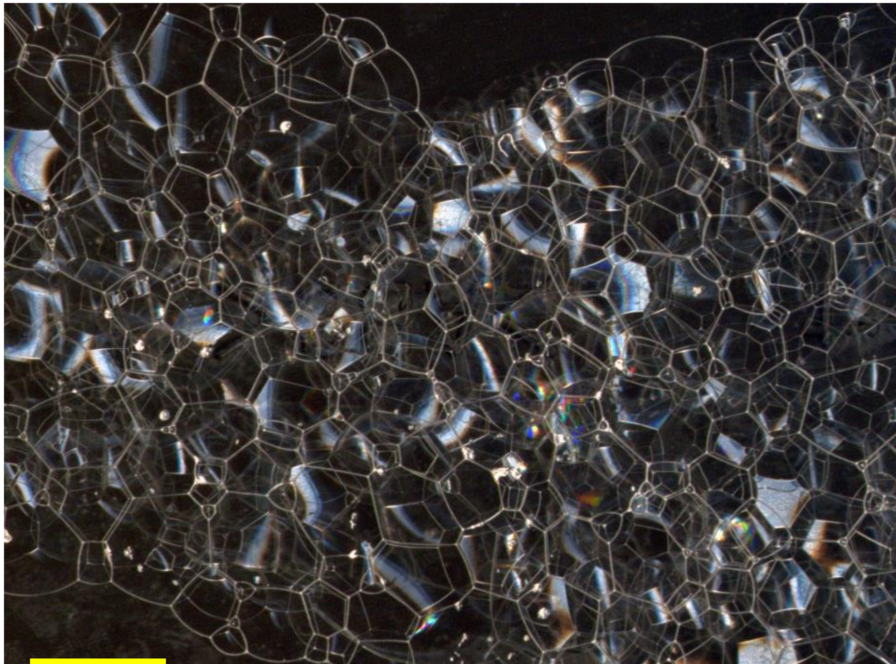
Physical Chemistry of Colloids



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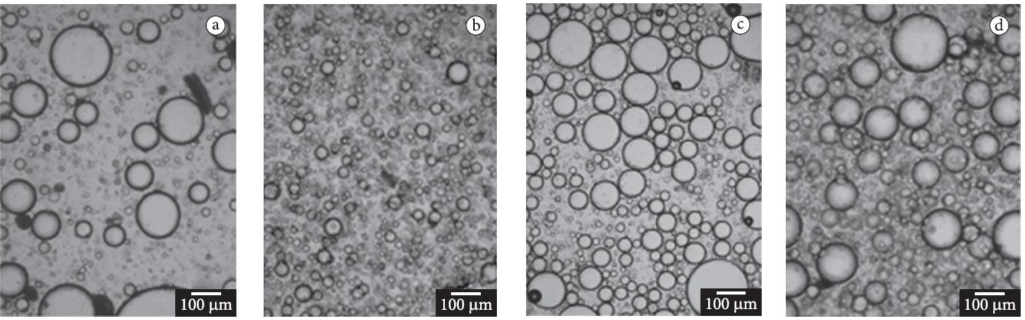
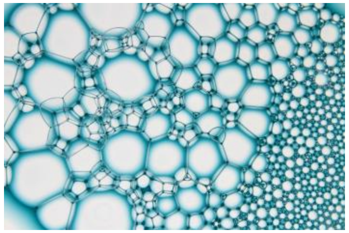


Ciênc. Tecnol. Aliment. **2010**, 3, 477



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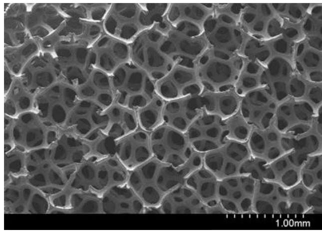


graphene-supermarket.com

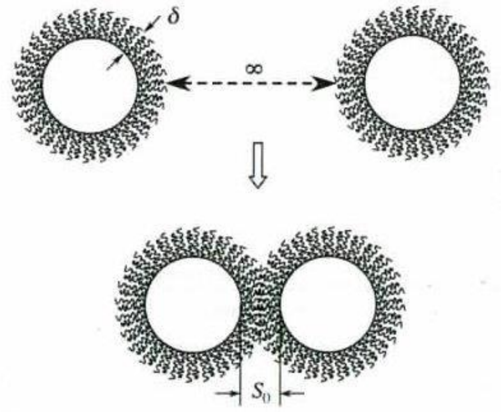
Lecture 10, *May 22, 2019*

Manos Anyfantakis

Physics & Materials Science Research Unit

Previously in ColloidsPhysChem…(I)

- *How is stability (against aggregation) achieved in aqueous media with high [salt] or non-aqueous solvents?*



$$\Delta G_R = G_{S_0} - G_\infty$$

Steric stabilization

-achieved by coating the particle surface with macromolecules (or other entities)

-very old method: Egyptians stabilzed pigment dispersions; Faraday used gelatin to stabilze Au sols

best steric stabilizers: block or graft copolymers that consist of both anchor groups & stabilizing moieties ("buoy" groups)

wsimag.com

entropic stabilization (more common in non-aqueous media)

- large configurational S decrease due to loss of volume accessible to the polymer chains during interpenetration
- ΔH_R small & negative (mon.-solv. interactions < than mon.-mon. & solv.-solv. interactions)

