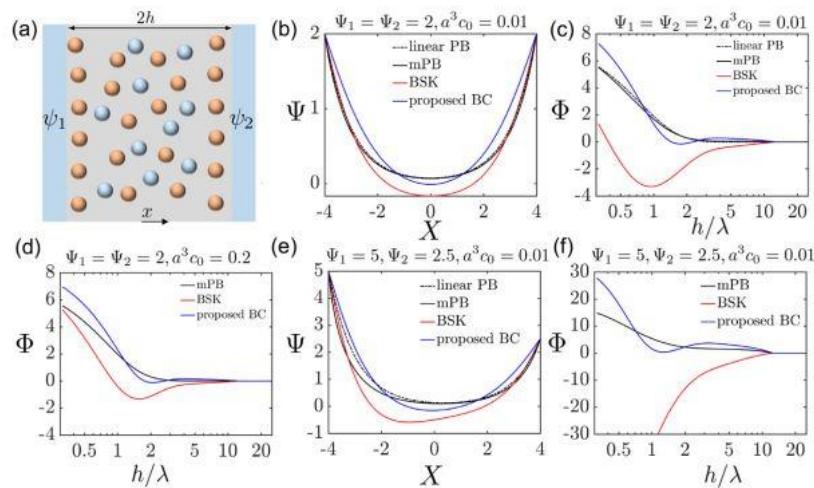
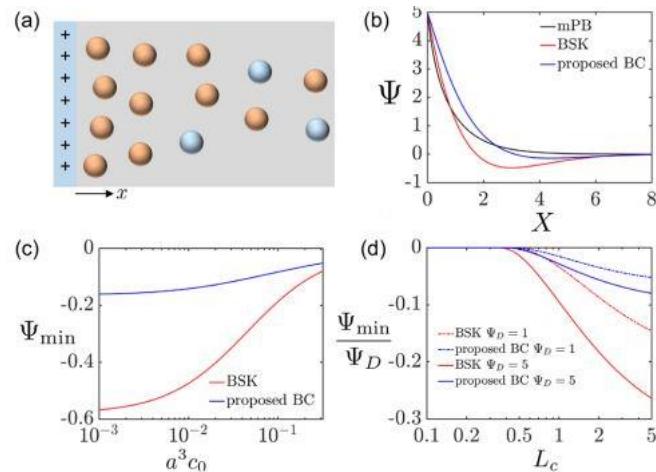
3.1.3.2 More rigorous model of electrical double layer

$$\frac{d^2\varphi}{dx^2} = \varphi \quad \text{linear PB equation} \quad (15)$$

$$-\nabla \cdot (\varepsilon \nabla \varphi) = \rho_e \quad BC: \text{at } \varphi = 0, \frac{\exp\left(-\frac{z_i e \varphi}{k_B T}\right)}{1 + \sum_i a^3 c_{i0} \left(\exp\left(-\frac{z_i e \varphi}{k_B T}\right) - 1\right)} = 1 \quad mPB \text{ equation} \quad (16)$$

$$\frac{d^2}{dX^2} \left(1 - L_c^2 \frac{d^2}{dX^2}\right) \varphi = \frac{\sinh \varphi}{1 + 4a^3 c_0 \sinh^2 \left(\frac{\varphi}{2}\right)} \quad BC: \frac{d^3 \varphi}{dX^3} \Big|_{X=0} = 0 \quad BSK \quad (17)$$

$$\frac{d^2}{dX^2} \left(1 - L_c^2 \frac{d^2}{dX^2}\right) \varphi = \frac{\sinh \varphi}{1 + 4a^3 c_0 \sinh^2 \left(\frac{\varphi}{2}\right)} \quad BC: \nabla^2 \varphi_j = 0 \quad \text{proposed BC} \quad (18)$$



Reference:

Gupta, A.; Govind Rajan, A.; Carter, E. A.; Stone, H. A. Thermodynamics of Electrical Double Layers with Electrostatic Correlations. *The Journal of Physical Chemistry C* **2020**, *124* (49), 26830–26842. <https://doi.org/10.1021/acs.jpcc.0c08554>.

3.2 Repulsive interactions

$$w(D)_{rep} = 2\kappa\varepsilon_R\varepsilon_0 R \varphi_0^2 \exp[-\kappa D] \quad (19)$$

Derivations:

Starting from (14) and the equilibrium requirement, we get Boltzmann distribution of counterions at any point x

$$\rho_x = \rho_0 e^{-ze\varphi(x)/kT} \quad (20)$$

Combined with Poisson equation (21), we get the Poisson-Boltzmann Equation

$$ze\rho_x = -\varepsilon\varepsilon_0 \frac{d^2\varphi}{dx^2} \quad (21)$$

$$\frac{d^2\varphi}{dx^2} = -\frac{ze\rho_x}{\varepsilon\varepsilon_0} = -\frac{ze\rho_0}{\varepsilon\varepsilon_0} e^{-\frac{ze\varphi(x)}{kT}} \quad (22)$$

If we consider the presence of electrolyte and redefine $x=0$ at the surface rather than the middle plane, we can modify (20)-(22) to (23)-(25)

$$\rho_{xi} = \rho_{\infty i} e^{-\frac{ze\varphi(x)}{kT}} \quad (23)$$

$$\rho_{0i} = \rho_{\infty i} e^{-\frac{ze\varphi(0)}{kT}} \quad (24)$$

$$ze\rho_{xi} = -\varepsilon\varepsilon_0 \frac{d^2\varphi}{dx^2} \quad (25)$$

$$\frac{d^2\varphi}{dx^2} = -\frac{1}{\varepsilon\varepsilon_0} \sum_i ze\rho_{\infty i} e^{-\frac{ze\varphi(x)}{kT}} \quad (26)$$

Then we apply the Debye-Hückel approximation (27)(28) to simplify (26)

$$\exp(x) = 1 + x + \frac{2x}{2!} + \frac{3x}{3!} + \dots \quad (27)$$

$$\text{when } ze\varphi \ll kT, \exp(x) \cong 1 + x \quad (28)$$

$$\frac{d^2\varphi}{dx^2} = -\frac{1}{\varepsilon\varepsilon_0} \sum_i ze\rho_{\infty i} \left(1 - \frac{ze\varphi(x)}{kT}\right) \quad (29)$$

Then apply the electro-neutrality condition (30), which eventually simplifies (29) to (32)

$$\sum_i ze\rho_{\infty i} = 0 \quad (30)$$

$$\frac{d^2\varphi}{dx^2} = \frac{\varphi}{\varepsilon\varepsilon_0 kT} \sum_i (ze)^2 \rho_{\infty i} \quad (31)$$

$$\frac{d^2\varphi}{dx^2} = \kappa^2 \varphi, \text{ where } \kappa^2 = \frac{\sum_i (ze)^2 \rho_{\infty i}}{\varepsilon\varepsilon_0 kT} \quad (32)$$

Solving (32) with boundary conditions (33) gives (34)

$$\text{BC: } \varphi \rightarrow \varphi_0 \text{ at } x = 0; \varphi \rightarrow 0 \text{ at } x = \infty \quad (33)$$

$$\varphi(x) = \varphi_0 e^{-\kappa x} \quad (34)$$

It is noticed that $1/\kappa$ is defined as the Debye Screening length or the thickness of the electrical double layer. It is dependent on the electrolyte concentration (decreases with increasing electrolyte concentration).

Then, we consider the repulsive potential between two charged surfaces. It has two origins: the electrical field emanating from the charged surfaces (35) and osmotic pressure difference (36).

$$F_{el} = \rho \frac{d\varphi}{dx} = 0 \quad \text{at midpoint} \quad (35)$$

$$\Pi_{osm} = \rho kT = kT \sum_i (\rho_i^{mid} - \rho_i^{bulk}) \quad (36)$$

Substituting (23)(24) into (36) and rearrange (*Both anions and cations are present in the electrolyte*)

$$\Pi_{osm} = \rho_{\infty i} kT \left(e^{-\frac{ze\varphi(\frac{D}{2})}{kT}} + e^{\frac{ze\varphi(\frac{D}{2})}{kT}} - 2 \right) = 2\rho_{\infty i} kT \left[\cosh\left(\frac{ze\varphi(\frac{D}{2})}{kT}\right) - 1 \right] \quad (37)$$

Then we simplify (37) by expanding $\cosh(x)$ as a power series (38)(39)

$$\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots \quad (38)$$

$$\text{when } ze\varphi \ll kT, \cosh(x) \cong 1 + \frac{x^2}{2!} \quad (39)$$

$$\Pi_{osm} = \rho_{\infty i} kT \left(\frac{ze\varphi(\frac{D}{2})}{kT} \right)^2 = \rho_{0i} kT \left(\frac{ze\varphi(\frac{D}{2})}{kT} \right)^2 \quad (40)$$

Substituting the definition of κ and calculating $\varphi\left(\frac{D}{2}\right)$ using (34), we achieve (41)(42)

$$\Pi_{osm} = \frac{\kappa^2 \varepsilon \varepsilon_0}{2} \left[\varphi\left(\frac{D}{2}\right) \right]^2 \quad (41)$$

$$\Pi_{osm} = 2\kappa^2 \varepsilon \varepsilon_0 \varphi_0^2 \exp(-\kappa D) \quad (42)$$

The interaction energy can then be determined by integrating (42) with respect to x

$$w(D)_{rep} = - \int \Pi_{osm} dx \quad (43)$$

$$w(D)_{rep} = 2\kappa \varepsilon \varepsilon_0 \varphi_0^2 \exp(-\kappa D) \quad (44)$$

If the geometry is spherical (with radius R), (44) can be modified by introducing a geometric factor

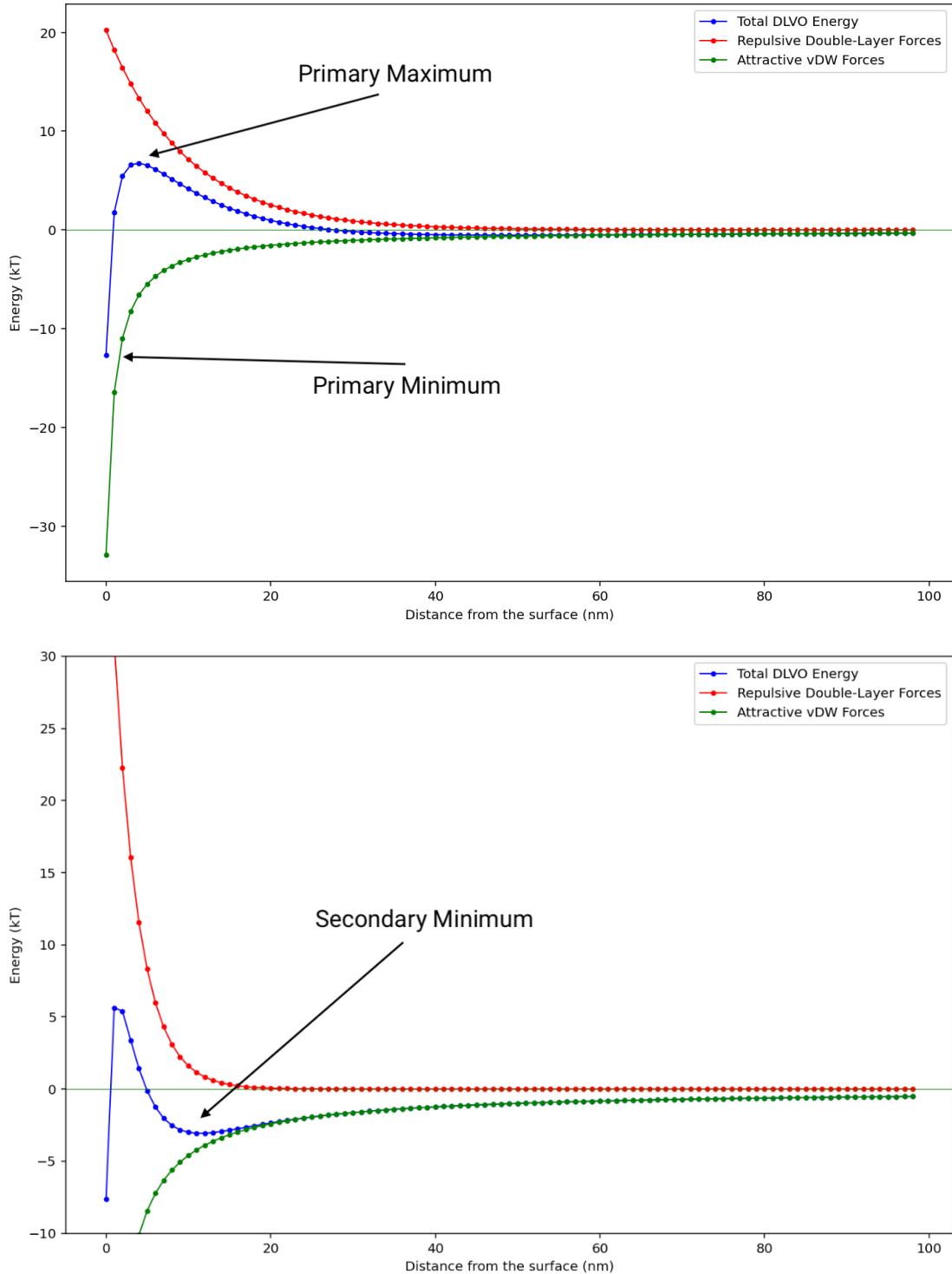
$$w(D)_{rep} = 2\pi \varepsilon \varepsilon_0 R \varphi_0^2 \exp(-\kappa D) \quad (45)$$

3.3 DLVO theory

Combining (45) with (5), the total interaction between charged particles is achieved

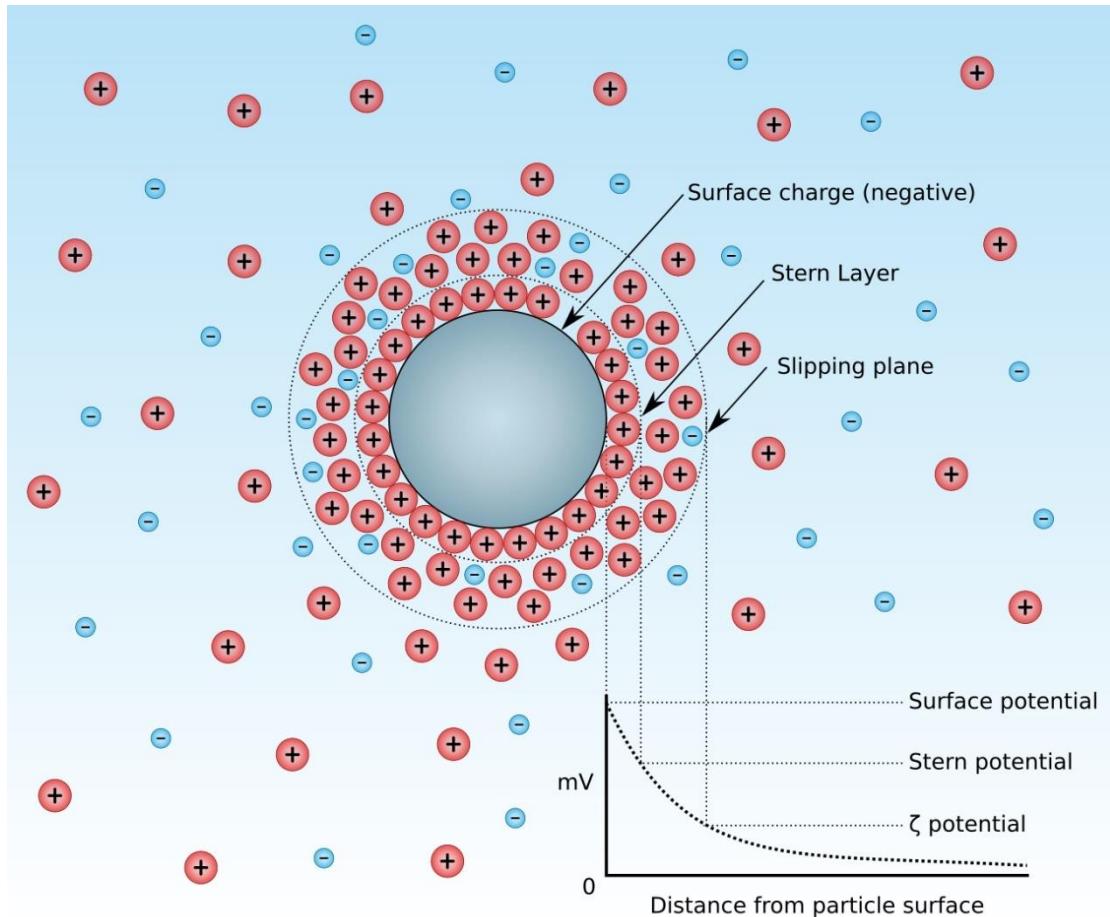
$$w(D)_{tot} = -\frac{AR}{12D} + 2\kappa \varepsilon \varepsilon_0 R \varphi_0^2 \exp(-\kappa D) \quad (46)$$

The key features for DLVO theory are a primary minimum and a primary maximum. In flocculation systems, a secondary minimum will appear. DLVO only explicitly accounts for repulsive forces related to the ion double-layer and attractive van der Waals forces, but ultimately for nothing else. Any corrections to this, such as H-bonding, cavitation, Lewis acid/base considerations, polyelectrolyte solutions, hydrophobicity, stabilizing polymers/steric stabilization are all considered additions to DLVO.



3.4 Zeta Potential

With everything we've done so far, there is one fundamental issue. We can't actually measure φ_0 . What we can measure instead is the zeta potential, that is, the potential at the slipping plane, which is the boundary between the EDL and the bulk. Since this is most extreme part of the EDL, it will represent the point that can interact with its surrounding.



3.4.1 Electrokinetic Phenomena

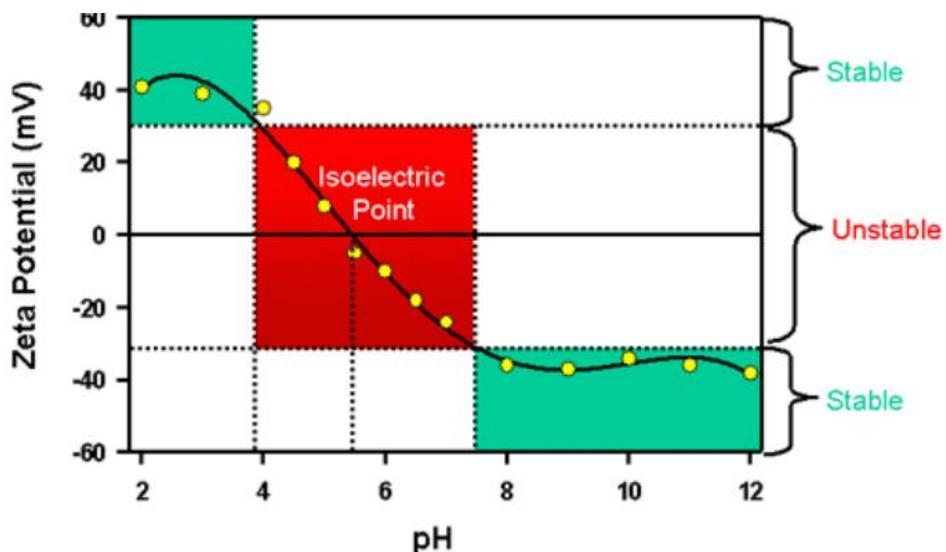
The zeta potential is linked with the electrophoretic mobility in the following way

$$u_E = \frac{v}{E} = \frac{4\pi\epsilon\epsilon_0\xi}{\eta} f(\kappa R) \quad (47)$$

$$f(\kappa R) = \begin{cases} 1.5 & \text{for large particles and high electrolyte} \\ 1 & \text{for small particles and dilute electrolyte} \end{cases} \quad (48)$$

3.4.2 Influencing Factor

The zeta potential is greatly influenced by the pH, as illustrated below.



References:

TECHNICAL NOTE. <https://www.research.colostate.edu/wp-content/uploads/2018/11/ZetaPotential-Introduction-in-30min-Malvern.pdf>.

Snow, A. *Zeta Potential (\$\zeta\$) - Adrea's Notebook and Journal.* Adreasnow.com. <https://adreasnow.com/Undergrad/Notes/Sem%20Surface%20and%20Colloids/Colloids/04a/#implications> (accessed 2023-04-11).

4. Brownian Motion and Sedimentation

4.1 Brownian Motion

$$x = \langle \langle x^2 \rangle \rangle^{1/2} = (2Dt)^{1/2} = \left(\frac{kT}{3\pi\eta R} t \right)^{1/2} \quad (49)$$

4.2 Sedimentation

$$x = \left(\frac{2R^2 \Delta \rho g}{9\eta} \right) t \quad (50)$$

5. Sample Problems and Solutions

5.1 Spherical colloidal particles of radius 30 nm, 300 nm, 3,000nm and 30,000nm and density 2000 kg.m⁻³ are suspended in water (temperature 25°C, density 1000 kg.m⁻³ viscosity 1.0·10⁻³ Pa.s). Calculate the average distance from the origin along a given axis travelled by a particle in 1 minute due to Brownian motion and sedimentation, respectively. Comment on the results and which particles would you expect to settle, given sufficient time

Solutions:

For Brownian motion and particle size of 30nm:

$$x = \left(\frac{kT}{3\pi\eta R} t \right)^{1/2} = \left(\frac{1.38 \times 10^{-23} \times (273 + 25)}{3\pi \times 1 \times 10^{-3} \times 30 \times 10^{-9}} \times 60 \right)^{0.5} = 2.95 \times 10^{-5} m$$

With the other parameters remaining the same, we find

$$x \propto \left(\frac{1}{R} \right)^{0.5}$$

Therefore

$$x = 2.95 \times 10^{-5} \times \left(\frac{1}{10} \right)^{0.5} = 9.33 \times 10^{-6} m \quad \text{for } R = 300 nm$$

$$x = 2.95 \times 10^{-5} \times \left(\frac{1}{100} \right)^{0.5} = 2.95 \times 10^{-6} m \quad \text{for } R = 3000 nm$$

$$x = 2.95 \times 10^{-5} \times \left(\frac{1}{1000} \right)^{0.5} = 9.33 \times 10^{-7} m \quad \text{for } R = 30000 nm$$

For Sedimentation and particle size of 30nm:

$$x = \left(\frac{2R^2 \Delta \rho g}{9\eta} \right) t = \frac{2 \times (30 \times 10^{-9})^2 \times (2000 - 1000) \times 9.81}{9 \times 1 \times 10^{-3}} \times 60 = 1.18 \times 10^{-7} m$$

With the other parameters remaining the same, we find

$$x \propto R^2$$

Therefore

$$x = 1.18 \times 10^{-7} \times 10^2 = 1.18 \times 10^{-5} m \quad \text{for } R = 300 nm$$

$$x = 1.18 \times 10^{-7} \times 100^2 = 1.18 \times 10^{-3} m \quad \text{for } R = 3000 nm$$

$$x = 1.18 \times 10^{-7} \times 1000^2 = 1.18 \times 10^{-1} m \quad \text{for } R = 30000 nm$$

Considering the difference in sedimentation velocity, where larger the particle size, greater the sedimentation velocity. It can be concluded that, given sufficient long time (that is reasonable), particles with size equal or greater than 300nm will eventually settle.

5.2 In an aqueous solution at 25°C the thickness of the double layer $1/\kappa$ surrounding a charged colloid was determined to be 3 nm. What is the electrolyte concentration, if the electrolyte was a 1-1, 2-2, or 3-3 electrolyte, respectively. Compare the stability of these three solutions under the assumption that there are only electrostatic interactions.

Recall the definition of κ

$$\kappa^2 = \frac{\sum_i (ze)^2 \rho_{\infty i}}{\epsilon \epsilon_0 kT}$$

Here we do not need to know the exact value of every parameter, since the combination of them gives characteristic numbers (which is valid at 298K)

$$\kappa \text{ (in nm}^{-1}) = \frac{z^2 c}{0.3 nm} \quad \text{where } c = \frac{\rho}{N_A} \text{ in M}$$

Rearrange

$$c = \frac{0.3 \times \kappa}{z^2} = \frac{0.3}{z^2 \left(\frac{1}{\kappa}\right)} = 0.1 M \quad \text{for 1 - 1 electrolyte}$$

$$c = \frac{0.3 \times \kappa}{z^2} = \frac{0.3}{z^2 \left(\frac{1}{\kappa}\right)} = 0.025 M \quad \text{for 2 - 2 electrolyte}$$

$$c = \frac{0.3 \times \kappa}{z^2} = \frac{0.3}{z^2 \left(\frac{1}{\kappa}\right)} = 0.011 M \quad \text{for 3 - 3 electrolyte}$$

Since the double layer thicknesses are the same, the stability should also be the same. This can be validated using the expression for electrostatic interactions, where z plays no role.

$$w(D)_{rep} = 2\pi\epsilon\epsilon_0 R\varphi_0^2 \exp(-\kappa D)$$

5.3 Spherical colloidal particles of radius 5 nm (effective Hamaker constant

$A = 12 kT$, surface potential $\varphi_0 = 75$ mV) are dispersed in 0.01 mol dm⁻³ aqueous 1-1 electrolyte at 25°C. Sketch the DLVO potential and its constituting potentials (Especially in the region of a few nm) and comment on its stability.

