

Emulsions and Foams

Emulsions

- Fundamental concepts
 - Thermodynamics
 - Spontaneous dispersion
- Emulsification
 - Turbulent regime
 - Laminar regime
 - Emulsifiers
 - Hydrophilic-lipophilic balance
- Properties and stability
 - Appearance, rheology
 - Aggregation, coalescence, Ostwald ripening
 - Creaming and break-down
- Pickering (Particle stabilised) Emulsions

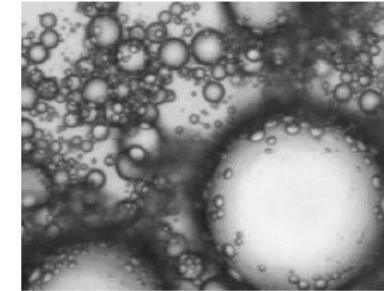
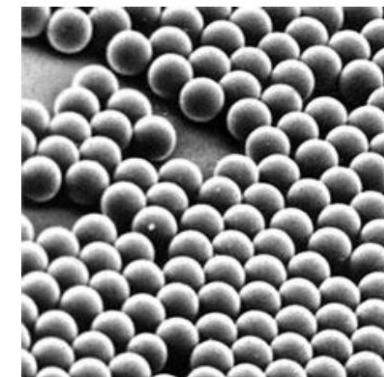
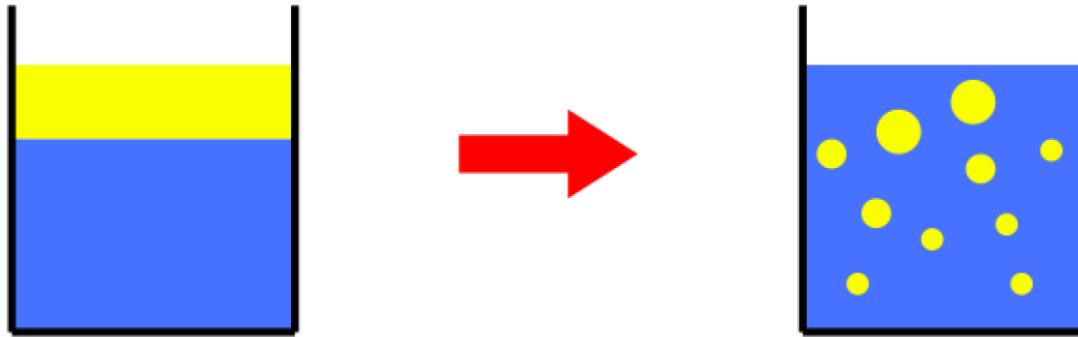


Image of a coarse emulsion

polystyrene microparticles
prepared by
emulsion polymerisation



What are emulsions?



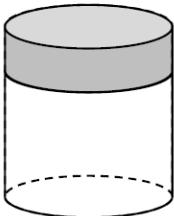
Liquid droplets dispersed in a second immiscible liquid (e.g. oil and water)



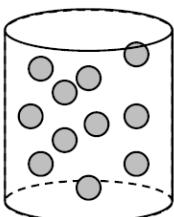
MILK: fat droplets dispersed in water

Emulsions

- 1) Estimate the energy cost of the extra interfacial area created upon emulsification:



A beaker (diameter 4 cm) is filled with water and an oil layer on top.



After emulsification, the oil is dispersed in water, forming 3×10^9 droplets of $10 \mu\text{m}$ radius.

What is the energy cost of the interface created upon emulsification? The surface tension between water and oil is $\gamma = 30 \text{ mN/m}$.

- 2) Milk is an emulsion of fat droplets in water, containing > 90% water. Water is transparent, why is milk not transparent?

Emulsions in daily life

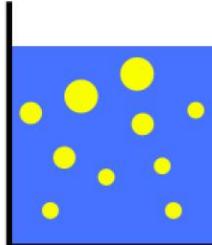


- Food products
- Pharmaceuticals
- Cleaning agents
- Cosmetics



consumer goods

emulsions



- Lubricants
- Fuels
- Herbicides
- Paints



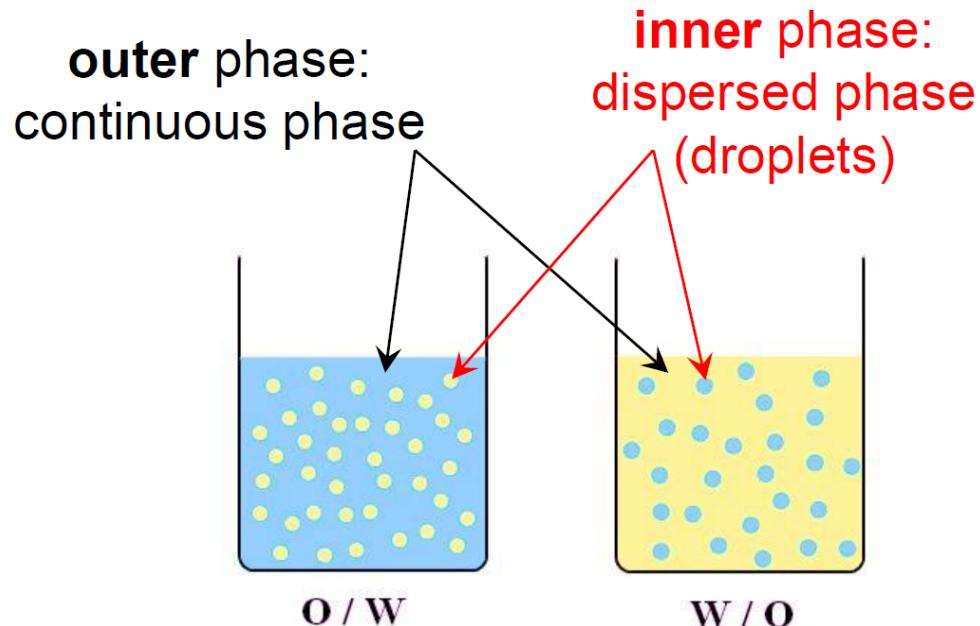
industrial applications

- Agriculture
- Paper industry
- Wood processing
- Mining

- Oil & gas industry
- Chemical industry
- Textile industry
- Construction industry



Classification of emulsions



Whether emulsion is **oil-in-water** or **water-in-oil**:

- volume ratio of inner/outer phases
- viscosity ratio of the two phases (phase of higher viscosity is typically continuous phase)
- Type and concentration of **emulsifier** (surfactant)
- Temperature

The science of making mayonnaise



- Mayonnaise contains up to **80% oil**
- Egg yolks contain **water** and proteins
- Proteins act as surfactant to stabilise emulsion
- Is mayonnaise **water-in-oil or oil-in-water emulsion?**

Making mayonnaise – Try this at home

Gordon Ramsay

<https://www.youtube.com/watch?v=qSHXG-5ShFk&feature=youtu.be&t=10s>



versus

Jamie Oliver
<https://www.youtube.com/watch?v=ypQuZX5MVsl&feature=youtu.be&t=11s>



Key concepts in emulsions

- How are droplets **formed**?
- How are they **stabilised**?
- How and how fast do they **coalesce**?
- How do liquids in emulsions **interact**?
- How do **additives** affect these processes?

Thermodynamics of emulsification

Change in Gibbs free energy upon dispersion:

$$\Delta G_d = \underbrace{\gamma \Delta A}_{(> 0)} - \underbrace{T \Delta S}_{(> 0)}$$

ΔA increase in interfacial area; ΔS increase in entropy

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

$$\Delta G_d < 0$$

However in practice

$$\gamma \Delta A > T \Delta S$$

So dispersion is not spontaneous

Spontaneous dispersion: microemulsion

Spontaneous dispersion is possible if:

$$\gamma \Delta A < T \Delta S$$

In practice this happens when $\gamma \leq 0.01 \text{ mN/m}$

A **microemulsion** is formed, with droplet diameter $\approx 10\text{-}50 \text{ nm}$

Drops are too small to scatter visible light: microemulsion is optically clear

Microemulsion = thermodynamically stable emulsion

Ultra-low γ may 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.

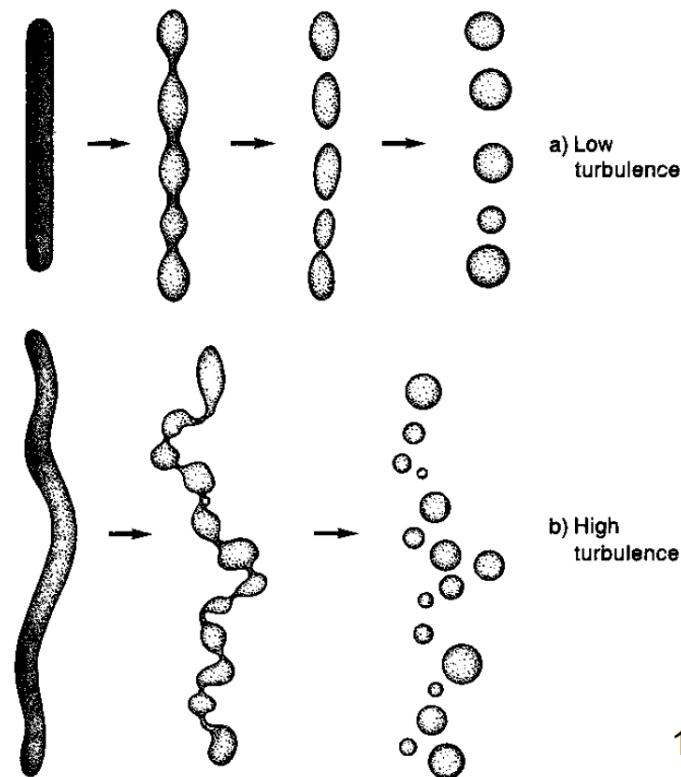
Emulsification

In most cases: $\gamma \cdot \Delta A \gg T \cdot \Delta S$

- Dispersion is not spontaneous
- Energy input is required for emulsification
- Fluid flow/mixing

$$Re = \frac{\rho v R}{\eta}$$

- Laminar regime: $Re \ll 1$
(dominated by viscosity)
- Turbulent regime: $Re \gg 1$
(dominated by inertia of fluid)



Balance of forces in turbulent regime

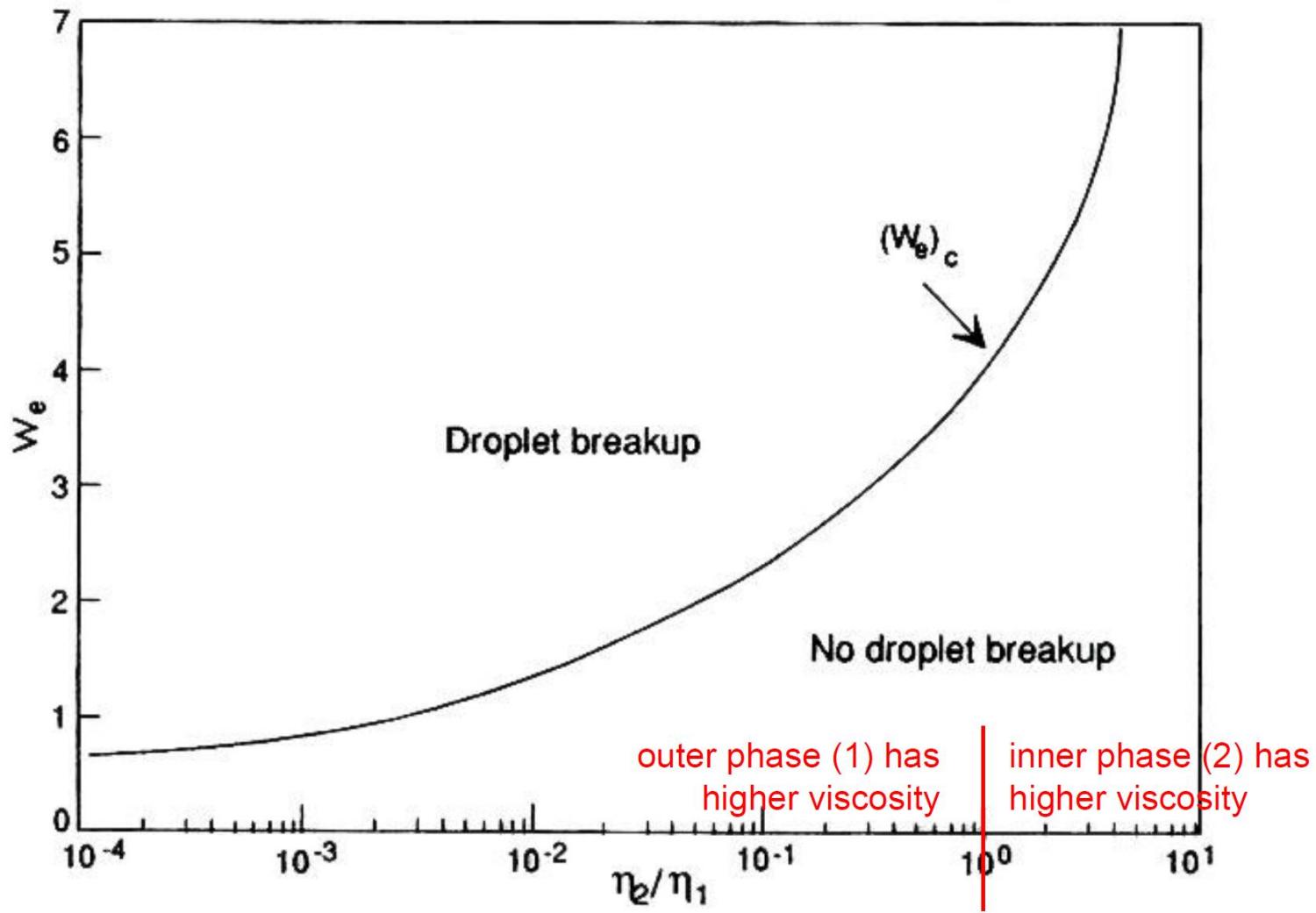
- Flow-induced deformation promotes drop break-up
- Surface tension forces resist drop deformation
- Balance is described by Weber number (fluid inertia vs surface tension):

$$We = \frac{\rho v^2 R}{\gamma_{12}}$$

ρ : density outer phase
 v : fluid velocity
 R : droplet radius
 γ_{12} : surface tension