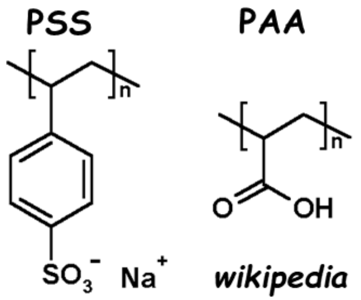
enthalpic stabilization (more common in aqueous media)

- occurs when ΔH_R relatively large & positive
- mon.-solv. > than mon.-mon. & solv.-solv. interactions
- often observed in aqueous dispersions stabilized by hydrated polymers; associated with partial dehydration of chains upon interpenetration

Previously in ColloidsPhysChem…(II)

electrostatic & steric stabilization may act synergistically
→ ***electrosteric stabilization***

- involves charged polymers that are adsorbed onto particles
- achieved using i) polyelectrolytes or ii) neutral polymers (particle surface has already a double layer)
- polyelectrolytes anchor to surfaces of opposite charge → excess molar mass & charge → thick charged layer
- electrosteric stabilization may be achieved in non-aqueous solvents
- electrosterically stabilized colloids may be very robust:
  -electrostatic stabil. insensitive to T & solvent composition
  -steric stabil. insensitive to small [electrolyte] changes



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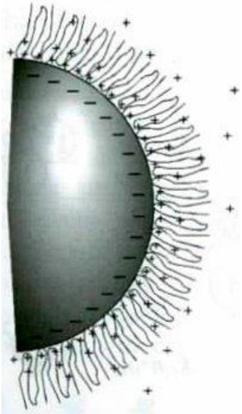


bridging flocculation

- a very high molecular weight polymer (@ very low concentrations) may adsorb onto two or more particles @ the same time
  → aggregation
- bridging flocculation important in wastewater clarification & paper making

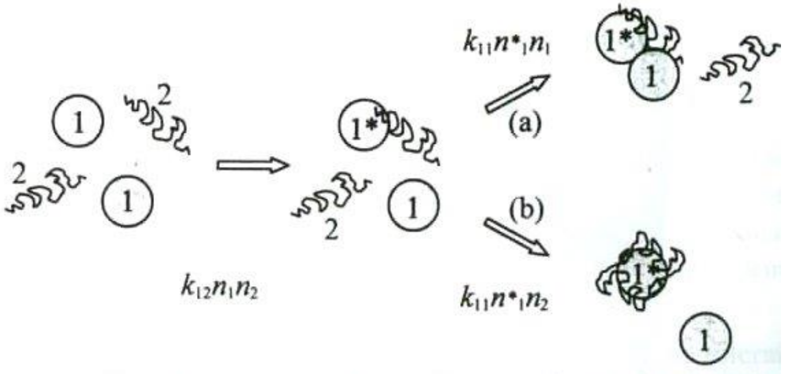


Fig. 7-30: Bridging flocculation. Polymer (2) adsorbs first to one particle (1) followed by adsorption to a second particle, as in route (a). In route (b), either the adsorbed polymer re-conforms, or a second polymer molecule adsorbs to the first particle.

Previously in ColloidsPhysChem…(III)

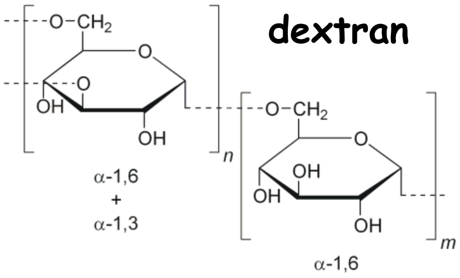
Depletion interactions arise when non-adsorbing polymers are added to colloidal dispersions

- neutral polymers (e.g. polysaccharides), polyelectrolytes/like-charged surface
- available surfaces already saturated with adsorbed polymers → free polymer

➢ When no (more) polymer adsorption is possible, free chains are excluded from a zone near the surface with thickness ~ ***R$_g$*** of polymer

two particles (with depletion layers) approaching so that polymer is excluded from the region between them → ***ΔΠ*** → flow toward this region → **attraction**

dextran



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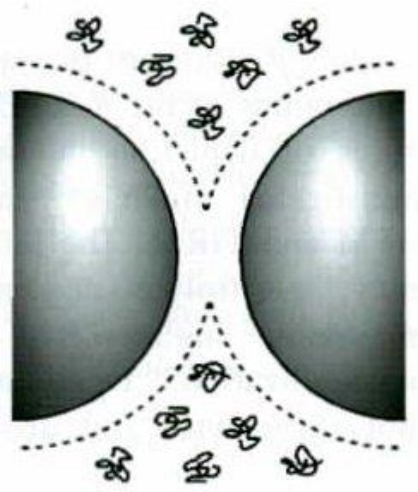


Fig. 7-31: Effect of free (unadsorbed) polymer: "depletion flocculation."

simple treatment

- non-adsorbed entities act as hard spheres with radius = ***R$_g$***
- completely excluded from depletion zone

$$\Delta G_{\mathrm{dep}} = -\left(\Pi_{\mathrm{soln}} - \Pi_{\mathrm{overlap}}\right)\Delta V_{\mathrm{overlap}} = -\Pi_{\mathrm{soln}}\,\Delta V_{\mathrm{overlap}} \qquad \Pi_{\mathrm{overlap}} = 0 \qquad \Pi_{\mathrm{soln}} = n_2 \mathrm{k_B} T$$

$$\Delta G_{\mathrm{dep}} = \Phi_{dep} = -\frac{2}{3}\pi n_2 \mathrm{k_B} T \left(R_g - \frac{S_0}{2}\right)^2 \left(3a + 2R_g + \frac{S_0}{2}\right)$$