Assume that the electrical double layer interaction can be given by the expression

$$w(D)_{rep} = 2\pi\epsilon\epsilon_0 R\varphi_0^2 \exp(-\kappa D)$$

For attractive forces, we can use

$$w(D)_{att} = \frac{-AR}{12D} = -\frac{5}{D}$$

For repulsive forces, we can use

$$w(D)_{rep} = 2\pi\epsilon\epsilon_0 R\varphi_0^2 \exp(-\kappa D)$$

where

$$\kappa = \frac{z^2 c}{0.3 nm} = \frac{1^2 \times 0.01}{0.3} = 0.033 nm^{-1}$$

In water $\varepsilon \varepsilon_0 = 78.54 \times 8.854 \times 10^{-12} \text{ C} \cdot (\text{V} \cdot \text{m})^{-1}$

Therefore

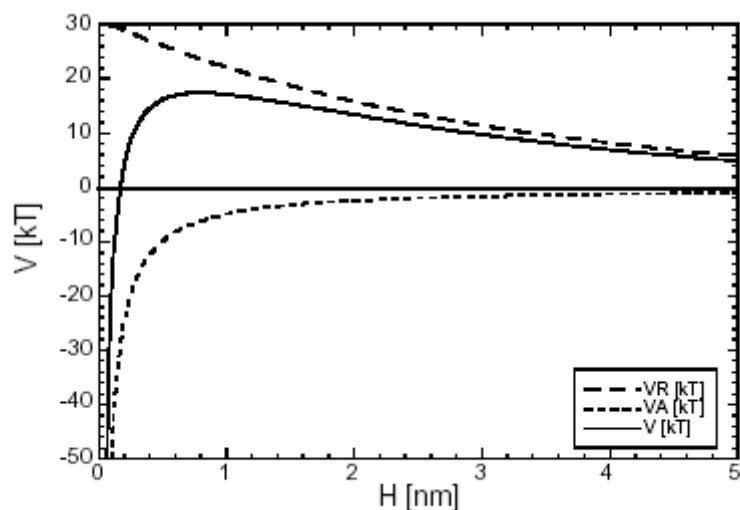
$$\begin{aligned} w(D)_{rep} &= 2\pi\varepsilon\varepsilon_0 R\varphi_0^2 \exp(-\kappa D) \\ &= 2 \times 3.14 \times 78.54 \times 8.854 \times 10^{-12} \times 5 \times 10^{-9} \times (75 \times 10^{-3})^2 \\ &\quad \times \exp(-0.033 \times D) \end{aligned}$$

If we convert the energy unit to kT ($kT = 4.11 \times 10^{-21} \text{ J}$), we get

$$w(D)_{rep} = 29.9 \times \exp(-0.033 \times D)$$

The total energy, according to DLVO theory, is the sum of $w(D)_{att}$ and $w(D)_{rep}$.

distance of surfaces H	$V_R [kT]$	$V_A [kT]$	$V [kT]$
0.1 nm	29.8	-50.0	-20.2
0.5 nm	26.1	-10.0	16.1
1 nm	22.1	-5.00	17.1
2 nm	15.8	-2.50	13.3
3 nm	11.3	-1.67	9.63
4 nm	8.12	-1.25	6.87
5 nm	5.82	-1.00	4.82



Lecture 3: The effect of polymers on particle interactions

Revision Time: 2023/4/12

1. Polymer properties

A polymer is a molecule compromised of many similar units. Unlike simple molecules, polymers do not have a unique length or molecular weight.

1.1 Polymer length

$\langle r^2 \rangle^{1/2}$	The root mean square end to end distance
$\langle s^2 \rangle^{1/2}$	The root mean square distance of the elements of the chain from its center of gravity, also known as the radius of gyration

Considering a simple polymer consists of a series of x links of length l , joined in a linear sequence with no restrictions on bond angle, we have

$$\langle r^2 \rangle^{1/2} = \langle 6s^2 \rangle^{1/2} \quad (1)$$

$$\langle r^2 \rangle^{1/2} = lx^{1/2} \quad (2)$$

The polymer length is usually considered to be proportional to the square root of its molecular weight

$$\langle r^2 \rangle^{1/2} \propto M^{1/2} \quad (3)$$

1.2 Polymer molecular weight

The molecular weight of polymer can be defined as number average molecular weight (osmotic pressure) and weight average molecular weight (light scattering), as shown in (4) and (5) respectively.

$$M_N = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad (4)$$

$$M_w = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i n_i M_i}{\sum_i n_i M_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \quad (5)$$

where n_i and w_i are the number and weight fractions respectively.

It is worth noticing that $M_w \geq M_N$ always holds.

2. Thermodynamics of polymers

2.1 Thermodynamics of simple liquid mixtures

$$\Delta G_A = kT \ln \frac{p_A}{p_A^0} \quad (6)$$

If the solution can be assumed as an ideal solution (where the molecules of component A and B have roughly the same size, shape and interactions), Raoult's Law is obeyed and (6) can be simplified.

$$\Delta G_A = kT \ln(n_A) \quad (7)$$

2.2 Thermodynamics of mixing

2.2.1 Ideal mixing

$$\Delta G = N_A \Delta G_A + N_B \Delta G_B = kT(N_A \ln(n_A) + N_B \ln(n_B)) \quad (8)$$

$$\Delta H = 0 \quad (9)$$

$$\Delta S = -k(N_A \ln(n_A) + N_B \ln(n_B)) \quad (10)$$

It can be seen that for ideal mixing $\Delta G < 0$ and $\Delta S > 0$. Therefore, by 2nd law, we concluded that spontaneous mixing occurs in all proportions.

2.2.2 Other types of mixing

Athermal Solutions	$\Delta H = 0, \Delta S \text{ non ideal}$
--------------------	--

Regular Solutions	$\Delta H \neq 0, \Delta S \text{ ideal}$
Irregular Solutions	$\Delta H \neq 0, \Delta S \text{ non ideal}$

2.2.3 Entropy of the polymer

$$\Delta S = -k(N_A \ln(\Phi_A) + N_B \ln(\Phi_B)) \quad (11)$$

where Φ_A and Φ_B is the volume fraction of solvent and polymer, respectively.

2.2.4 Deviation from ideal solutions

In ideal solutions, we assume all intermolecular interactions in a solution are the same, which is highly unlikely in reality. Therefore, we introduce a new parameter ($\Delta\epsilon$) to account for the difference between like-unlike and like-like molecular interactions.

$$\Delta\epsilon = \epsilon_{A,B} - \frac{(\epsilon_{A,A} + \epsilon_{B,B})}{2} \quad (12)$$

And accordingly, the enthalpy of mixing is modified as

$$\Delta H_{mix} = zN_A n_B \Delta\epsilon \quad (13)$$

$$\chi = \frac{z\Delta\epsilon}{kT} \quad (14)$$

$$\Delta H_{mix} = kTN_A n_B \chi \quad (15)$$

For polymer solutions, similar to (11), we replace n_B with Φ_B

$$\Delta H_{mix} = kTN_A \Delta H_{mix} = kTN_A \Phi_B \chi \quad (16)$$

It is noticed that, as long as χ is positive (which is always true), the enthalpy of mixing is positive, suggesting that mixing is unfavorable enthalpically. Combing (16) with (11), we have

$$\Delta G = kT(N_A \ln(\Phi_A) + N_B \ln(\Phi_B) + N_A \Phi_B \chi) \quad (17)$$

If the temperature is decreased, we expect the favorable entropy term to have less contribution to the ΔG , leading to phase separation. However, this is in general not true for water soluble polymers.

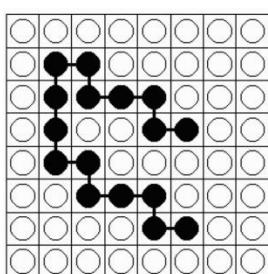
2.2.5 Flory-Huggins theory

We define n as a degree of polymerization, where a segment is said to be equal to the size of the solvent molecule. Here, we can link Φ_i with N_i .

$$\Phi_A = \frac{N_A}{N_A + nN_B} \quad (18)$$

$$\Phi_B = \frac{nN_B}{N_A + nN_B} \quad (19)$$

In the example below, $n = 16, N_A = 48, N_B = 1$. Accordingly, we can calculate $\Phi_A = 0.75$ and $\Phi_B = 0.25$, which agrees with the definition of volume fraction.



2.2.6 Water soluble polymers

In water soluble polymers, hydrogen bonding plays a critical role. Hydrogen bonding decreases as temperature increases, where χ is temperature dependent.

2.2.7 Change in chemical potentials

To derive the change in chemical potentials, we must first calculate the derivative of Φ_A and Φ_B with respect to N_A

$$\frac{d\Phi_A}{dN_A} = \frac{(N_A + nN_B) - N_A}{(N_A + nN_B)^2} = \frac{nN_B}{(N_A + nN_B)^2} = \frac{\Phi_A \Phi_B}{N_A} \quad (20)$$

$$\frac{d\Phi_B}{dN_A} = \frac{0 - nN_B}{(N_A + nN_B)^2} = \frac{-nN_B}{(N_A + nN_B)^2} = \frac{-\Phi_A \Phi_B}{N_A} \quad (21)$$

Then recall the definition of change in chemical potential

$$\Delta\mu = \left. \frac{d\Delta G}{dN_A} \right|_{N_B} = kT \left(\ln(\Phi_A) + N_A \frac{d\ln(\Phi_A)}{d\Phi_A} \frac{d\Phi_A}{dN_A} + N_B \frac{d\ln(\Phi_B)}{d\Phi_B} \frac{d\Phi_B}{dN_A} + \Phi_B \chi + N_A \chi \frac{d\Phi_B}{dN_A} \right) \quad (22)$$

Substituting (20) and (21) to (22)

$$\Delta\mu = kT \left(\ln(\Phi_A) + \Phi_B - \frac{N_B \Phi_A}{N_A} + \Phi_B \chi - \chi \Phi_A \Phi_B \right) \quad (23)$$

Rearranging

$$\Phi_B - \frac{N_B \Phi_A}{N_A} = \Phi_B - \frac{1}{n} \Phi_B = \left(1 - \frac{1}{n}\right) \Phi_B \quad (24)$$

$$\Phi_B \chi - \chi \Phi_A \Phi_B = \left(\frac{nN_B(N_A + nN_B)}{(N_A + nN_B)^2} - \frac{nN_A N_B}{(N_A + nN_B)^2} \right) \chi = \Phi_B^2 \chi \quad (25)$$

Substituting (24) and (25) to (23)

$$\Delta\mu = kT \left(\ln(\Phi_A) + \left(1 - \frac{1}{n}\right) \Phi_B + \Phi_B^2 \chi \right) \quad (26)$$

Apply Taylor series expansion of $\ln(1 - x)$

$$\ln(1 - x) = -x - \frac{1}{2}x^2 + \dots \quad (27)$$

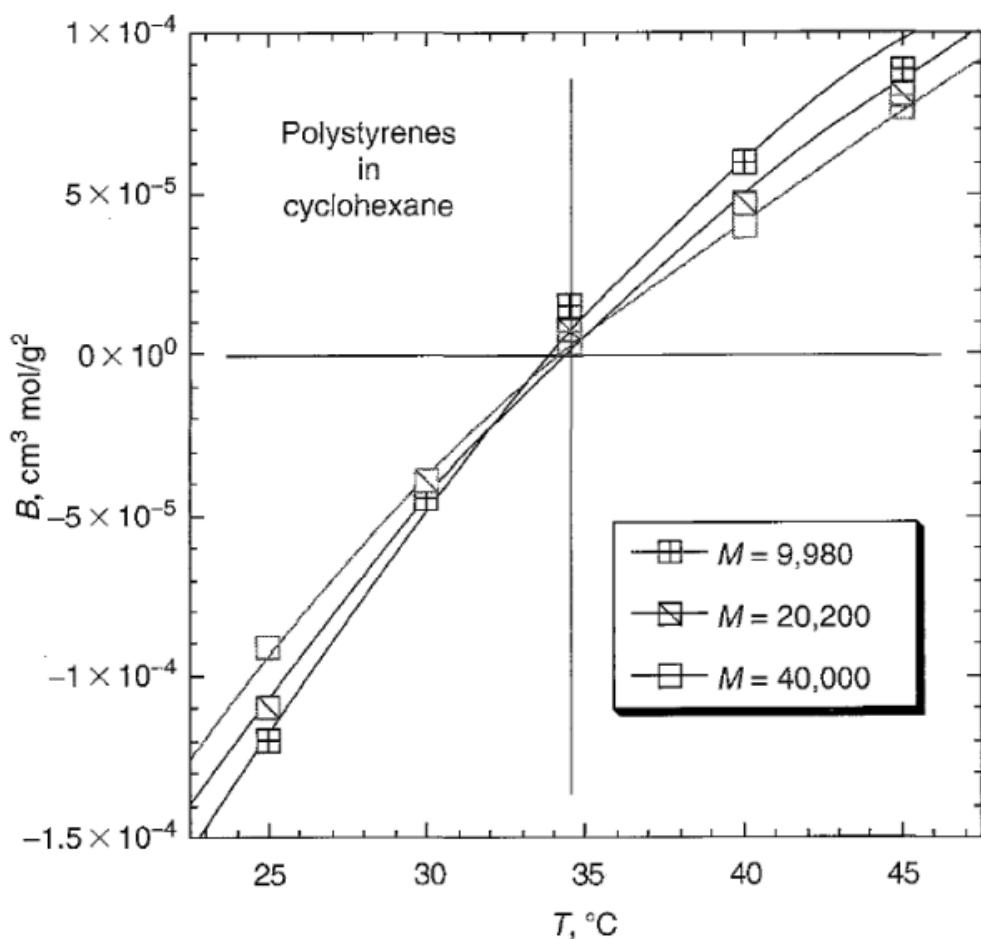
Substituting (27) to (26)

$$\Delta\mu = kT \left(-\frac{1}{n} \Phi_B + \left(\chi - \frac{1}{2} \right) \Phi_B^2 \right) \quad (28)$$

Rearranging in terms of osmotic pressure

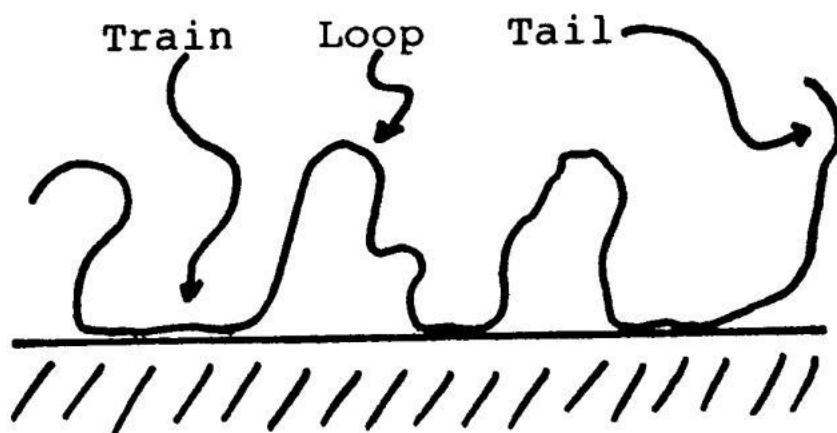
$$\Pi = \frac{-\Delta\mu}{V_A} = \frac{kT}{V_A} \left(\frac{1}{n} \Phi_B + \left(\frac{1}{2} - \chi \right) \Phi_B^2 \right) \quad (29)$$

(29) is analogous to the virial equation for gases, where the first term is the ideal term and the second term is the non-ideal term. It can be seen that when $\chi = \frac{1}{2}$, the properties of the polymer solution are ideal, which is also known as θ condition. Furthermore, it turns out when $\chi < \frac{1}{2}$: the polymer dissolves in the solvent, and the solvent is known as good solvent; when $\chi > \frac{1}{2}$, the polymer does not dissolve in the solvent, and the solvent is known as poor solvent. The non-ideal term is predicted to be independent of M, while experiments show some weak dependencies.

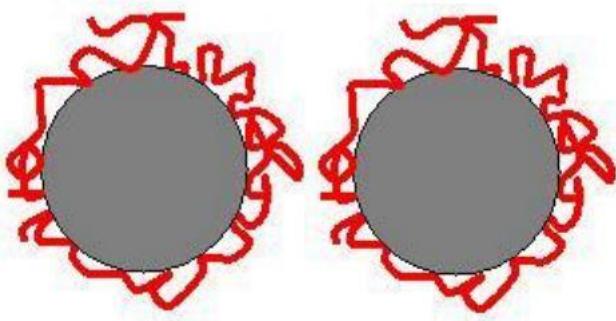


3. Polymer Adsorption

3.1 Configurations of polymer adsorption



It is noticed that, for polymer adsorption processes, the polymers might interfere with each other before van der Waals forces play a significant role and aggregate the particles. Therefore, the adsorbed polymer provides a physical buffer, preventing the cores of the particles from coming together and hence prevents the van der Waals attractions becoming significant. As a result, instead of a compact layer, a fuzzy, relatively thick monolayer is formed, where only 5% of the layer is polymer (the rest is solvent).



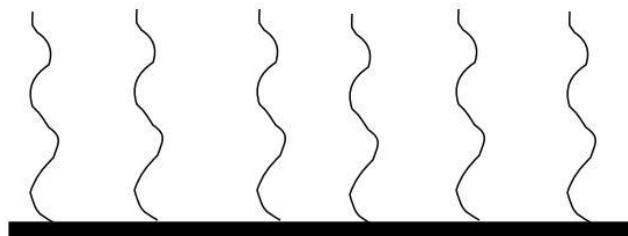
3.2 Polymer as stabilizing agent

Criteria: The polymer should be strongly adsorbed onto the surface and to extend sufficiently far away from the surface (5-10 nm), so that the van der Waals forces are less than kT . (*The criteria are mutually exclusive for homopolymers*)

Examples: A Graft or Comb copolymer (*one part of the polymer adsorb onto the surface, while the other part not*)

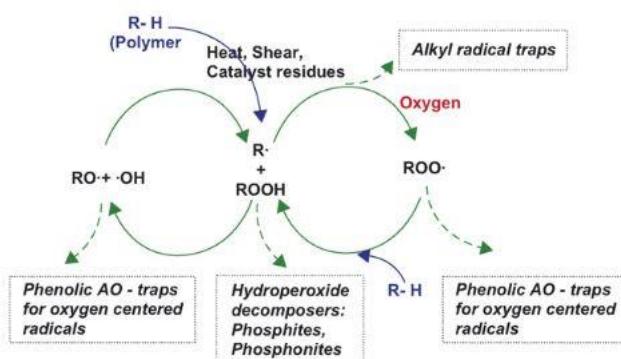


An AB Block Co-polymer

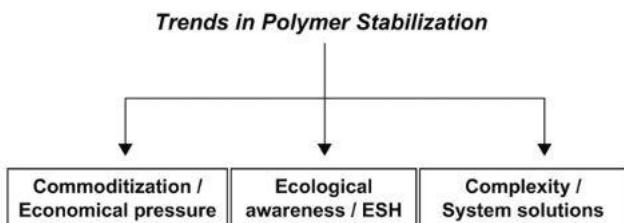


A Graft or Comb copolymer

Stabilization mechanisms of polymeric materials



Future trends in polymer stabilization

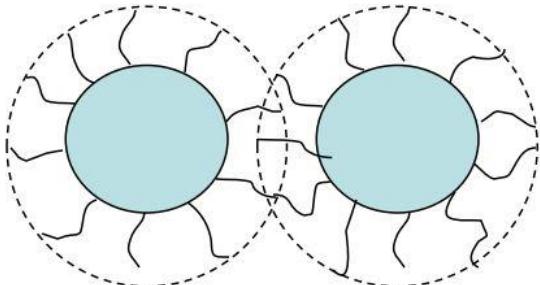


Reference: Malík, J.; Kröhnke, C. Polymer Stabilization: Present Status and Possible Future Trends. *Comptes Rendus Chimie* **2006**, 9 (11-12), 1330–1337.
<https://doi.org/10.1016/j.crci.2006.02.009>.

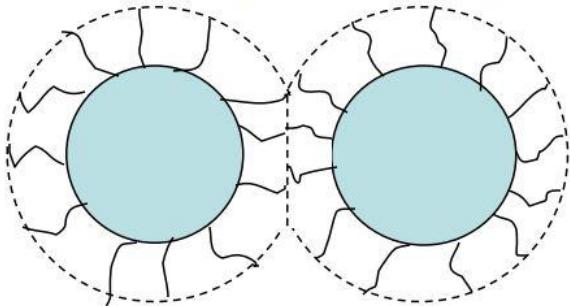
4. Interactions between adsorbed polymer layers

4.1 Effects of interaction

When two particles coated with polymers interact the two polymer layers overlap and compress. There are two effects associated with it.



Overlap of adsorbed layer



Compression of adsorbed layer

Osmotic effect	The concentration of polymer in the gap is increased, this increases the osmotic pressure and the particles are forced apart
Entropic effect	A consequence of the compression of the polymer layer decreasing the number of configurations the polymer can adopt

4.2 Modelling of the interactions

4.2.1 Osmotic contribution

$$\Delta G_{mix} = \frac{2\pi RkTV_p^2 n^2 \tau^2 \left(\frac{1}{2} - \chi\right)}{V_l} S_{os} \quad (30)$$

The osmotic contribution is summarized in (30). V_p, V_l are the molar volume of the polymer segments and the liquid respectively. n is the number of polymer segments overlapping and τ is the amount of polymers adsorbed. S_{os} is a geometric term that depends on the particle size and the thickness of the polymer layer.

The sign of the Gibbs free energy and therefore the nature of the interaction force depends on the value of χ .

$\chi < \frac{1}{2}$	Repulsive interaction
$\chi > \frac{1}{2}$	Attractive interaction
$\chi = \frac{1}{2}$	No contribution

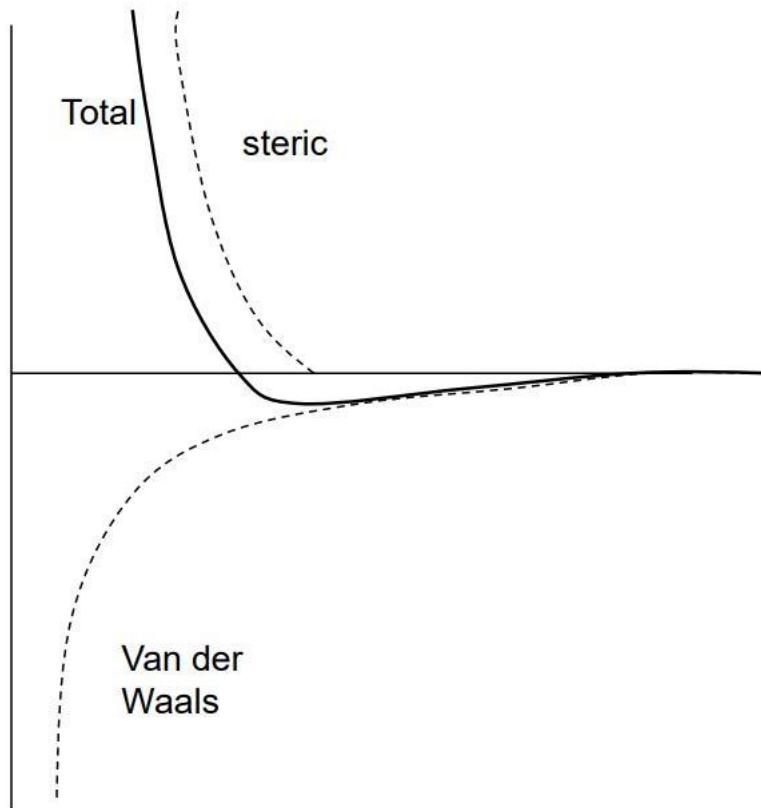
4.2.2 Entropic contribution

$$\Delta G_{ent} = 2\pi RkT\tau S_{ent} \quad (31)$$

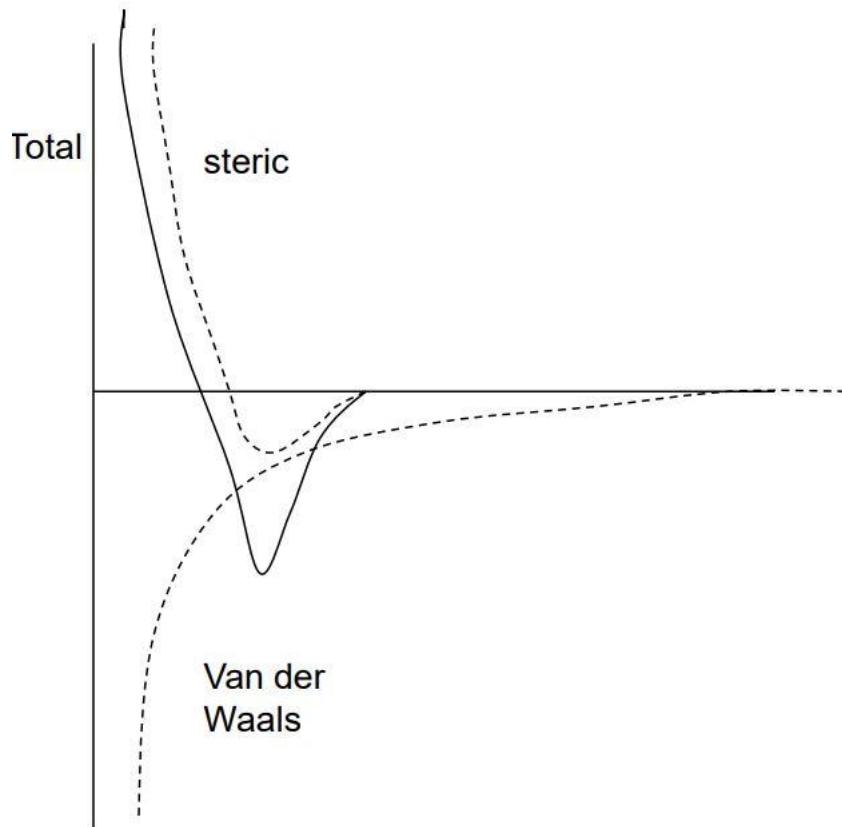
where S_{ent} is another geometric term. It is noticed that the entropic contribution is always repulsive.

4.2.3 Total interaction

when $\chi < \frac{1}{2}$:



when $\chi > \frac{1}{2}$:



The depth of the minimum can be adjusted by the thickness of the polymer layer.