- Drops will break up into smaller droplets if Weber number exceeds a critical value:

$$We > (We)_c$$



Critical Weber number (We_c) depends on viscosity ratio of dispersed and continuous phases

Balance of forces in laminar regime

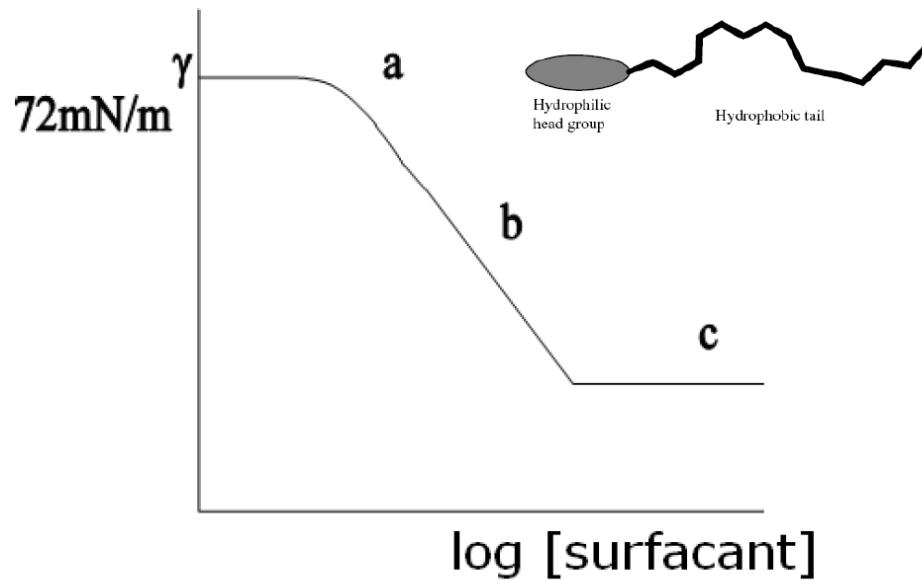
- Viscous forces are responsible for droplet deformation
- Surface tension resists deformation
- Mechanical instabilities lead to break-up. Governed by capillary number Ca :

$$Ca = \frac{\eta v}{\gamma_{12}} = \frac{\eta \dot{\gamma} R}{\gamma_{12}}$$

η : viscosity outer phase
 v : velocity of outer phase
 R : droplet radius
 γ_{12} : surface tension
 $\dot{\gamma} = dv/dy$ shear rate

- Large deformations require:
 - high η
 - high dv/dy
 - low γ
- Addition of surfactants favours emulsification by: decreasing γ , increasing η

Interfacial stabilisation by surfactants



1. Adding surfactant lowers surface tension of liquid as described by **Gibbs adsorption equation**:

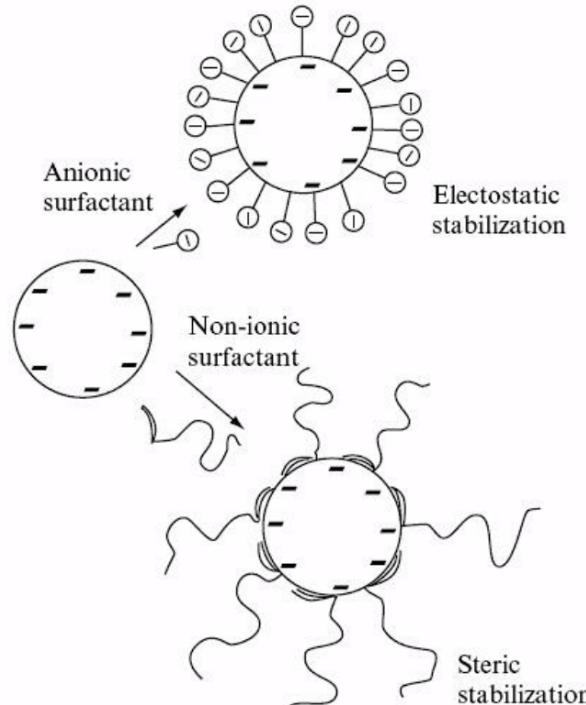
$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln c}$$

2. But also increases the **interfacial dilational elasticity**:

$$E_0 = - \left[\frac{d\gamma}{d \ln \Gamma} \right]_A = \left[\frac{d\gamma}{d \ln A} \right]_\Gamma$$

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.

Interfacial stabilisation by surfactants



3. Ionic surfactants provide electrostatic repulsion

4. Non-ionic surfactants can provide steric repulsion

Bancroft Rule

- Type of emulsion (O/W or W/O) is also determined by type of surfactant used
- **Bancroft rule** (a rule of thumb): **phase in which emulsifier is more soluble becomes continuous phase**

- Example: Sodium and other alkali metal soaps (i.e. ionic surfactants) are more soluble in water than oil → They tend to stabilise O/W emulsions.
- The reverse is true for oil-soluble surfactants → They stabilise W/O emulsions.

- How to determine in which phase a surfactant is more soluble? Hydrophilic-lipophilic balance HLB

Hydrophilic-Lipophilic Balance (HLB)

A number assigned to a surfactant describing its hydrophilic-lipophilic balance at 20° C:

$$\text{HLB} = xH - yL + 7$$

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		

HLB numbers

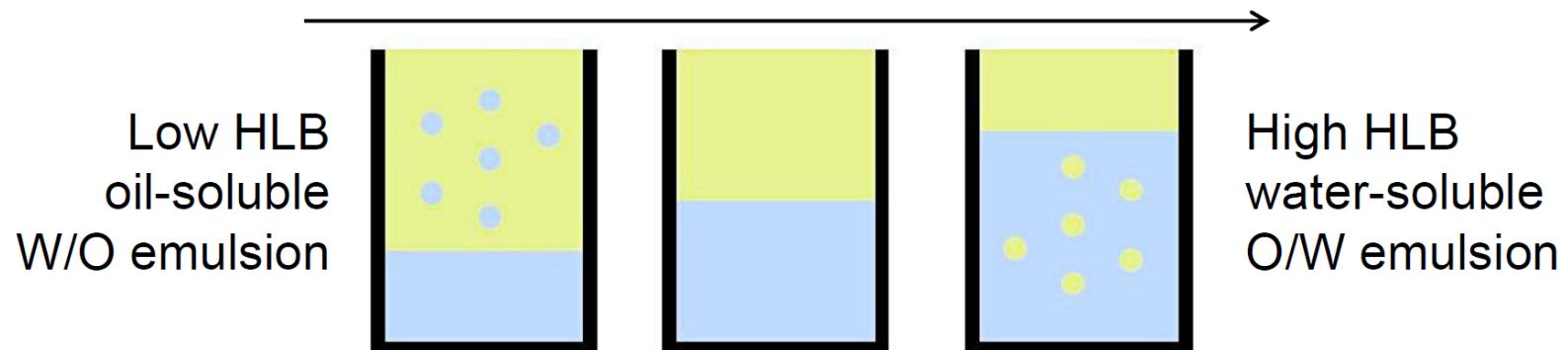
Surfactant	HLB value
Oleic acid	0.5
Span 85 (sorbitan trioleate)	1.0
Cetyl alcohol	1.3
Sorbitan tristearate	2.1
Span 80 (sorbitan monoleate)	4.3
Span 20 (sorbitan monolaurate)	8.6
Tween 81 (sorbitan monolaurate ethanoxide ₆)	10.9
Triethanolamine oleate	12.0
Nonyl phenol ethanoxide ₃₀	17.1
Potassium oleate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

HLB values for selected surfactants at 20° C (Adamson 1990).

Example: HLB number for cetyl alcohol, C₁₆H₃₃OH is determined according to: 7 + 1.9 (for OH) - 16 × 0.475 (for the hydrocarbon chain) = **1.3**

Effect of HLB on emulsification

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 Clear Solution	12	Detergent (O/W emulsifier)
	14	
	16	
	18	Solubiliser (O/W emulsifier)



General properties: Appearance

Emulsions are *transparent* if

- droplet size is much smaller than wavelength of light (as in microemulsion)
- or refractive index of liquids is matched



General properties: Rheology

- Volume fraction ϕ : ratio of the volume of the inner phase to the outer phase
- For very dilute emulsions inner phase droplets are spheres;
- Assuming rigid spheres, **Einstein law for viscosity** of a very dilute emulsion:

$$\eta = \eta_o \left(1 + \frac{5}{2} \phi\right)$$

where η_o is viscosity of the outer phase.

- Concentrated emulsions exhibit non-Newtonian rheological behaviours, e.g., yield stress and shear thinning. Viscosity depends on: volume fraction ϕ ; viscosities of inner/outer phase; droplet size; droplet deformability; nature of droplet-droplet interactions.

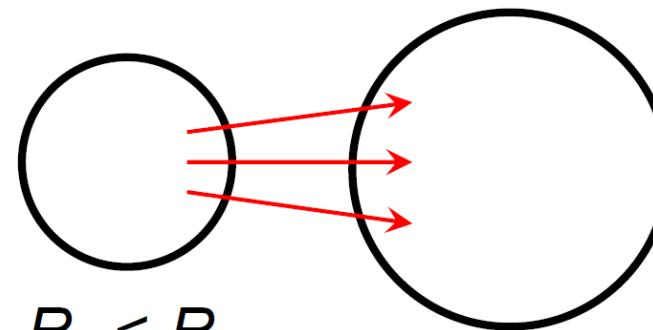
Stability: Ostwald ripening

Occurs in *Polydisperse emulsions* → larger droplets grow at the expense of the smaller ones

Solubility S increases with Laplace pressure $2\gamma/R$

$$\frac{s_1}{s_2} = \exp\left(\frac{2\gamma}{R_1 + R_2}\right) \left(\frac{V}{RT}\right)$$

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



$$R_1 < R_2$$

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

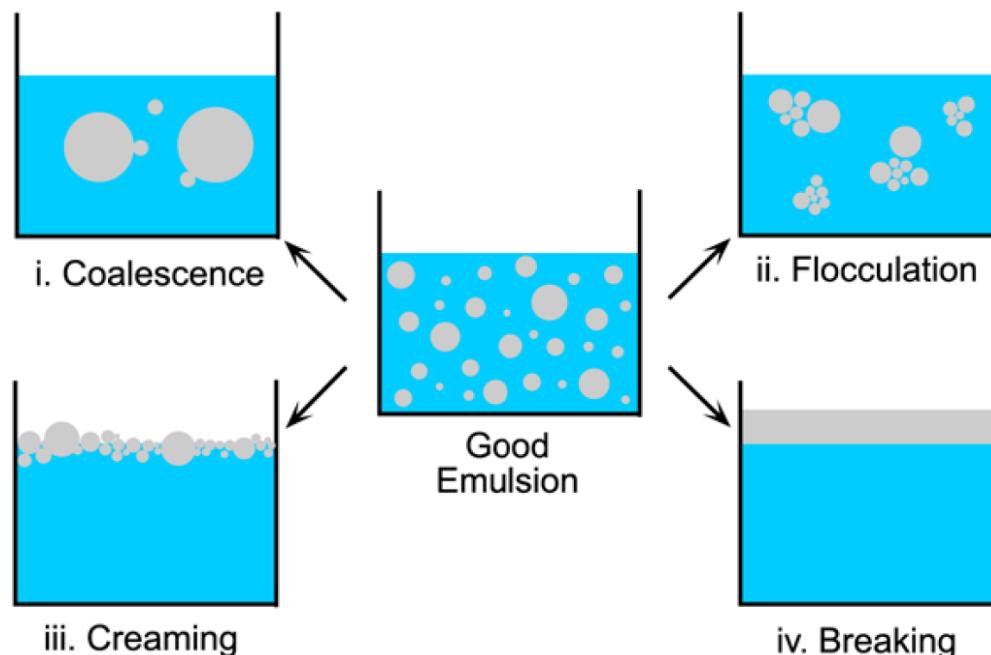
This undesirable process eventually leads to separation.

