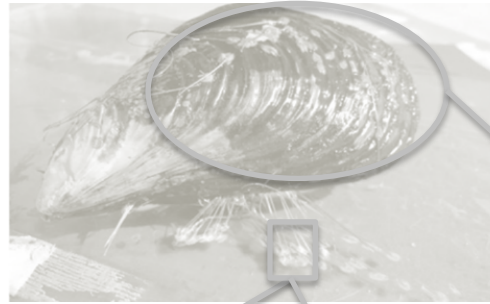
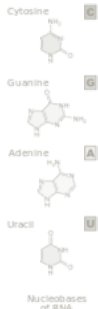


Following the book
 "Introduction to Soft
 Matter" by Ian W. Hamley

Course outline

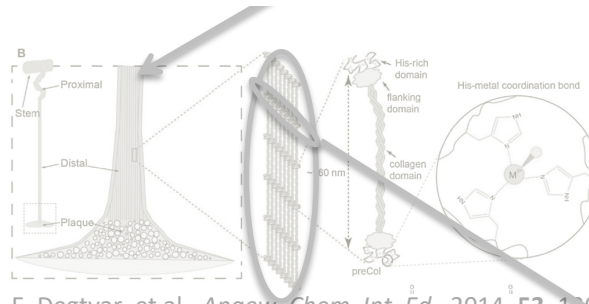


Introduction



Ordered materials

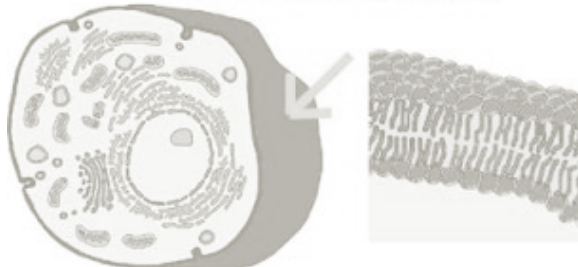
Thermotropic liquid crystals



E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

Lyotropic liquid crystals

Cell Membrane

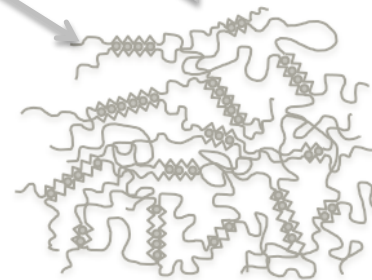


Disordered materials

Polymers



Gels



Colloids

Nanoparticles

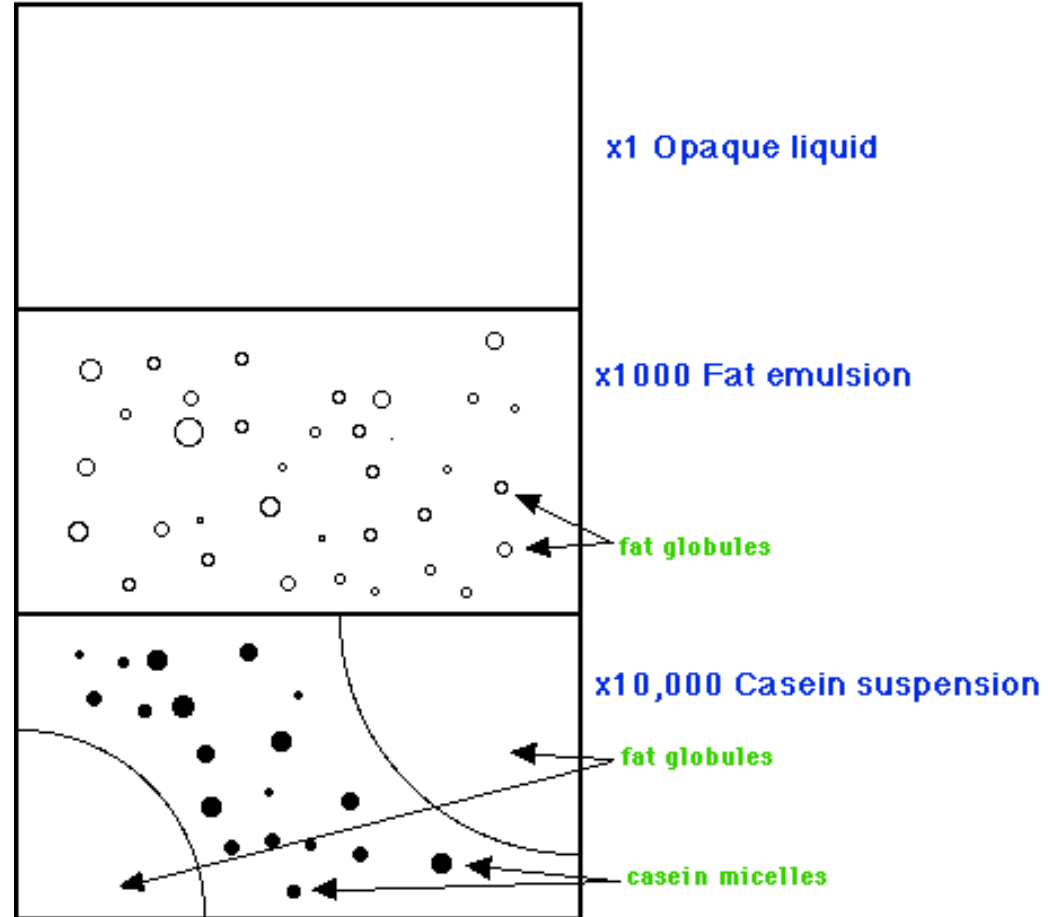


Emulsions



Milk

Milk Structure



<https://www.uoguelph.ca/foodscience/book/export/html/1883>

Outline

- Introduction
- Production of emulsions
- Stabilization of emulsions
 - Surfactants
 - Particles
- Applications of emulsions
- Foams

Outline

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Colloids

Colloid: Short synonym for colloidal system.

Colloidal: Either molecules or polymolecular particles that are dispersed in a medium and have at least one dimension between approximately 1 nm and 1 μm , or discontinuities in a system that are of this order.

The energy of inter-particle interactions is around $k_B T$.

		continuous phase		
		gas	liquid	solid
dispersed phase	gas		soap sud cappuccino froth	pillow foam styrofoam packaging
	liquid	fog hair spray	mayonnaise milk	ice cream
	solid		paints	
		smoke	blood	

Colloids in our daily life

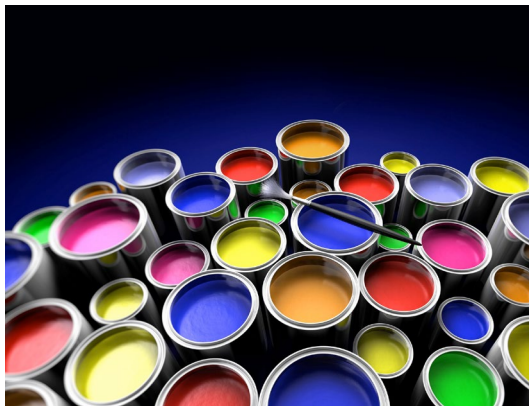
Dispersion: certain sun creams



Emulsion: mayonnaise



Polymer latex dispersion: paint



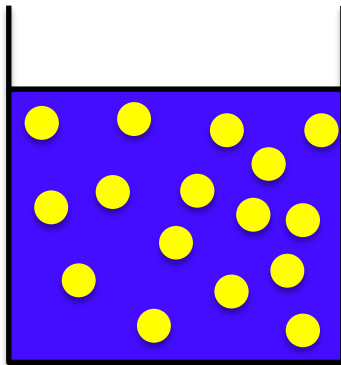
Emulsion: salad dressing



Emulsions

Emulsions are drops of a liquid dispersed in a second, immiscible liquid.