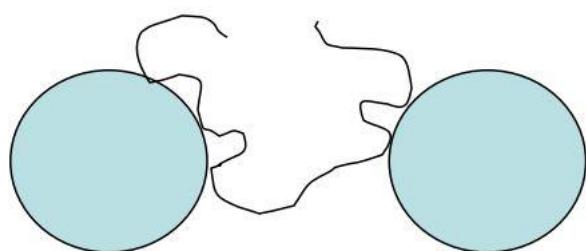
4.3 Polymer Flocculation

4.3.1 Temperature dependency of flocculation

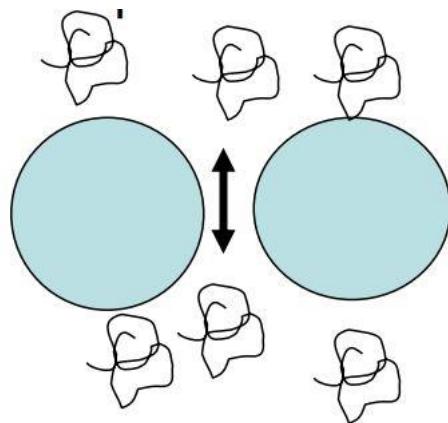
From (14), we understand the Flory-Huggins interaction parameter χ decreases as the temperature increases, where the particle flocculation follows the same trend. For water soluble polymers, the opposite is true.

4.3.2 Flocculation types

Bridging (under very dilute polymer concentrations)

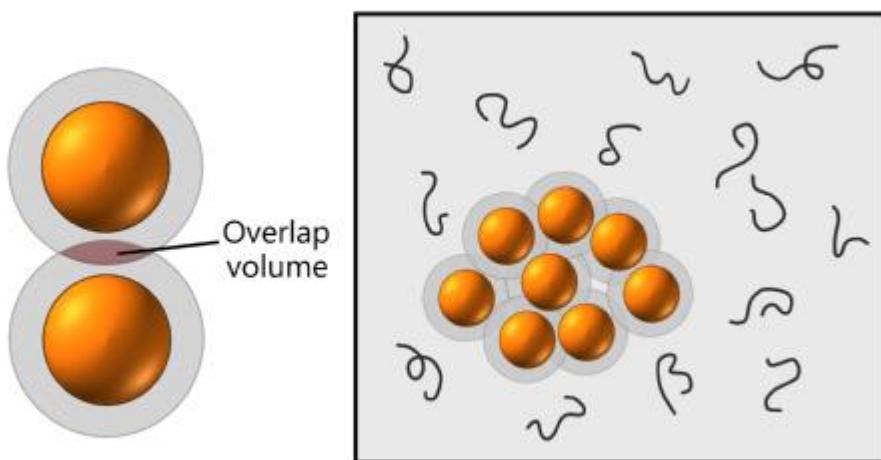


Depletion flocculation (when the polymer is non-adsorbing and the gap between two particles becomes very small)



Less polymers between the two particle surfaces than in the bulk → solvent flow from the dilute to the concentrated region → particles moving toward each other

Entropic view of depletion flocculation:



The presence of hard objects in a polymer solution reduces the configurational entropy of the polymers by reducing the accessible volume, both from the objects themselves and the surrounding depletion region. Nothing can be done about the objects' actual volume, but the polymers stand to gain available volume if the depletion regions overlap.

Thus polymers maximize their entropy if the hard objects cluster together. However, this also reduces the entropy of the hard objects, as only the relatively small number of arrangements in which they are all next to each other are allowed.

In practice, the additional conformational entropy of the polymers means they dominate, and the system separates into clusters (called 'flocs') and polymer-rich phases. This is aptly named depletion flocculation.

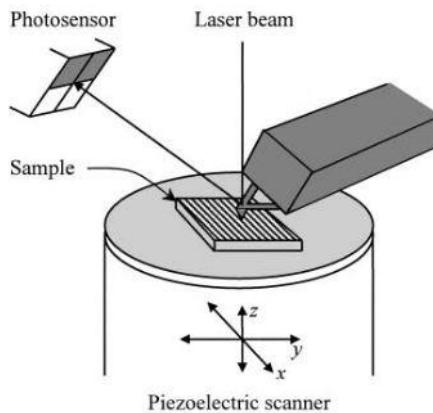
Reference:

Entropic phase separation and depletion flocculation. warwick.ac.uk.
https://warwick.ac.uk/fac/cross_fac/transcription/modelling/entropy/ (accessed 2023-04-13).

5. Measurement of particle interactions

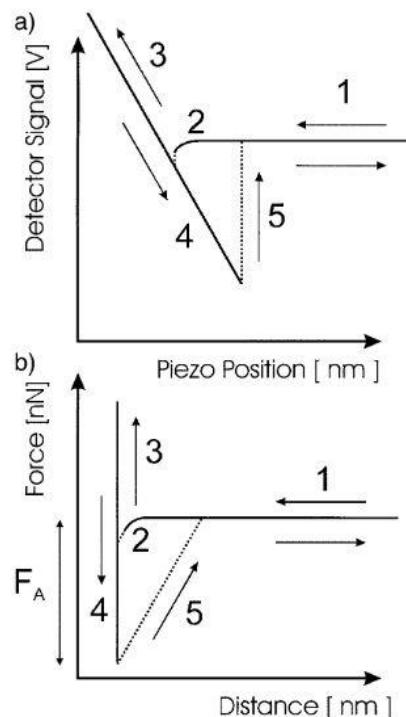
5.1 Atomic Force Microscope (AFM)

Particle interactions can be measured by modifying an atomic force microscope. In this experiment the interaction between a sharp tip attached to the end of a cantilever can be determined by monitoring the bending of the cantilever using laser light. By replacing the tip by a particle, particle surface and particle-particle interactions can be measured.



Principle of AFM: the sample is mounted onto a piezoelectric scanner and can be raster-scanned while in contact with the sharp tip that sits at the end of a cantilever. The deflection of the cantilever is detected with an optical lever technique. Therefore, a laser beam is reflected from the backside of the cantilever onto a split photodiode, and the change in position of the laser spot is recorded.

5.2 Schematic of deflection signal and forces



- (1) When the probe gets close to the substrate, the (in this case attractive) surfaces forces will cause a bending of the cantilever towards the surface.
- (2) As soon as the attractive force gradient becomes larger than the spring constant of the cantilever, the probe jumps in contact of the surface. From this moment, probe and surface will move in parallel. The resulting straight line corresponds to the so called “constant compliance” region.
- (3) Upon retracting the sample, the probe will usually adhere to the surface, causing the cantilever to bend downwards.
- (4) Eventually the bending force will become larger than the adhesive or pull-off force, and the cantilever will snap off the surface into its equilibrium position.
- (5) Linear fit of the constant compliance region.

Reference: Kappl, M.; Butt, H.-J. The Colloidal Probe Technique and Its Application to Adhesion Force Measurements. *Particle & Particle Systems Characterization* **2002**, *19* (3), 129. [https://doi.org/10.1002/1521-4117\(200207\)19:3%3C129::aid-ppsc129%3E3.0.co;2-g](https://doi.org/10.1002/1521-4117(200207)19:3%3C129::aid-ppsc129%3E3.0.co;2-g).

6. Problem sheet

- 6.1 It is observed that 0.01 M sodium sulfate will aggregate charged stabilised particles, whilst 0.6M sodium sulfate is needed to aggregate particles stabilised by a copolymer containing polyethyleneoxide, why?

Solutions: *Basically in 0.01 M Sodium sulfate the edl is very short, around 2nm, and so the particles are not sufficiently repulsive to prevent the particles from aggregating, the addition of polymer stops this aggregation, via a steric mechanism. However as the electrolyte concentration increases, the polyethyleneoxide becomes less soluble as there is a competition between the hydrated ions of the electrolyte and the polymer for water, which will hydrogen bond. At sufficiently high electrolyte concentrations this competition is such that at room temperature the polymer comes out of solution. Thus also the adsorbed polymer layer also begins to precipitate, but as it does so it collapses onto the particle surface, making the polymer layer very thin (also the interactions between the polymer layers become attractive) so that the PEO stabilised particles no longer remain stable and aggregate.*

- 6.2 If you had to choose to study a colloidal suspension either by light or electron microscopy, which would you prefer and why? Comment on the possibility to get a sharp picture of a colloidal particle with radius 30 nm which is not immobilised.

Solutions:

	light microscopy	electron microscopy
magnification	~ 1000x	≥ 10 000x
resolution	~ 300 nm	~ 0.2 nm
contrast	low, but still reasonable for most samples	good for heavy atoms
samples	'wet', thin	immobilised, have to withstand low pressure, thin (~10 to 100nm), sample preparation might introduce artefacts

It thus depends on the specific sample and the availability of the techniques, but most often electron microscopy is preferable. The particle will move due to Brownian motion an average distance of about 3 μm , i.e. about 60 times its diameter, within 1 second, which is a typical time to take a picture (see question 1). The picture will thus be blurred. Further more it turns out that an electron microscope needs a very high vacuum to work, such that only dry samples can be investigated, thus it is not actually possible to take pictures of very small particles in liquids. What is normally done is that samples are frozen, very quickly to form a dispersion in a frozen liquid (ice). The sample is then micro-tomed, the ice allowed to sublime to some extent and then the surface replicated with a very thin carbon film. This carbon film is then put in the AFM. This process is called Freeze Fracture. It is fraught with artefacts, so you have to be very careful.

Note the AFM would not work as the particles are in a liquid, the AFM can only image surfaces, although it would work if you could put particles on the surface in some way, although of course now its immobilised.

For these reasons you cannot currently get pictures of particles smaller than 100 nm or so in liquids

Lecture 4: Surface Tension and Wetting

Revision Time: 2023/4/14

1. Surface Tension

1.1 Thermodynamic definition of surface tension

Surface tension is a venerable scientific concept; Gibbs defined it as the excess of the grand potential of an inhomogeneous system with respect to its bulk value per interface area [J. W. Gibbs, "The Collected Works" in Thermodynamics (1928), Vol. 1].

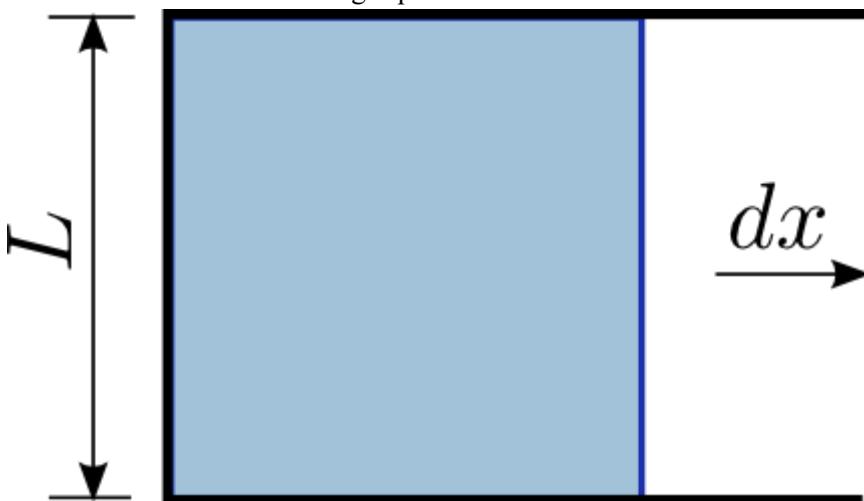
$$\Omega(\mu, T, V, A) = \Omega^{\text{bulk}}(\mu, T, V) + \hat{\gamma}\delta \quad (1)$$

where Ω is the grand potential, $\hat{\gamma}$ is the surface tension and δ is the surface area.

Rearranging, we get the definition of surface tension (2)

$$\gamma = \hat{\gamma} = \left(\frac{\partial \Omega}{\partial \delta} \right)_{\mu, T, V} \quad (2)$$

1.2 Surface tension for sliding liquid film



Amount of reversible work (dW) to increase the area of the film by dA

$$(dG)_{T,P} = dW = \gamma dA \quad (3)$$

Notice that the rigorous thermodynamical definition of surface tension uses grand potential. However, for the purpose of the course, it can be used as exchangeable with the Gibbs free energy

Substituting the definition of work (4) and the geometric calculation of area (*noticed that there are two faces for the surface area*) (5), we get (6)

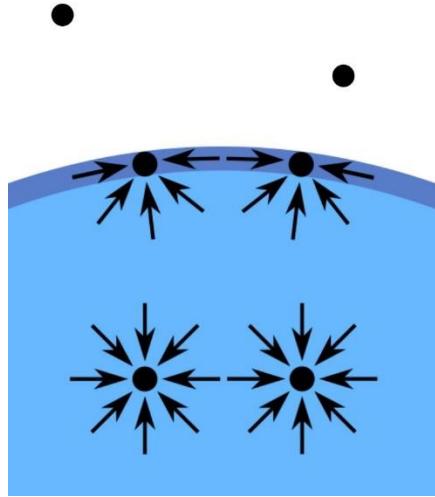
$$dW = Fdx \quad (5)$$

$$dA = 2Ldx \quad (6)$$

$$\gamma = \frac{F}{2L} \quad (7)$$

1.3 Origin of surface tension

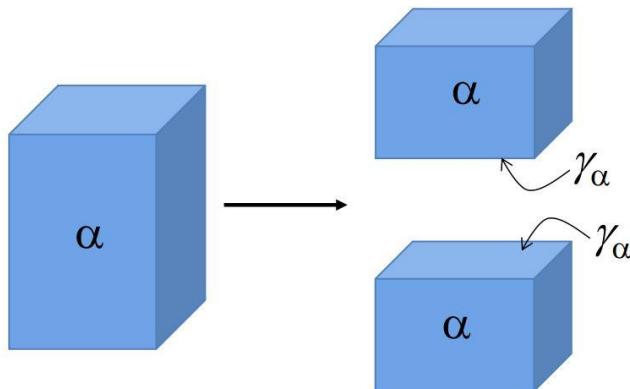
Liquid/Vapor Interface	Cohesive forces towards the liquid bulk are not balanced; the molecules are attracted inwards
Bulk Liquid	Cohesive forces are balanced in all directions; the molecule do not experience any net force



Cohesive forces include van der Waals interactions (Keesom, Debye, and London) and other specific interactions (polar, metallic, and hydrogen bonding). Each interaction contributes (approximately independent of each other) to total surface tension.

1.4 Work of cohesion

Work of cohesion: work required to pull apart a volume of unit cross sectional area ($A=1$)

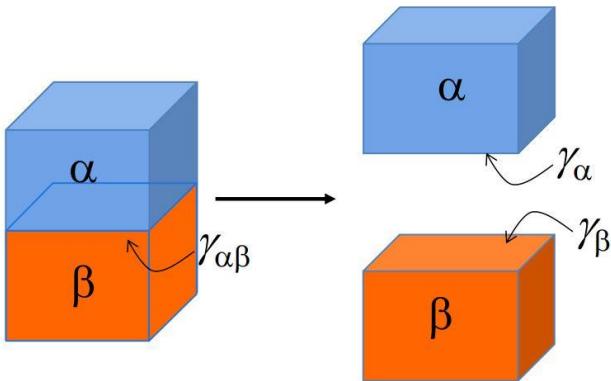


$$W_{cohesion} = 2\gamma_\alpha \quad (8)$$

where γ_α is the surface energy per unit area (or surface tension)

1.5 Work of adhesion

Work of adhesion: work required to separate a unit area of interface between two phases (α and β) to form a new surface of each phase



$$W_{adhesion} = \gamma_\alpha + \gamma_\beta - \gamma_{\alpha\beta} \quad (9)$$

where $\gamma_{\alpha\beta}$ is the interfacial energy per unit area (interfacial tension)

1.6 Spreading Coefficient



**olive oil on water:
no spreading**

If oil spreads on water, area of oil-water interface increases; area of water-vapor interface decreases. Therefore,

$$dG \sim (\gamma_{ov} + \gamma_{ow} - \gamma_{wv})dA \quad (10)$$

Spreading is said to spontaneous when $dG < 0$. Here, we define the spreading coefficient

$$S = \gamma_{wv} - (\gamma_{ov} + \gamma_{ow}) = W_{adhesion\ oil-water} - W_{cohesion\ oil} \quad (11)$$

For spontaneous spreading $S > 0$, indicating that the oil adheres to the water more strongly than it coheres to itself.

1.7 Dispersion forces

The van der Waals interaction can be described following (12)

$$w(r) = -\frac{3}{4} \frac{\alpha^2 I}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \quad (12)$$

Introduce the Hamaker constant and interaction energy between two planar surfaces can be described as

$$w(D) = -\frac{A}{12D^2} \quad (13)$$

The surface energy per unit area (energy needed to separate two flat surfaces from contact to infinity) is

$$\gamma = \frac{A}{24\pi D_0^2} \quad (14)$$

$$D_0 \sim 0.165 \text{ nm} \quad (15)$$

The (15) gives an approximation of D_0 , showing a good agreement with experiment.

However, it fails for polar substance because dispersion interactions are not the dominant interactions in that case.

1.8 Fowkes equation

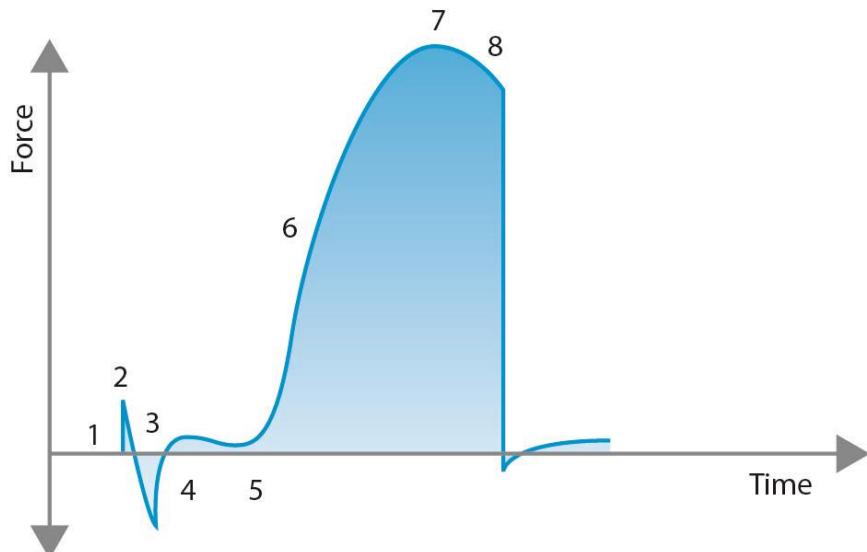
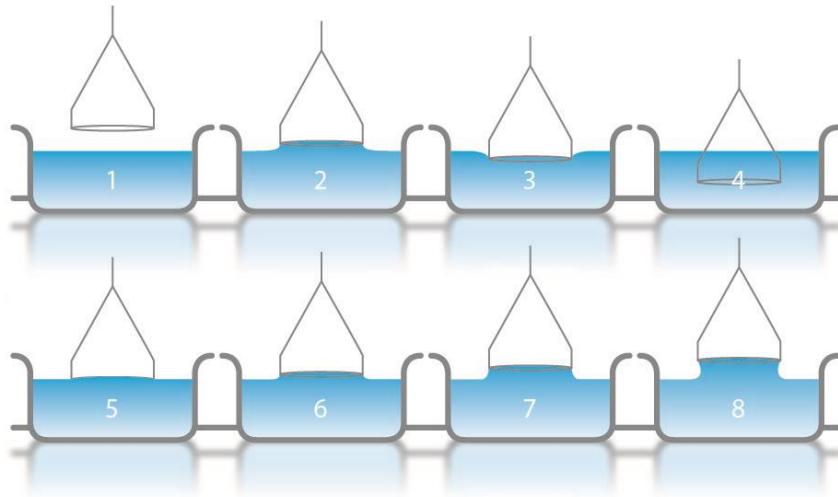
$$\gamma_{\alpha\beta}^{total} = \gamma_{\alpha}^{total} + \gamma_{\beta}^{total} - 2\sqrt{\gamma_{\alpha}^d \gamma_{\beta}^d} \quad (16)$$

Assumption: the cross-interaction term across interface (work of adhesion) is due exclusively to dispersion forces. It can be used for hydrocarbon-hydrocarbon interactions and hydrocarbon-water interactions.

1.9 Liquid surface tension measurements

1.9.1 Du Noüy ring method

Du Noüy method utilizes the interaction of a platinum ring with the surface of the liquid. The ring is submerged below the interface by moving the stage where the liquid container is placed. After immersion, the stage is gradually lowered, and the ring pulls up the meniscus of the liquid. Eventually this meniscus tears from the ring. Before this event, the volume (and thus the force exerted) of the meniscus passes through the maximum value and begins to drop before the actual tearing event.

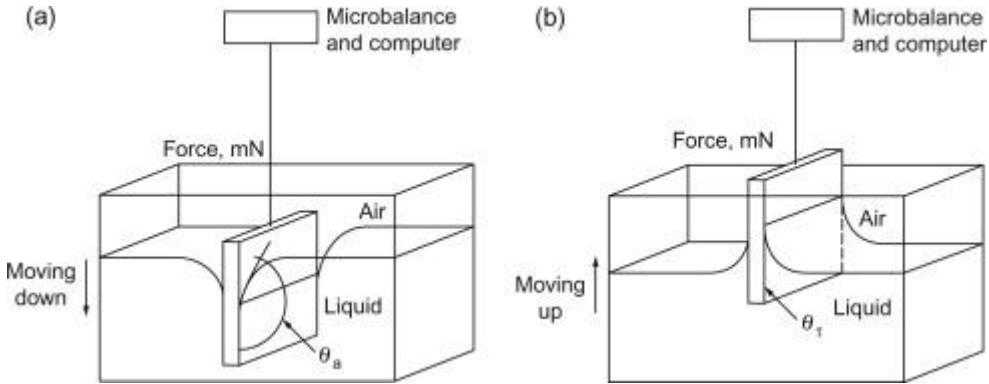


$$\gamma = \frac{F_{max}}{L \cos \theta} \quad (17)$$

where L is the wetted length of the ring. The ring is typically made of material that is well

wetted by liquid, so that $\cos\theta \approx 1$.

1.9.2 Wilhelmy plate method

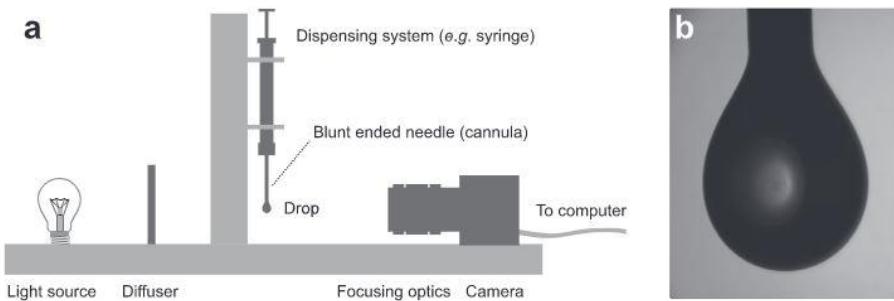


$$\gamma = \frac{F}{L \cos\theta} \quad (18)$$

As the interface is not ruptured during measurement, this method is suitable to measure interfacial tension as a function of time.

1.9.3 Pendant drop method

Configuration and typical result:



Mechanisms and calculation:

A pendant drop at equilibrium obeys the Young-Laplace equation, which relates the Laplace pressure across an interface with the curvature of the interface and the interfacial tension γ

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P \equiv \Delta P_0 - \Delta \rho g z \quad (19)$$

where R_1 and R_2 are principal radii of the curvature

Taking advantages of asymmetry and using the cylindrical coordinates, the Young-Laplace equation can be obtained as a coupled set of dimensionless differential equations (20)-(22) with boundary conditions (23)

$$\frac{d\varphi}{d\bar{s}} = 2 - Bo\bar{z} - \frac{\sin\varphi}{\bar{r}} \quad (20)$$

$$\frac{d\bar{r}}{d\bar{s}} = \cos\varphi \quad (21)$$

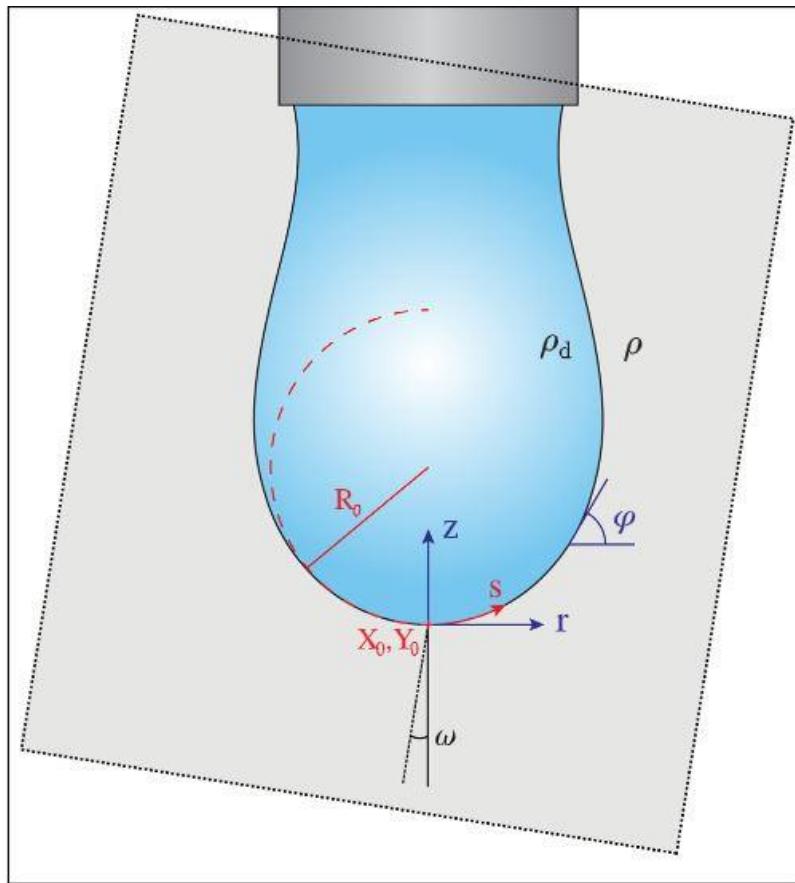
$$\frac{d\bar{z}}{d\bar{s}} = \sin\varphi \quad (22)$$

$$BC: \varphi = 0, \bar{r} = 0, \bar{z} = 0 \quad \text{when } \bar{s} = 0 \quad (23)$$

Bo denotes for bond number, as defined in (24)

$$Bo \equiv \frac{\Delta \rho g R_0^2}{\gamma} \quad (24)$$

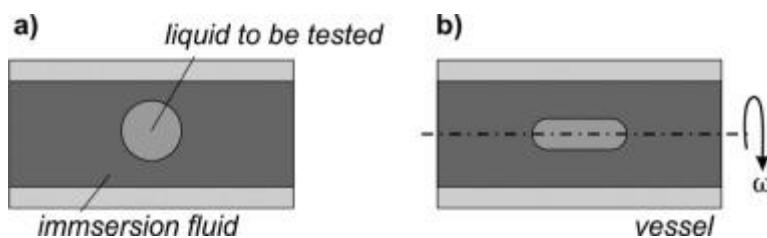
Numerical fit of shape returns surface tension. If Bo is too large, drop can detach (exceptionally low surface tension)



Reference: Berry, J. D.; Neeson, M. J.; Dagastine, R. R.; Chan, D. Y. C.; Tabor, R. F. Measurement of Surface and Interfacial Tension Using Pendant Drop Tensiometry. *Journal of Colloid and Interface Science* **2015**, 454, 226–237. <https://doi.org/10.1016/j.jcis.2015.05.012>.