Surfactants reduce γ (and hence S_1/S_2) and reduce molecular diffusion across interface.

Stability: key issues

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

- due to aggregation/flocculation of droplets ([see Lectures on colloidal interactions](#))
- or due to **creaming**/sedimentation
- followed by **coalescence**

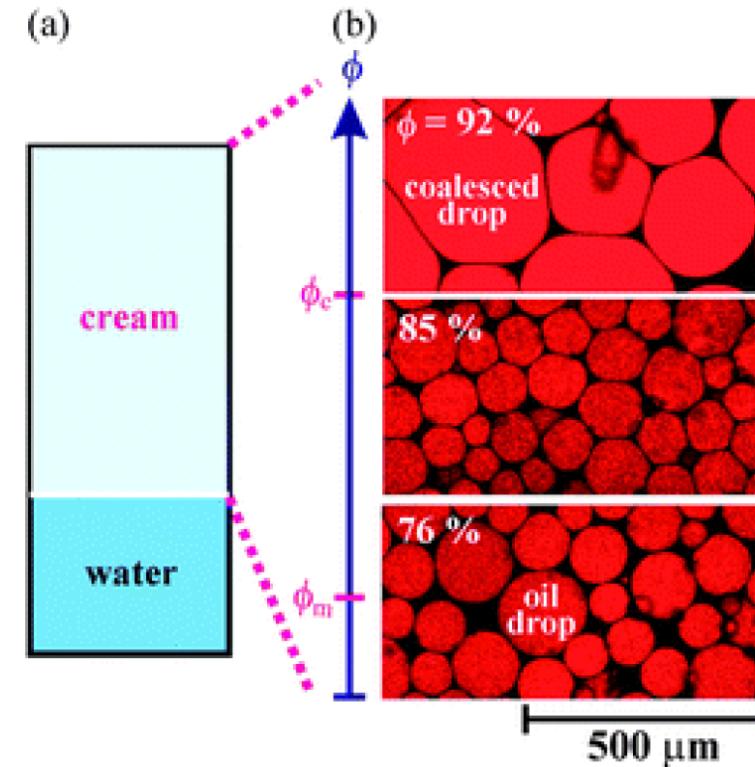


Stability: creaming

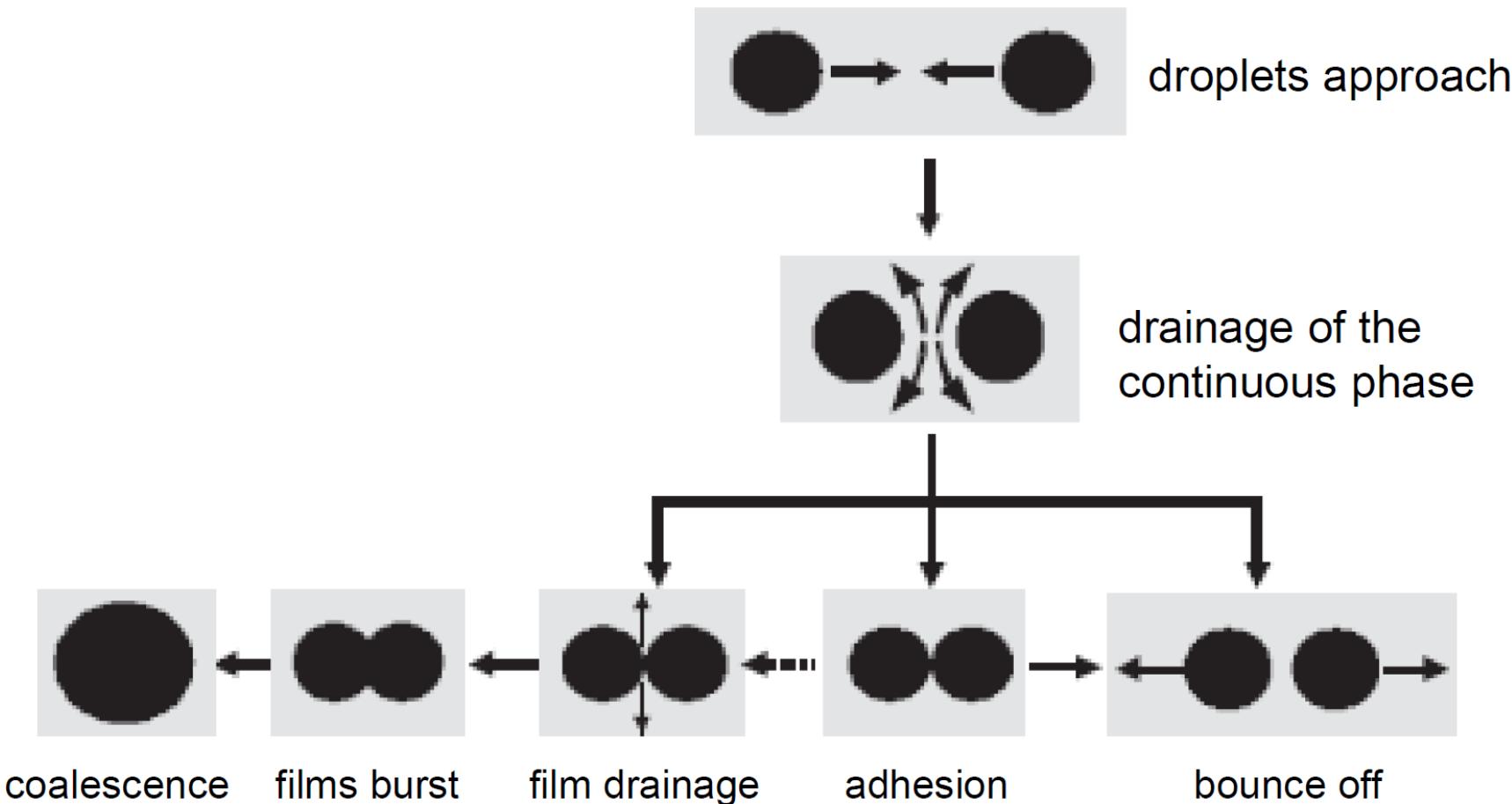
Settling velocity for dilute emulsions:

- increases with droplet size R
- increases with density difference
- decreases with viscosity η_o

$$u_0 = \frac{2}{9} \left(\frac{\rho_i - \rho_o R^2 g}{\eta_o} \right)$$



Stability: coalescence



Outcome of drop impact depends on Weber number

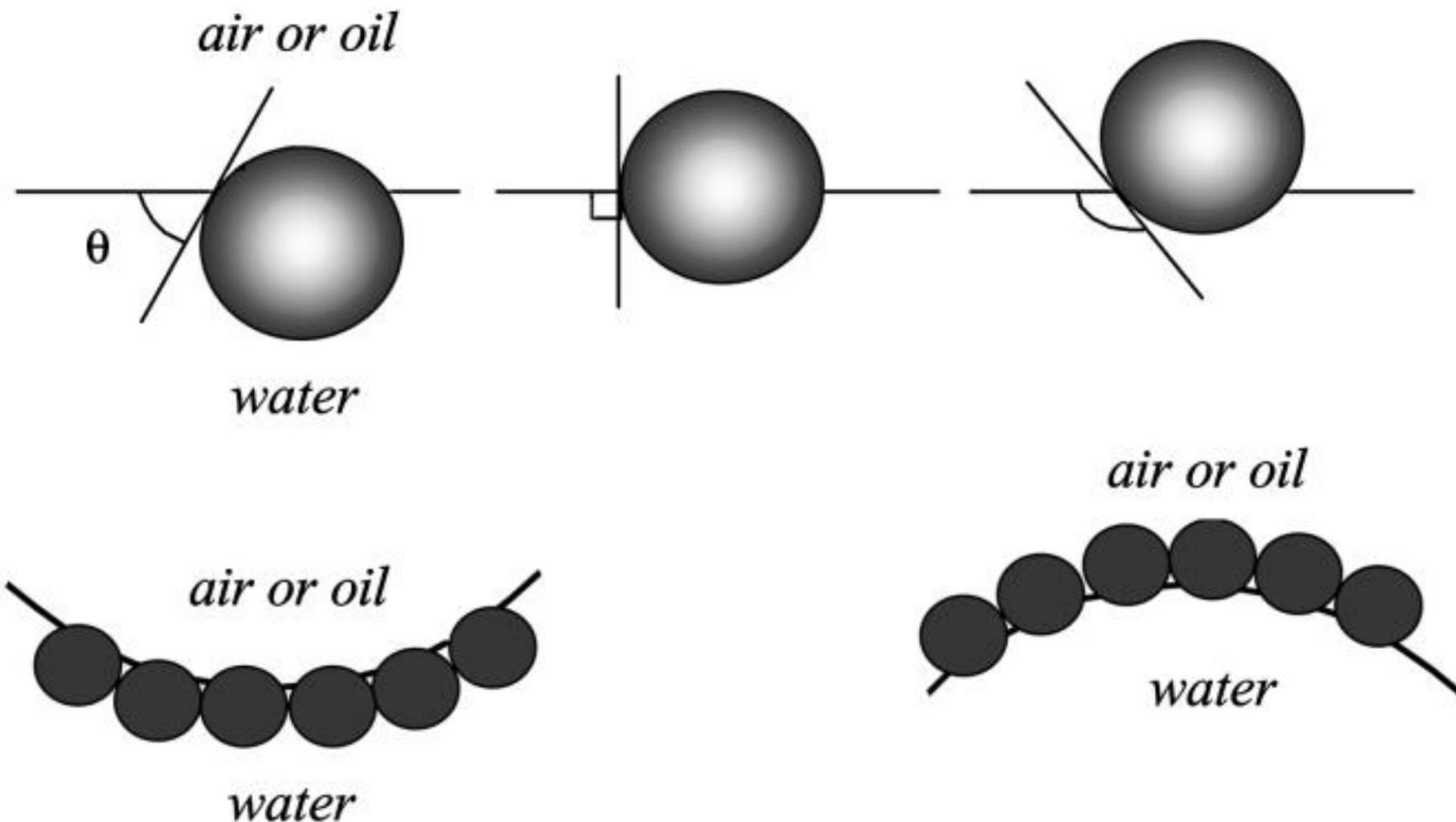
<http://www.youtube.com/watch?v=QSIZEjHjipg>

Stability against coalescence

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

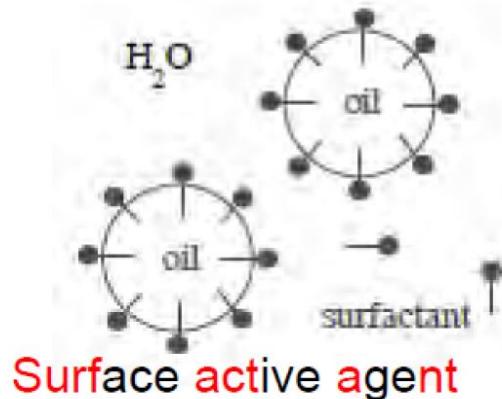
Pickering (Particle stabilised) Emulsions