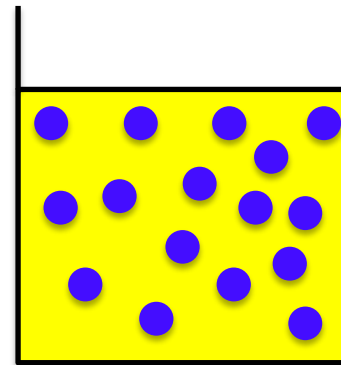
oil in water emulsions



Example: milk



water in oil emulsions



Example: margarine



Examples of emulsions



Outline

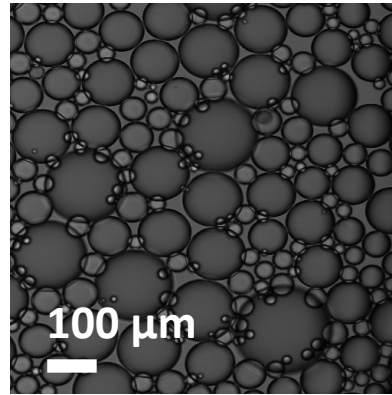
- Introduction
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Production of emulsions

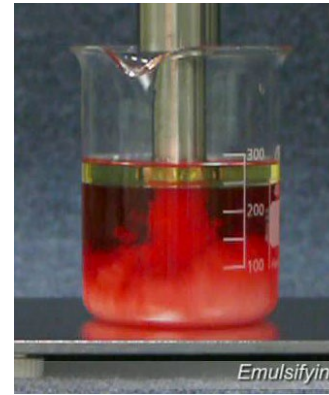
mechanical mixing



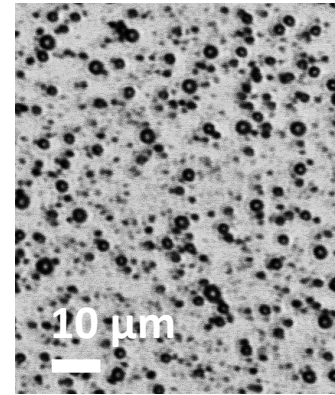
<http://www.csiro.au>



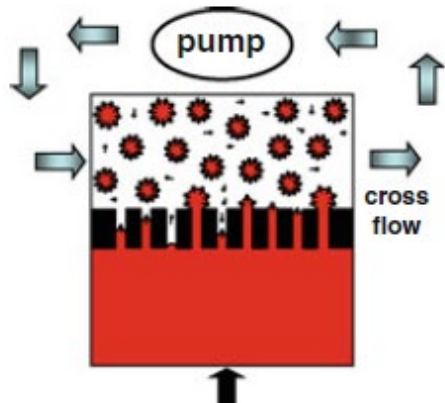
sonication



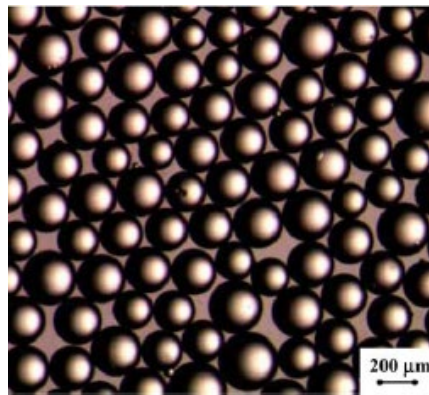
<http://www.hielscher.com>



membrane emulsification

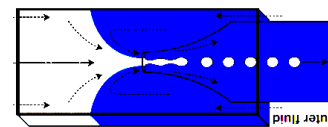


Vladisavljevic, G.T., et al.,
*Microfluidics and
Nanofluidics*, 2012. **13**(1)

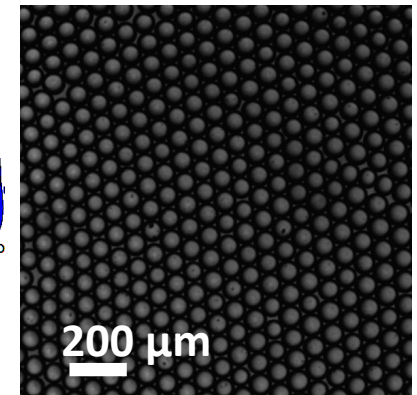


Vladisavljevic, G. T. et al., 2006,
*Journal of Colloid and Interface
Science* **299**(1)

microfluidics



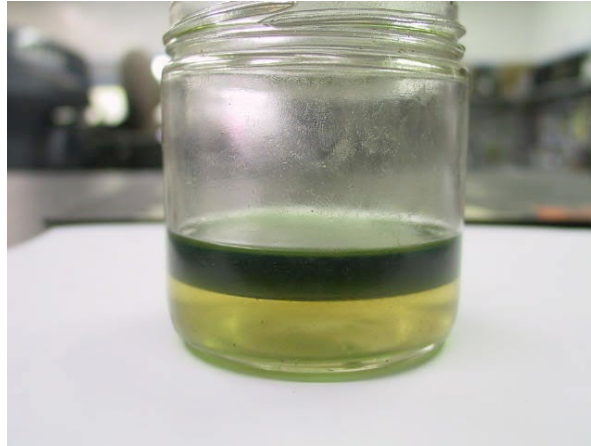
Utada, A.S., et al., Mrs
Bulletin, 2007. **32**(9):



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Emulsions



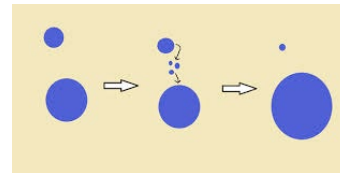
If two immiscible liquids are mixed they usually phase separate.

Phase separation of emulsions can occur through:

coalescence of drops



Ostwald ripening



Free energy required to form emulsions

Free energy of undispersed systems:

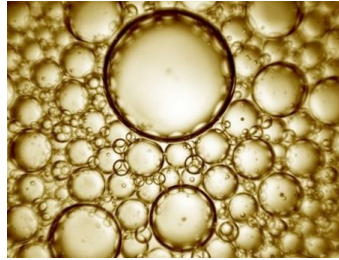
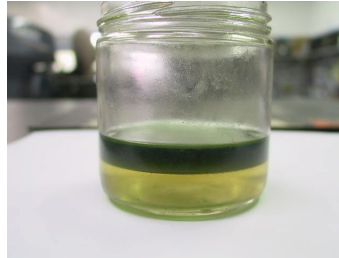
$$G^I = G_a^I + G_b^I + G_{ab}^I$$

$$G_{ab}^I = \gamma_{ab} A^I$$

Free energy of emulsified systems:

$$G^{II} = G_a^{II} + G_b^{II} + G_{ab}^{II} - TS^{II}(conf)$$

↑
reflects decrease in the
order of the system



G^I : free energy of undispersed system [J]

G_a^I : free energy of liquid a [J]

G_b^I : free energy of liquid b [J]

G_{ab}^I : excess free energy associated with liquid-liquid interface [J]

γ : interfacial tension [N/m]

A^I : interface area [m²]

Φ : volume fraction [-]

N : number of drops [-]

ΔA : increase in surface area [m²]

$$NS^{II}(config) = -Nk_B \left[\ln \phi_b + \frac{1 - \phi_b}{\phi_b} \ln(1 - \phi_b) \right]$$

$$\Delta G = G_{ab}^{II} - G_{ab}^I - T\Delta S$$

$$\Delta G = \gamma_{ab} \Delta A - TS^{II}(conf)$$

$$\Delta G \approx \gamma_{ab} A^{II} - TS^{II}(conf)$$

Emulsion formation

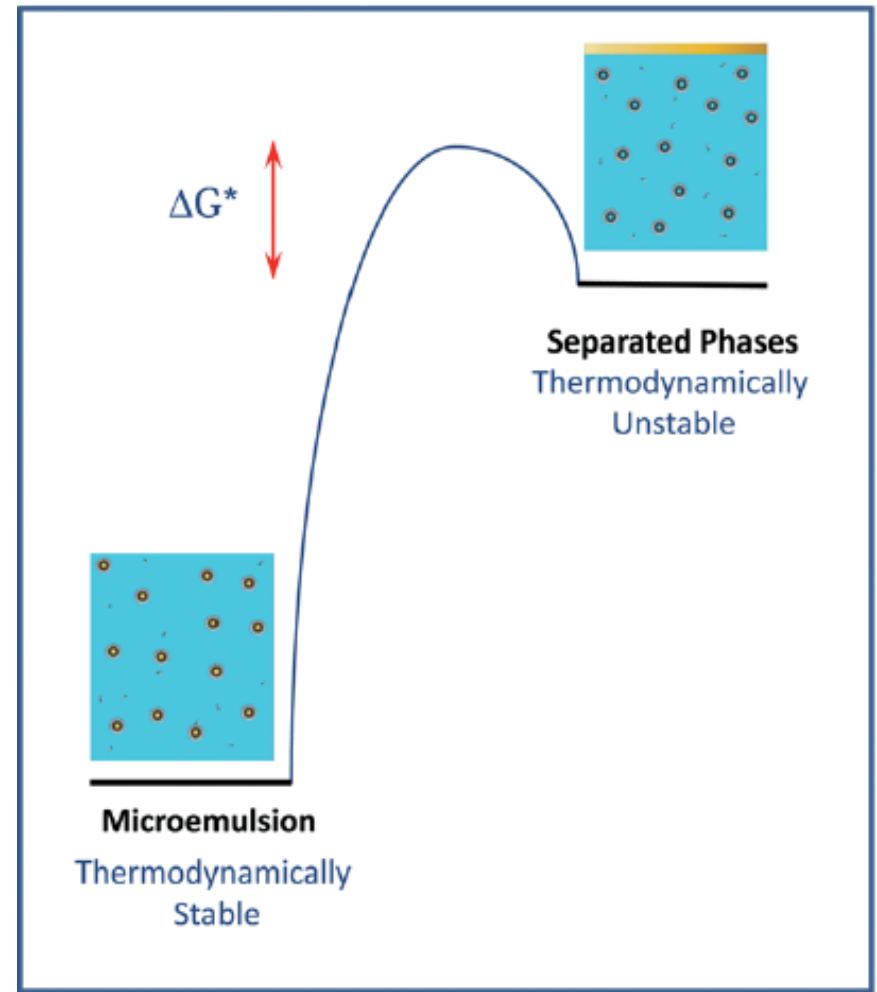
What is the maximum γ_{ab} for which it is energetically favorable to form emulsions?