1.9.4 Spinning drop method

This method uses a droplet of a liquid or a gas that is suspended in a second immersion fluid. If the whole setup is rotated at high speeds, the drop will deform under the action of the centrifugal force. The deformation of the droplet allows deriving the surface tension.



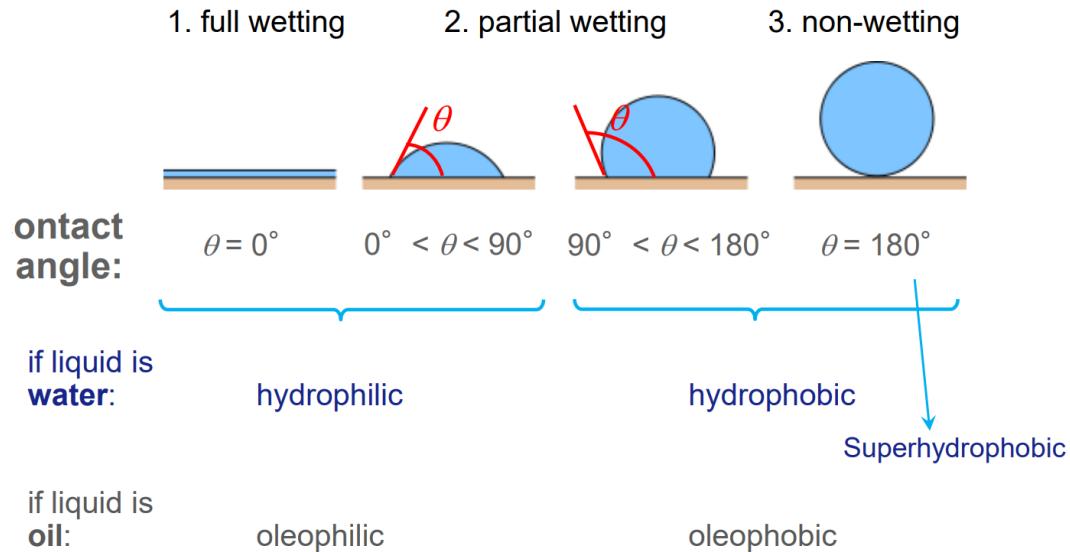
Interfacial tension is calculated from Vonnegut's equation

$$\gamma = \frac{\Delta \rho R^3 \omega^2}{4} \quad (26)$$

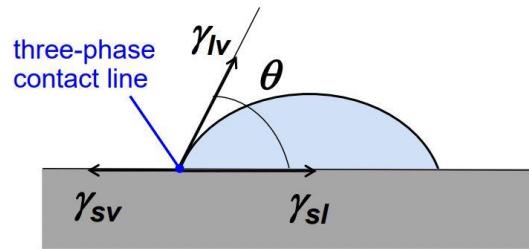
The spinning drop method is very precise, and therefore is suitable for very low surface tensions ($\gamma < 0.1 \text{ mN/m}$).

2. Wetting

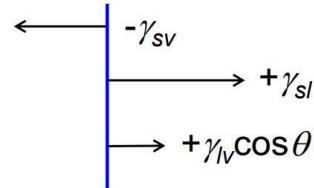
2.1 Configuration



2.2 Young's equation



Force balance on contact line (per unit length):



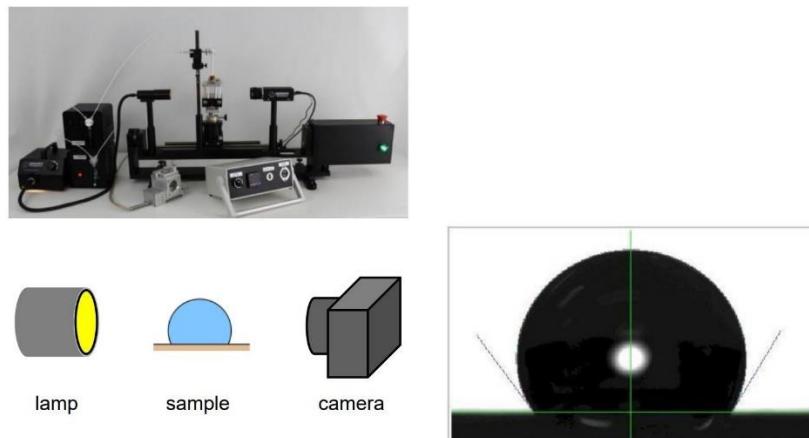
Apply force balance on the contract line (per unit length)

$$-\gamma_{sv} + \gamma_{sl} + \gamma_{lv}\cos\theta = 0 \quad (27)$$

Rearrange for $\cos\theta$

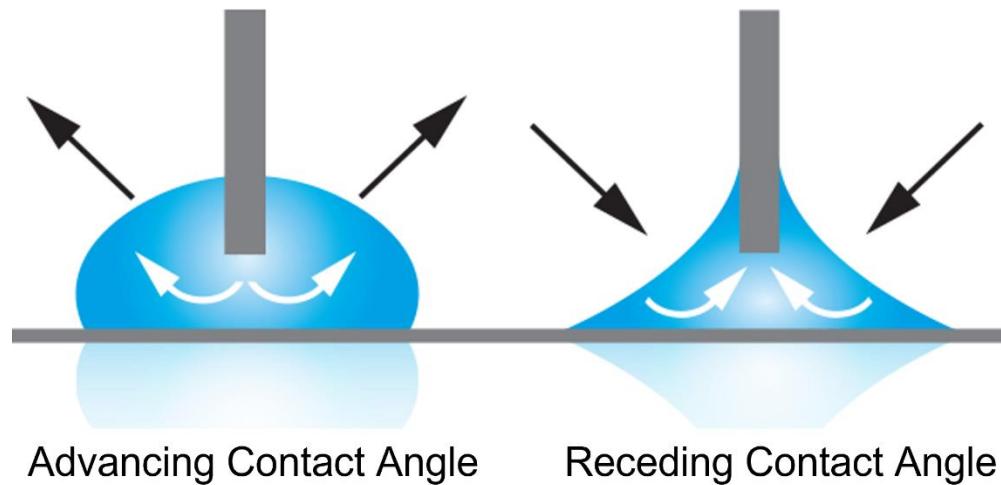
$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (28)$$

2.3 Contact angle measurement: sessile drop



2.4 Advancing and receding contact angle

In effect, the advancing contact angle is the largest contact angle in the free energy range, while the receding contact angle is the lowest contact angle in the free energy range. Because of this, these measurements are theoretically the most reproducible.



Force (per unit length) needed to make a drop slide over a solid surface:

$$f = \frac{\gamma_{lv}(\cos\theta_r - \cos\theta_a)}{2} \quad (29)$$

At angle α , a liquid drop with perimeter L and mass m slides on a smooth surface. Sliding constant:

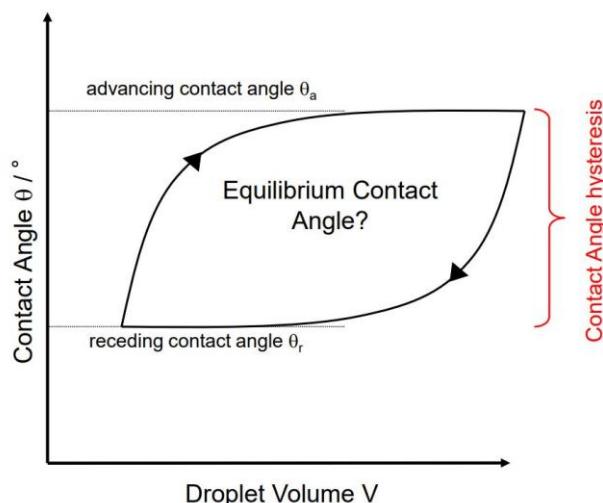
$$k_\alpha = mgsin\frac{\alpha}{L} \quad (30)$$

2.5 Contact angle hysteresis

Contact angle hysteresis is a reflection of the activation energy required for movement of a droplet from one metastable state to another on a surface. This can be expressed quantitatively in terms of changes in the interfacial area and thus interfacial free energy. It is caused by non-ideal surfaces (roughness, chemical heterogeneity)

Increasing droplet volume: approaching maximum (advancing) contact angle

Decreasing droplet volume: approaching minimum (receding) contact angle



$$\Delta\theta = \theta_a - \theta_r \quad (31)$$

Simple dynamic model for contact angle hysteresis (Whyman et al.)

$$\theta_a - \theta_r = \left(\frac{8U}{\gamma_{lv} R_0} \right)^{\frac{1}{2}} \frac{(1 - \cos\theta^*)^{\frac{1}{12}} (2 + \cos\theta^*)^{\frac{2}{3}}}{2^{\frac{1}{3}} (1 + \cos\theta^*)^{\frac{1}{4}}} \quad (32)$$

where θ^* is the apparent contact angle at equilibrium.

Applications:

- Control of contact angle hysteresis by electrowetting: sliding droplet and coffee stain
- Mechanical vibrations for the reduction of contact angle hysteresis
- Curtain coating
- Wire coating

Reference:

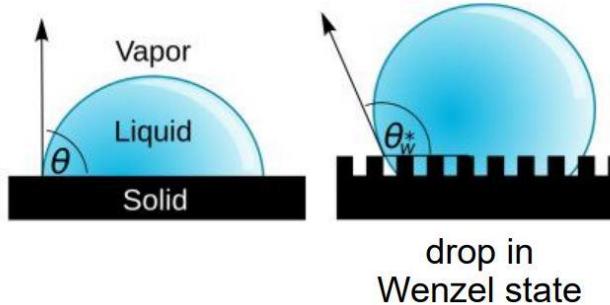
Eral, H. B.; t Manneke, D. J. C. M.; Oh, J. M. Contact Angle Hysteresis: A Review of Fundamentals and Applications. *Colloid and Polymer Science* **2012**, *291* (2), 247–260.
<https://doi.org/10.1007/s00396-012-2796-6>.

2.6 Wenzel equation

$$\cos\theta_w^* = R_w \cos\theta \quad (33)$$

$$R_w = \frac{A_{true}}{A_{apparent}} \quad (34)$$

where θ_w^* is the apparent contact angle, R_w is the roughness factor.

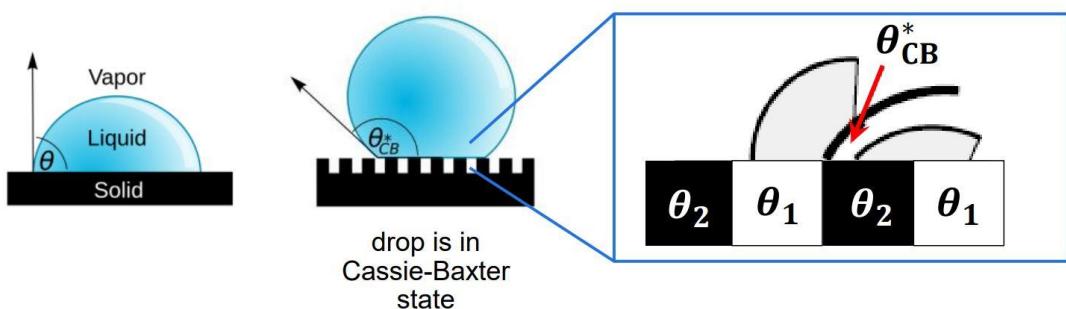


2.7 Cassie-Baxter Equation

$$\cos\theta_{CB}^* = f_1 \cos\theta_1 + f_2 \cos\theta_2 \quad (35)$$

$$f_1 + f_2 = 1 \quad (36)$$

where θ_{CB}^* is the apparent contact angle, f_1 and f_2 are the surface fractions.

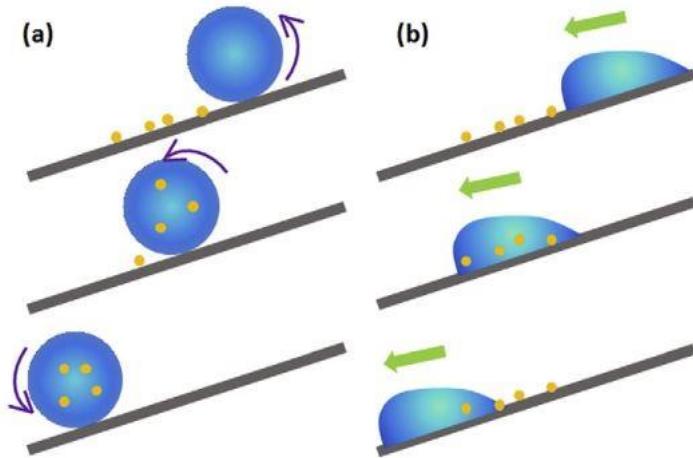


2.8 The Lotus effects

Superhydrophobicity is defined by two criteria: a very high water contact angle and a very low roll-off angle. Since it is very difficult to calculate the latter for rough surfaces, it is proposed here to use the criterion of a very low wet (solid-liquid) contact area as a simple, approximate substitute for the roll-off angle criterion. It is concluded that nature employs metastable states in the heterogeneous wetting regime as the key to superhydrophobicity on Lotus leaves.

Link between roughness and self-cleaning:

- (a) On smooth surfaces, dirt particles are redistributed by water
- (b) On rough surfaces, dirt adheres to drop and is removed from leaves when droplets roll off

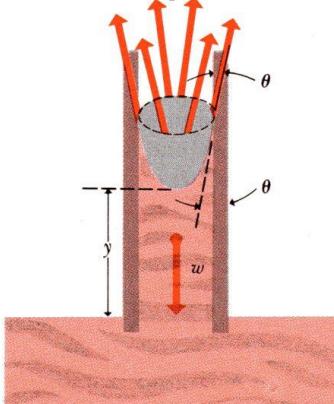


Reference:

- Marmur, A. The Lotus Effect: Superhydrophobicity and Metastability. *Langmuir* **2004**, *20* (9), 3517–3519. <https://doi.org/10.1021/la036369u>.
- Zhang, M.; Feng, S.; Wang, L.; Zheng, Y. Lotus Effect in Wetting and Self-Cleaning. *Biotribology* **2016**, *5*, 31–43. <https://doi.org/10.1016/j.biotri.2015.08.002>.

3. Capillary action

3.1 Types of capillary action

$\theta < 90^\circ$	 <p>(a)</p> <p>Small surface tension liquid on a high energy surface, water or clean glass</p>	adhesive forces are greater than the cohesive forces
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$\theta > 90^\circ$	<p>(b)</p>	Adhesive forces are less than cohesive forces
	Large energy tension liquid (such as Hg)	

3.2 Laplace pressure and equilibrium height

The Laplace pressure is the pressure difference between the inside and the outside of a curved surface that forms the boundary between two fluid regions.

3.2.1 Capillary pressure in a tube

The Laplace pressure in a tube can be expressed by (37)

$$\Delta P = \frac{2\gamma}{R} \quad (37)$$

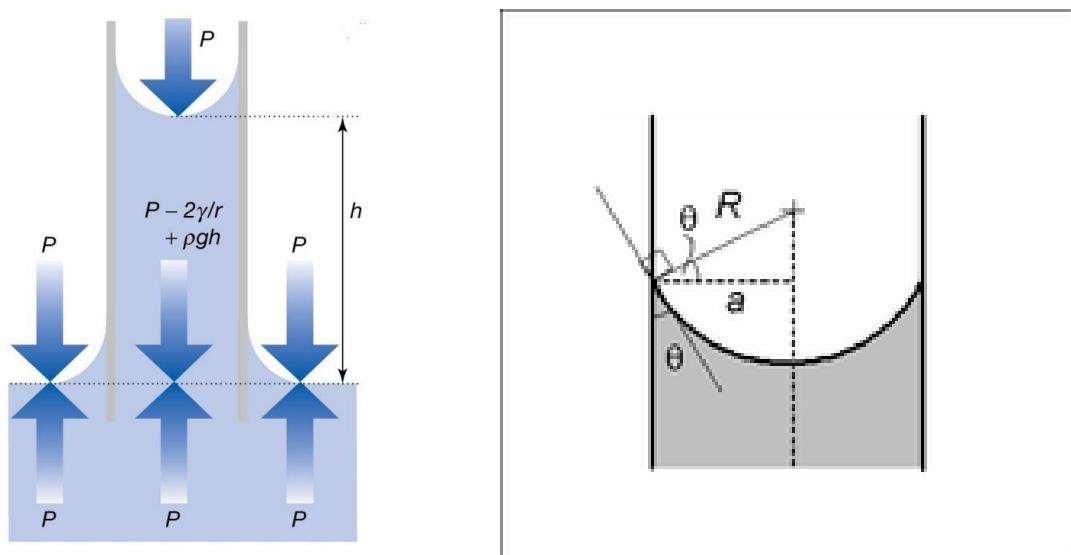
Considering the force balance (38) and the geometry of the tube

$$\Delta P = \rho gh \quad (38)$$

$$R = \frac{a}{\cos\theta} \quad (39)$$

Substituting (37)(39) into (38) and rearrange, we get the equilibrium height

$$h = \frac{2\gamma\cos\theta}{\rho ga} \quad (40)$$



3.2.2 Capillary pressure in general

(37) only applies for spherical shapes, such as bubble or droplets. For non-spherical shapes,

(37) can be generalized into (41)

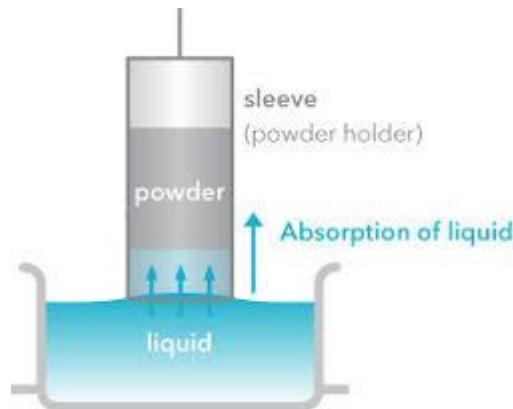
$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (41)$$

Note that if there are two surfaces, the total pressure difference is calculated by summing the pressure difference of individual surfaces.

3.3 Capillary rise in porous medium: Washburn equation

$$h^2 = \frac{r\gamma_{lv}\cos\theta}{2\eta} t \quad (42)$$

where r is the effective interstitial pore radius, η is the liquid viscosity and γ_{lv} is the liquid/vapor surface tension.

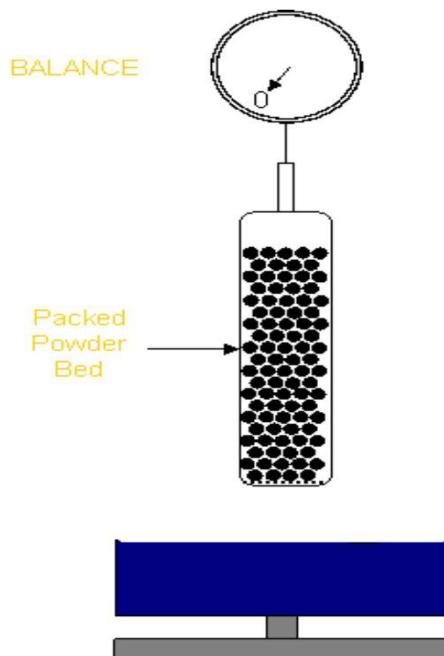


$$m^2 = \frac{C\rho^2\gamma\cos\theta}{\eta} t \quad (43)$$

$$C = \frac{rA^2\varepsilon^2}{2} \quad (44)$$

where A is the cross-section of the tube and ε is the porosity of the packing in the tube. It is noticed that (42) and (43) are linked via (45)

$$m = \rho Ah\varepsilon \quad (45)$$



4. Problem Sheet

4.1 A liquid β spreads spontaneously on another immiscible liquid α . Show that the spreading coefficient is given by the difference between the work of adhesion between α and β , and the work of cohesion of β .

Solutions:

$$S = \gamma_{\alpha v} - (\gamma_{\beta v} + \gamma_{\alpha\beta}) = (\gamma_{\alpha v} + \gamma_{\beta v} - \gamma_{\alpha\beta}) - 2\gamma_{\beta v} = W_{adhesion\alpha\beta} - W_{cohesion\beta}$$

4.2 Show that if a liquid β spreads on another immiscible liquid α , then liquid α cannot spread on liquid β .

Solutions:

Suppose we have

$$S = \gamma_{\alpha v} - (\gamma_{\beta v} + \gamma_{\alpha\beta}) > 0 \quad \text{for liquid } \beta \text{ spreading on } \alpha$$

Then we can express

$$S' = \gamma_{\beta v} - (\gamma_{\alpha v} + \gamma_{\alpha\beta}) \quad \text{for liquid } \alpha \text{ spreading on } \beta$$

Substituting S into S'

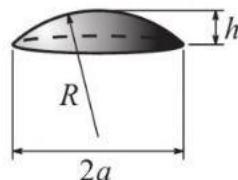
$$S' = \gamma_{\beta v} - (\gamma_{\alpha v} + \gamma_{\alpha\beta}) < \gamma_{\beta v} - (\gamma_{\beta v} + \gamma_{\alpha\beta} + \gamma_{\alpha\beta}) = -2\gamma_{\alpha\beta} < 0$$

Therefore, if a liquid β spreads on another immiscible liquid α , then liquid α cannot spread on liquid β .

4.3 A liquid resin is sprayed in droplets of volume 10^{-3} mm^3 on a smooth solid surface on which the droplets have a contact angle of 35° . The droplets solidify into an array of bumps that provides an anti-stick coating. Calculate the height of the bumps.

Solutions:

Based on the problem, we can conclude a spherical cap configuration



First, we need to relate the volume with the height

$$V = \int_{R-h}^R \pi r^2 dy$$

where r is the radius of the surface cap at different y (For instance $r = a$ when $y = R - h$)

The geometries of the spherical cap can be related through Pythagorean theorem

$$r^2 = R^2 - y^2$$

Substituting, we get

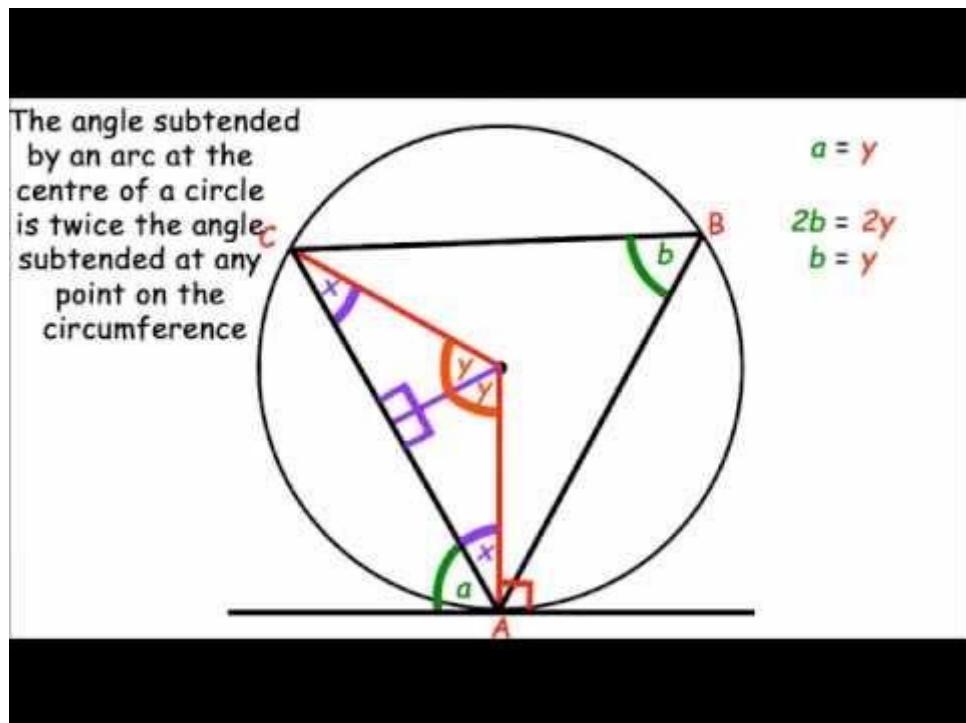
$$\begin{aligned} V &= \int_{R-h}^R \pi(R^2 - y^2) dy = \left[\pi R^2 y - \frac{1}{3} \pi y^3 \right]_{R-h}^R = \pi R^2 h - \frac{1}{3} \pi R^3 + \frac{1}{3} \pi (R - h)^3 \\ &= \pi R h^2 - \frac{1}{3} h^3 \end{aligned}$$

If we introduce the contact angle to the above equation

$$a = r \sin \theta$$

$$h = R(1 - \cos \theta)$$

$$V = \frac{1}{3} \pi R^3 [3(1 - \cos \theta)^2 - (1 - \cos \theta)^3] = 0.0922 \frac{1}{3} \pi R^3$$



Solving the equation, we get

$$R = 0.218 \text{ mm}$$

$$h = R(1 - \cos\theta) = 0.0394 \text{ mm}$$

4.4

3. A continuous problem in older buildings is rising damp, which might result in structural damage to buildings. The phenomenon is caused by ground water travelling up through porous building materials by capillarity.