Particles at liquid-liquid interfaces



Emulsions

Conventional emulsion

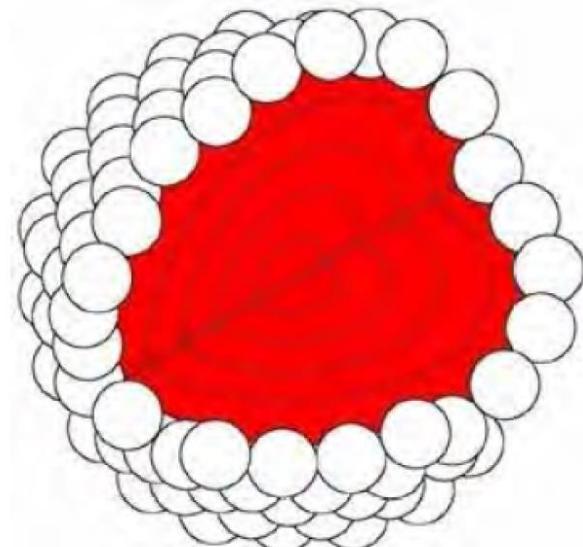


Trapping energy
 $\Delta E \sim k_B T$

i.e. surfactants
hop on and off

"Infinitessimal" increase
in area is covered by
fresh surfactant

γ is decreased



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

i.e. particles
irreversibly trapped

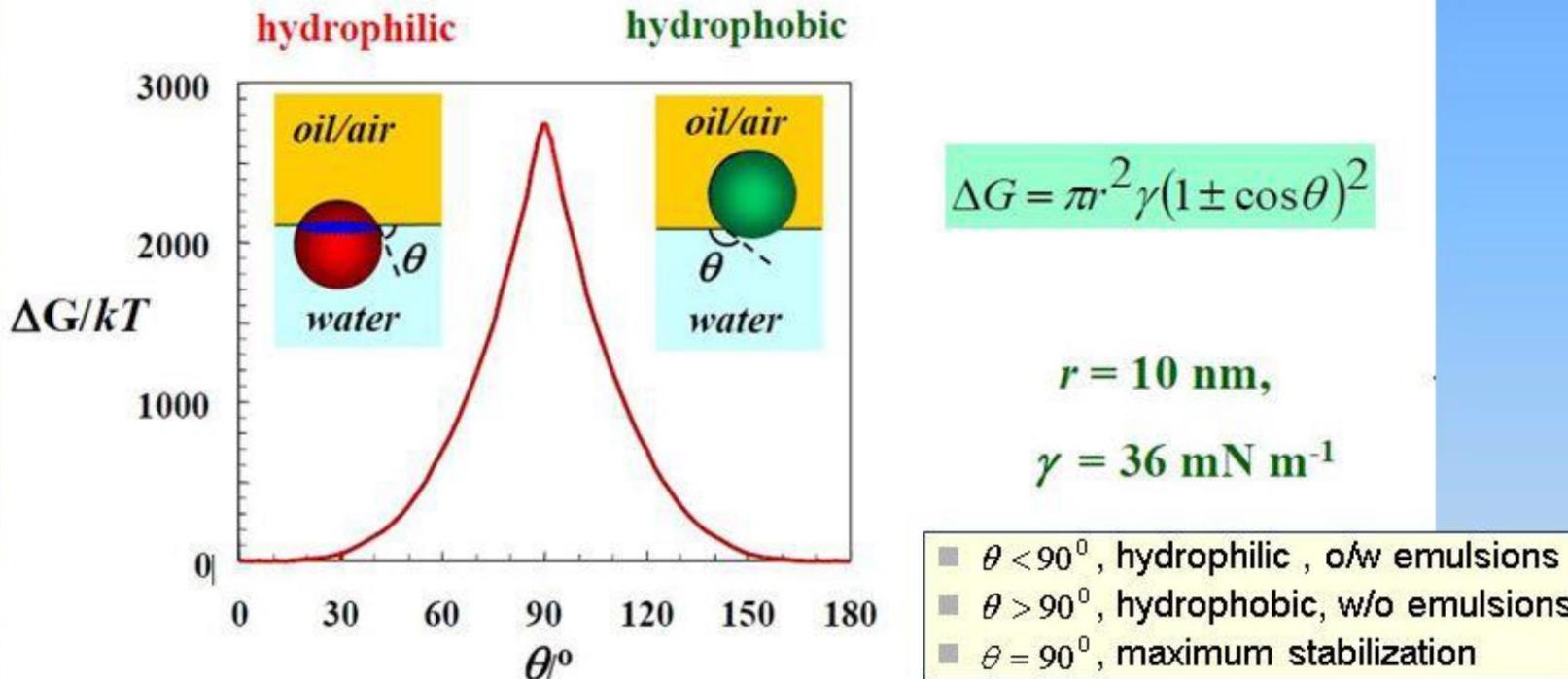
"Infinitessimal" increase
in area cannot be
covered by mesoscale
colloids

γ unchanged or
inappropriate

Pickering emulsion

Pickering Emulsions: Stabilising O/W and W/O Emulsions Solely by Solid Hydrophobic Particles

Free energy gain by losing an area of fluid-fluid interface



Particles strongly held at interfaces: irreversibly adsorbed

Contact angle is particle equivalent of surfactant HLB number

Hydrophobic particles (colloidal silica, mod. bentonite or TiO_2 , etc.) tend to curve the interfacial layer by the way, when the better wetting liquid ($\theta < 90^\circ$) becomes the dispersion (continuous) medium.

Emulsions

- recall: definition of emulsion
- recall: applications of emulsions
- understand: change in free energy upon dispersion
- understand: conditions for spontaneous dispersion
- understand: mechanical energy input required if dispersion is not spontaneous
- understand: significance of Weber number in emulsification
- understand: significance of capillary number in emulsification
- understand: role of emulsifiers and mechanisms of stabilisation
- recall: Bancroft's rule
- apply: hydrophilic-lipophilic balance
- understand: conditions under which emulsion is optically transparent
- understand: role of Laplace pressure in Ostwald ripening
- recall: mechanisms that can destabilize emulsions
- apply: settling velocity of dilute emulsions
- Recall Pickering emulsions
- Understand why they are stable

Foams

Outline of Lecture

- **Foam Structure and terminology**
- **Foam chemistry and stability**
- **Foam physics; surfaces and liquid behaviour**
- **Particles in Foams**
- **Foams in Industry**

Why Study Foams?

Foams in Processes

Desirable Foams

- **Froth Flotation**
 - Mineral separation
 - Paper de-inking
 - Water treatment



Tiete River, Brazil
Foam caused by
industrial and
residential runoff
from Sao Paulo

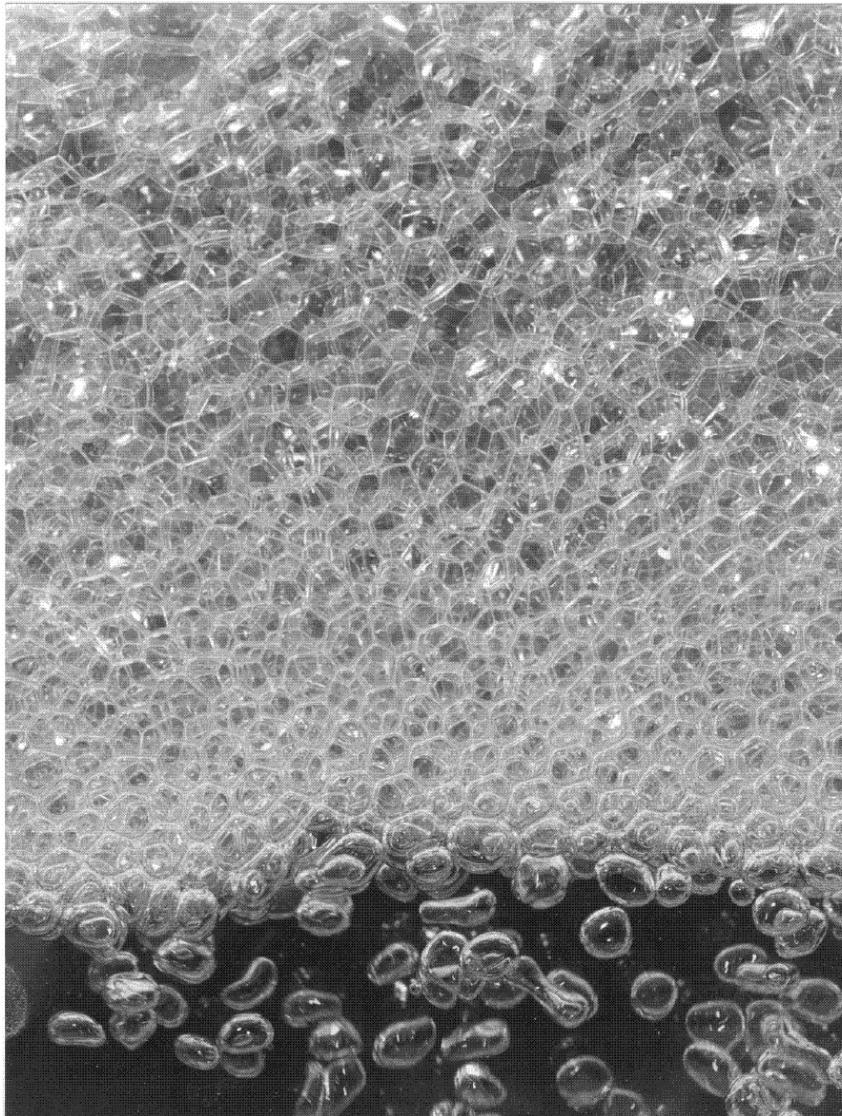
Problem Foams

- **Thickeners**
- Distillation columns
- Oil/water separators

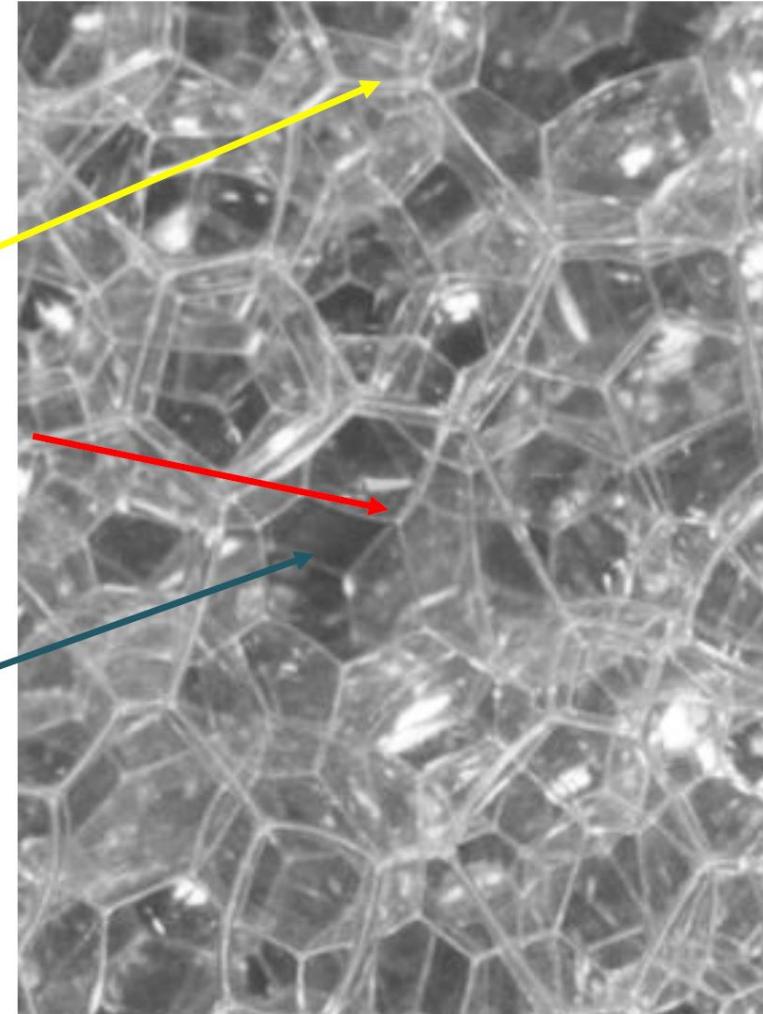
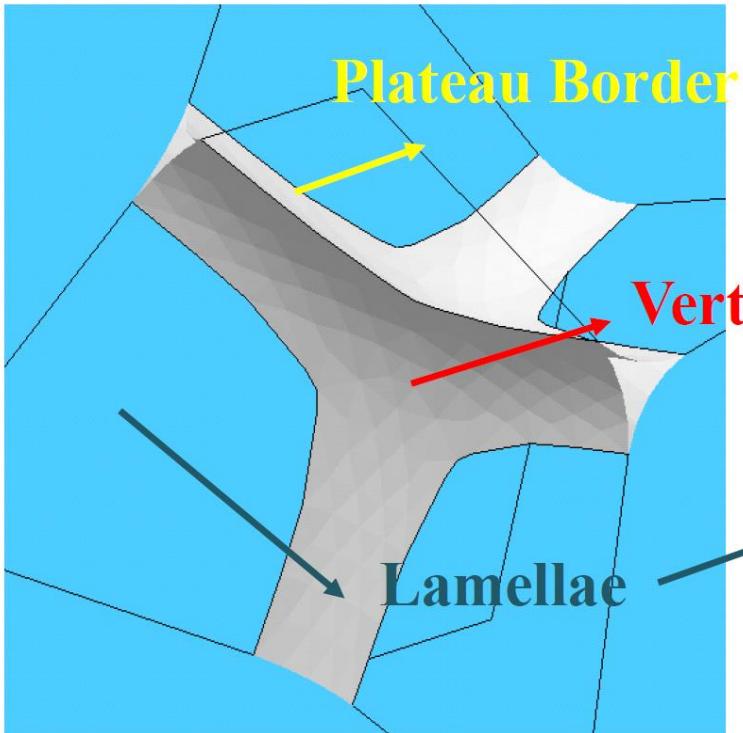