The emulsion still forms if $\Delta G = 0$.

$$\gamma_{ab,crit} = -\frac{k_B T}{4\pi r^2} \left[\ln \phi_b + \frac{1 - \phi_b}{\phi_b} \ln(1 - \phi_b) \right]$$

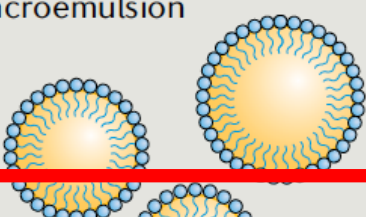
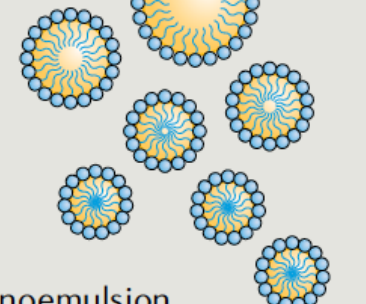
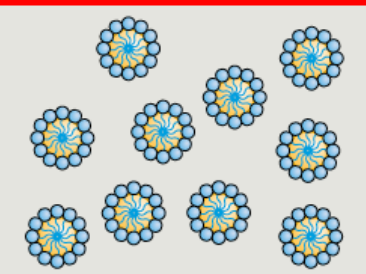
Emulsions

Microemulsion Formation



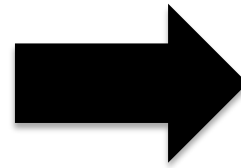
They are thermodynamically stable.

Emulsion classes

Emulsion type	Size	Stability	Requirements
 <p>Macroemulsion</p>	<p>Large ($>1 \mu\text{m}$), limited by large surface tension. Droplets tend to be polydisperse.</p>	<p>Unstable. Droplets coarsen into phase-separated mixtures in minutes or hours.</p>	<p>Simple to produce through low-energy agitation or, more precisely, using microfluidic devices.</p>
 <p>Nanoemulsion</p>	<p>Small ($\sim 100 \text{ nm}$). Lower size dispersity than macroemulsions but not monodisperse.</p>	<p>Kinetically stable. Phase separation may be slowed to occur over weeks or months.</p>	<p>High-energy processing required to overcome the large energy of highly curved droplets.</p>
 <p>Microemulsion</p>	<p>Very small ($\sim 10 \text{ nm}$). Monodisperse droplets from thermodynamic self-assembly.</p>	<p>Thermodynamic phase. Micelles remain dispersed indefinitely if state variables do not change.</p>	<p>Form spontaneously if immiscible phases and surfactants are in the correct concentration.</p>

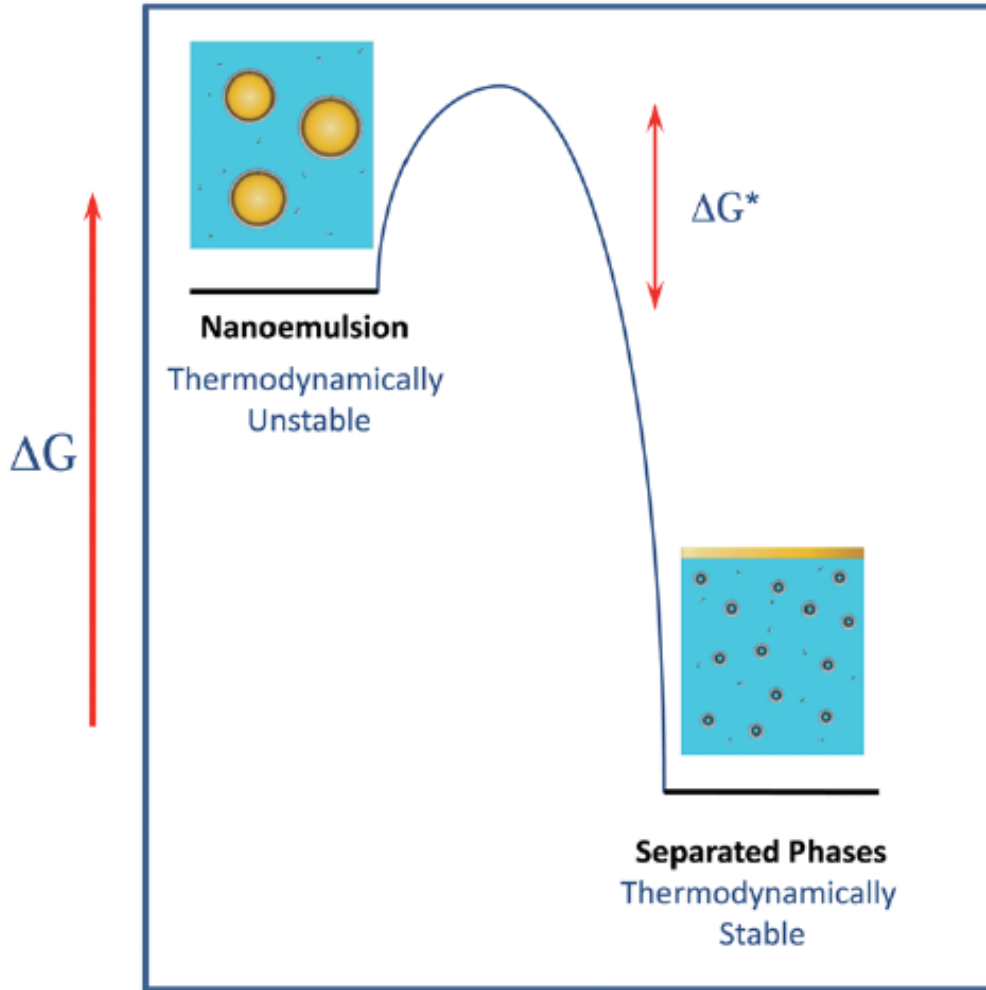
Decreasing size

Coalescence



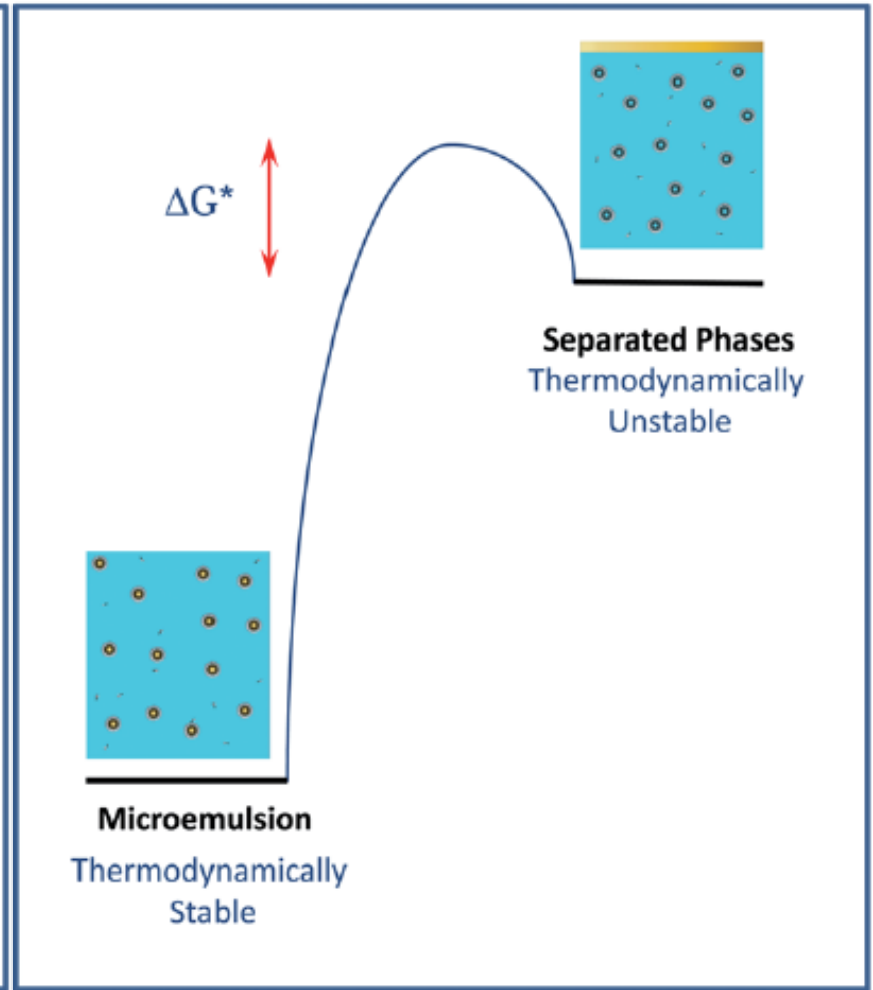
Emulsions

Nanoemulsion Formation



They are thermodynamically unstable.