- a) considering the building material as a porous network of capillaries of an average diameter of about $1 \mu\text{m}$, calculate the maximum rising height. **5 Marks**
- b) Explain why typically only rising heights of about 1.5 m are observed. **3 Marks**
- c) You can determine the contact angle of water on a cylindrical sample of a unknown porous building block by fixing it in a tight sleeve and pressing water in the block with increasing but known pressure. How would you calculate the contact angle? Which quantity do you need to determine via an independent measurement and how would you do it? **5 Marks**
- d) Which contact angle do you have to measure? **2 Marks**
- e) How else could you determine the wetting behaviour of a porous building block? **2 Marks**
- f) What would you do to avoid the penetration of water into a building block (from ground water as well as rain splash)? **2 Marks**
- g) In oil recovery you have to displace the oil from a porous reservoir, which could also be sandstone (such as the building blocks above). Water flooding is used to do so. How could you determine the oil/water contact angle in such a porous medium? Consider which contact angle (measured into water) is important. Which quantities do you need to determine by independent measurements? **6 Marks**

Solutions:

(a) Assuming single capillary

$$h = \frac{2\gamma \cos\theta}{\rho g a}$$
$$h_{max} = \frac{2\gamma}{\rho g a} = \frac{2 \times 72.8 \times 10^{-3}}{1000 \times 9.81 \times 1 \times 10^{-6}} = 14.84 \text{ m}$$

(b) Water adsorption is balanced with evaporation, which limits the height.

(c)

$$\Delta P = \frac{2\gamma}{R} = \frac{2\gamma \cos\theta}{a}$$

We need to measure the capillary pressure (ΔP) and the radius of the capillary cylinder. The capillary pressure can be measured at force equilibrium using $\Delta P = \rho gh$.

(d)

Advancing contact angle: As the plate or rod is immersed, the advancing contact angle is measured and when the plate is emerged, the receding angle is obtained.

(e)

Using Capillary rise in porous medium: Washburn equation

(f)

Using coarser (with larger R) or hydrophobic building blocks

(g)

$$\cos\theta = \frac{\Delta Pa}{2\gamma_{ow}}$$

We need to measure the capillary pressure (ΔP) and the radius of the capillary cylinder. The capillary pressure can be measured at force equilibrium using $\Delta P = \rho gh$.

The difference here is that the contact angle we measured is receding contact angle. This is because we are measuring by water flooding (not oil flooding).

4.5

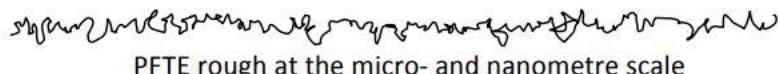
Q3. Various structured PTFE (Teflon) surfaces are brought into contact with water (SFT = 72.8 mN/m) and n-decane (SFT = 23.8 mN/m).

- a) What is the difference between wetting and wettability? (2 marks)
- b) Draw the expected droplet shape for water and dodecane on the following PTFE surfaces (10 marks)
- c) Explain what governs the wetting behaviour and the wettability of these surfaces. (5 marks)
- d) What is a self-cleaning surface? Why does self-cleaning occur? Which of the surfaces in part (b) would exhibit self-cleaning? (5 marks)
- e) If you bring two smooth PTFE surfaces attached to a sensitive balance under water in contact, what will you observe? Now try to separate the two PTFE surfaces. Explain your observation. (3 Marks)

PTFE Surface Smooth at micro and nano-scales



PTFE rough at the micro-scale, smooth at the nano-scale



Solutions:

- (a) When we talk about wetting, we describe the behavior of liquids on contact with the surface of solids. The corresponding property of the surface of the solid is the so-called wettability.
(b)(c)

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

$$\cos\theta_w^* = R_w \cos\theta$$

$$R_w = \frac{A_{true}}{A_{apparent}}$$

$$\cos\theta_{CB}^* = f_1 \cos\theta_1 + f_2 \cos\theta_2$$

From the equations above, we have made several observations:

- (1) Since γ_{lv} is greater for water, we expect $\cos\theta$ to be smaller for water. PTFE is in general considered to be hydrophobic and oleophilic.
- (2) For more and more rough surface, we have greater R_w and therefore larger $\cos\theta_w^*$. If $\theta > 90^\circ$, we expect the contact angle to be bigger for a rough surface. If $\theta < 90^\circ$, we expect the contact angle to be smaller for a rough surface.
- (3) A rough nanostructure introduces air inclusion ($\cos\theta_2 = 1$), which makes $\cos\theta_{CB}^*$ increases. Again, $\theta > 90^\circ$, we expect the contact angle to be bigger for a rough surface. If $\theta < 90^\circ$, we expect the contact angle to be smaller for a rough surface.
- (4) Surfaces with re-entrant topography pins the wetting front and results in a high θ ($\approx 180^\circ$)

The drawings should satisfy the above observations.

(d)

A self-cleaning surface is any surface with the ability to readily remove any dirt or bacteria on it by rinsing with water.

Superhydrophobic, self-cleaning surfaces are based on high water contact angles. A drop of water is almost spherical on the surface and readily rolls off taking the dirt away with it. Superhydrophobicity is achieved by combination hydrophobic surface chemistry and surface roughness.

Surfaces (3) and (4), which has very high water contact angles.

(e)

The surface will jump into contact and it is hard to separate them again. The process is driven by hydrophobic interactions and the non-wetting feature makes the separation difficult.

Lecture 5: Introduction to surfactants

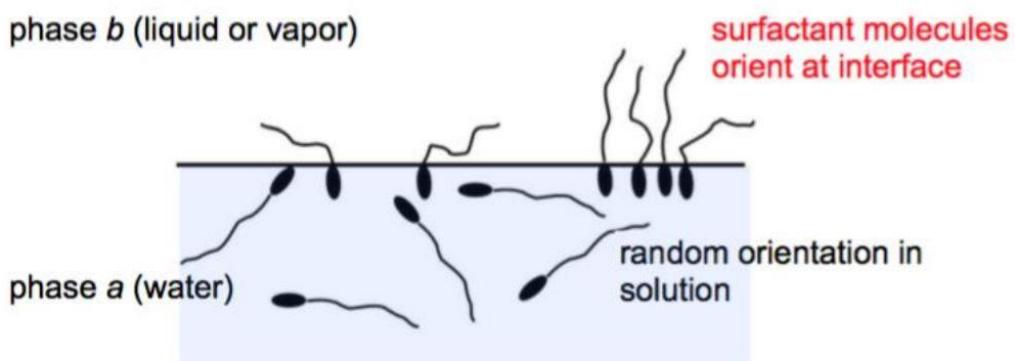
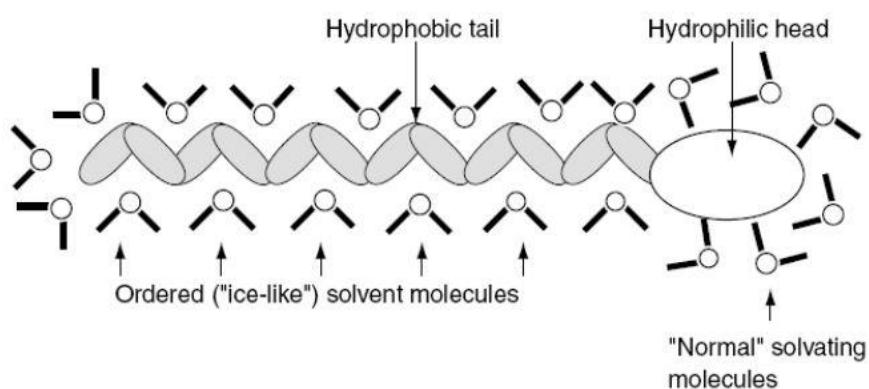
Revision Time: 28/4/2023

1. Introduction to surfactants

1.1 Definition and structure

Definitions: The word surfactant denotes for surface active agents. Surfactants are chemical compounds that decrease the surface tension or interfacial tension between two liquids, a liquid and a gas, or a liquid and a solid.

Structure: Energetically favorable to be at interface because of molecular structure: typical surfactant is amphiphilic, i.e., it combines hydrophilic groups and hydrophobic groups



Hydrophilic group (head)	Sulfonate, Sulfate, Carboxylate, Hydroxyl, etc.
Hydrophobic group (tail)	Hydrocarbons: linear chain or aromatic groups

1.2 Classification and application of surfactants

Non-ionic	Stability in varying pH, used in detergents, food products, pharmaceuticals, cosmetics, pesticides	Examples: Fatty alcohol ethoxylate Fatty acid ethoxylate Fatty amide ethoxylate
Anionic	Detergents, adsorption on polar surfaces, used in pesticide formulations and toothpastes	Examples: Alkyl sulfate Alkyl ether carboxylate Alkyl phosphate
Cationic	Adsorption on surfaces, used in hair and fabric conditioners	Examples: Fatty amine salt

		Alkyl ‘quat’ Ester ‘quat’
Zwitterionic	Found in cell membranes, and used in drug delivery and cosmetics	Examples: Betaine Amido betaine Amine oxide

1.3 Surfactants as detergents

Surfactants are used as detergents, emulsifiers, encapsulants, lubricants, etc.

Grease does not mix with water because the main interactions between water molecules are hydrogen bonding, whilst those between molecules of oils and fats are dispersion forces.

To get water and grease to mix we use surfactants as detergents. The hydrophobic ‘tail’ can form van der Waals bonds with non-polar grease molecules, whilst the polar ‘head’ can form hydrogen bonds with water.

1.4 Problems with surfactants

- Dermatological problems (*emulsification of lipids on skin can cause removal of protective layer; loss of water by the skin*)
- Biocidal effects
- Environmental issues (*aquatic toxicity, biodegradability, bioaccumulation*)

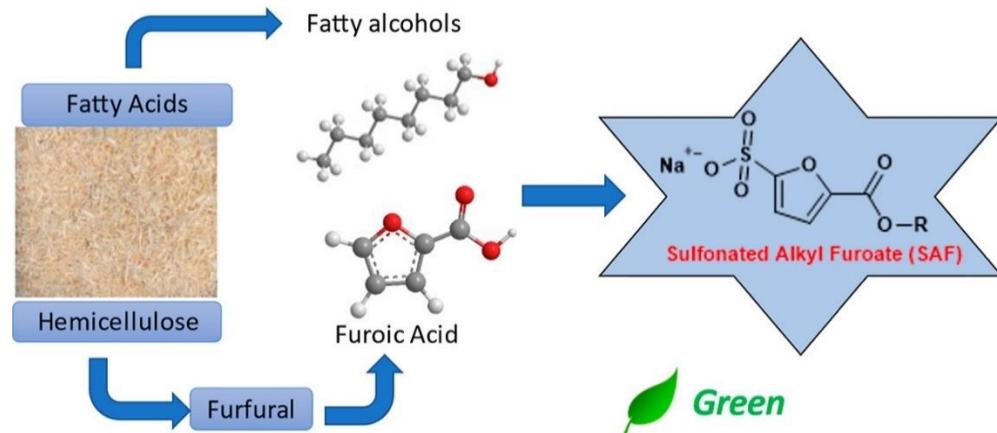
1.5 Research into green surfactant

Green surfactant-producing companies with different industrial applications.

Company	site	Tensioactive	Application
Fraunhofer IGB – Germany	https://www.igb.fraunhofer.de/	Glycolipid and cellobiose lipid biosurfactants	Cleaning products, dishwashing liquids, pharmaceutical products (bioactive properties
AGAE Technologies – USA	https://www.agatech.com/	Rhamnolipid biosurfactants	Pharmaceuticals, cosmetics, personal care products, bioremediation (<i>in situ</i> and <i>ex situ</i>), enhanced oil recovery (EOR)
TeeGene Biotech – UK	http://www.teegene.co.uk/	Rhamnolipids and lipopeptides	Pharmaceutical products, cosmetics, antimicrobials and anticarcinogen ingredients
Jeneil Biosurfactant – USA	http://www.jenelbiotech.com/	Rhamnolipid biosurfactants	Cleaning and oil recovery from storage tanks, EOR
Allied Carbon Solutions (ACS) Ltd – Japan	https://www.allied-c-s.co.jp/english-site	Sophorolipids	Agricultural products, ecological research
Rhamnolipid Companies – USA	http://rhamnolipid.com/	Rhamnolipid biosurfactants	Agricultura, cosmetics, EOR, bioremediation, food products, pharmaceutical products
Saraya Co. Ltd. – Japan	http://worldwide.saraya.com/	Sophorolipid biosurfactants	Cleaning products, hygiene products
BioFuture – Ireland	https://biofuture.ie/	Rhamnolipid biosurfactants	Washing of fuel tanks
TensioGreen – USA	http://www.tensiogreen.com/index.php	Rhamnolipid biosurfactants	Petroleum industry, cleaning, and oil recovery from storage tanks, EOR
EcoChem Organics Company – Canada	http://www.biochemica.co.uk/	Rhamnolipid biosurfactants	Dispersant of insoluble hydrocarbons in water
Logos Technologies – USA	https://www.natsurfact.com/	Rhamnolipid biosurfactants	Petroleum industry, cleaning, and oil recovery from storage tanks, EOR
Synthezyme – USA	http://www.synthezyme.com/index.html	Sophorolipid biosurfactants	Emulsification of crude oil, petroleum, and gas
EnzymeTechnologies – USA		Bacterial biosurfactant (unknown)	Oil removal; oil recovery and processing, EOR
Ecover Eco-Surfactant – Belgium	https://www.ecover.com/	ACS-Sophor/Sophorolipid	Oil recovery and processing, EOR; biofilm removing agent, biofilm growth inhibitor; detergent action
Cognis (BASF) – Germany, USA	http://saifuusa.com/portfolio-item/mildsurfactants/	Green surfactant alkyl polyglucoside (APG) – 0810-65	Shampoo, body wash; facial wash; liquid hand soap; moistened towelettes, laundry, hard surface cleaning
Cognis (BASF) – Germany, USA	http://saifuusa.com/portfolio-item/mildsurfactants/	Green surfactant alkyl polyglucoside (APG) – 0810H-70N	Industrial and institutional surface cleaning
Cognis (BASF) – Germany, USA	http://saifuusa.com/portfolio-item/mildsurfactants/	Green surfactant alkyl polyglucoside (APG) – 0810-70DK	Hard surface cleaning
Paradigm Biomedical Inc – USA	http://www.akama.com/company/Paradigm_Biomedical_Inc_a7bcb2680775.html	Rhamnolipid biosurfactant	Pharmaceutical products
Kaneka Corporation – Japan	https://www.kaneka.co.jp/en/business/qualityoflife/nbd_002.html	Sodium surfactin	Cosmetics
Sabo S.p.A. – Italy	www.sabo.com/sabo/home.php	Sodium surfactin	Cosmetics
Groupe Soliance – France	http://www.soliance.com/dtproduit.php?id=42	Sopholiance S (Sophorolipid)	Cosmetics and pharmaceuticals

Reference: Production of Green Surfactants: Market Prospects. *Electronic Journal of Biotechnology* 2021, 51, 28–39. <https://doi.org/10.1016/j.ejbt.2021.02.002>.

Green surfactant research at Imperial College



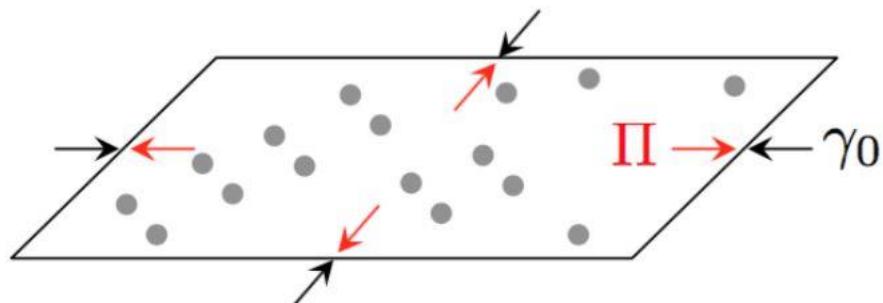
Reference: Al Ghatta, A.; Aravenas, R. C.; Wu, Y.; Perry, J. M.; Lemus, J.; Hallett, J. P. New Biobased Sulfonated Anionic Surfactants Based on the Esterification of Furoic Acid and Fatty Alcohols: A Green Solution for the Replacement of Oil Derivative Surfactants with Superior Properties. *ACS Sustainable Chemistry & Engineering* 2022, 10 (27), 8846–8855. <https://doi.org/10.1021/acssuschemeng.2c01766>.

2. Interfacial thermodynamics

2.1 Surface pressure

As defined, surfactants decrease the surface tension

$$\gamma = \gamma_0 - \Pi \quad (1)$$



where γ and γ_0 are surface tensions with or without surfactant respectively, Π is the surface pressure of surfactant monolayer.

2.2 Surface excess

2.2.1 Gibbs ideal interface model

With Gibbs model, the interface is ideally thin with effectively no volumes

$$V^\sigma = 0 \quad (2)$$

$$V = V^\alpha + V^\beta \quad (3)$$

All other extensive quantities can be written as a sum of three components: one of bulk phase α , one of bulk phase β , one of interfacial region σ .

$$U = U^\alpha + U^\beta + U^\sigma \quad (4)$$

$$S = S^\alpha + S^\beta + S^\sigma \quad (5)$$

$$N_i = N_i^\alpha + N_i^\beta + N_i^\sigma \quad (6)$$

where N_i is the number of molecules of the i th substance.

Rewriting U^α , U^β in terms of internal energy per unit volume and N_i^α, N_i^β in terms of concentration (number of molecules per unit volume), we have

$$U^\sigma = U - u^\alpha V^\alpha - u^\beta V^\beta \quad (7)$$

$$N_i^\sigma = N_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta \quad (8)$$

With (7), it is possible to define a quantity, which is given as the number of molecules per unit area, so called interfacial excess

$$\Gamma_i = \frac{N_i^\sigma}{A} \quad (9)$$

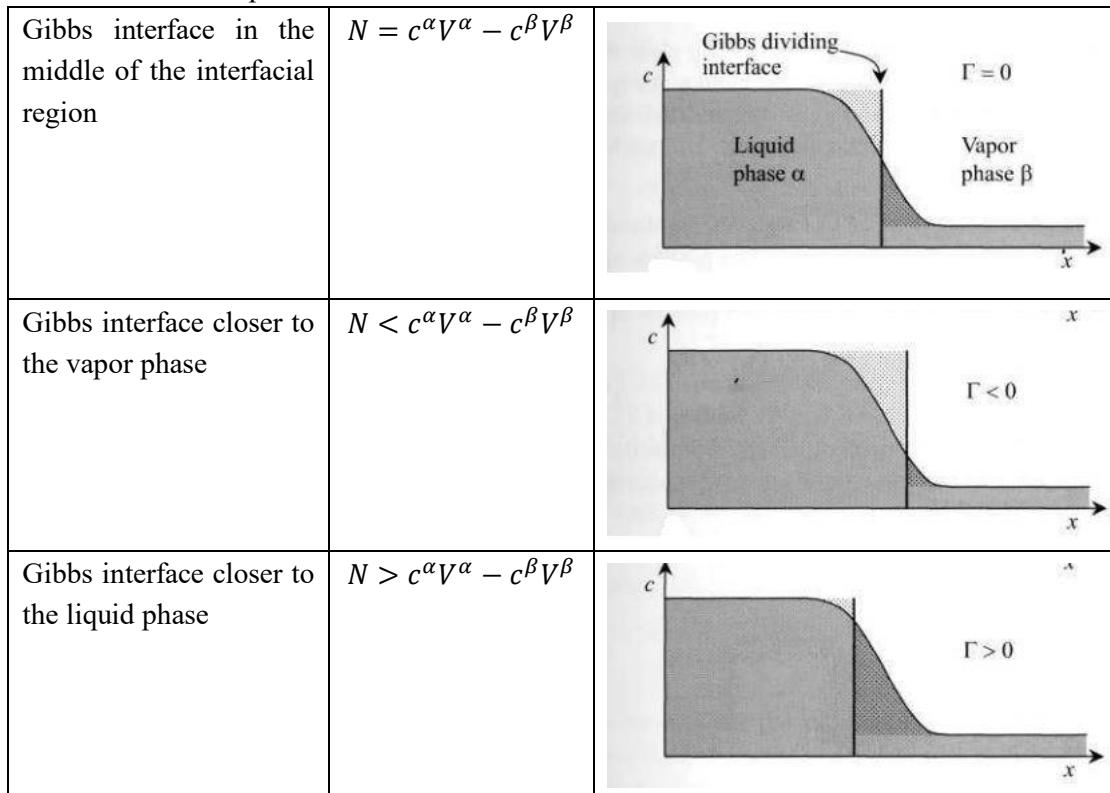
Alternatively it can also be defined in terms of moles, so called specific interfacial excess

$$\Gamma_{i,s} = \frac{n_i^\sigma}{A} \quad (10)$$

From (7), it is not hard to see that the surface excess represents the excess material at the interface compared to the bulk

$\Gamma_i > 0$	Interfacial excess (e.g., surfactants)
$\Gamma_i < 0$	Interfacial depletion (e.g., salts)

It is conventional to place the Gibbs interface at where the surface excess of solvent is 0.

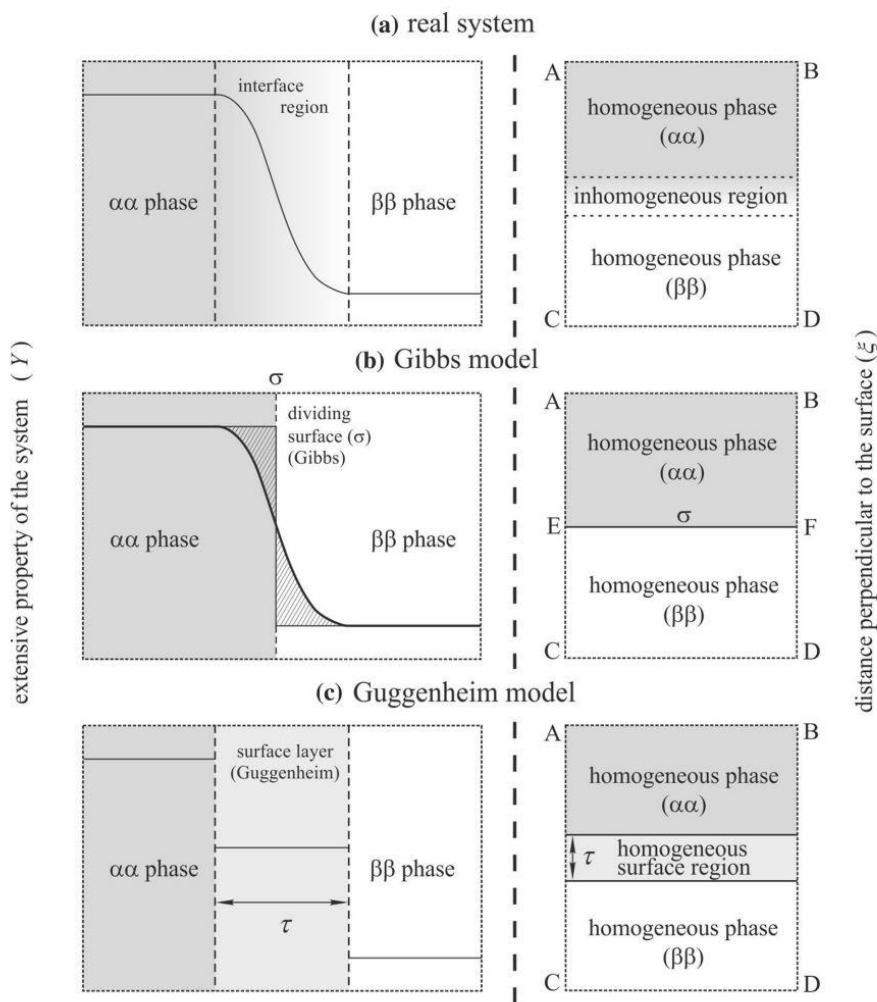


Notice that N is represented by the area under the graph for the above discussion.

Measurement of surface excess can be normally done via radioactive tracers or neutron reflectivity.

Besides Gibbs model, there are some other models that illustrating the interface in different

ways, as shown below



Reference: Láng, G. G. Basic Interfacial Thermodynamics and Related Mathematical Background. *ChemTexts* 2015, 1 (4). <https://doi.org/10.1007/s40828-015-0015-z>.

2.2.2 Gibbs adsorption isotherm

First, we start with the definition of internal energy for a two-phase system

$$dU = TdS - PdV + \sum \mu_i dN_i + dW \quad (11)$$

Apply (10) to the interfacial excess internal energy

$$dU^\sigma = TdS^\sigma + \sum \mu_i dN_i^\sigma + \gamma dA \quad (12)$$

Note that following Gibbs interfacial model, the term $PdV^\sigma = 0$

Integrating (11) yields (*notice that the integration of (11) has some mathematical subtlety, which far exceeds the scope of the course and therefore is not proved here*)

$$U^\sigma = TS^\sigma + \sum \mu_i N_i^\sigma + \gamma A \quad (13)$$

Differentiate (12) yields (*it might seem strange to first integrate and immediately differentiate back, but if you recall, similar methodology is used in second year thermodynamics*)

$$dU^\sigma = TdS^\sigma + S^\sigma dT + \sum \mu_i dN_i^\sigma + \sum N_i^\sigma d\mu_i + \gamma dA + Ad\gamma \quad (14)$$

Equating (13) with (11)

$$0 = S^\sigma dT + \sum N_i^\sigma d\mu_i + Ad\gamma \quad (15)$$

At constant temperature, it simplifies to

$$d\gamma = - \sum \Gamma_i d\mu_i \quad (16)$$

(15) is well-known as the Gibbs adsorption isotherm, which relates change in surface tension to surface excess and change in chemical potential (i.e., concentration) of the bulk surfactant solution.