Foam Definition

- **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



Foam Structure & Terminology



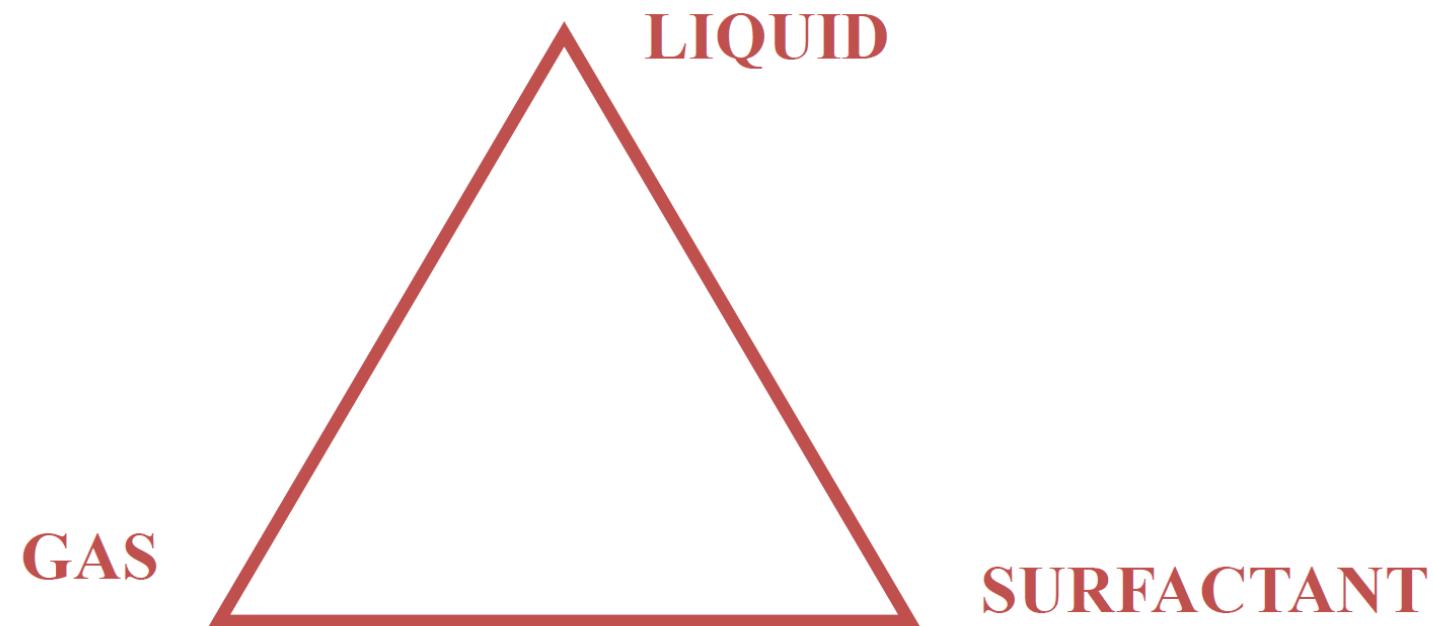
Foam Chemistry

- Foam Structure - chemical view
- Foam Components, the foam triangle
- Foam Stability and its cause
- Foaming and Foam Stability
 - **Role of surfactants and interfaces**
 - **Gas and bubbles**

Foam Chemistry

Foam Structure - a chemical view

The Foam Triangle



Eliminate foam by removing one component
No pure liquid can form a stable foam

Foam Chemistry

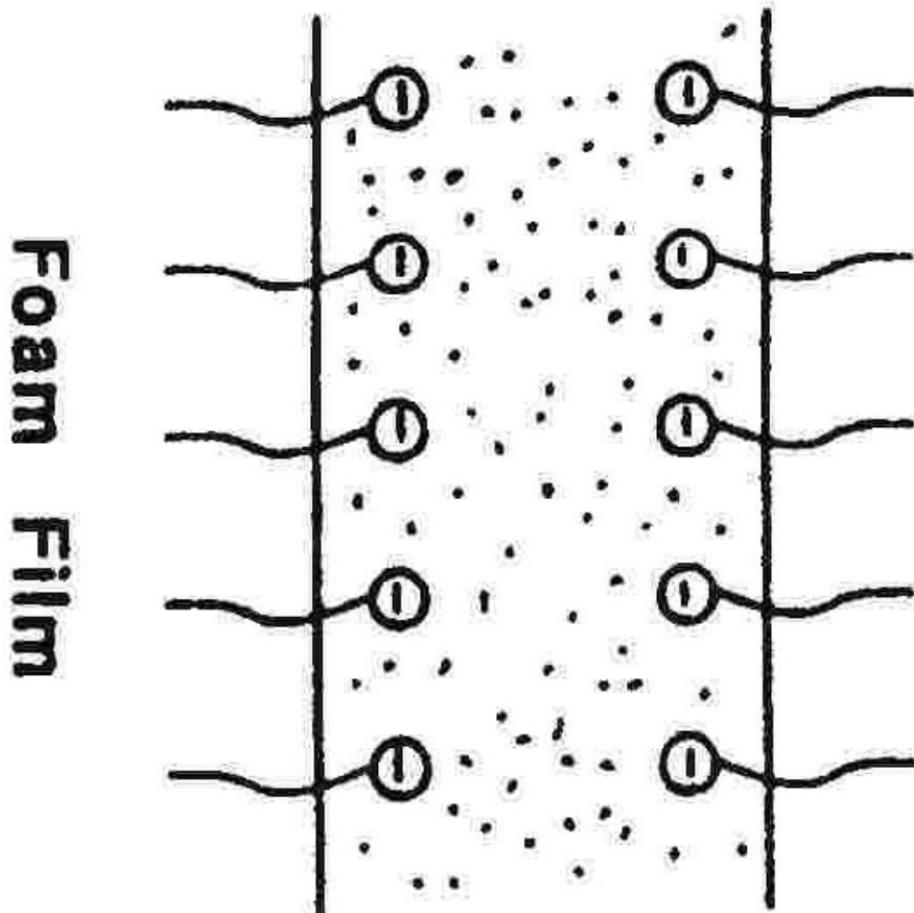
The Foam Triangle: I. Surfactants

Foaming requires a stable gas-liquid interface,
the role of surfactant molecules

- Hydrophobic and hydrophilic component
- At interface between gas and liquid
- Reduces liquid surface tension
- Keeps lamellae surfaces apart
- Can self-associate (micelles) at high conc's

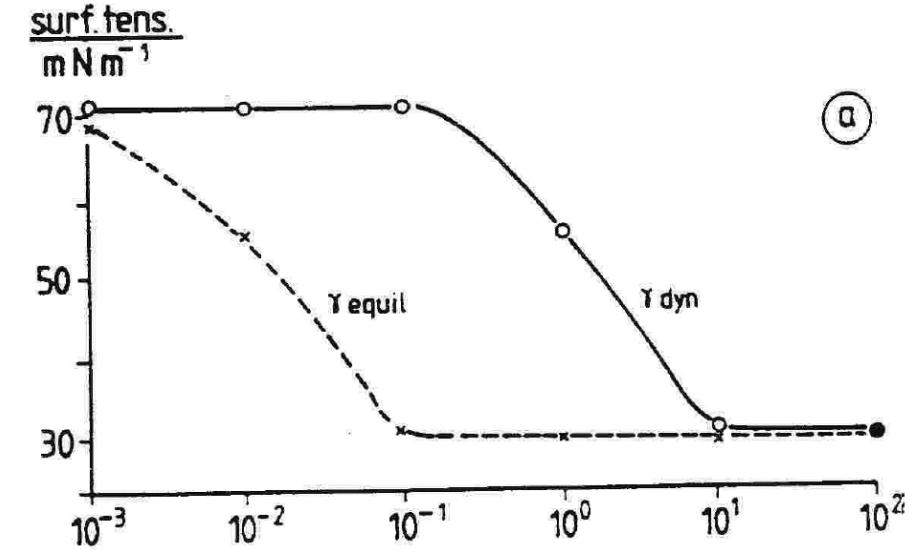
Foam Stability

Foam Stability and its Cause

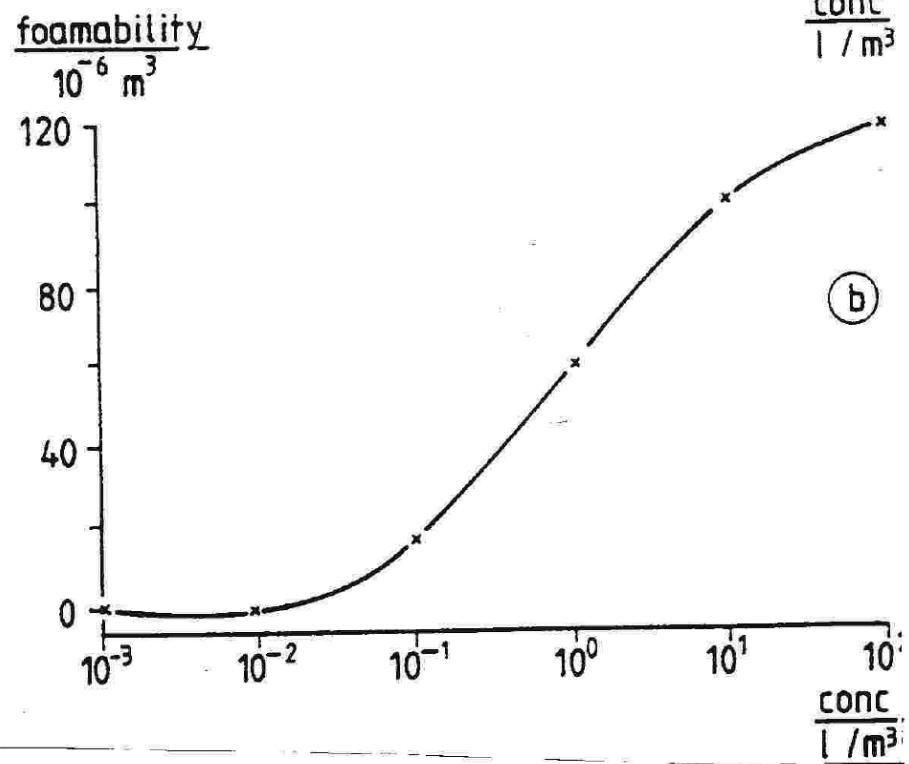


Surfactant at interface

- Lowers surface tension
- Electric double layer between planes
 - Opposite ions in liquid attracted to charged head groups.
 - Results in repulsive charged “layers”



(a)



(b)