- ***R$_g$***: influence of T, molecular weight, solvency, & [salt]

Previously in ColloidsPhysChem…(IV)

late-stage aggregation: structure of "particle assembly" depends on preceding events

gelation

- formation of very voluminous flocks due to rapid aggregation (attraction-driven)
- entire dispersion percolates into a network that can span the whole sample volume

glass transition

- [particle] increase: particles "pack" randomly, still liquid-like structure
- viscosity increases dramatically as transition is approached
- above glass transition: sample cannot equilibrate (frozen)
- colloids as model ("big atoms") for studying this univeral effect

crystallization

- occurs for colloids with size dispersity < 10% that are stable to aggregation (repulsion-driven)
- colloidal crystallization is an entropic effect

Jeroen Appel, *PhD thesis* **2017**, Wageningen Univ. (NE)

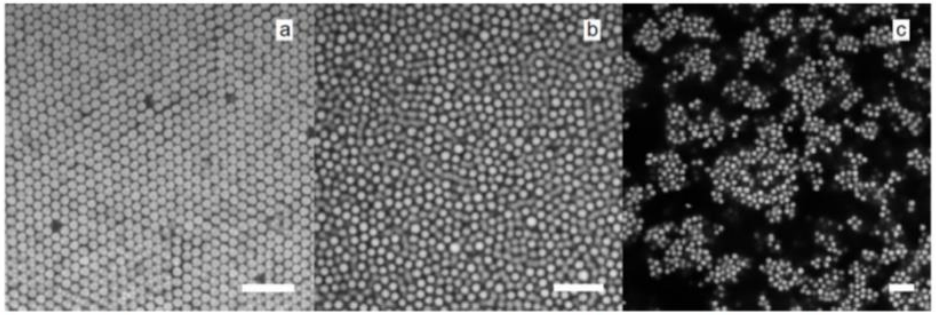
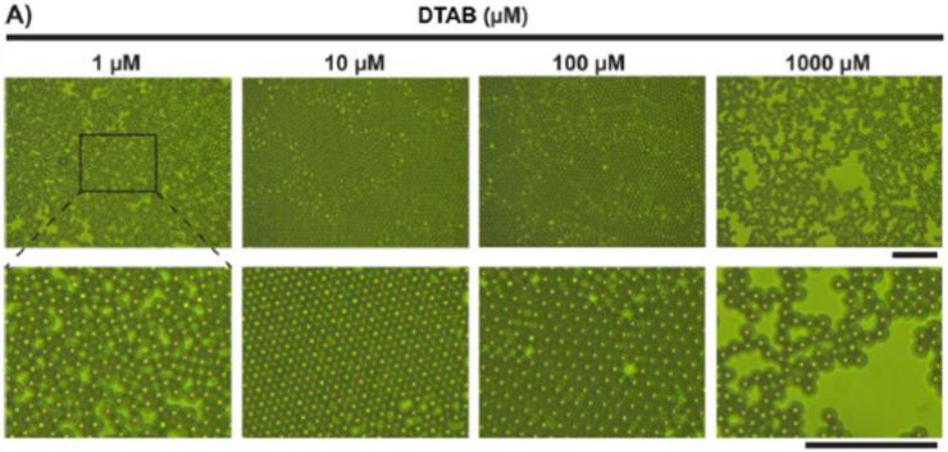


Figure 1.4: Confocal microscopy images of pTFEMA-pTBMA colloids in three different solid-like phases. A colloidal crystal (a), colloidal glass (b) and colloidal gel phase (c). Scale bars 10 μm.



Langmuir **2018**, *34*, 15526

Classification & examples of emulsions

word "emulsion" comes from Latin *"mulgere"* (= to "milk")

emulsion (general)

a two-phase system where droplets of one liquid are dispersed in another immiscible liquid (continuous phase)

macroemulsions

- droplets usually an order of magnitude larger than in microemulsions, large size dispersity
- lyophobic colloids, thermodynamically unstable

microemulsions (IUPAC)

- dispersions made of water, oil & surfactant(s) that are isotropic & thermodynamically stable with dispersed domain diameter from ~ 1 to 100 nm

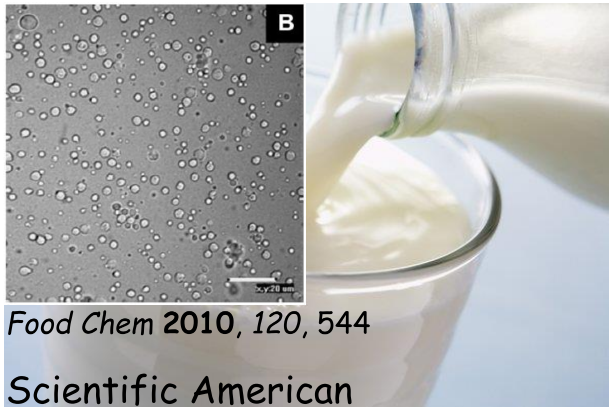
Physical properties like viscosity, flow-ability, pump-ability, color, mouth-feeling, texture & flavor are influenced by droplet size distribution