For simple two-components system

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (17)$$

The ideal interface is defined when $\Gamma_1 = 0$, and therefore

$$d\gamma = -\Gamma_2 d\mu_2 \quad (18)$$

The standard chemical potential is expressed as

$$\mu_2 = \mu^0 + RT \ln \frac{a}{a_0} \quad (19)$$

Differentiating with respect to $\frac{a}{a_0}$

$$d\mu_2 = RT \frac{da}{a} \approx RT \frac{dc}{c} \quad (20)$$

Substituting back to (17)

$$\Gamma_2 = -\frac{c}{RT} \left. \frac{\partial \gamma}{\partial c} \right|_T \quad (21)$$

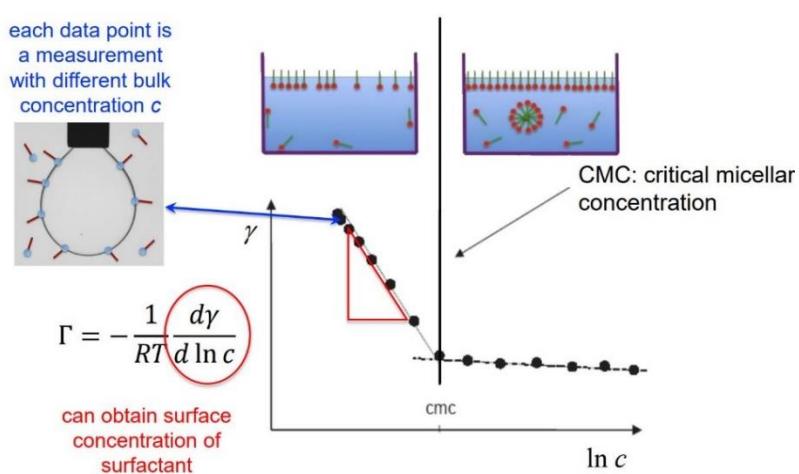
Equivalent it can be written as

$$\Gamma_2 = -\frac{1}{RT} \left. \frac{\partial \gamma}{\partial \ln c} \right|_T \quad (22)$$

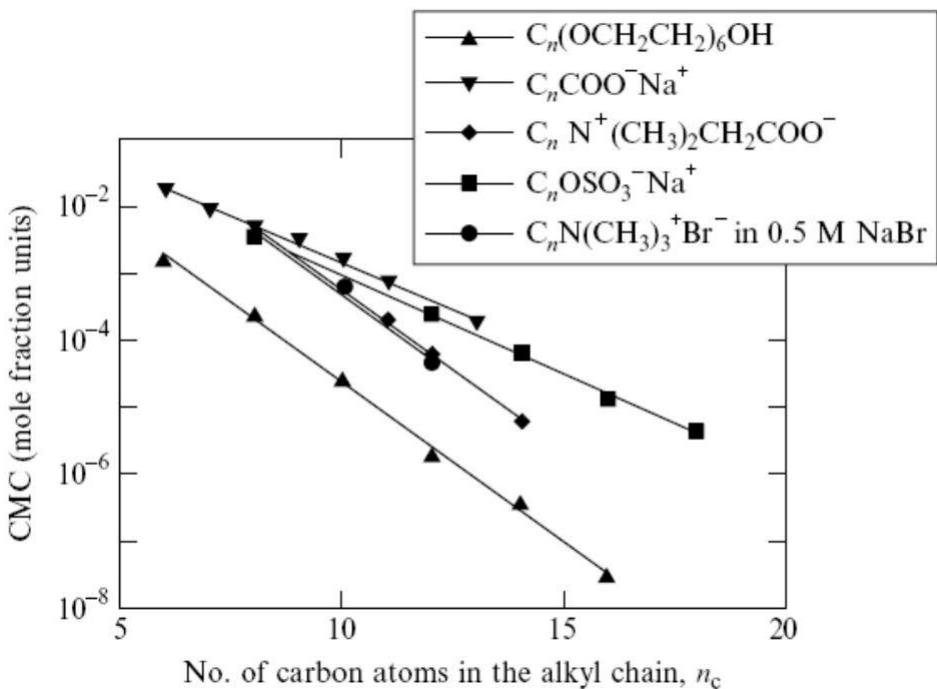
Note that in the slides it states the derivation is for Gibbs adsorption equation for one component. However, it is not true since the simplest application of the equation is for a system of two components, where you have a solvent and a solute (in this case, possibly a surfactant).

2.3 Critical micellar concentration

Critical micelle concentration (CMC) is defined as the surfactant concentration at which micelle formation is first seen in the solution.



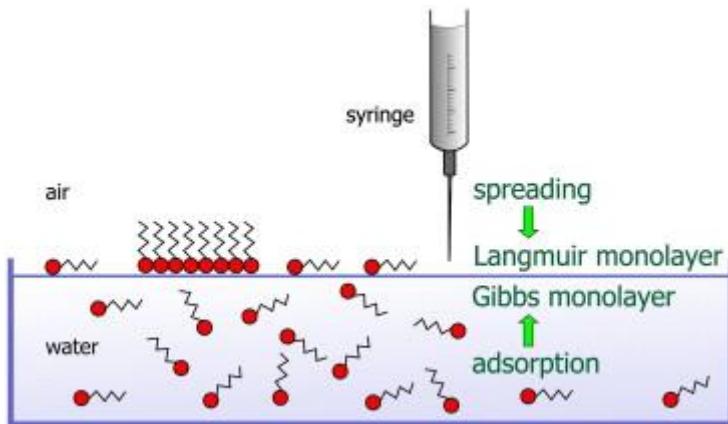
CMC decreases exponentially with alkyl chain length for a variety of headgroups.



2.4 Langmuir monolayer

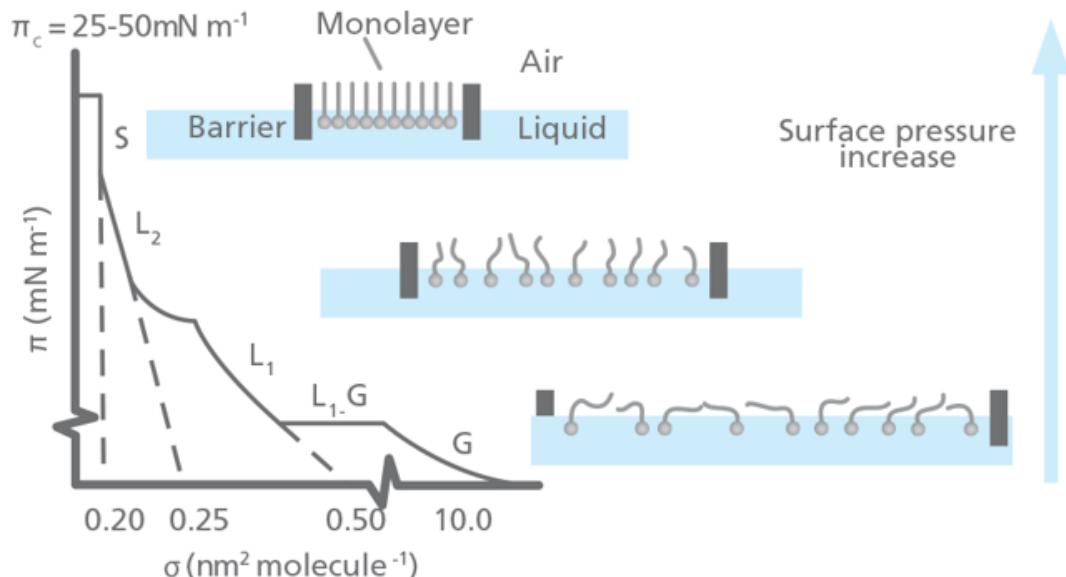
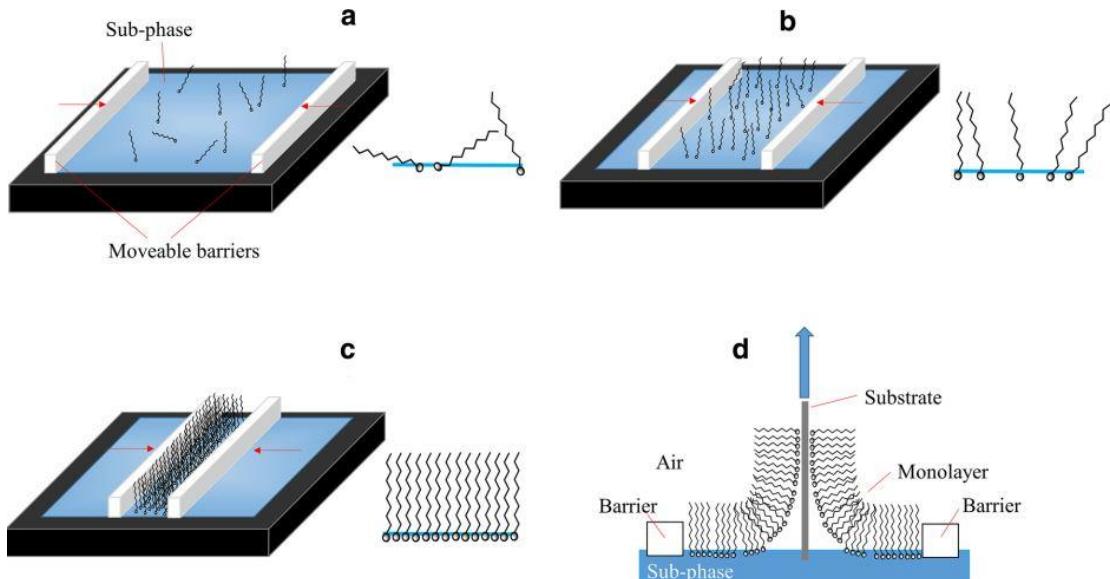
A *Langmuir monolayer* or *insoluble monolayer* is a one-molecule thick layer of an insoluble organic material spread onto an aqueous subphase in a Langmuir-Blodgett trough. Traditional compounds used to prepare Langmuir monolayers are amphiphilic materials that possess a hydrophilic headgroup and a hydrophobic tail.

Langmuir monolayers typically have really low CMC, indicating that they always form micelles in water. Therefore, Langmuir monolayer deposits on the interface by spreading; whereas Gibbs monolayer undergoes spontaneous adsorption.



Langmuir trough (as shown in the diagram below): used to measure Γ ($\Gamma_{i,s} = \frac{n_i^\sigma}{A}$, n_i^σ is constant while A is changing by compression of the barrier)

Wilhelmy plate (as discussed in Lecture 4): used to measure γ continuously. Together with Langmuir trough, we can determine Π as a function of Γ .



2.5 Surface equation of state

At infinite dilution	$\Pi A = n^\sigma RT$ (23) $\Pi = \Gamma RT$ (24)	2D analogy to $PV = nRT$
At higher concentration	$\Pi(A - A_0) = n^\sigma RT$ (25)	Volmer equation. A_0 is molecular co-area (measures effective crosssectional area of adsorbed molecule)
At even higher concentrations	$(\Pi - \frac{\alpha}{A^2})(A - A_0)$ $= n^\sigma RT$ (26)	In analogy to the van der Waals equation of state for gases, it accounts for intermolecular interactions through parameter α

From (1) we can get

$$d\Pi = -d\gamma \quad (27)$$

Combining with (27) with (16)(22), we can get the adsorption isotherm in terms of surface pressure of the monolayer

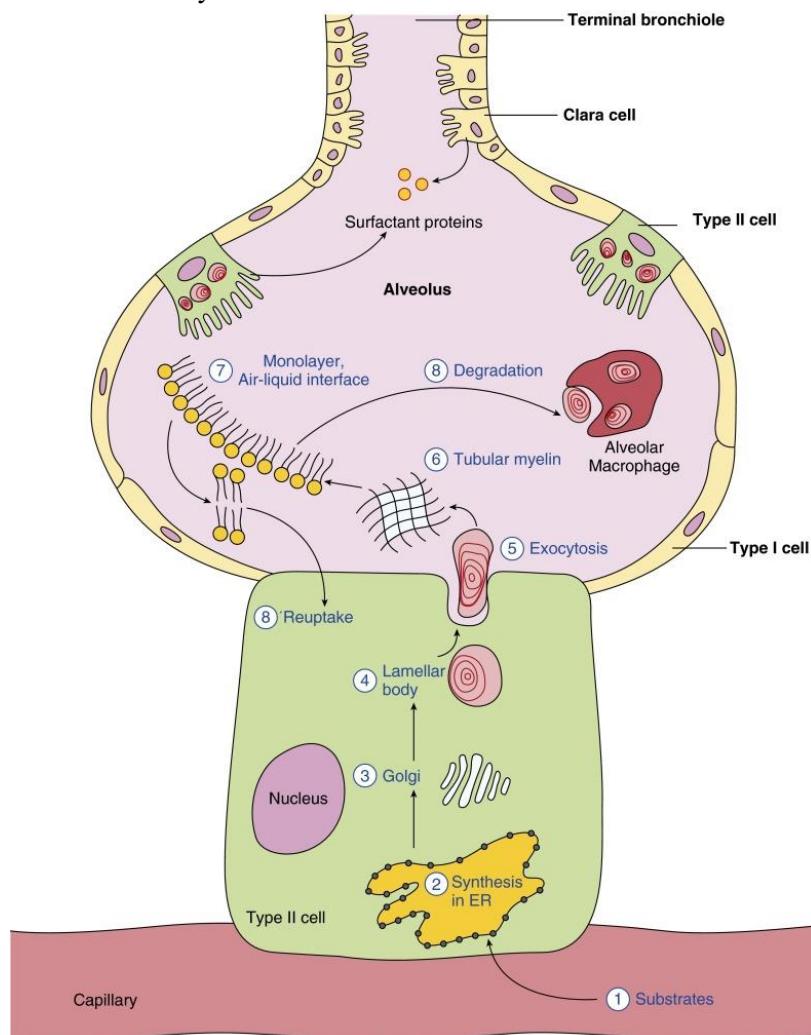
$$d\Pi = \sum \Gamma_i d\mu_i \quad (28)$$

$$\Gamma_2 = \frac{1}{RT} \frac{\partial \Pi}{\partial \ln c} \Big|_T \quad (29)$$

2.6 Lung surfactants

Lung surfactant, a lipo-protein complex, is a highly surface-active material found in the fluid lining the air-liquid interface of the alveolar surface. Surfactant plays a dual function of preventing alveolar collapse during breathing cycle and protection of the lungs from injuries and infections caused by foreign bodies and pathogens.

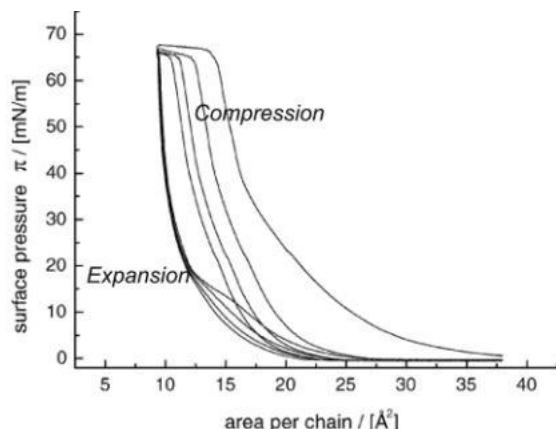
Surfactant life cycle



Surfactant life cycle—synthesis, secretion, and recycling. Alveolar type II cells, which cover about 7% of alveolar epithelial surface, are mainly responsible for surfactant production using dietary substrates (1). Surfactant is synthesized in the endoplasmic reticulum (ER) (2) of alveolar type II cells, and transported to the Golgi (3) for further modification. Most of the surfactant components are stored in the lamellar bodies (4) until they are secreted into liquid

hypophase on the alveoli by exocytosis (5). Surfactant forms a lattice-like structure, called tubular myelin (6), which is transported to the air–liquid interface to form a monolayer of surfactant film (7). The phospholipids are either internalized and degraded by macrophages (8) or recycled back to the type II cells for reuse (8'). Note that surfactant protein (SP)-A, SP-B, and SP-D are also synthesized in club cells in terminal bronchioles.

Isotherm for lung surfactants



Alveoli are lined with surfactant monolayer, which reduces surface tension, hence reduces work of breathing

Reference:

Saxena, S. Lung Surfactant. *Resonance* **2005**, 10 (8), 91–96.

<https://doi.org/10.1007/bf02866749>.

Han, S.; Mallampalli, R. K. The Role of Surfactant in Lung Disease and Host Defense against Pulmonary Infections. *Annals of the American Thoracic Society* **2015**, 12 (5), 765–774.

<https://doi.org/10.1513/annalsats.201411-507fr>.

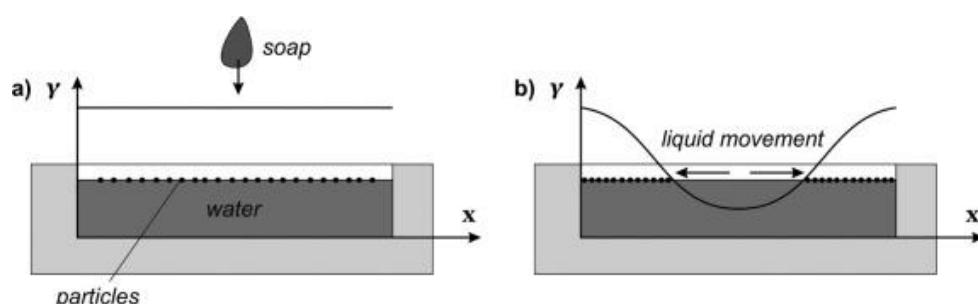
Brinzeu, F.; Pinkerton, K. E.; Zasadzinski, J. A. Environmental Tobacco Smoke Effects on the Primary Lipids of Lung Surfactant. *Langmuir* **2003**, 19 (7), 2900–2907.

<https://doi.org/10.1021/la026455e>.

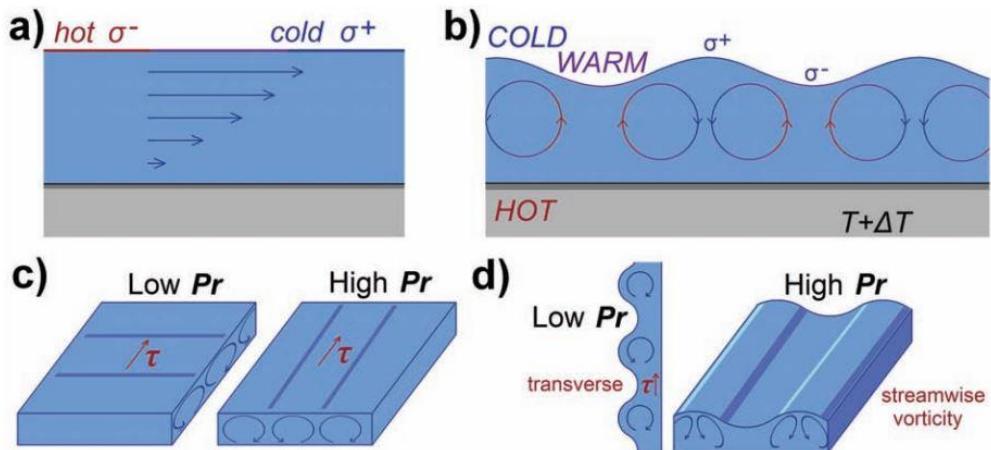
2.7 The Marangoni effect

The Marangoni effect (also called the Gibbs–Marangoni effect) is the mass transfer along an interface between two phases due to a gradient of the surface tension.

Demonstration of the Marangoni effect



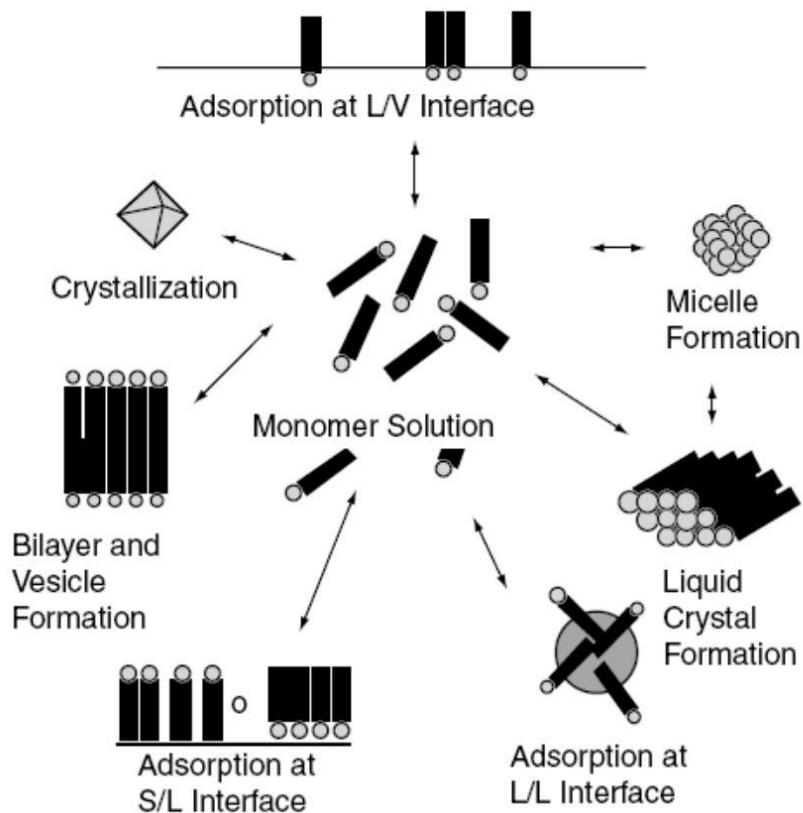
After adding a soap (surfactant), the surface tension in the middle decreases, resulting in a noticeable liquid movement.



Marangoni convection in a shear layer may lead to transverse surface waves or streamwise rolls. Surface deflection may accompany both instabilities depending on the value of Pr.

3. Self-assembly of surfactants

3.1 Surfactant self-assembly



Surfactant self-assembly leads to different structures. It depends on shape, type & concentration of surfactant, as well as the ratio of polar/non-polar solvent.

3.2 Examples of hydrophobic interactions

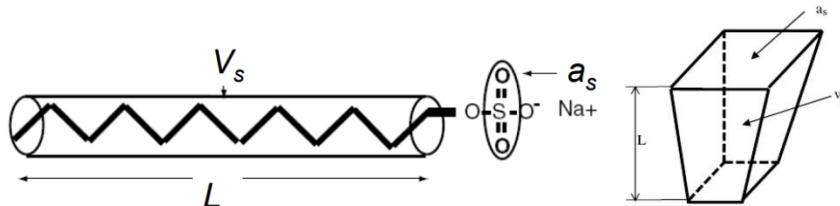
- water and oil are immiscible, with strong driving force to expel hydrocarbons from water
- self-assembly of surfactants
- other types of hydrocarbon chain association
- strong adhesion between hydrophobic surfaces in water

- non-wetting of water on hydrophobic surfaces
- rapid coagulation of hydrophobic particles in water
- attachment of hydrophobic particles to air bubbles

3.3 Surfactant packing factor

Surfactant packing parameter P allows prediction of shape & size of surfactant aggregates that will produce a minimum in free energy for a given surfactant structure

$$P = \frac{V_s}{a_s L} \quad (30)$$

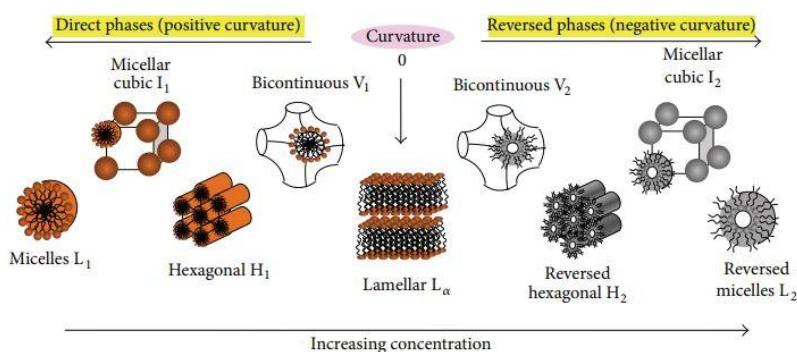


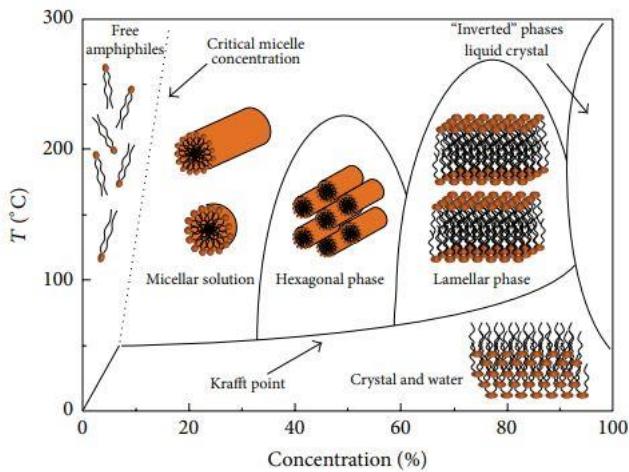
P	Surfactant Shape	Self-Assembly Shape
$< 1/3$	cone 	Spherical micelles
$1/3-1/2$	Truncated cone 	Cylindrical micelles
$1/2-1$	Truncated cone 	Flexible bilayers, vesicles
~ 1	Cylinder 	Planar bilayers
> 1	Inverted truncated cone or wedge 	Inverted micelles

Expected aggregate characteristics in relation to surfactant packing parameter P (critical value P_c)

P_c	General Surfactant Type	Expected Aggregate Structure
< 0.33	Simple surfactants with single chains and relatively large head groups	Spherical or ellipsoidal micelles
$0.33-0.5$	Simple surfactants with relatively small head groups, or ionics in the presence of large amounts of electrolyte	Relatively large cylindrical or rod-shaped micelles
$0.5-1.0$	Double-chain surfactants with large head groups and flexible chains	Vesicles and flexible bilayer structures
1.0	Double-chain surfactants with small head groups or rigid, immobile chains	Planar extended bilayers
> 1.0	Double-chain surfactants with small head groups, very large and bulky hydrophobic groups	Reversed or inverted micelles

3.4 Phase Diagrams and Lyotropic Liquid Crystal Structures of Amphiphiles



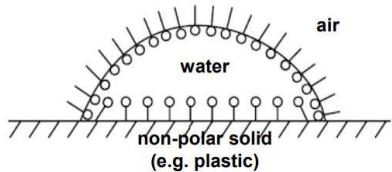


Reference:

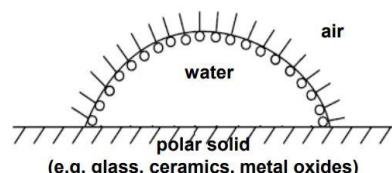
Lombardo, D.; Kiselev, M. A.; Magazù, S.; Calandra, P. Amphiphiles Self-Assembly: Basic Concepts and Future Perspectives of Supramolecular Approaches. *Advances in Condensed Matter Physics* **2015**, 2015, 1–22. <https://doi.org/10.1155/2015/151683>.