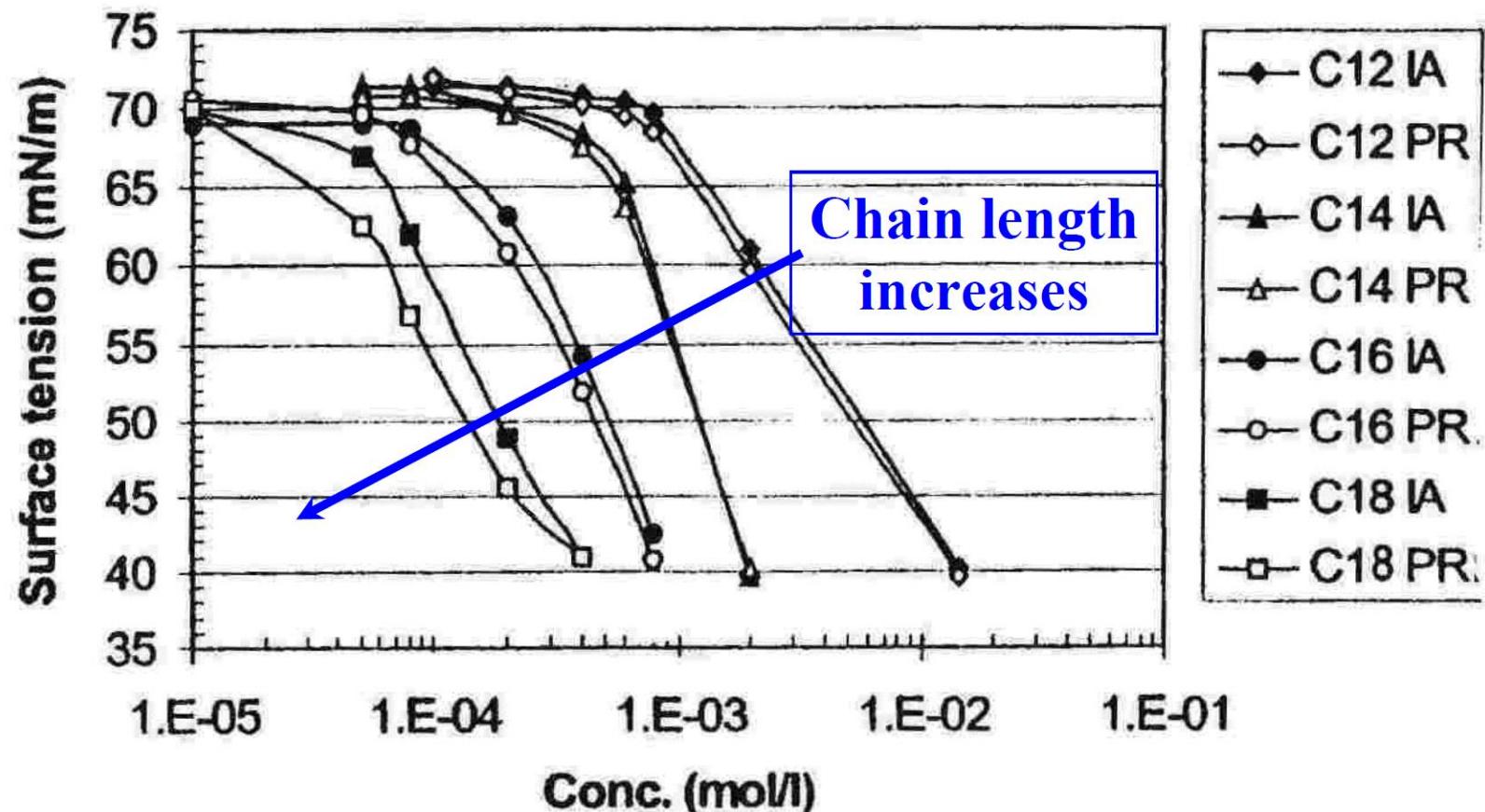
Foam Chemistry Surfactants

- Surface Tension and Foamability strongly related

Foam Chemistry

Foam Structure - a chemical view

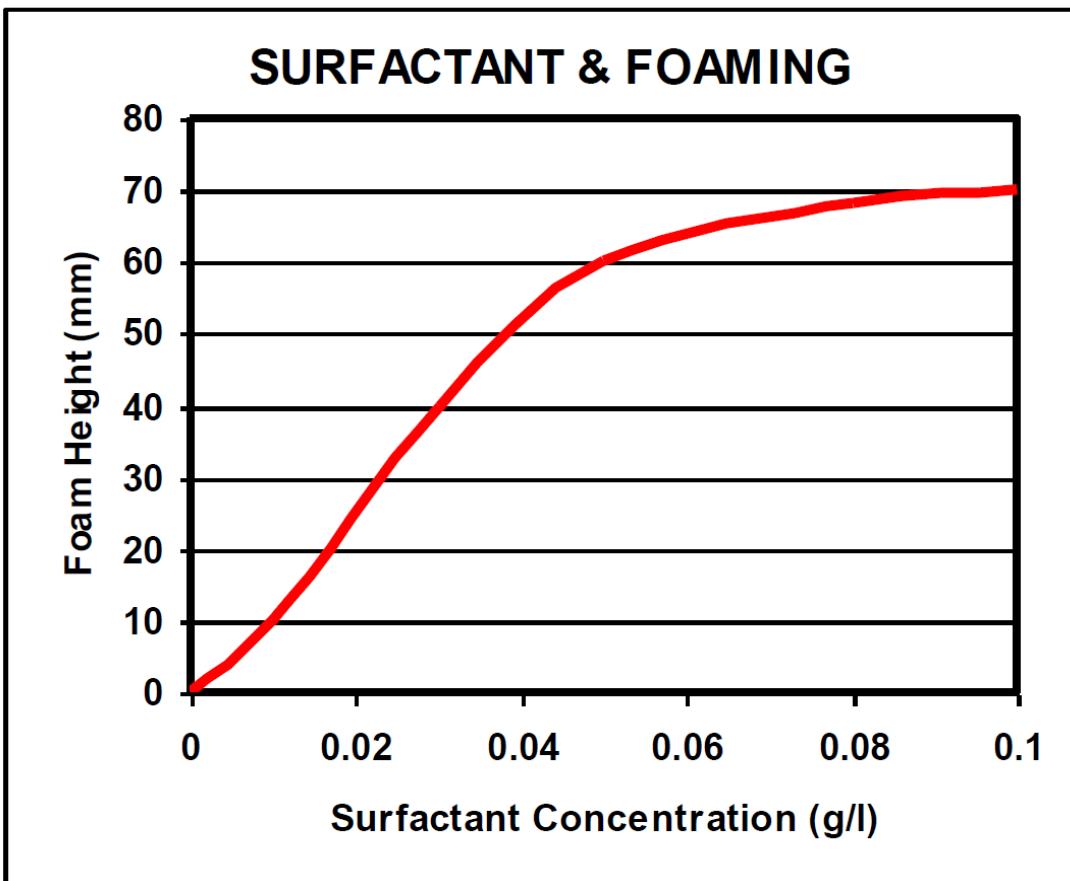
Surfactant types and Surface Tension



Surface tension of the cationic surfactants

Foam Chemistry

Foaming Effects: Concentration



- Higher concentration, greater foam volume
- Above CMC little further increase
- CMC is critical micelle concentration
 - Micelles form when surfactant clumps with itself rather than at the interface

The Effect of Pressure

- Interfaces curve when subjected to pressure differences (Young-Laplace Law):

$$\Delta P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

r_1, r_2 : radius of curvatures in perpendicular directions

γ : surface tension

ΔP : pressure difference across interface

Pressure inside a single bubble

- Remember that there are two interfaces:

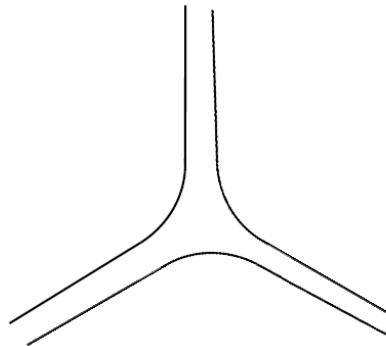
$$\Delta P = \frac{4\gamma}{r}$$

- What happens to the pressure in a ball when you pump more gas into it?
- What happens to the pressure in a bubble when you pump more gas into it?

Foam Chemistry

Foam Stability and Causes

Liquid content also affects foam stability:



- Plateau borders draw liquid from lamellae
- Opposed by repulsion between lamella surfaces

Enhanced drainage will increase breakdown

Quantifying the Forces on Films

DLVO Theory

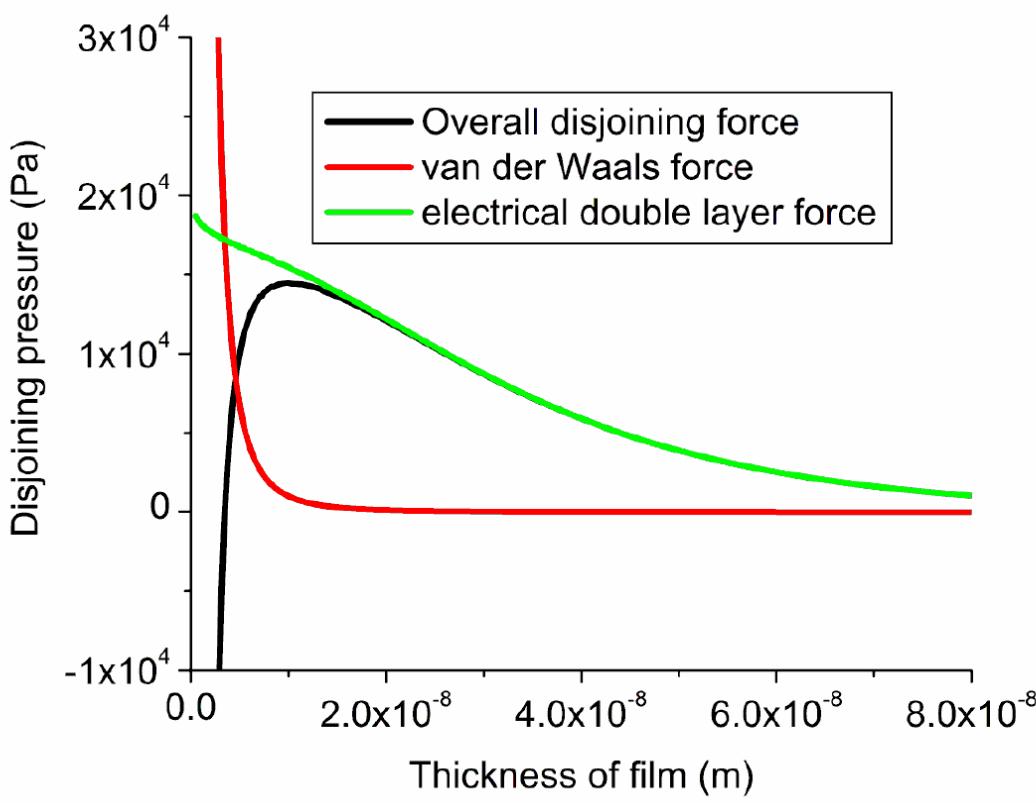
Three main forces exerted on the films:

- Van der Waals forces
 - In a foam these intermolecular forces are **attractive** and try to thin the film
- Electric double layer or steric interaction
 - Caused by the charged layers brought about by the polar surfactant heads, this is a **repulsive** force that tends to stabilise the film
- Capillary suction
 - Caused by the curvature of the Plateau borders, it tries to thin the film

Quantifying the Forces on Films

DLVO Theory

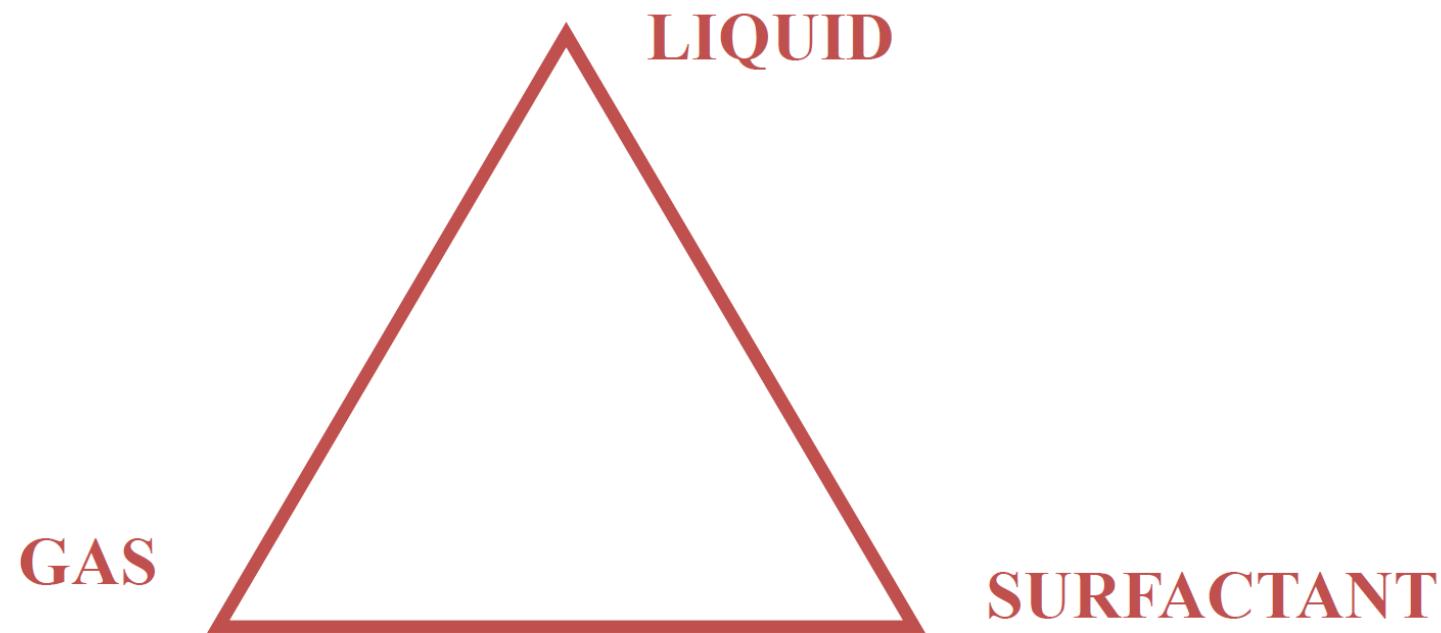
The net force due to van der Waals and electric double layer forces can be plotted as a function of film thickness:



Foam Chemistry

Foam Structure - a chemical view

- The Foam Triangle - GAS



How is gas added to the system?