Microemulsion Formation

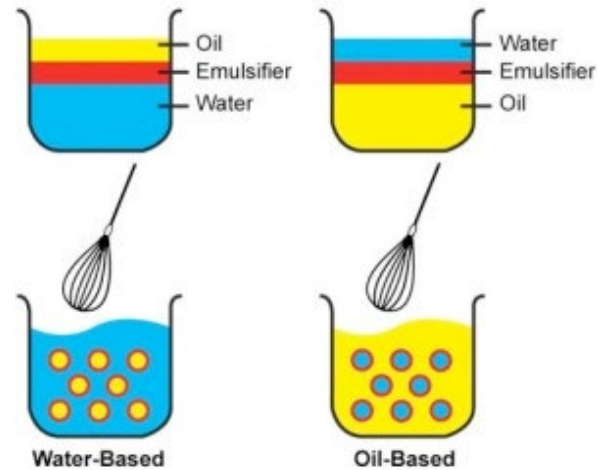


They are thermodynamically stable.

What can you do to facilitate the formation of oil in water emulsions and to increase their stability?

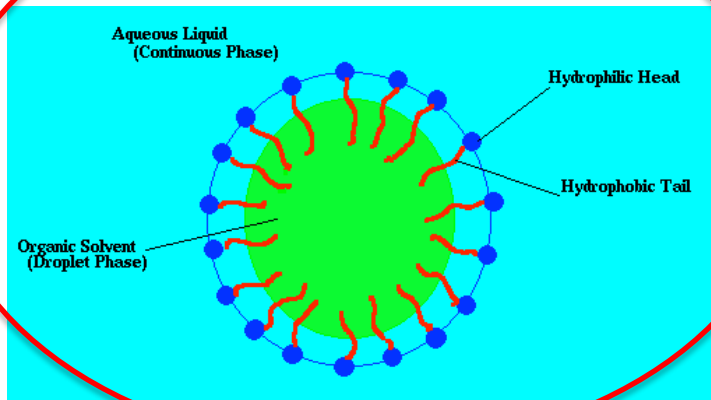
- A. decrease the temperature
- B. increase the volume fraction of oil
- C. lower the interfacial tension
- D. stir vigorously

Stabilization of emulsions



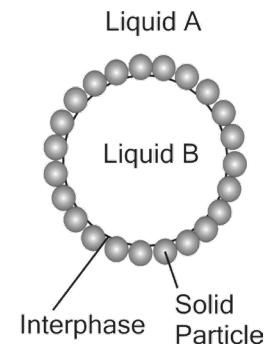
<http://www.dermaessence.com.au>

Surfactants



<http://www.physics.emory.edu/faculty/weeks//lab/emulsion/>

Nanoparticles (Pickering emulsions)



<https://www.mtm.kuleuven.be/Onderzoek/Ceramics/Porous>

Outline

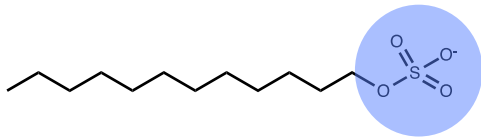
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Surfactants

Surfactants are molecules composed of parts that have a chemical preference to one solvent and other parts with a chemical preference to the other solvent.

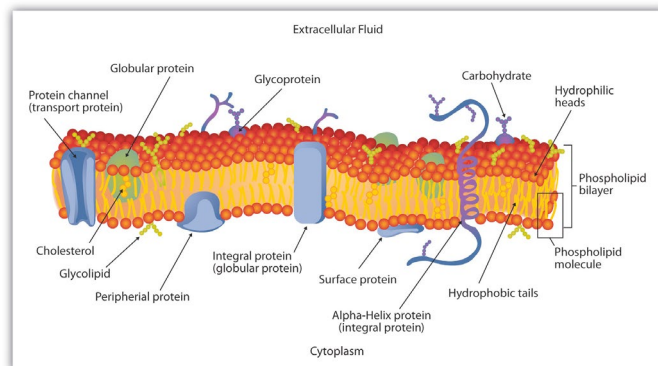
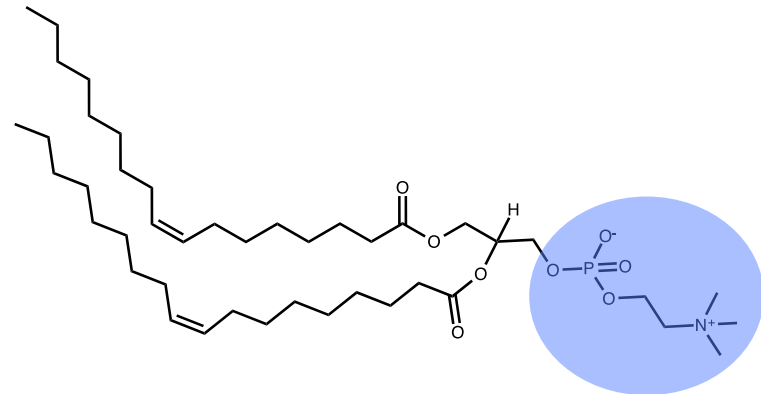
Example:

sodium dodecyl sulfate (SDS)

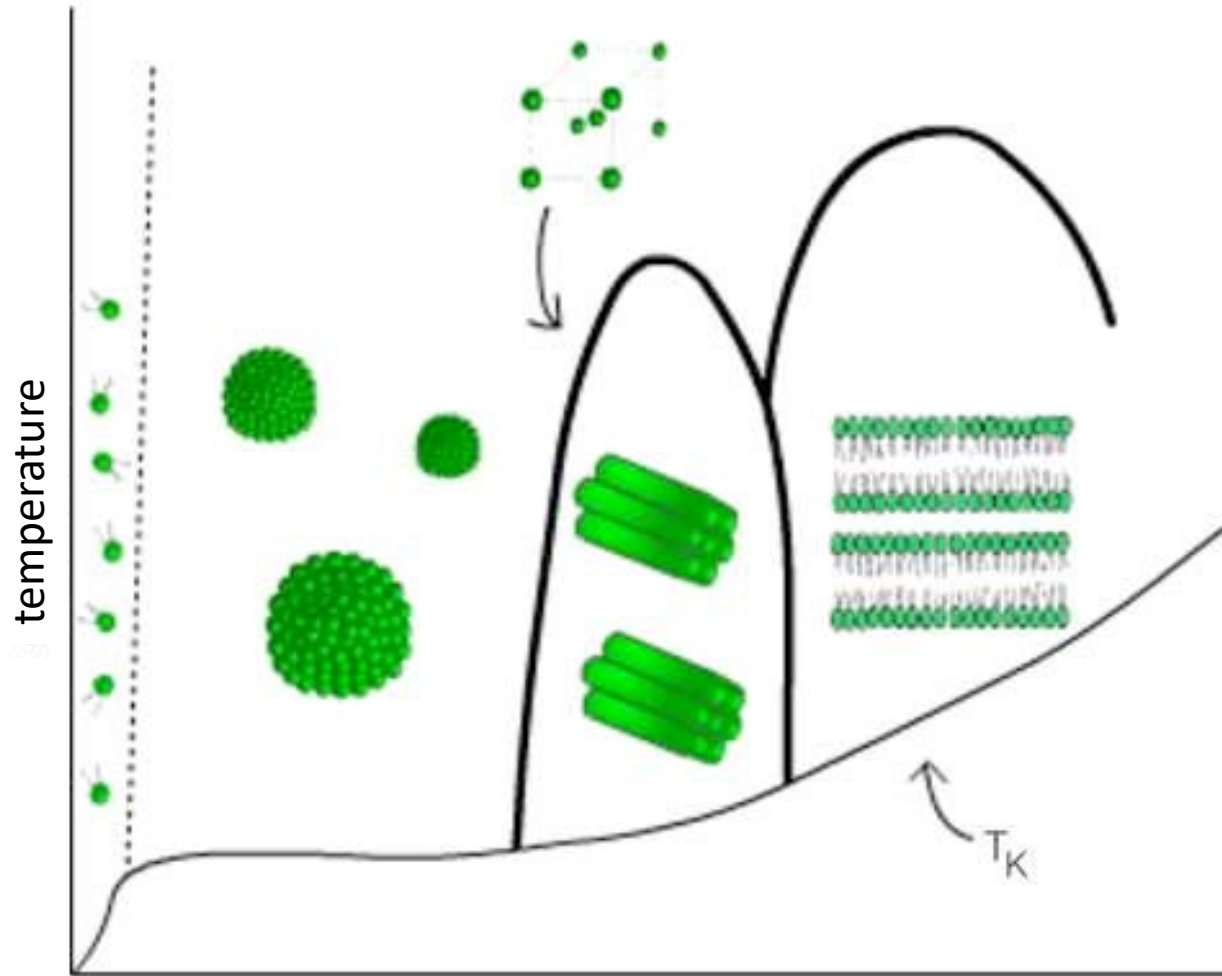


Example:

1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC)



What are surfactants?



concentration of amphiphilic molecules

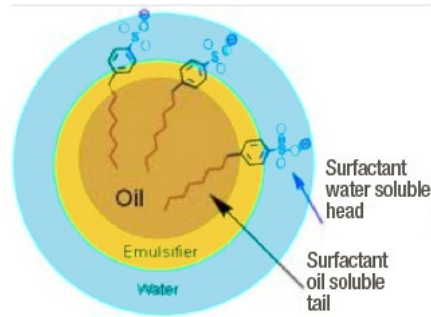
Surfactant are usually lyotropic liquid crystals.

<http://plc.cwru.edu/tutorial/enhanced/files/lc/phase/phase.htm>

What is the main function of surfactants in emulsions?

- A. Increase viscosity
- B. Decrease pH
- C. Reduce interfacial tension
- D. Promote coalescence

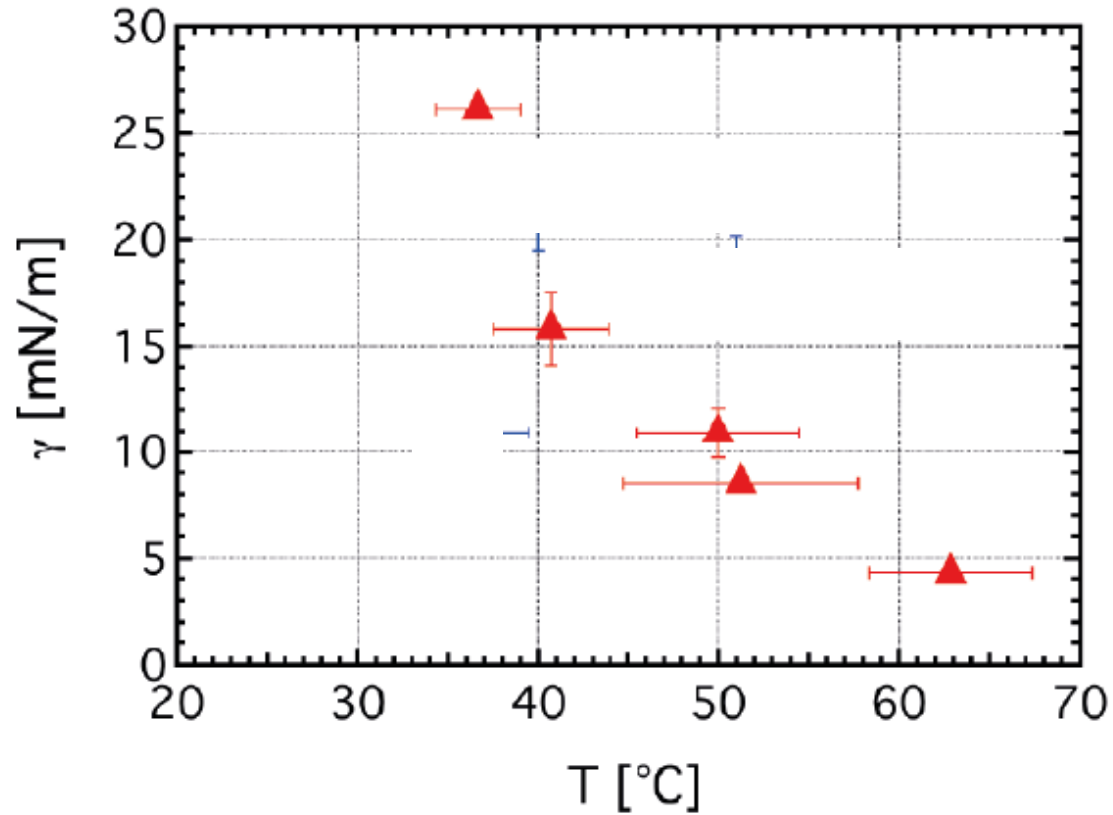
What do surfactants do?



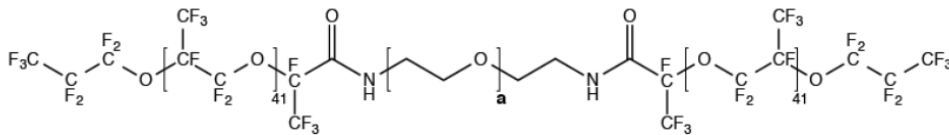
<http://www.verutek.com>

- Surfactants adsorb at liquid-liquid or liquid-air interfaces.
- They lower the interfacial tension.

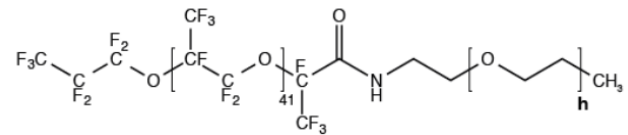
Surfactants



Triblock-copolymers



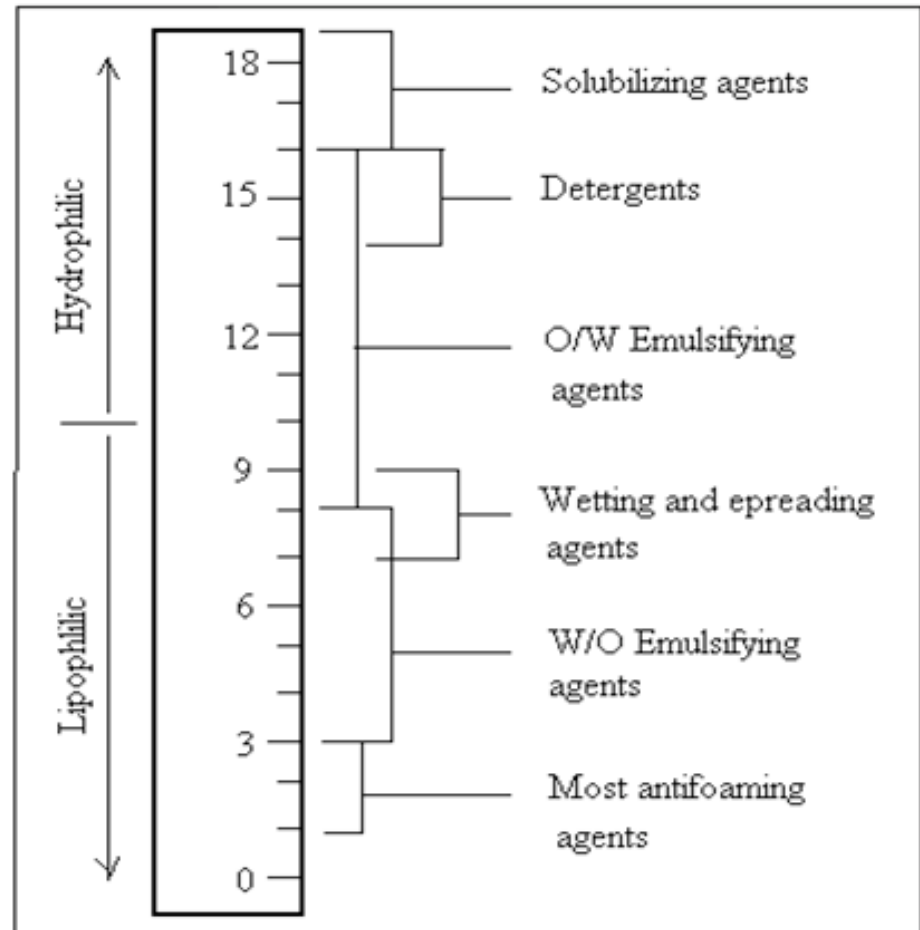
Diblock-copolymers



Activity of surfactants

The activity of surfactant is measured as the hydrophile-lipophile balance (HLB). The HLB value ranges from 1 (very hydrophobic) to 20 (very hydrophilic).