4. Surfactant adsorption on solid surface

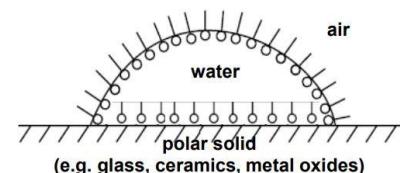
4.1 Types of surfactant adsorption



1. Non-polar surface: surfactant adsorbs at SL (due to hydrophobic effect) and LV interfaces. Result: **decrease in θ ; increased wetting.**



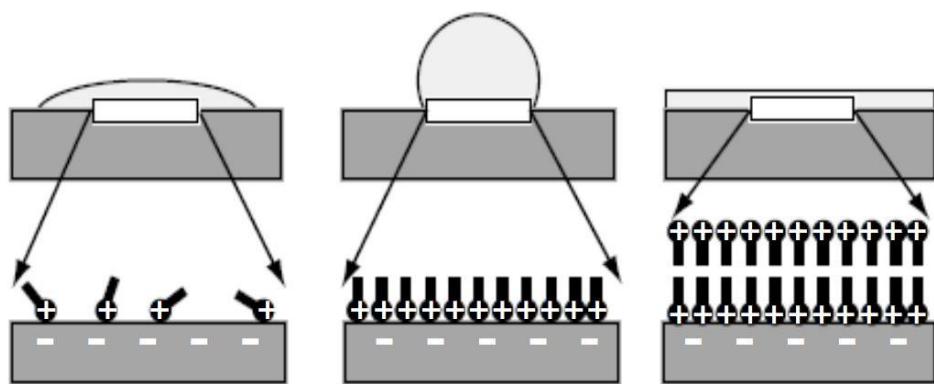
2. Polar surface. (a) Surfactant and surface have same charge. Surfactant adsorbs at LV interface. Surfactant is repelled by like-charged surface. Result: **decrease in θ ; increased wetting.**



2. Polar surface. (b) Surfactant and surface have opposite charge. Surfactant adsorbs to SL (due to opposite charge) and LV interface. Result: **increase in θ ; decreased wetting. Autophobic effect.**

4.2 Contact angle cycle

When an ionic surfactant in water adsorbs on an oppositely charged solid surface, the orientation of molecules will be such that one may observe a contact angle cycle as the adsorption increases:



The initial surface will be hydrophilic and have a small contact angle

As adsorption proceeds, surface becomes more hydrophobic and contact angle increases to a maximum

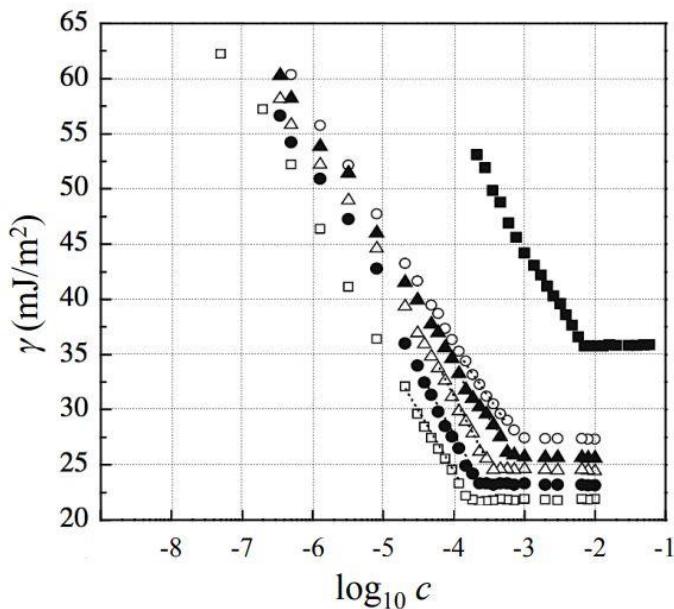
Further adsorption (if it occurs) will reverse the process leading to more polar surface and smaller contact angle.

5. Problem Sheets

5.1

a) Silicone surfactants are often used in formulations together with hydrocarbon surfactants. Figure 1 shows surface tension isotherms for mixtures of trisiloxane-type silicone surfactant with sodium dodecyl sulphate (SDS) [from: J Surfact Deterg 16, 829-840 (2013)].

The surface tension is plotted as a function of $\log_{10} c$, where c is the bulk concentration of the mixture in moles, for various mole fractions x_{SDS} of SDS: $x_{\text{SDS}} = 1.0$ (filled squares), $x_{\text{SDS}} = 0.9$ (circles); $x_{\text{SDS}} = 0.8$ (filled triangles); $x_{\text{SDS}} = 0.6$ (triangles); $x_{\text{SDS}} = 0.4$ (filled circles); $x_{\text{SDS}} = 0$ (squares). All the isotherms are at a temperature $T = 30^\circ\text{C}$.



(i) The surface tension stops decreasing for a threshold of concentration of the surfactant mixture in solution. Explain why. **[2 marks]**

(ii) Discuss the qualitative differences between the behaviours of pure SDS and pure silicone surfactant. **[2 marks]**

(iii) Estimate the surface excess of pure silicone surfactant before the plateau of the surface tension. Recall that $\ln x = \frac{\log_{10} x}{\log_{10} e}$ and gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ **[5 marks]**

- (a) *The threshold of surfactant concentration when surface tension stops decreasing is called critical micellar concentration (CMC). After which, micellar starts to form in the solution and hence no surface tension reduction (no more surfactant on the interface) is seen.*
- (b) *Qualitatively, it can be seen that, at a certain surfactant concentration, pure silicon surfactant results in smaller surface tension compared to pure SDS, leading to better performance. However, pure silicon surfactant also has a lower CMC.*
- (c)

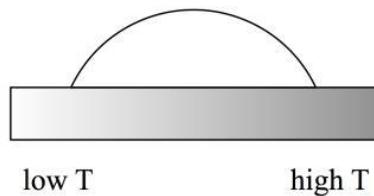
$$\Gamma_2 = -\frac{1}{RT} \frac{\partial \gamma}{\partial \ln c} \Big|_T$$

Before CMC, $\frac{\partial \Pi}{\partial \ln c} \Big|_T$ is constant, represented by the slope of the linear region of the curve.

$$slope = \frac{25 - 30}{\frac{-4 - (-4.5)}{\log_{10} e}} = -4.34 \text{ mJ/m}^2$$

$$\Gamma_2 = -\frac{slope}{RT} = 1.72 \times 10^{-6} \text{ mol/m}^2$$

- b) The surface tension of a pure fluid typically decreases with increasing temperature. Temperature-induced surface tension gradients give rise to Marangoni flow, which can cause drops to move. Consider the system in Figure 2: a temperature gradient is applied to a solid substrate, and a drop is deposited on the solid.



(i) What is the direction of the temperature-induced surface tension gradient?

[1 mark]

(ii) What is the direction of the tangential force on the liquid-vapour interface resulting from the temperature-induced surface tension gradient? **[2 marks]**

(iii) In what direction is the drop going to move and why? **[2 marks]**

[5 marks]

- (a) Surface tension decreases with temperature. Therefore, temperature-induced surface tension gradient is from right to left.
- (b) The surface tension on the right is smaller than the surface tension on the left. Since, by definition, surface tension points inward, the direction of the tangential force is from right to left.
- (c) Since the tangential force is from right to left, according to Newton's second law, the drop moves from right to left.

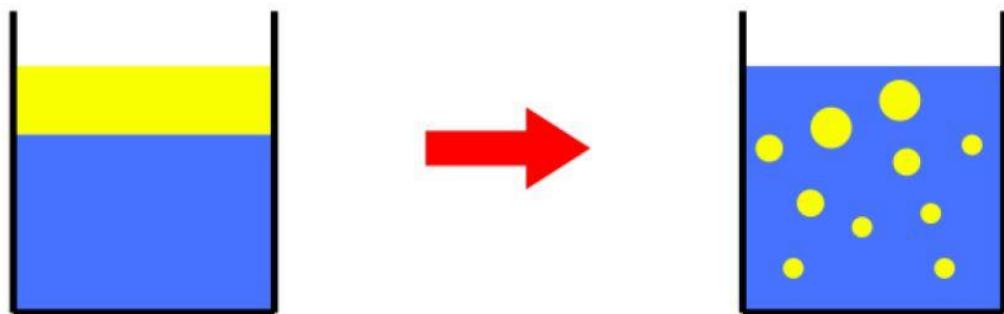
Lecture 6-7: Emulsions and Foams

Revision Time: 4/5/2023

1. Introduction to emulsions

1.1 Definitions of emulsions

Liquid droplets dispersed in a second immiscible liquid (e.g., oil and water).

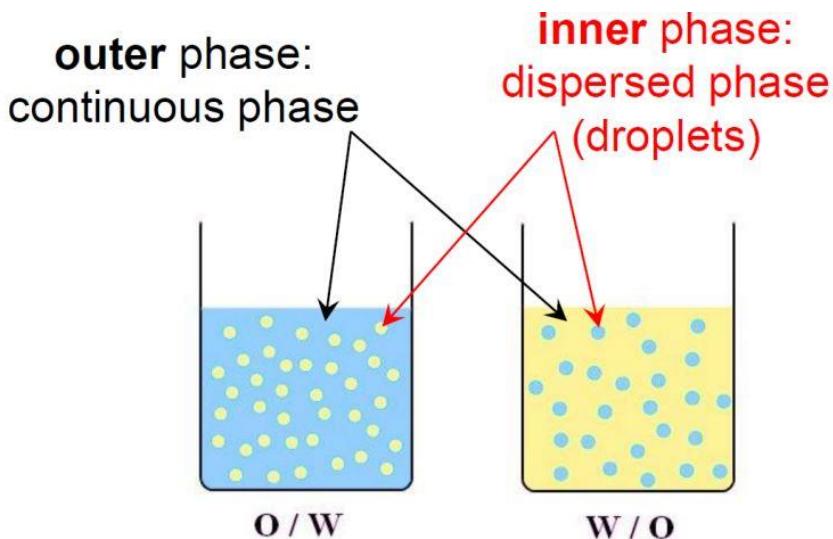


An emulsion is a mixture of two or more liquids that are normally immiscible (unmixable or unblendable) owing to liquid-liquid phase separation. --- Wikipedia

1.2 Applications of emulsions

Consumer goods	Food products, pharmaceuticals, cleaning agents, cosmetics, lubricants, fuels, herbicides, paints
Industrial applications	Agriculture, paper industry, wood processing, mining, oil & gas industry, chemical industry, textile industry, construction industry

1.3 Classification of emulsions



The formation of the inner and outer phases is influenced by several factors:

- Volume ratio of inner/outer phases
- Viscosity ratio of the two phases (phase of higher viscosity is typically continuous phase)
- Type and concentration of emulsifiers (surfactants)
- Temperature

1.4 The science of mayonnaise

Mayonnaise is an example of an oil-in-vinegar emulsion. Mayonnaise, like all emulsions,

contains an emulsifier-in this case, the incredible, edible egg. Egg yolk contains the phospholipid lecithin. Each lecithin molecule contains a polar end that is attracted to water and a non-polar end that is attracted to oil. The result is that the lecithin dissolves half of itself in water and the other half in oil. Thus, droplets of oil can be dissolved in vinegar, creating mayonnaise.

2. Thermodynamics of emulsification

2.1 Gibbs free energy

Change in Gibbs free energy upon emulsification can be expressed as follows

$$\Delta G_d = \gamma \Delta A - T \Delta S \quad (1)$$

where ΔA is increase in interfacial area, ΔS is increase in entropy.

For spontaneous dispersion to occur, the change in free energy must satisfy

$$\Delta G_d < 0 \quad (2)$$

$$\gamma \Delta A < T \Delta S \quad (3)$$

In practice, this only happens when $\gamma \leq 0.01 \text{ mN/m}$. Thermodynamically stable emulsion is called microemulsion, where the droplet diameter is approximately 10-50 nm. Microemulsion is always optically clear because the drops are too small to scatter visible light. Ultra-low γ can be achieved for oil-water interface by adding:

- Co-surfactants (e.g., medium chain length alkanol, to ionic surfactants)
- Certain ionic surfactant such as AOT (no co-surfactant)
- Non-ionic surfactant (e.g., alkyl or alkylphenylethoxylates)

Therefore, in practice we normally have

$$\gamma \Delta A \gg T \Delta S \quad (4)$$

(4) indicating that the dispersion is not spontaneous, suggesting that energy input is required for emulsification.

2.2 Balance of forces

2.2.1 Dimensionless numbers

To understand the balance of forces in laminar/turbulent regions, we need to define the following dimensionless numbers: Reynolds number (to justify the flow region), Weber number (to describe the force balance in turbulent regime), and capillary number (to describe the force balance in laminar regime)

$$Re = \frac{\text{inertia of fluid}}{\text{viscosity}} = \frac{\rho v R}{\eta} \quad (5)$$

$$We = \frac{\text{fluid inertia}}{\text{surface tension}} = \frac{\rho v^2 R}{\gamma_{12}} \quad (6)$$

$$Ca = \frac{\text{viscous force}}{\text{surface tension}} = \frac{\eta v}{\gamma_{12}} = \frac{\eta \dot{v} R}{\gamma_{12}} \quad (7)$$

2.2.2 Balance of forces in distinct flow regions

Laminar region	$Re \ll 1$	Large deformations require: large η , large $\frac{dv}{dy}$, and low γ
Turbulent region	$Re \gg 1$	Drops will break up into smaller droplets if Weber number exceeds a critical value: $We > (We)_c$ where critical weber number $(We)_c$

		depends on viscosity ratio of dispersed and continuous phases
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2.3 Interfacial stabilization by surfactants

The effects of surfactants can be summarized as the followings:

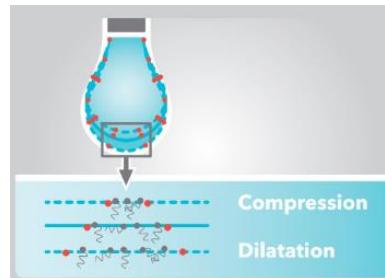
- Surfactant lowers the surface tension of liquid as described by Gibbs adsorption equation:

$$\Gamma_2 = -\frac{1}{RT} \frac{\partial \gamma}{\partial \ln c} \Big|_T \quad (8)$$

- Surfactant increases the interfacial dilational elasticity (E_0)

$$E_0 = - \left[\frac{d\gamma}{d \ln \Gamma} \right]_A = \left[\frac{d\gamma}{d \ln A} \right]_T \quad (9)$$

E is a measure of mechanical strength of an interface, it reflects the ability of a film to adjust its surface tension in an instant of stress.



- Ionic surfactants provide electrostatic repulsion
- Non-ionic surfactants can provide steric repulsion

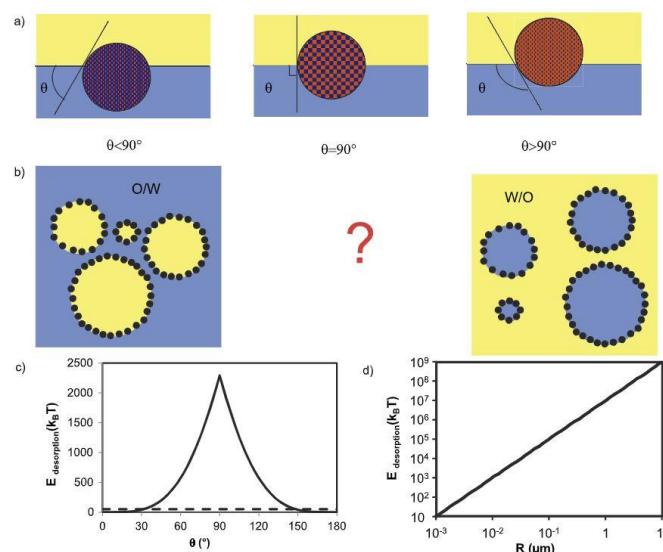
3. Properties of emulsions

3.1 Bancroft rule and Finkle rule

Bancroft rule (a rule of thumb): phase in which emulsifiers is more soluble becomes continuous phase

Finkle rule: the emulsion type (O/W or W/O) is mainly determined by the relative particle wettability in both liquids, characterized by θ . The most wetting liquid becomes the continuous phase. The energy needed to desorb a particle from the interface and to suspend it in its preferred suspending phase is given by $E_{desorption}$.

$$E_{desorption} = \gamma_{o/w} \pi R^2 (1 - |\cos \theta|)^2 \quad (10)$$



Reference:

Schmitt, V.; Destribats, M.; Backov, R. Colloidal Particles as Liquid Dispersion Stabilizer: Pickering Emulsions and Materials Thereof. *Comptes Rendus Physique* **2014**, *15* (8), 761–774. <https://doi.org/10.1016/j.crhy.2014.09.010>.

3.2 Hydrophilic-Lipophilic Balance (HLB)

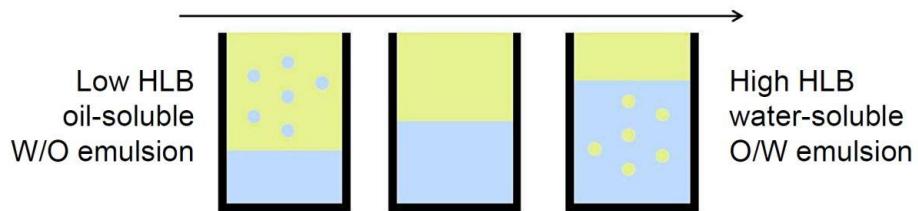
A number assigned to a surfactant describing its hydrophobic-lipophilic balance at 20°C.

$$HLB = xH - yL + 7 \quad (11)$$

Hydrophilic groups	H	Lipophilic groups	L
SO ₄ Na	38.7	CH	0.475
COOK	21.1	CH ₂	
COONa	19.1	CH ₃	
Sulphonate	~ 11.0	C=	
N (tertiary amine)	9.4	(CH ₂ CH ₂ CH ₂ O)	0.15
Ester (sorbitan ring)	6.8		
Ester (free)	2.4		
COOH	2.1		
OH(free)	1.9		
O	1.3		
OH (sorbitan ring)	0.5		

Surfactant	HLB value
Oleic acid	0.5
Span 85 (sorbitan trioleate)	1.0
Cetyl alcohol	1.3
Sorbitan tristearate	2.1
Span 80 (sorbitan monoleate)	4.3
Span 20 (sorbitan monolaurate)	8.6
Tween 81 (sorbitan monolaurate ethanoxide ₆)	10.9
Triethanolamine oleate	12.0
Nonyl phenol ethanoxide ₃₀	17.1
Potassium oleate	20
Sodium lauryl sulphate	40

Solubility in water	HLB number	Application
No dispersibility in water	0	W/O emulsifier
	2	
	4	
Poor dispersibility	6	
Milky dispersion; unstable Milky dispersion; stable	8	Wetting agent
	10	
Translucent to clear solution	12	Detergent (O/W emulsifier)
	14	
	16	
	18	Solubiliser (O/W emulsifier)



3.3 Appearance

Emulsions are transparent if

- Droplet size is much smaller than the wavelength of light (as in microemulsion)
- Or refractive index of liquids is matched

3.4 Rheology

Dilute emulsions	For very dilute emulsions, the inner phase droplets are spheroid. Assuming rigid spheres, Einstein law for viscosity can be applied: $\eta = \eta_0 \left(1 + \frac{5}{2} \Phi\right) \quad (12)$ where η_0 is the viscosity of the outer phase, Φ is the volume fraction of inner phase to the outer phase.
Concentrated emulsions	Concentrated emulsions exhibit non-Newtonian rheological behaviors (e.g., yield stress and shear thinning). Viscosity depends on: volume fraction; viscosities of inner/outer phases; droplet size; droplet deformability; nature of droplet interactions.

3.5 Stability

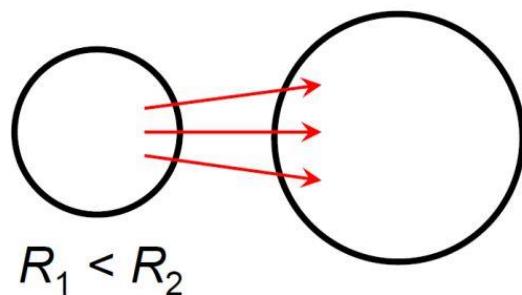
3.5.1 Ostwald ripening

Ostwald ripening happens in polydisperse emulsions. It is a phenomenon where larger droplets grow at the expense of smaller ones.

The solubility is found to increase with Laplace pressure $\frac{2\gamma}{R}$ as follows

$$\frac{S_1}{S_2} = \exp\left(\frac{2\gamma}{R_1 + R_2}\right)\left(\frac{V}{RT}\right) \quad (13)$$

where S_1, S_2 are solubility values of molecules of internal phase (total volume V) in external phase.



$$2\gamma/R_1 > 2\gamma/R_2$$

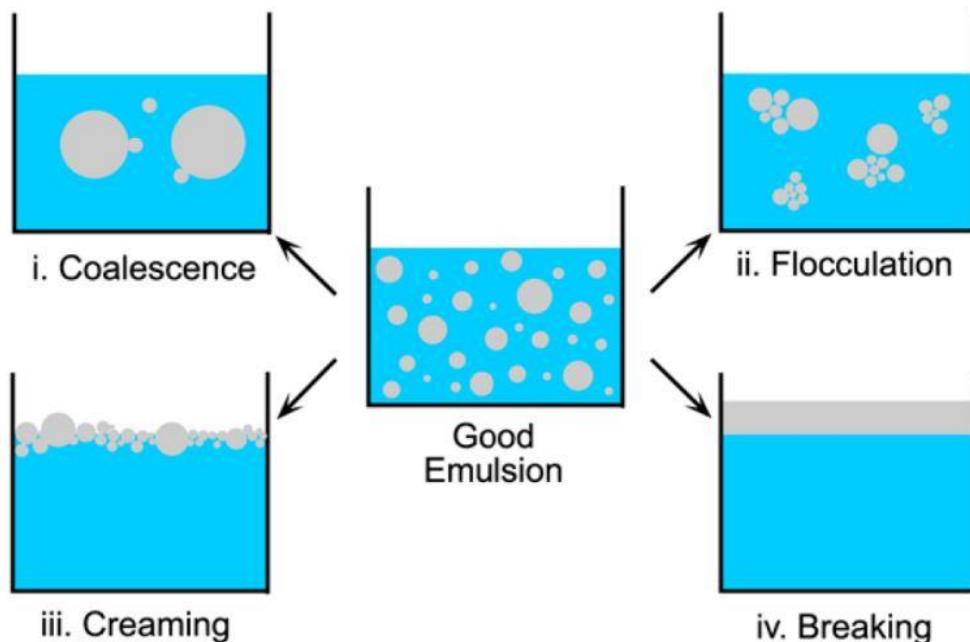
Ostwald ripening is observed in liquid-liquid systems. For example, in an oil-in-water emulsion polymerization, Ostwald ripening causes the diffusion of monomers from smaller to larger droplets due to greater solubility of the single monomer molecules in the larger monomer droplets. The rate of this diffusion process is linked to the solubility of the monomer in the continuous (water) phase of the emulsion. This can lead to the destabilization of emulsions (for example, by creaming and sedimentation).

This undesirable process eventually leads to phase separation. Adding surfactants will decrease γ (and hence $\frac{S_1}{S_2}$), and thus the molecular diffusion across interface.

3.5.2 Key issues

Emulsions are generally unstable to separation of the two liquid phase:

- Due to aggregation/flocculation of droplets
- Due to creaming/sedimentation
- Followed by coalescence



3.5.3 Creaming

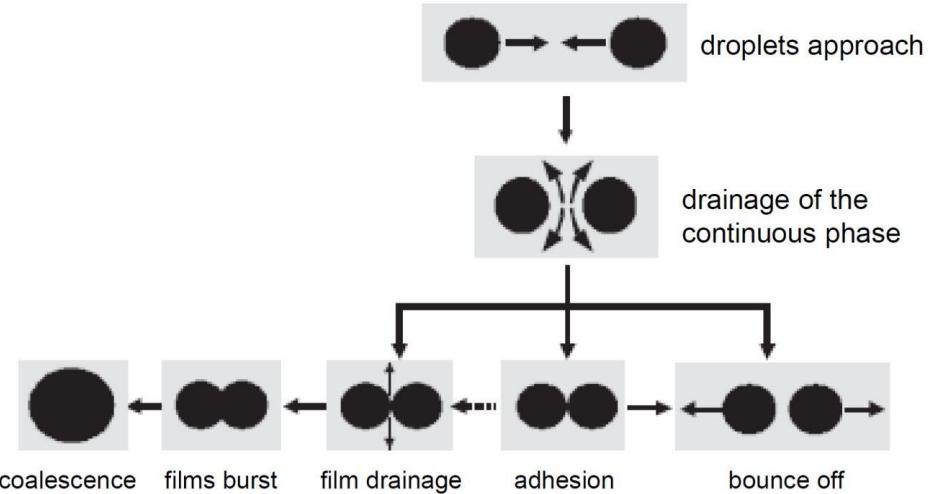
Creaming and sedimentation take place due to gravitational effect and both of them are referred as gravitational separation. They are frequently observed forms of instability in emulsions. Depending on relative densities of dispersed and continuous phase, creaming, or sedimentation may occur. If the density of dispersed phase is lower than continuous phase, droplets move upward and get separated from continuous phase forming a separate layer at the top of the continuous phase. This phenomenon is termed as creaming. On the other hand, sedimentation takes place when density of dispersed phase is higher than continuous phase forcing droplets to move downward and forming a layer at the bottom of continuous phase.