water-in-oil (W/O) emulsions

an aqueous phase dispersed in an organic liquid

oil-in-water (O/W) emulsions

water-insoluble organic droplets dispersed in water

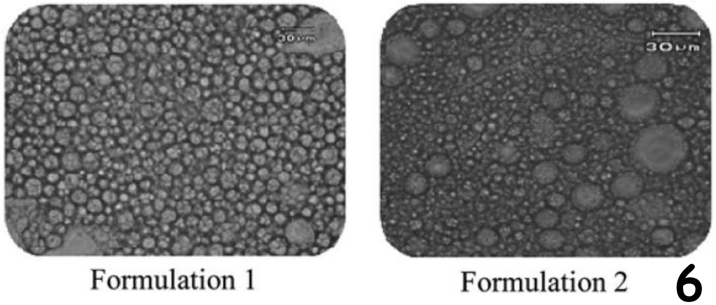


Food Chem **2010**, *120*, 544

Scientific American

wikipedia

Food Hydrocolloid **2012**, *28*, 344



Formulation 1 Formulation 2

Thermodynamics of emulsion formation & breakdown

(activation) energy to produce an emulsion from two phases » min. energy: $E_a^e \gg \Delta G^e$

ΔG^{emul} for volume of oil → **N** droplets

- interfacial area increase (**ΔG^{area}**)
- increase of configurational entropy of oil droplets (**ΔS^{config}**)

$$\Delta G^{\text{emul}} = \Delta G^{\text{area}} - T\Delta S^{\text{config}}$$

$$= \sigma \Delta A + TNk_B \left[\ln\phi_0 + \left(\frac{1-\phi_0}{\phi_0}\right) \ln(1-\phi_0) \right]$$

$\phi_{0:}$ *volume fraction of oil droplets*

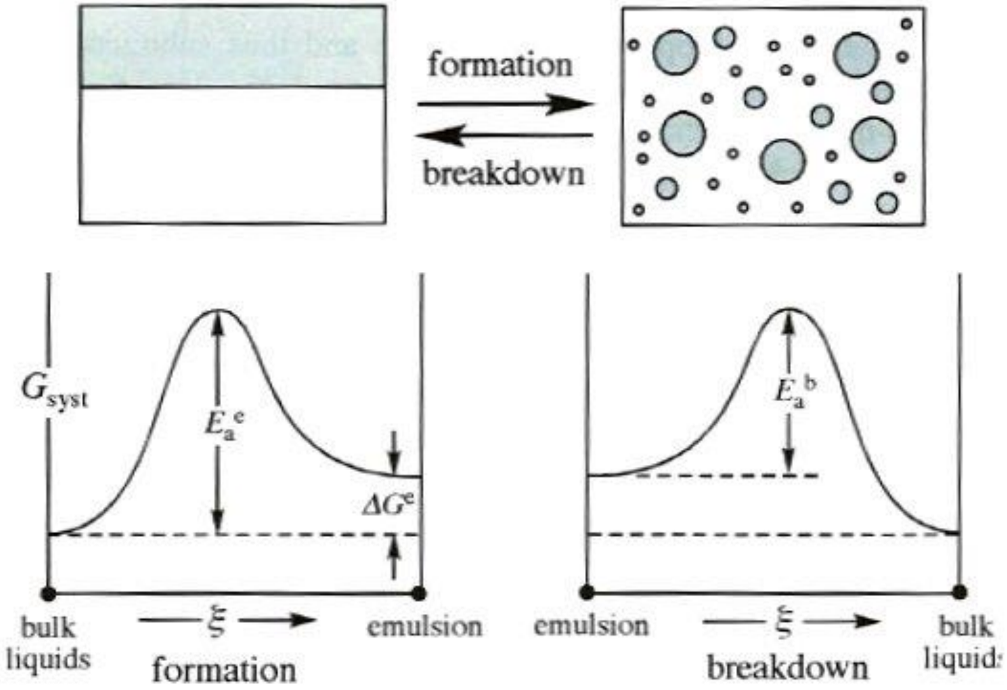


Fig. 9-5: Simplified thermodynamic description of emulsion formation and breakdown.

high & intermediate σ:
ΔS^{config} negligible → **ΔG^{emul}** > 0

low σ: **ΔS^{config}** negligible → **ΔG^{emul}** $\leq$ 0
→ spontaneous emulsification

$$\sigma^{crit} = -\frac{k_B T}{4\pi\alpha^2} \left[\ln\phi_0 + \left(\frac{1-\phi_0}{\phi_0}\right) \ln(1-\phi_0) \right]$$

α: *droplet radius*

$$\left.\begin{array}{c} \phi_0 = 0.5 \\ T = 298\,K, \\ a = 100\text{ nm} \end{array}\right\} \quad \sigma^{crit} \approx 5\times 10^{-5}\text{ mN/m}$$

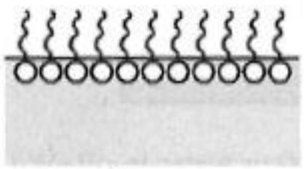
realized in equilibrium with surfactants with CPP ≈ 1 → microemulsion formation

Emulsifiers & stability

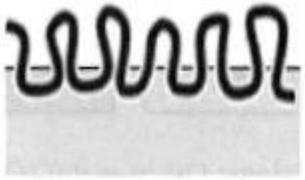
emulsions are kinetically stable due to the presence of an emulsifier @ the interface between the two liquids

emulsifier

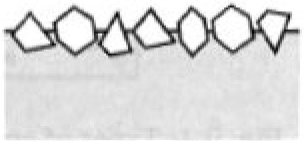
- a substance that adsorbs @ the fluid interface & stabilizes the dispersed liquid within the continuous phase
- different types: surfactants, polymers (proteins, starches, cellulose-based, polyelectrolytes), particles, inorganic anions
- assist in emulsion formation by reducing interfacial tension
- ***mainly:*** preserve drops from coalescence by forming a mechanical & interaction barrier between the two phases