$$HLB = 20 \frac{M_{hydrophil}}{M_{tot}}$$



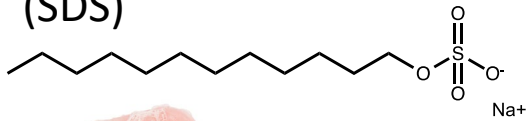
$M_{hydrophil}$: molecular weight of hydrophilic part [g/mol]
 M_{tot} : molecular weight of surfactant [g/mol]

Types of surfactants

Anionic surfactants

Example:

sodium dodecyl sulfate (SDS)

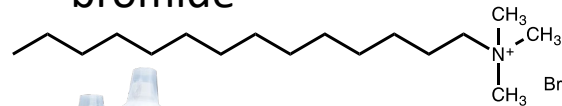


use: soaps, detergents

Cationic surfactants

Example:

alkyl trimethylammonium bromide

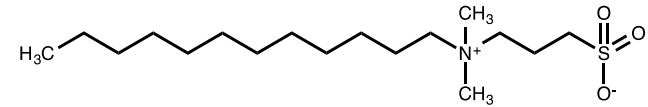


more expensive than anionic surfactants
use: bactericides, to kill bacteria

Zwitterionic surfactants

Example:

sulfobetaine

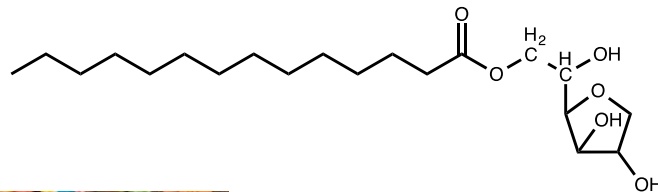


use: cosmetic products, as it is non-irritating to skin and eyes

Nonionic surfactants

Example:

sorbitan alcanoate (Span)

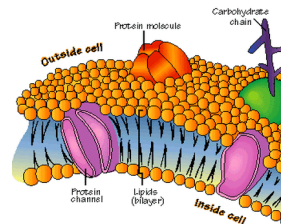
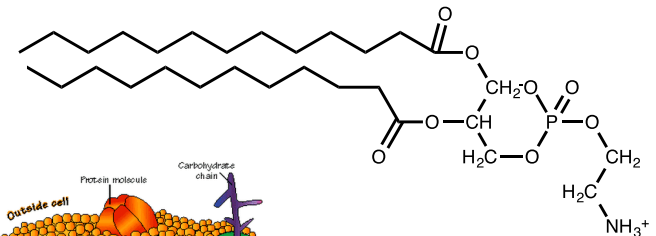


use: food as some of them are non-toxic (e.g. sorbitol)

Lipids

Example:

phosphatidylethanolamine (PE)



abundant in cell membranes

Coalescence



<https://www.sciencefriday.com/educational-resources/salad-dressing-science-emulsions/>

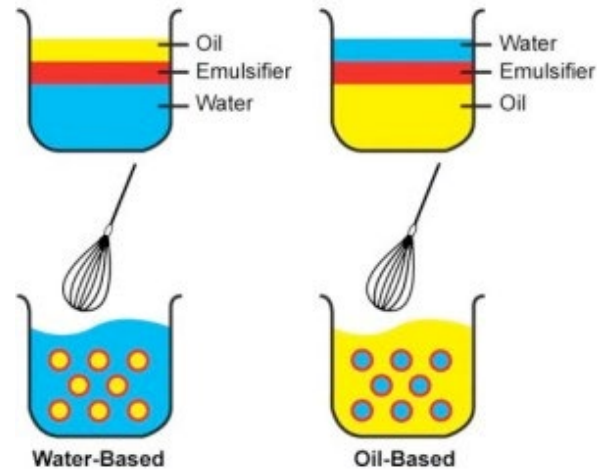
Which of the following will help stabilize an oil-in-water emulsion?

- A. Increasing temperature
- B. Reducing interfacial tension
- C. Adding salt
- D. Increasing the oil droplet size

Outline

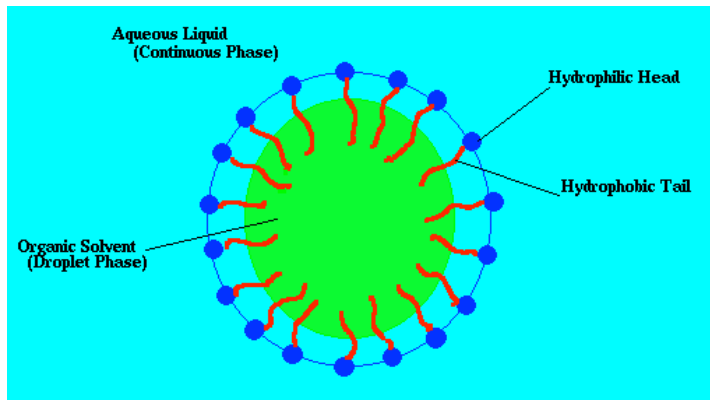
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Stabilization of emulsions



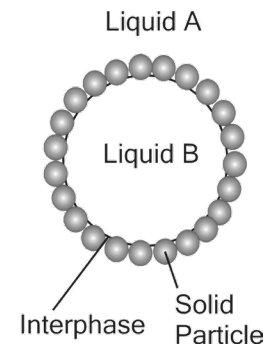
<http://www.dermaessence.com.au>

Surfactants



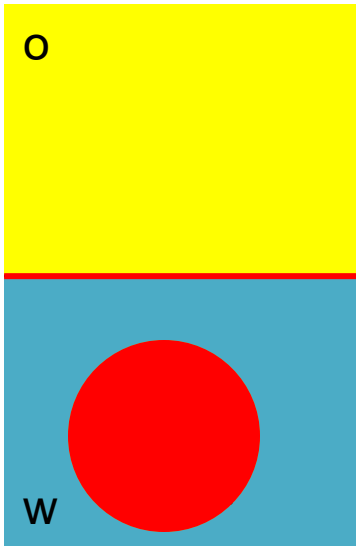
<http://www.physics.emory.edu/faculty/weeks//lab/emulsion/>

Nanoparticles (Pickering emulsions)

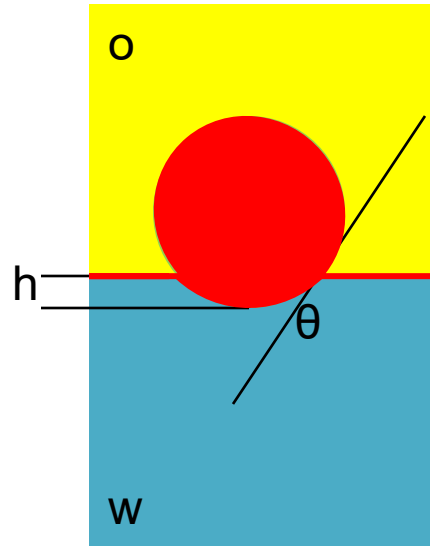


<https://www.mtm.kuleuven.be/Onderzoek/Ceramics/Porous>

Particle adsorption at liquid-liquid interfaces



$$E_0 = \gamma_{pw}A_p + \gamma_{ow}A_{ow}$$



$$E_1 = \gamma_{pw}A_p + \gamma_{po}A_{po} + \gamma_{ow}A_{ow} - \gamma_{ow}A_i$$

$$\cos\theta = \frac{\gamma_{po} - \gamma_{pw}}{\gamma_{ow}} \quad \text{Young's equation}$$

$$A_p = A_{pw} + A_{po} = 4\pi r^2$$

$$A_{pw} = 2\pi r h = 2\pi r^2 (1 + \cos\theta)$$

$$A_i = \pi (r \sin\theta)^2$$

$\theta < 90^\circ$ hydrophilic

$\theta = 90^\circ$ neutrally-wetting

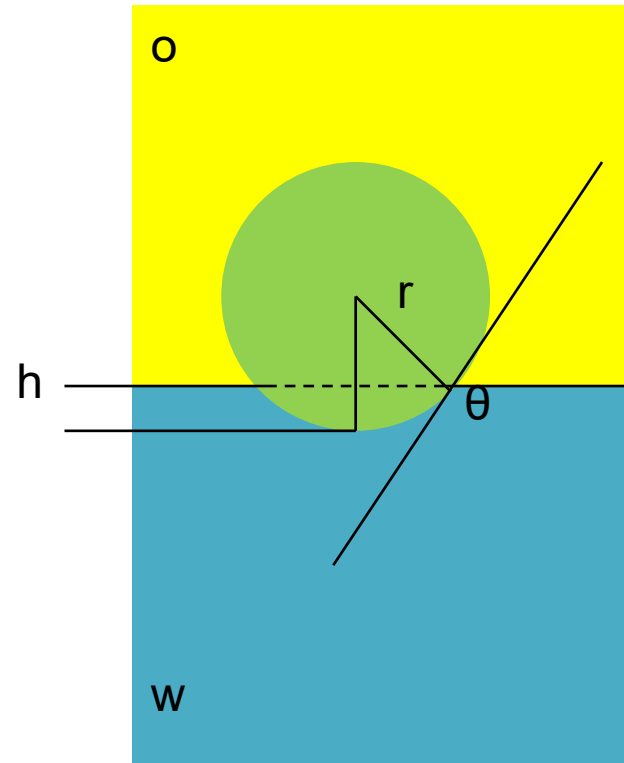
$\theta > 90^\circ$ hydrophobic

Colloidal particles: stabilization mechanism

$$\Delta E = E_1 - E_0 = \gamma_{pw}A_{pw} + \gamma_{po}A_{po} + \gamma_{ow}A_{ow} - \gamma_{ow}A_i - \gamma_{pw}A_p - \gamma_{ow}A_{ow}$$