The rate of creaming is expressed in terms of creaming velocity, which can be calculated from Stokes' law:

$$v = \frac{2gr^2(\rho_{outer} - \rho_{inner})}{9\eta_{outer}} \quad (14)$$

Notice that the equation on the slide is wrong!

3.5.4 Coalescence



To avoid/reduce coalescence:

- Lower interfacial tension γ
- Marangoni effect: local fluctuations are damped by local gradients of interfacial tension created
- Mechanically strong interfacial films with large values of interfacial elasticity E
- High viscosity of continuous phase retards drainage of thin films
- Colloidal stability: repulsive interactions between droplets (steric, electrostatic) prevent aggregation

3.6 Pickering emulsions

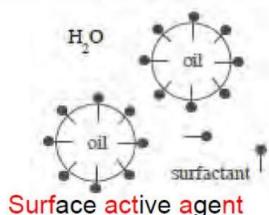
Pickering emulsions are systems composed of two immiscible fluids stabilized by organic or inorganic solid particles. These solid particles of certain dimensions (micro- or nano-particles), and desired wettability, have been shown to be an alternative to conventional emulsifiers.

Pickering emulsion, a kind of emulsion stabilized only by solid particles locating at oil–water interface, has been discovered a century ago, while being extensively studied in recent decades.

Substituting solid particles for traditional surfactants, Pickering emulsions are more stable against coalescence and can obtain many useful properties. Besides, they are more biocompatible when solid particles employed are relatively safe *in vivo*. Pickering emulsions can be applied in a wide range of fields, such as biomedicine, food, fine chemical synthesis, cosmetics, and so on, by properly tuning types and properties of solid emulsifiers.

Emulsions

Conventional emulsion



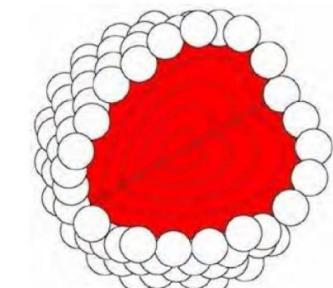
Surface active agent

Trapping energy
 $\Delta E \sim k_B T$

i.e. surfactants
hop on and off

"Infinitessimal" increase
in area is covered by
fresh surfactant

γ is decreased



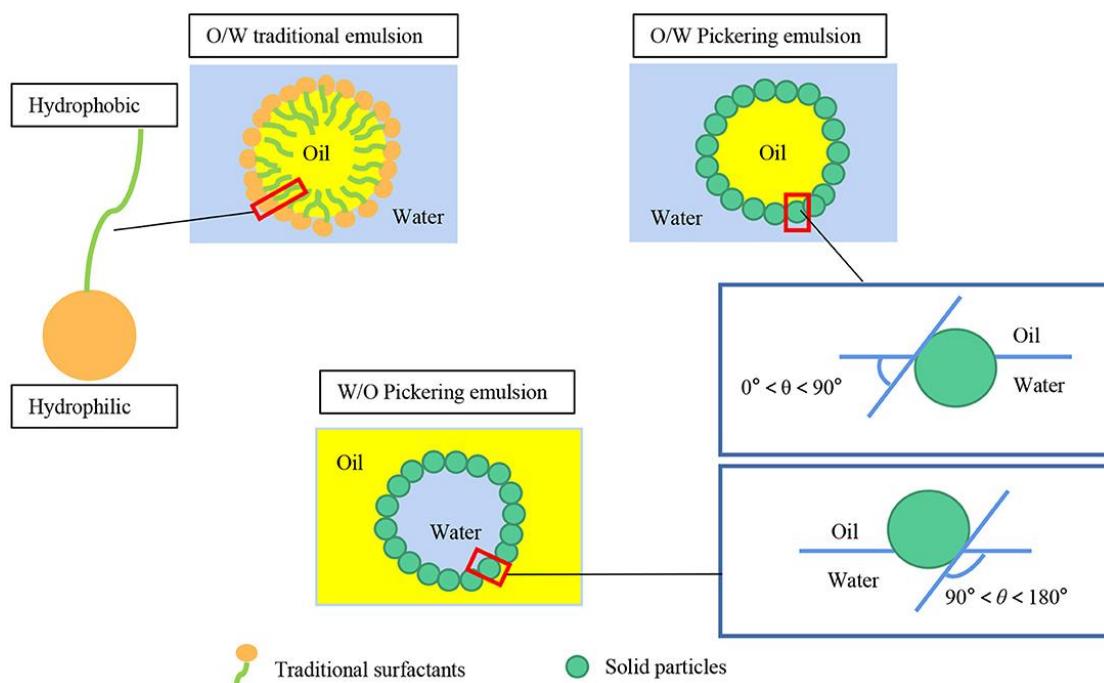
Pickering emulsion

Trapping energy
 $\Delta E > 10,000k_B T$

i.e. particles
irreversibly trapped

"Infinitessimal" increase
in area cannot be
covered by mesoscale
colloids

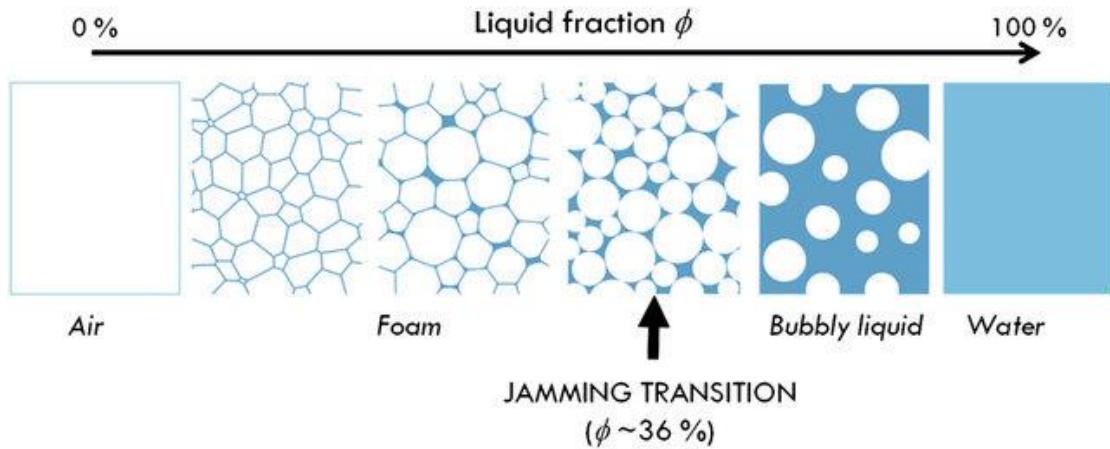
γ unchanged or
inappropriate



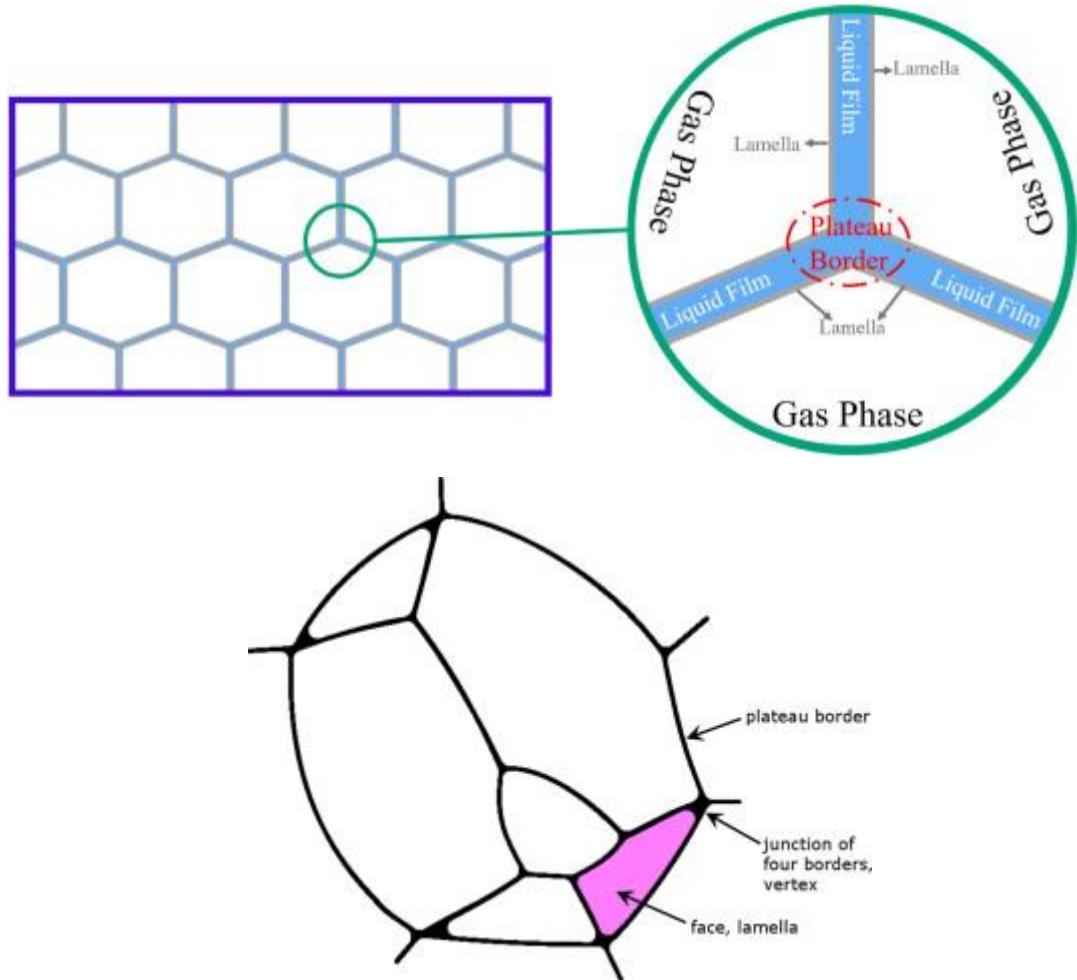
4. Introduction to foams

4.1 Definition of foams

Foam is air dispersed in a liquid as a stable mass of bubbles. Foam has relatively low liquid content; maximum about 30%, rapid change to <1% in many foams.



4.2 Foam structure & terminology



4.3 Foam in real life

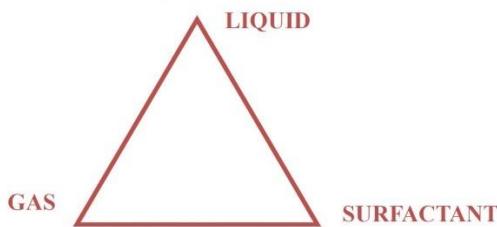
Desirable foams	Froth flotation (mineral separation; paper de-inking; water treatment)
Problem foams	Thickeners; Distillation Columns; Oil/water

	separator
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5. Foam chemistry

5.1 The foam triangle

The Foam Triangle



Foam can be eliminated by removing any one component. No pure liquid can form a stable form.

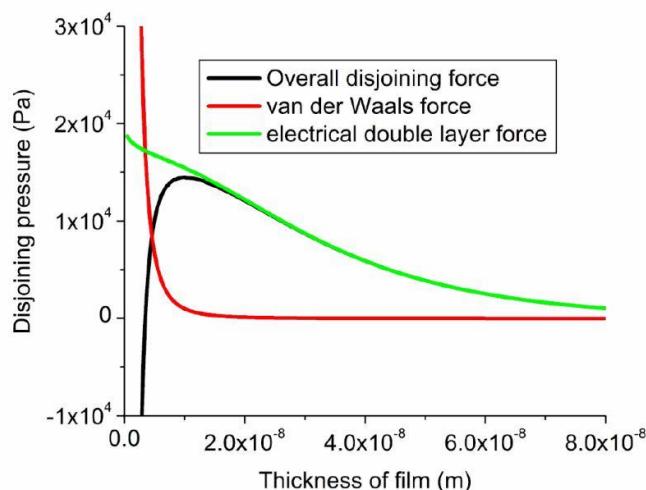
5.2 Surfactants

Foaming requires a stable gas-liquid interface, where surfactant can play a significant role. Surfactant can reduce the surface tension and form electrical double layer between planes (*opposite ions in liquid attached to charged head groups, resulting in repulsive charged layers*), and hence keep the lamellae surfaces apart.

Below the CMC, the foam volume increases with increasing concentration. Above the CMC, little further increase is seen. With increasing chain length of the surfactant, the surface tension reduces more, resulting in more stable foams.

5.3 Forces on films

Van der Waals forces	In a foam these intramolecular forces are attractive and try to thin the film
Electrical double layer or steric interaction	Caused by charged layers brought about by the polar surfactant heads, this is a repulsive force that tends to stabilize the film
Capillary suction	Caused by the curvature of the Plateau borders, it tries to thin the film (Plateau boarder draw liquid from lamellae, opposed by repulsion between lamella surfaces, therefore enhanced drainage will increase breakdown)



5.4 Gas addition

The gas can be added to the system by the following ways:

- Sparging (blowing in gas)
- From solution --- evolution, boiling, cavitation
- By entrainment --- plunging jets, turbulence, vortex formation

6. Foam physics

6.1 Principles of foam physics

Surface tension (surface energy) governs foam structure. All systems try to minimize their energy (either global minimum or local minimum). Foam therefore tries to minimize their surface area.

6.2 Plateau's rule

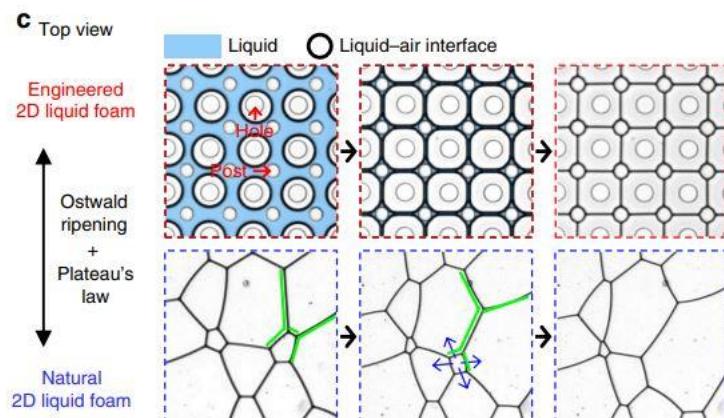
Topology

- 3 films meet at lines (lines are now called Plateau borders)
- 4 Plateau borders meet at a junction (vertex)
- More than 3 films at a Plateau border or 4 Plateau borders at a vertex are unstable

Geometry

- The 3 films at the Plateau border always meet at 120°C
- The 4 Plateau borders at the vertex always meet at the tetrahedral angle (about 109°C)

It should be noticed that Plateau's rule is valid for natural foams. With engineering foams, these rules can be violated.



Reference:

Bae, J.; Lee, K.; Seo, S.; Park, J. G.; Zhou, Q.; Kim, T. Controlled Open-Cell Two-Dimensional Liquid Foam Generation for Micro- and Nanoscale Patterning of Materials. *Nature Communications* **2019**, *10* (1). <https://doi.org/10.1038/s41467-019-11281-y>.

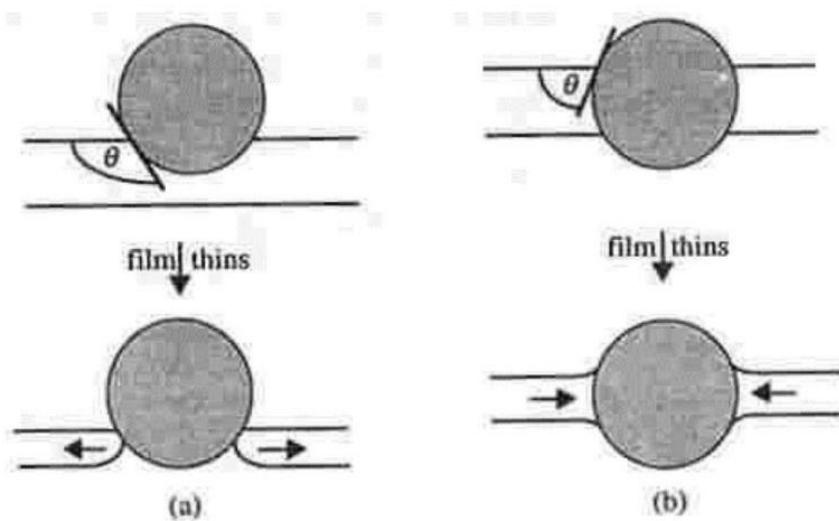
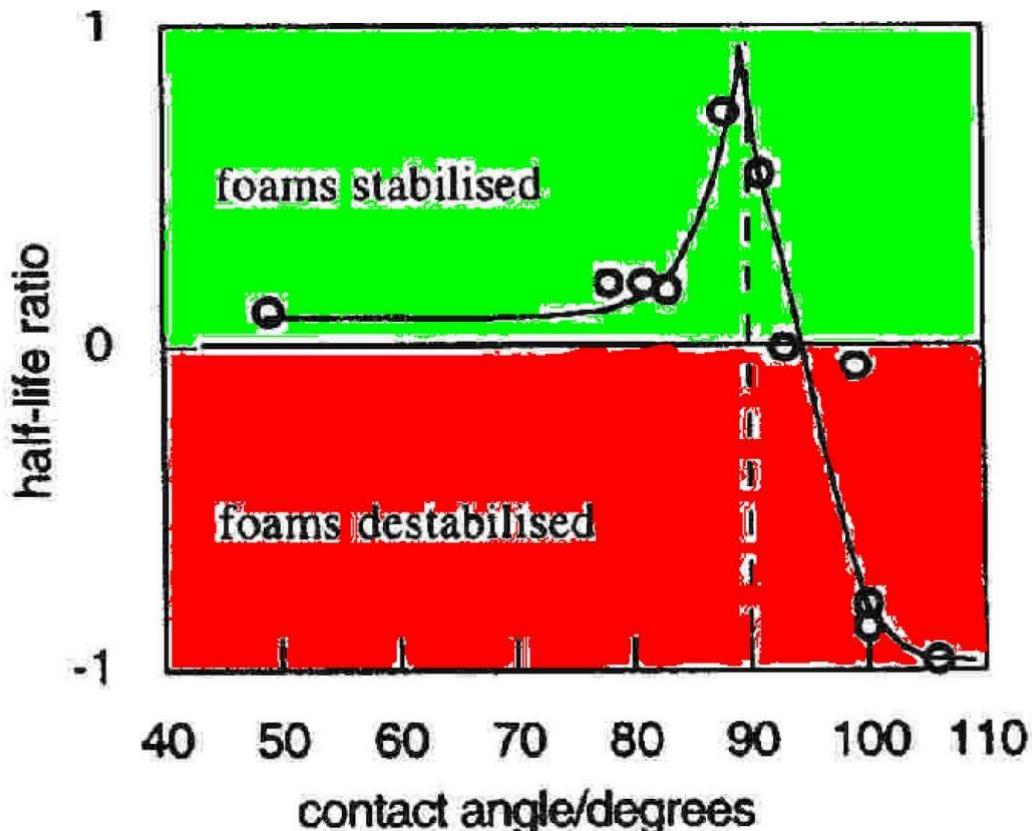
6.3 Particles in foams

High contact angle ($> 90^\circ$): Hydrophobic	Liquid moves away from particle, breaks the film
Low contact angle ($< 90^\circ$): Hydrophilic	Liquid moves towards the particle, film stabilized

Applications: (foams stabilized by particles)

- Mineral processing
- Paper de-inking

- Water treatment (dissolved air flotation)



6.4 Froth flotation

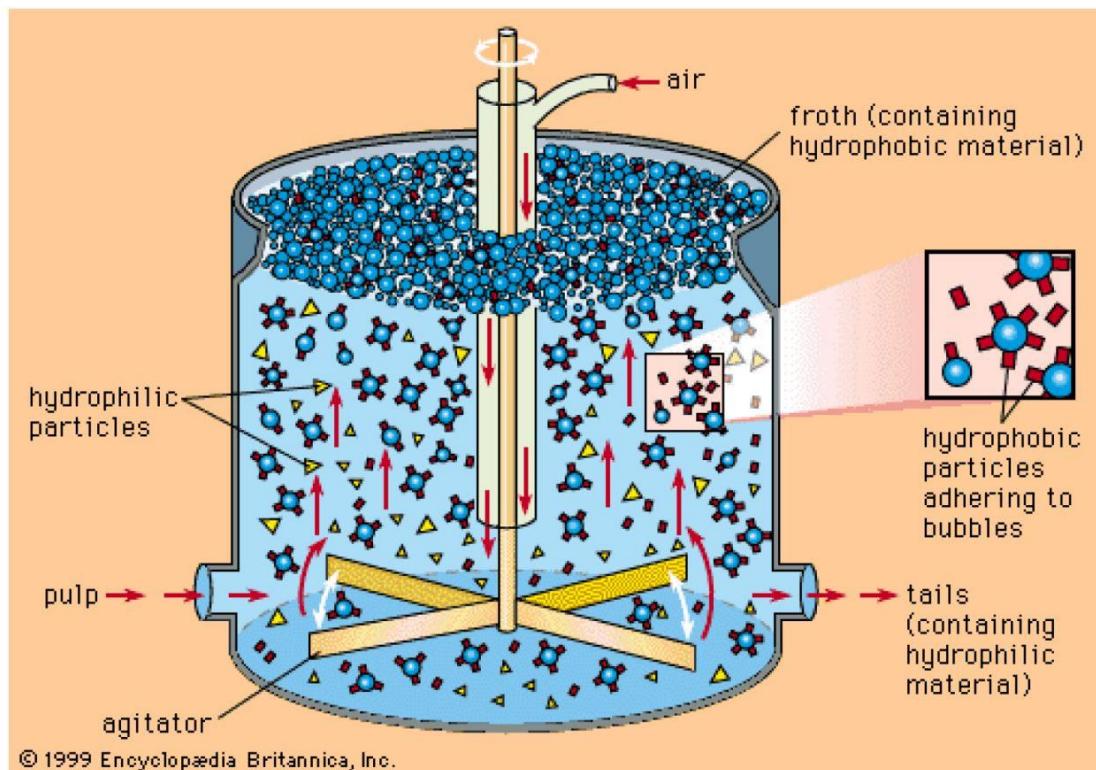
Principles: Hydrophobic particles attach to bubble lamellae, hydrophilic particles in Plateau borderers. Separation by hydrophobicity.

Applications: Waster water treatment (usually using dissolved air flotation); mineral processing; paper de-inking; foam fractionation (essentially the same process as flotation, but used to concentrate surfactants)

Froth is important in flotation: (1) The amount of water that is collected into the concentrate is dictated by the froth (increasing water content would reduce purity, the amount of water

collected is roughly inversely proportional to the bubble size). (2) As bubble size changes in the froth (from 1 mm to more than 1 cm), particles that were attached fall off and thus reduce the recovery.

Schematic:



7. Problem Sheet

IMPINGING AIR JETS MAY BE USED TO CLEAN PARTICLES FROM SURFACES.

The kinetic energy per unit volume (J/m^3) of an air jet at a surface, E_r , may be written as:

$$E_r = \frac{\rho v^2}{2} k d^{-1.3}$$

Where:

ρ = density of air (1.3 kg/m^3),

v = air velocity

k = proportionality constant ($0.4 \text{ mm}^{1.3}$)

d = distance from the jet nozzle (10 mm).

For a sphere adhered to a flat surface ($A_{11} = 1 \times 10^{-19} \text{ J}$), plz., find:

- (1) What size of particle (diameter) could a hurricane force wind ($v = 15 \text{ m/s}$) remove from a surface?
- (2) What size of particle can be removed at $v = 340 \text{ m/s}$ (speed of sound)?
- (3) What air velocity would be required to remove a 1 mm particle and a 100 nm particle?

Given that the separation distance is 0.3nm

Governing equation:

$$E_r V = \frac{A R}{6H}$$

$$V = \frac{4}{3} \pi R^3$$

$$E_r = \frac{A}{8\pi R^2 H}$$

(1)

$$E_r = \frac{\rho v^2}{2} k d^{-1.3} = \frac{1.3 \times 15^2}{2} \times 0.4 \times 10^{-1.3} = 2.93 \text{ J/m}^3$$

$$R = \sqrt{\frac{A}{8\pi E_r H}} = 2.13 \times 10^{-6} \text{ m}$$

$$D = 2R = 4.26 \times 10^{-6} \text{ m}$$

(2)

$$E_r = \frac{\rho v^2}{2} k d^{-1.3} = \frac{1.3 \times 340^2}{2} \times 0.4 \times 10^{-1.3} = 1506.4 \text{ J/m}^3$$

$$R = \sqrt{\frac{A}{8\pi E_r H}} = 9.38 \times 10^{-8} \text{ m}$$

$$D = 2R = 1.88 \times 10^{-7} \text{ m}$$

(3) for $D=1mm$, $R=0.5mm$

$$E_r = \frac{A}{8\pi R^2 H} = 5.31 \times 10^{-5} J/m^3$$

$$v = \sqrt{\frac{2E_r}{\rho k d^{-1.3}}} = 0.0638 m/s$$

It is not hard to observe

$$v \propto \sqrt{E_r} \propto \frac{1}{R}$$

Therefore, for $D=100nm$

$$v = 0.0638 \times \frac{1 \times 10^{-3}}{100 \times 10^{-9}} = 638 m/s$$

Notice that the solutions on blackboard is incorrect!