Surfactants



Macromolecules



Fine particles

interactions

- electrostatic repulsion (e.g. ionic surfactant)
- steric repulsion (e.g. non-ionic surfactant or polymer)

mechanical stability

- stabilization of thin film between adjacent droplets that can otherwise become unstable & rupture (Gibbs elasticity)
- polymer or particle stabilizers form interfacial gels that stop drainage

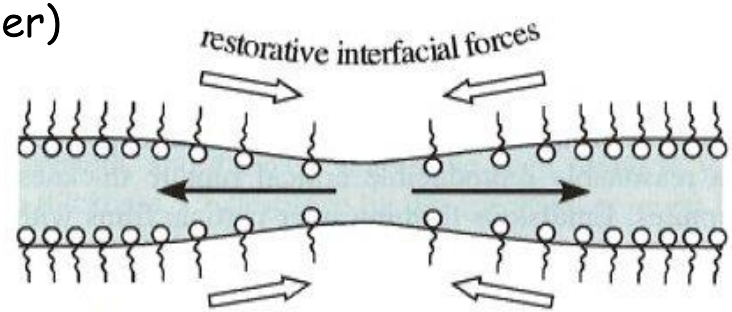


Fig. 9-4: The mechanism of Gibbs elasticity stabilizing the film between emulsion droplets.

Destabilization of emulsions

result of thermodynamic instability: emulsions tend to reduce total free energy by reducing total interfacial area (increase in drop diameter)

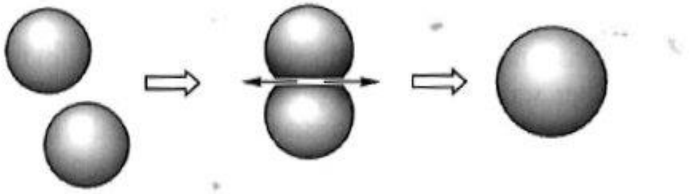
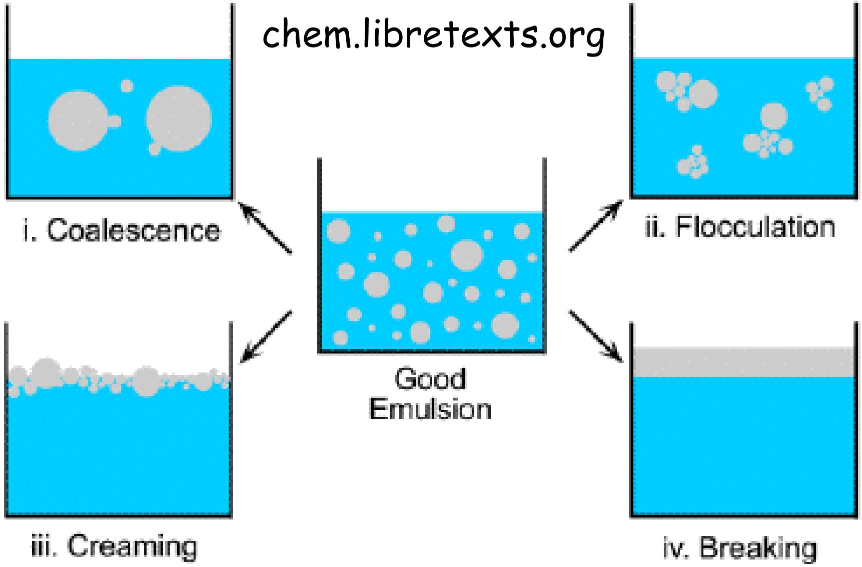


Fig. 9-2: The breakdown of emulsions through flocculation and coalescence.

destabilization mechanisms

- same as for other lyophobic colloids
- flocculation: reversible clustering of droplets
- coalescence: merging of droplets into larger droplets (irreversible)
- macroscopic phase separation: gravity-induced sedimentation or creaming
- Ostwald ripening



chem.libretexts.org

Ostwald ripening

- droplet proximity is not required
- mass transfer between drops of different curvature through the surrounding solvent
- concentration of dispersed phase material @ drop surface inversely related to radius of curvature → small drops: higher surface concentration → concentration gradient
- mass transfer from small to large drops → latter grow @ the expense of former

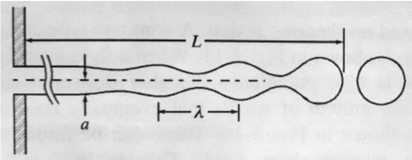
Energy input for emulsification

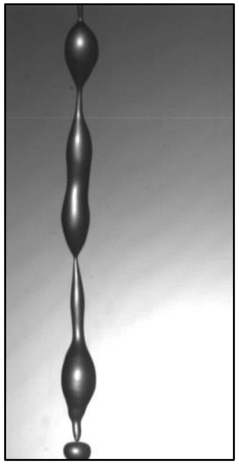
energy input required in to prepare an emulsion