For spherical particles

$$\Delta E = -\gamma_{ow}\pi r^2(1 - |\cos \theta|)^2$$



What is the energy required to take a particle with a radius of 5 nm away from a water-oil interface with

$$\gamma_{ow} = 30 \text{ mN/m at } 25^\circ \text{ C if}$$
$$\theta = 90^\circ \text{ ?}$$

- A. $0.6 k_B T$
- B. $6 k_B T$
- C. $60 k_B T$
- D. $600 k_B T$
- E. $60000 k_B T$

$$\Delta E = -\gamma_{ow} \pi r^2 (1 - |\cos \theta|)^2$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$T = 298 \text{ K}$$

What is the energy required to take a particle with a radius of 5 nm away from a liquid-oil interface with

$$\gamma_{ow} = 30 \text{ mN/m at } 25^\circ \text{ C if}$$
$$\theta = 10^\circ \text{ ?}$$

- A. $0.1 k_B T$
- B. $1 k_B T$
- C. $10 k_B T$
- D. $100 k_B T$
- E. $10000 k_B T$

$$\Delta E = -\gamma_{ow} \pi r^2 (1 - |\cos \theta|)^2$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$T = 298 \text{ K}$$

What is the energy required to take a particle with a radius of 100 nm away from a liquid-oil interface with

$$\gamma_{ow} = 30 \text{ mN/m at } 25^\circ \text{ C if}$$

$$\theta = 10^\circ \text{ ?}$$

- A. $0.5 k_B T$
- B. $5 k_B T$
- C. $50 k_B T$
- D. $500 k_B T$
- E. $50000 k_B T$

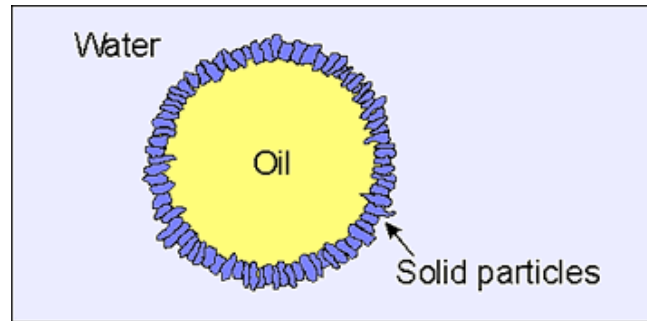
$$\Delta E = -\gamma_{ow} \pi r^2 (1 - |\cos \theta|)^2$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$T = 298 \text{ K}$$

Pickering emulsions

Pickering emulsions are usually more stable than emulsions stabilized with surfactants.



<http://www.azonano.com/article.aspx?ArticleID=1293>



Sunscreens are often Pickering emulsions.

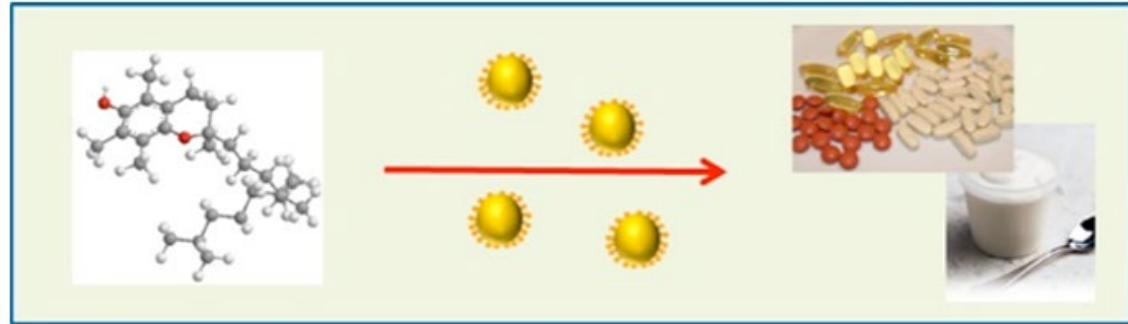
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- Foams