Foam Chemistry

The Foam Triangle: II. Gas Addition

- Sparging (blowing in gas)
- From Solution - evolution, boiling, cavitation
- By Entrainment
 - Plunging jets (pipes, overflows etc.)
 - Turbulence
 - Vortex formation

Foam Chemistry: Summary

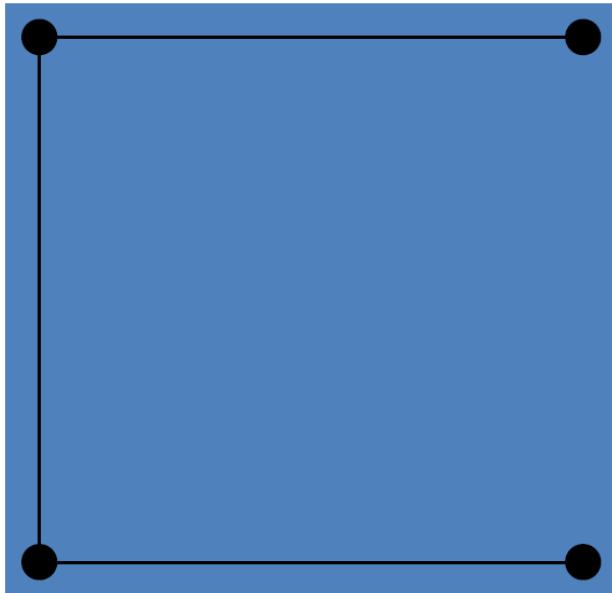
- Surfactants keep foams stable; more for longer chains and higher concentrations
- Gas required for foaming
- What about particles?
 - wait a bit....

Foam Physics & Structure

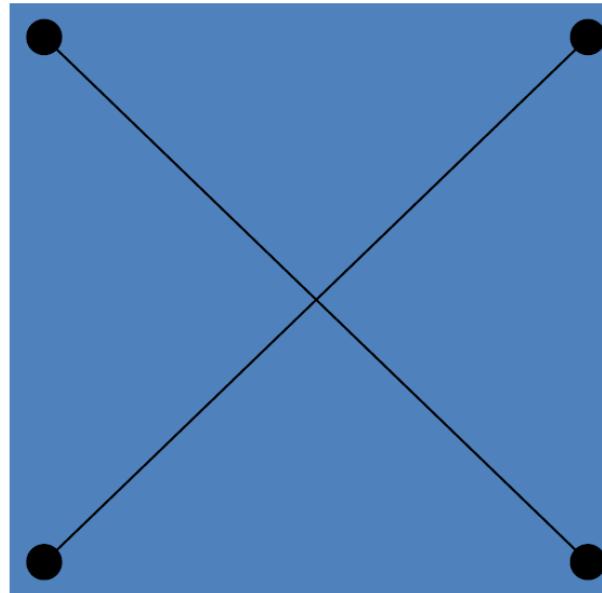
- Surface tension (surface energy) governs foam structure
- All systems try to minimise their energy.
 - Stable systems are those that are at an energy minimum
 - The minimum need not be the global minimum
- Foams therefore try to minimise their surface area

Look at 2-D example:

- What is the shortest length of lines that can connect the corners of a square?



or

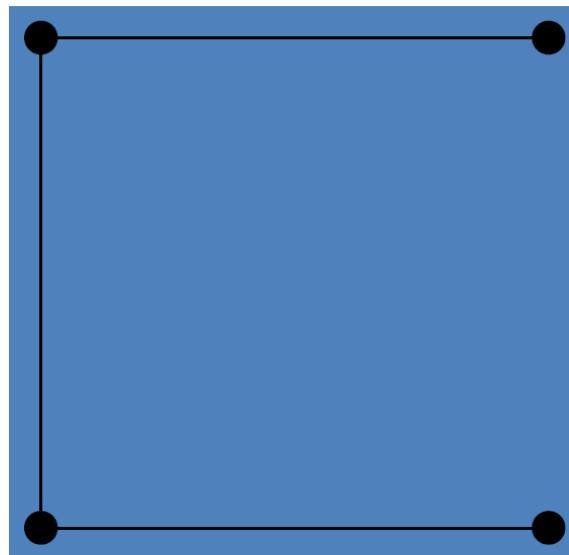


or another option?

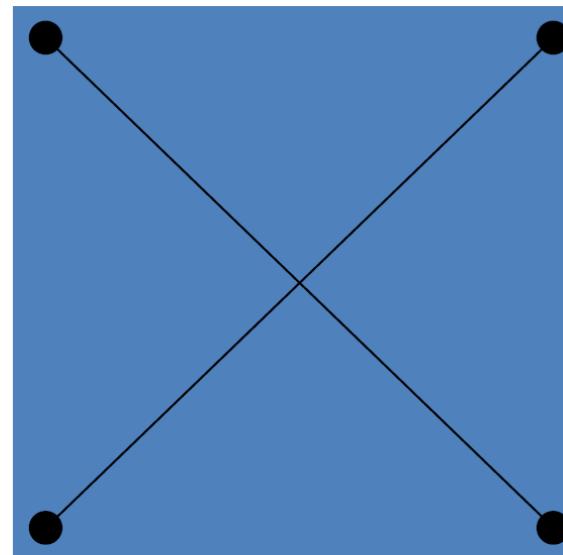
The Answer: Another Option!

- What is the shortest length of lines that can connect the corners of a square?

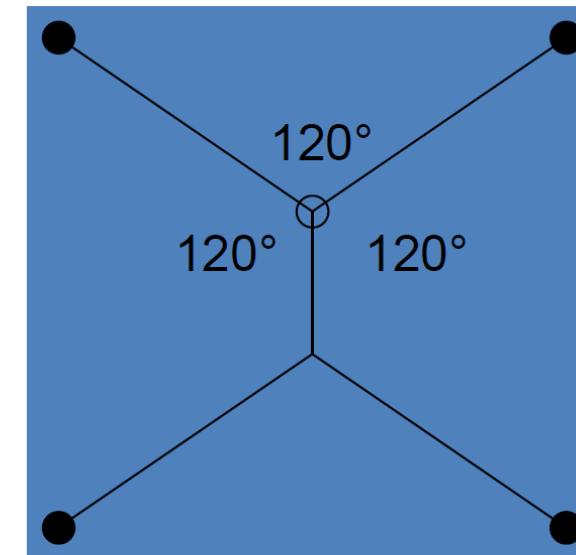
[Soap bubbles in tetraeder and cube - YouTube](#)



Line Length: = 3



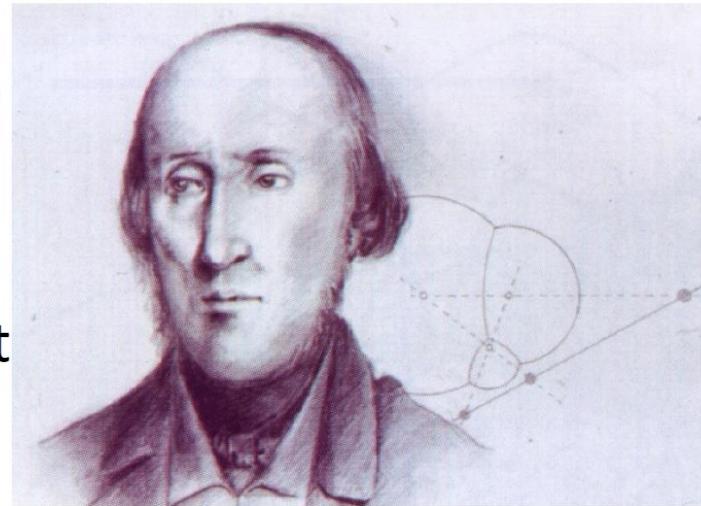
≈ 2.828



≈ 2.736

Foam Structure

- Joseph Plateau
(1801 – 1883)
- Belgian physicist
- Derived the rules governing foam structure
- Went blind in 1844 and carried out most of his most famous work while blind



Plateau's Rules

- **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°
 - The 4 Plateau borders at the vertex always meet at the tetrahedral angle (about 109°)

Particles in Foams

- Applications
- Effect on foam stability - can both stabilise and destabilise foams.

Particles in Foams

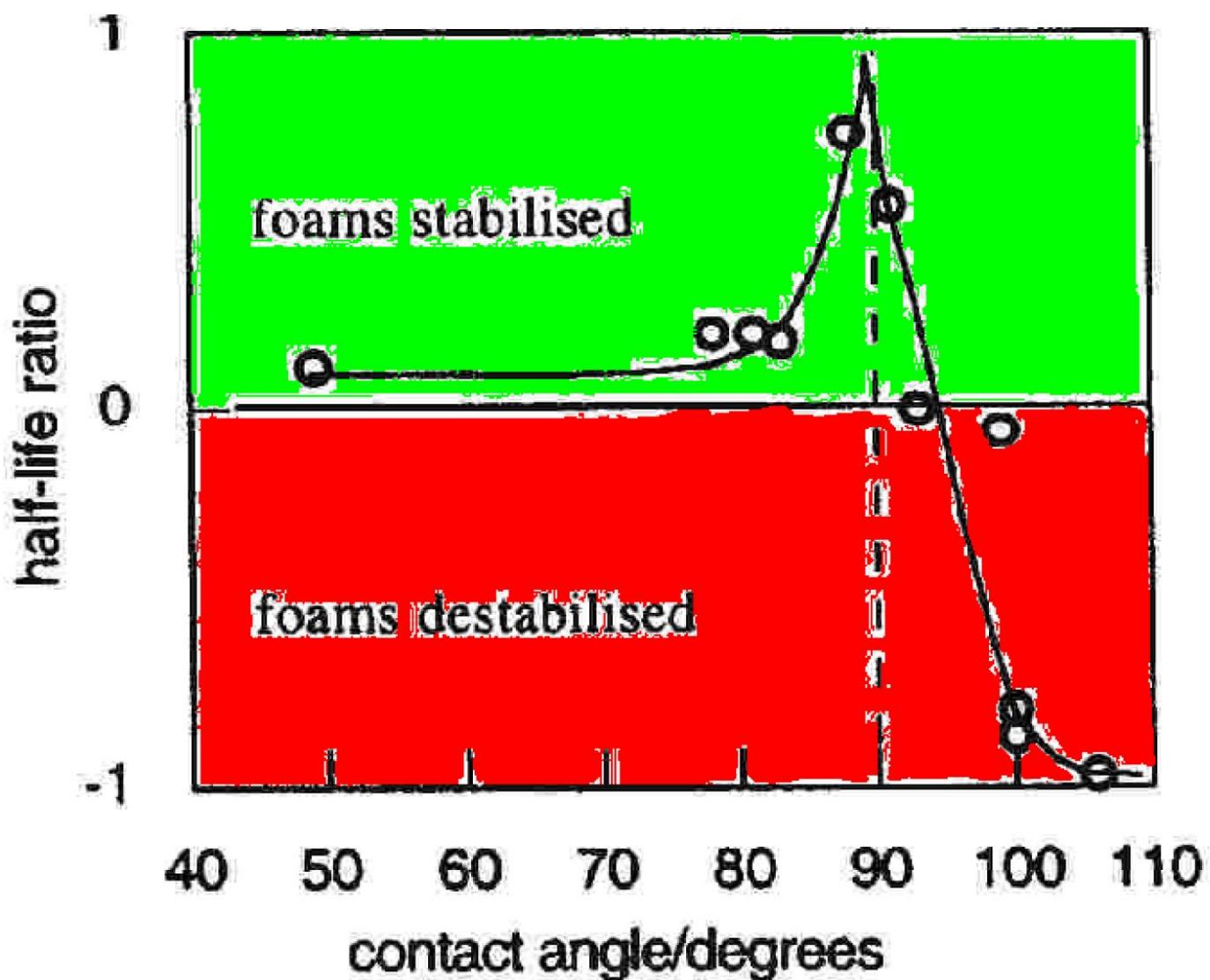
Hydrophobicity and Contact Angle

- **High contact angle ($>90^\circ$) = Hydrophobic,**
liquid moves away from particle, breaks film
- **Low contact angle ($<90^\circ$) = Hydrophilic,**
liquid moves towards particle, film stabilised

Continuous spectrum of hydrophobicity...