- liquids break into large drops via hydrodynamic instabilities
- next, large drops break down to droplets (additional *E* input)

youtube.com/watch?v=-Igf3AyDSCg

Rayleigh-Plateau instability



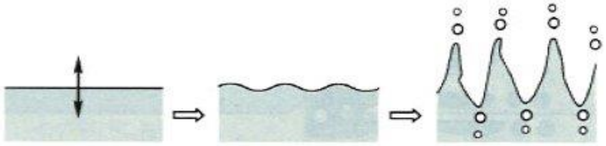


youtube.com/watch?v=UYRGEINpO50

$$L \propto U\left(\frac{\rho\alpha^3}{\sigma}\right)^{\frac{1}{2}}$$

wikipedia

Rayleigh-Taylor instability

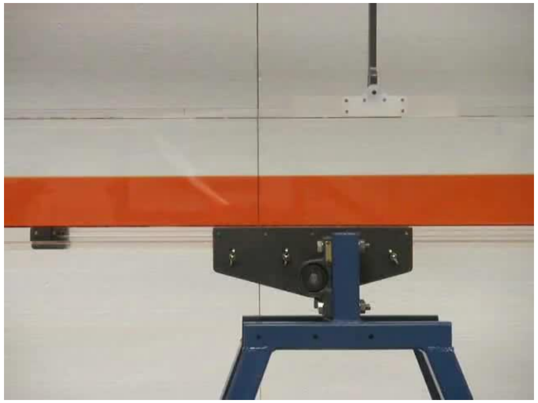


Breakup by shaking (Rayleigh-Taylor instability)

youtube.com/watch?v=yabqo7VFTYs

Kelvin-Helmholtz instability

Breakup by shearing (Kelvin-Helmholtz instability)



youtube.com/watch?v=UbAfvcaYr00

size distribution depends on type & concentration of emulsifier, duration of *E* input…

empirical relations

$$d_{\max} \propto \tilde{\Pi}^{-\frac{2}{5}}\,\sigma^{\frac{3}{5}}\,\rho_C^{-\frac{1}{5}}$$

$\tilde{\Pi}$: power input/volume

σ: interfacial tension

ρ_C: continuous phase density

Coffee break

clipart-library.com

paigeeworld.com

youtube.com/watch?v=sF3n9P0VTwc

Mario is wondering:

"What is the role of all those mayonnaise ingredients?"

O/W or W/O emulsions?

- *Which phase will be the dispersed one when we shake a mixture of liquids 1 & 2 & emulsifier?*

energy input → both types of droplets formed

emulsifier determines which type will survive

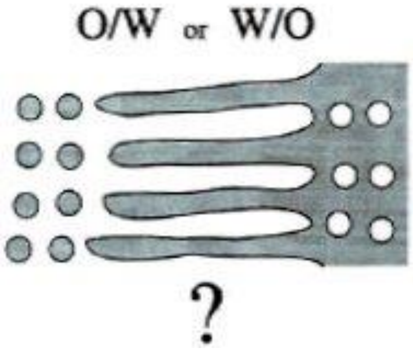


Fig. 9-7: Which type of emulsion forms depends on which type coalesces the faster.

Bancroft rule

- phase being better solvent for emulsifier → continuous phase
- larger emulsifier part must lie in continuous phase to satisfy curvature requir. of droplet (oriented wedge rule)

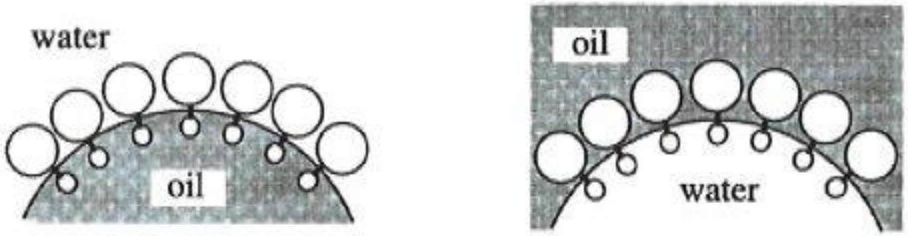
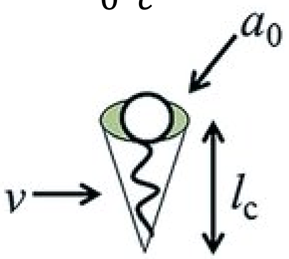


Fig. 9-8: The driving force for coalescence is related to curvature.

Critical Packing Parameter criterion

$$p = \frac{v}{a_0 l_c}$$



p < 1: oil on concave side of interface (→ dispersed phase)

p > 1: water on concave side of drop interface

criterion based on ***p*** explains influence of various parameters on type of emulsion formed (e.g. salt influence & T)

A special case of stabilizer: particles

Pickering emulsions

- emulsions in which the disperded phase droplets are stabilized by solid particles
- particles @ drop interface effective in slowing down/stopping film thinning
- particles hold interfaces apart by distance larger than critical film thickness

particle adsorption @ fluid interfaces

- finite particle contact angle (*θ*) req.; particle wettability controlled by surface treatment (e.g. silanization)
- energy of detachment of particles related to Pickering emulsion stability

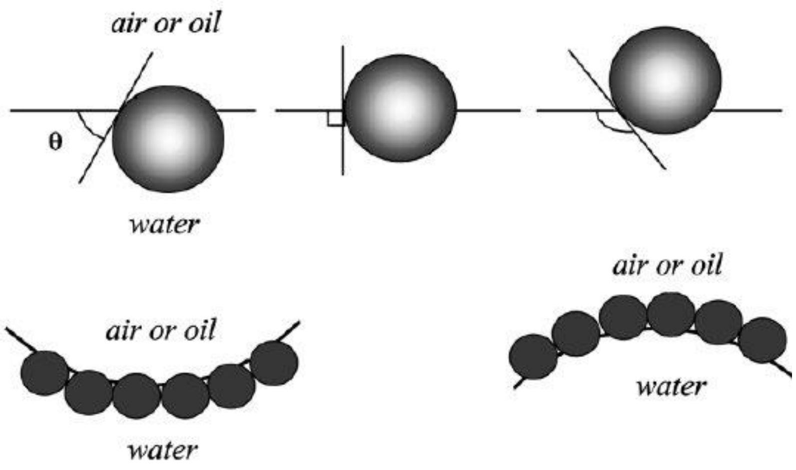
$$E_{detach} = \pi\alpha^2\sigma_{12}(1 \pm \cos\theta)^2$$

α: particle radius

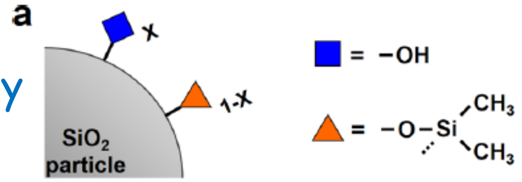
σ_{12}: interfacial tension (fluids 1 & 2)

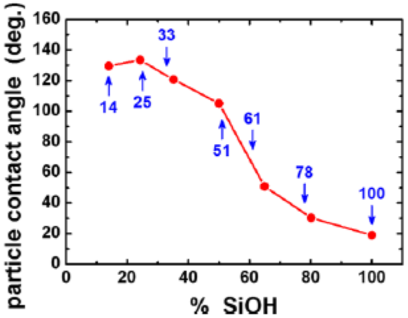
- phase that preferentially wets the solid particles → continuous phase

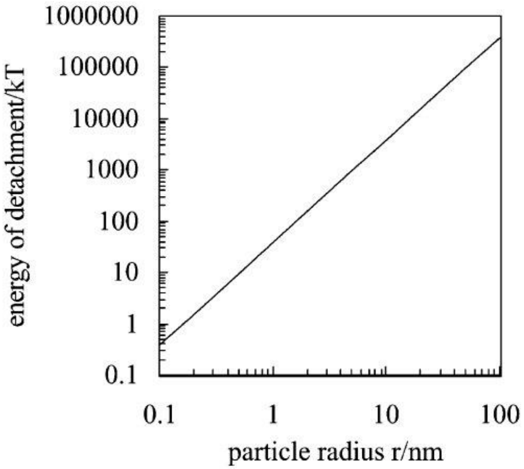
Curr. Opin Colloid Interface Sci. **2002**, *7*, 21



Langmuir **2017**, *33*, 5025







θ = 90°
σ_{12} = 50 mN/m

Foams & comparison to emulsions

foam (IUPAC)

- dispersion in which a large proportion of gas (by volume) in form of bubbles, is dispersed in a liquid, solid or gel
- bubble diameter usually > 1 μm, but thickness of lamellae between bubbles often in colloidal range

froth (IUPAC)

- particle-stabilized bubbles, in contrast to foams which are stabilized by soluble substances

similarities to emulsions

- foam breakdown depends on bubble approaching followed by drainage of continuous phase from the film between them & its rupture (→ coalescence)
- **foaming agent:** additional component required to ensure a reasonable lifetime

differences with emulsions

- large Δρ between bubbles & solvent → phase segregation by gravity → pressed bubbles form polyhedral structure
- larger draininng films between large bubbles → complex hydrodynamics
- bubble gases diffuse rapidly across thin films → disproportionation important (larger P in small bubbles)

wikipedia

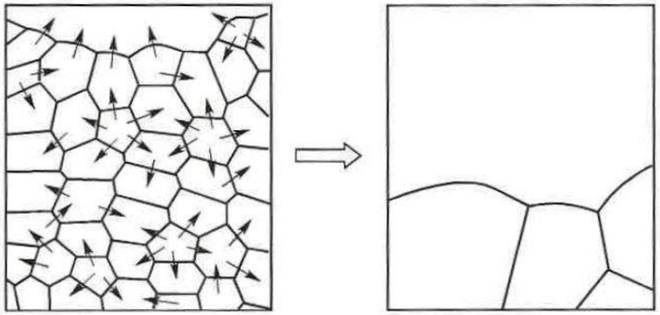


Fig. 9-30: Evolution of foam structure due to gas diffusion across foam lamellae and film breakage.

Preparation & importance of foams

preparation of foams

- spraying gas inside a liquid (as individual bubbles or as gas jets that quickly break up into bubbles)
- mixing liquids that are in contact with gas → waves @ liquid surface entrain pockets of gas
- plunging liquid masses from the gas into liquid pools
- precipitation of dissolved gases from the liquid (dispersed particles or container irregularities act as nucleation sites) → micro- & nanobubbles

foams often created unintentionally & are unwanted in numerous processes (air trapping into process lines, mixers, distillators etc.)