Particles in Foams

Contact Angle & Foam Stability



Particles in Foams

Particle mechanism

High contact angle, liquid flows away, film thins and fails (and the opposite)

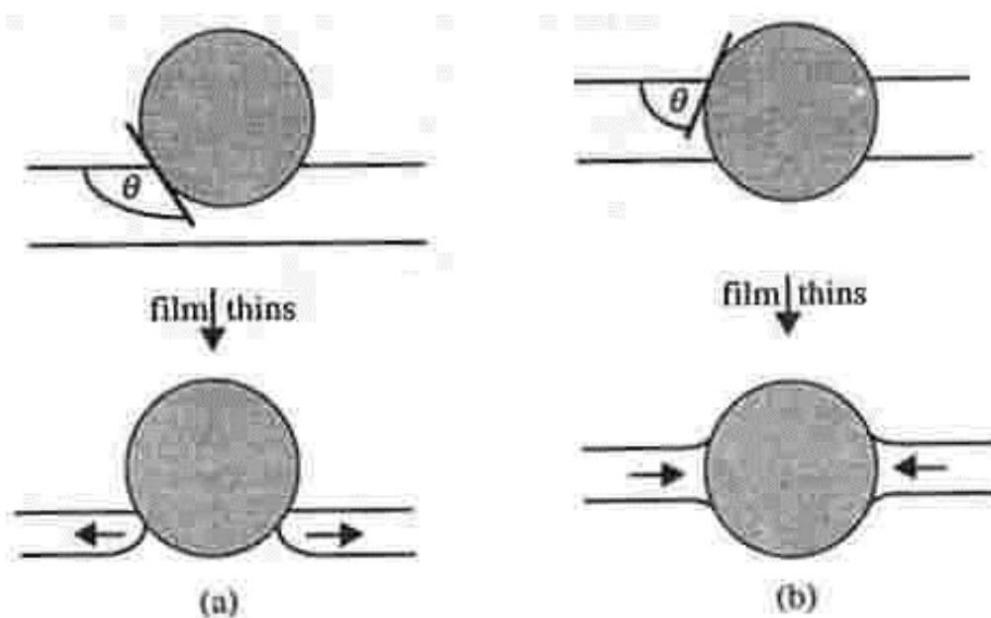


Figure 9. (a) Hydrophobic particle in aqueous film. When the bridge is formed as the film thins, the Laplace pressure generated in the curved meniscus which forms forces liquid away from the particle and causes rupture. (b) For a hydrophilic particle a stable bridging configuration is possible (upper diagram). As the film drains curvature is generated which draws liquid towards the particle, which thus opposes film thinning.

Particles in Foams

Applications

- Minerals Processing
- Paper De-inking
- Water Treatment (dissolved air flotation)

.....These foams are stabilised by particles

Froth Flotation

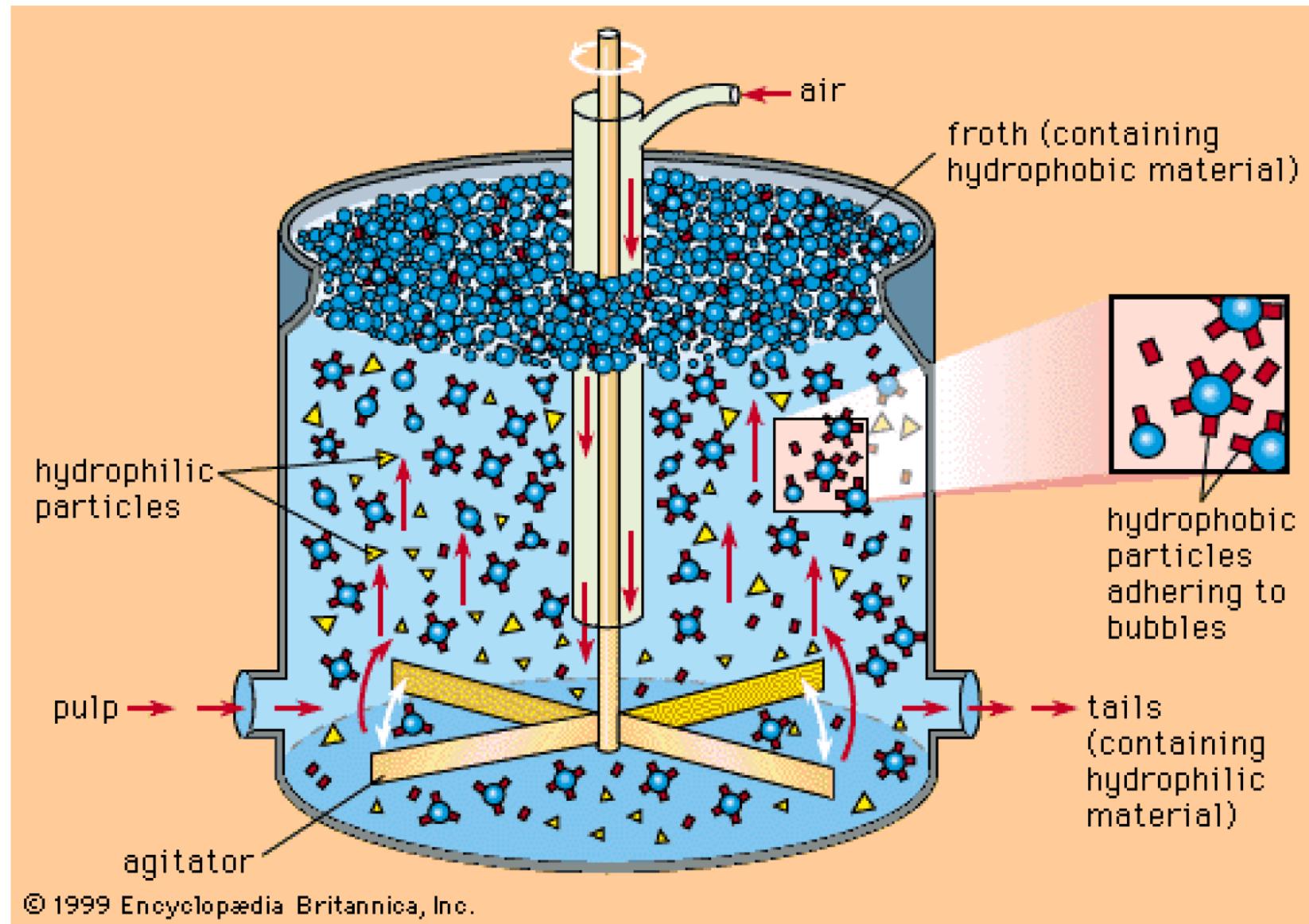
Mineral Separation using Froth Flotation

Conceptually simple:

- Make the valuable mineral hydrophobic using surface chemistry, and add air bubbles
- Hydrophobic particles stick to the bubbles, and float to the surface.
- An overflowing froth is formed that holds the valuable particles
- The waste stays in the liquid and is disposed.

Chemically and physically complex.

Froth Flotation Schematic



Mineral Flotation

- Hydrophobic particles attach to bubble lamellae
- Hydrophilic particles in Plateau borders

Separation by hydrophobicity

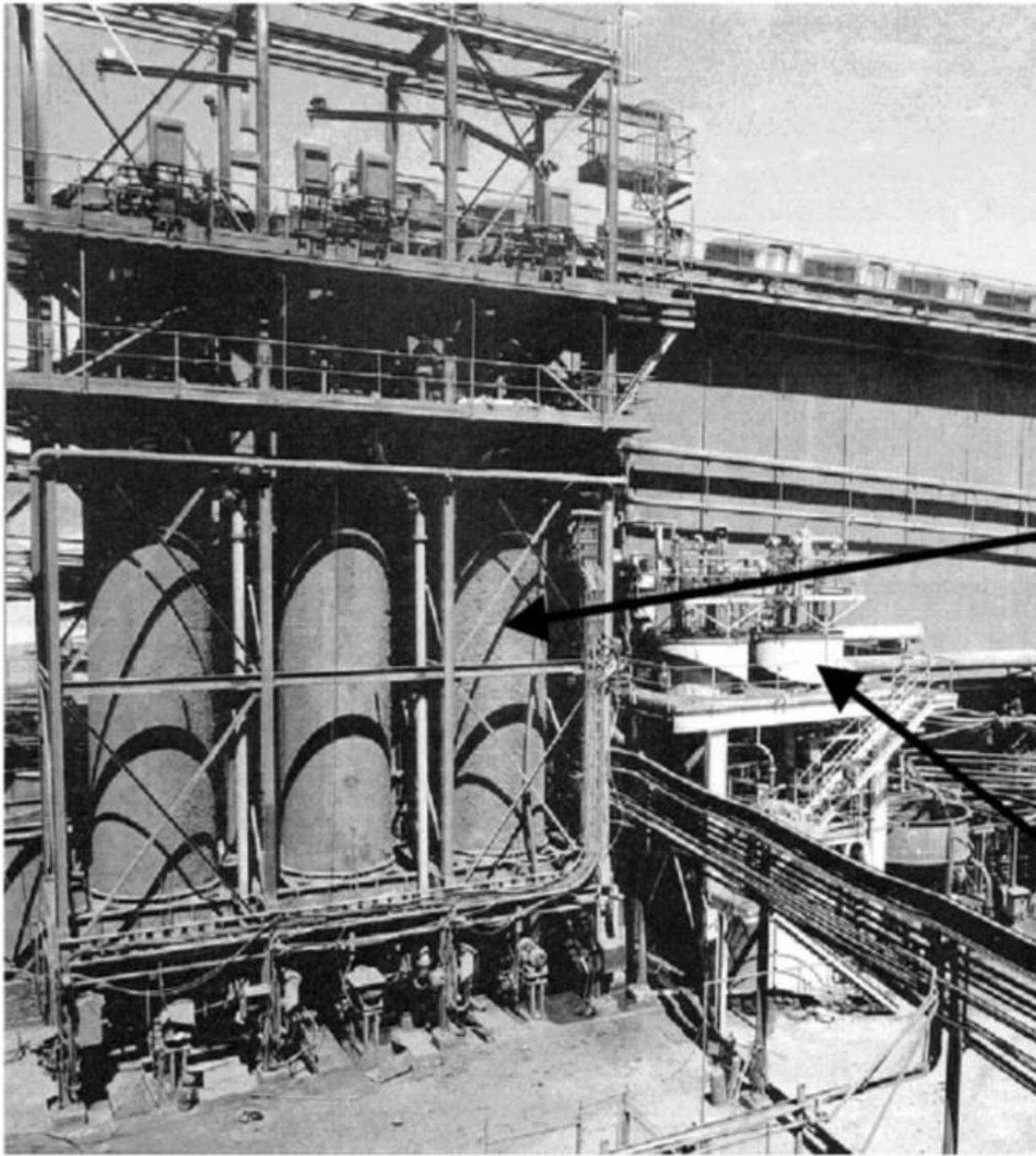


Flotation cells – bigger & bigger



Why is the Froth Important in Flotation?

- The amount of water that is collected into the concentrate is dictated by the froth
 - The water contains non-selectively entrained material and so reduces grade (purity) of the product
 - The amount of water collected is a strong function of bubble size (approximately inverse squared)
- As bubble size changes in the froth (changing from about 1mm to more than 1cm in average diameter) particles that were attached fall off and thus reduce the recovery
 - The froth is a major factor in the balance between the overall recovery and the grade of the product



Column
Flotation
Cells

Jameson
Cells

Other Froth Flotation Applications:

- Waste water treatment
 - Usually using Dissolved Air Flotation (DAF)
- Paper deinking
- Foam fractionation
 - Essentially the same process as flotation, but used to concentrate surfactants