anti-foaming agents → lead to fast draining films
foam inhibiters: branch-chained alcohols, apolar oils
foam breakers: displace surfactant from films (hydrophobic particulates)

foams have many important uses

- cleansing action
- capturing of fine particulates from gases
- liquid foams: precusrsors of solid foams
- fire fighting applications

youtube.com/watch?v=dGAN1QlVgq0

buildersontario.com

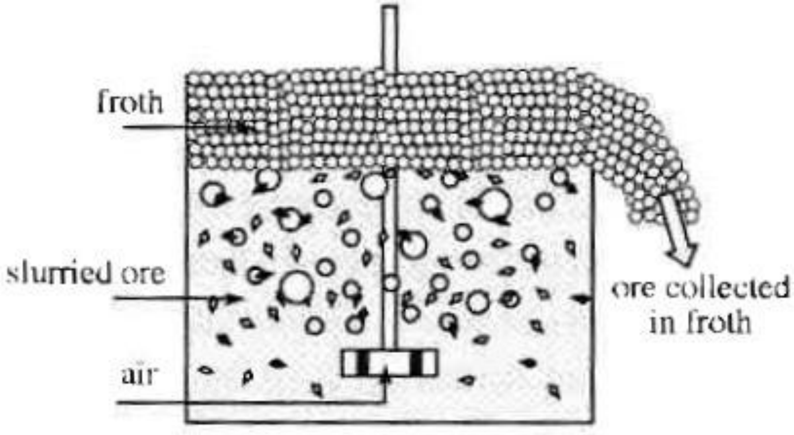
cfdsolution.com

Froth flotation

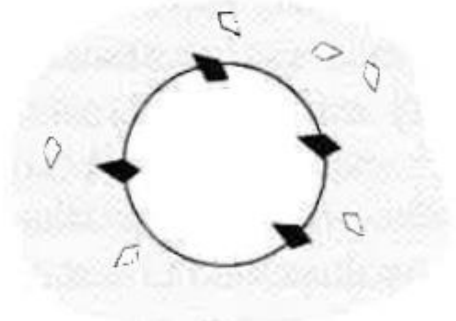
- process in which valuable materials (e.g. in the form of particles) are separated from a slurry that contains other materials too
- separation based on differences in wettability of different solids by water

ore flotation

- valuable ores like Pb, Zn & Cu sulfides are separated from siliceous gangue by passing bubbles through a mixed slurry of both
- after agitation of the water suspension & bubble introduction: sulfide particles are adsorbed on the bubbles ($\theta \approx 90^o$) whereas silica particles ($\theta \approx 0^o$) do not
- sulfide partiles floated to surface (attached to bubbles) & trapped in a froth which is then removed by mechanical means
- often not good separation due to θ variability; addition of a collector which makes sulfides more hydrophobic
- unstable bubbles (coalescence or bursting at the surface); addition of frother
- important in other separation processes (de-inking of recycled paper, ion flotation)



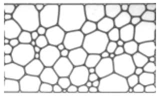
(a)



(b)

Stages in foam lifetime

- foam lifetimes may vary a lot depending on conditions
- kinetic arrest @ some intermediate stage → long lifetime
- weak metastability: small disturbance → breakdown



youtube.com/watch?v=HPRGa3_On6s

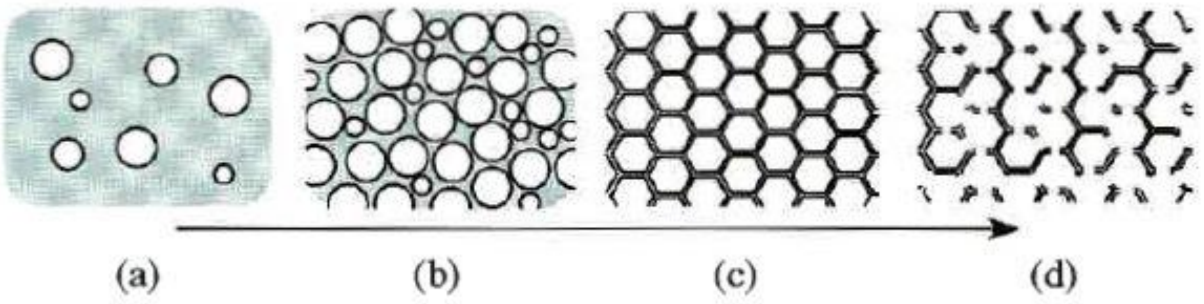
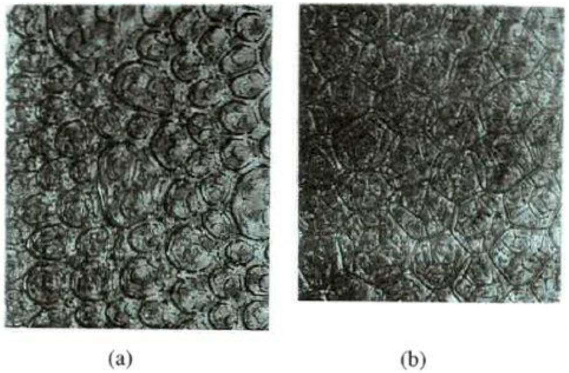


Fig. 9-31: Stages in a foam lifetime: (a) *Kugelschaum* period (independent gas bubbles), (b) gravity drainage period, (c) lamella thinning period, (d) film rupture.



(a) (b)

Fig. 9-32: Foams formed from 600-800 mg/L of Aerosol OT surfactant in water at 25°C. (a) gravity-draining froth; (b) lamellae thinning period. From [Hartland, S., and Barber, A., *Trans. Inst. Chem. Engrs.*, **52**, 43 (1974).]

1st stage

- foam formation → independent, spherical bubbles; transient state for low η liquids

2nd stage

- structure drains by gravity → film thickness ~ 10 μm – 1 mm; lasts ~ few s - min

3rd stage

- lamellae thinning period: bubbles pressed together → honeycomb structure; lasts longer

4th stage

- film reaches a critical thickness & is ruptured → foam collapses