Emulsions in our daily life



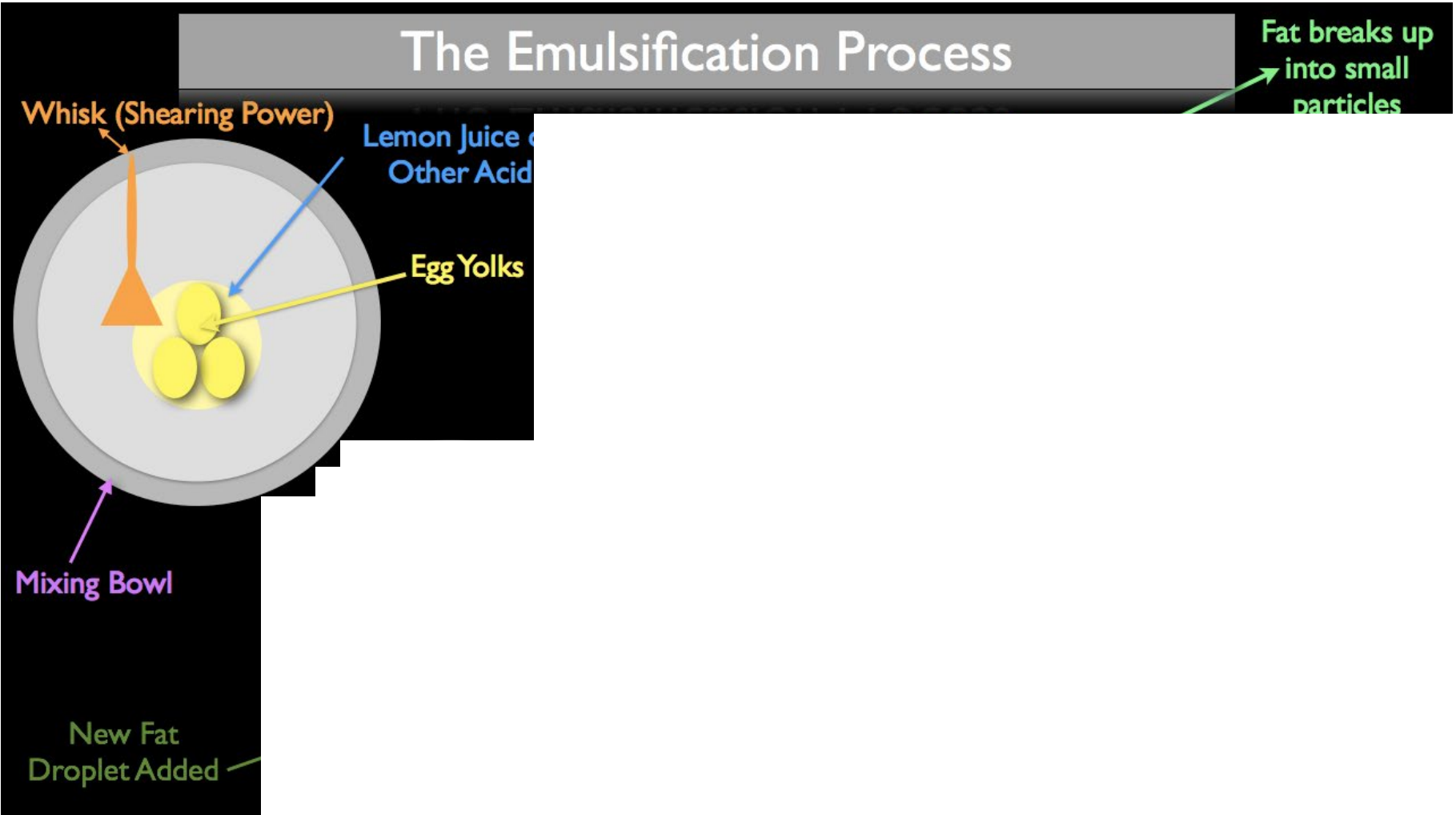
Emulsion



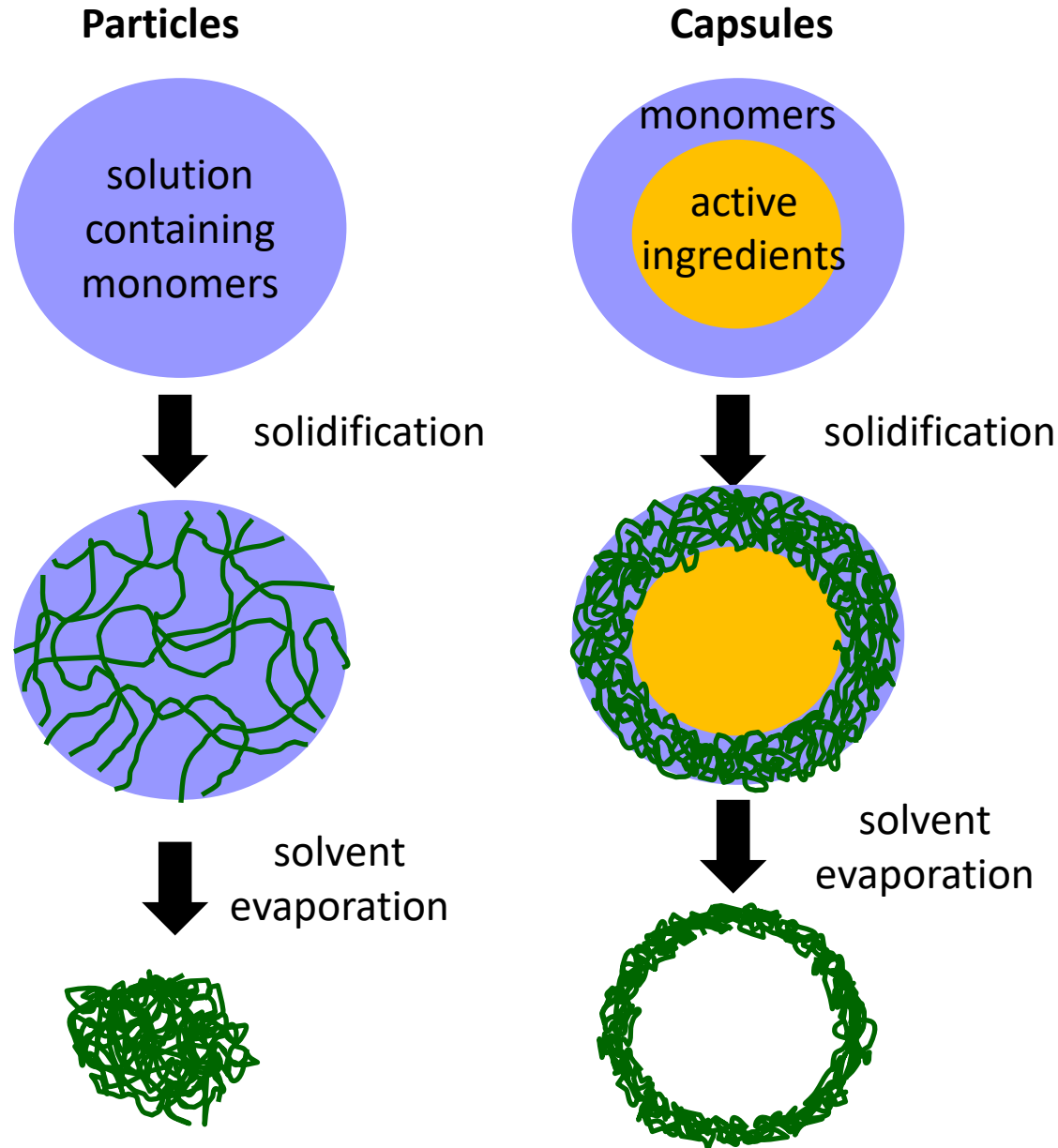
<https://www.umass.edu/cbd/emulsion-based-delivery-systems-oil-soluble-vitamins>

Mayonnaise

The Emulsification Process

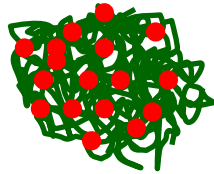


Drops as templates to produce carriers

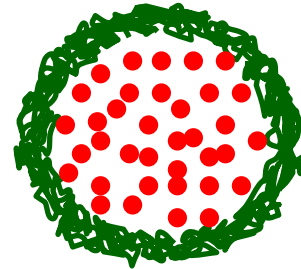


Why do you need to encapsulate substances?

Microparticles



Microparticles



Protection

- Degradation
- Consumption prior to use



<http://entitledtorevelation.com>

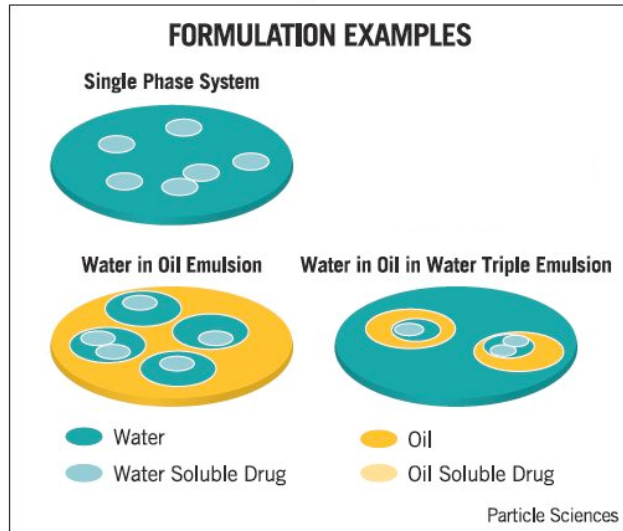
Localized release

- Minimize the dose of actives
- Minimize side-reactions

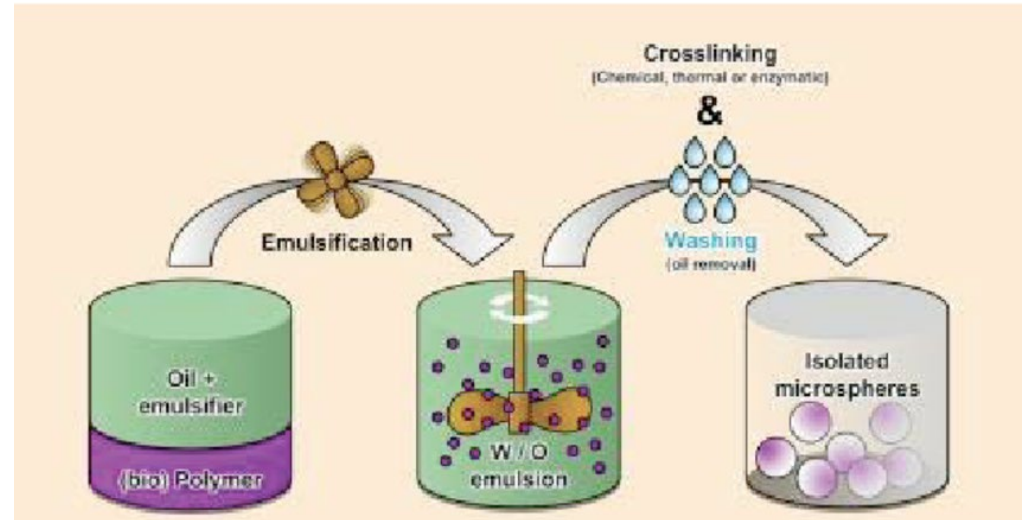


<http://www.indiamart.com>

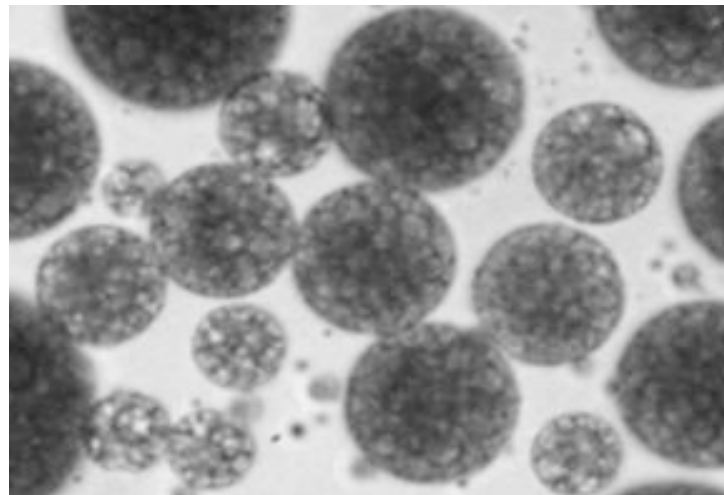
Production of double emulsions



<http://www.particlesciences.com/news/technical-briefs/2009/emulsions-and-emulsification.html>



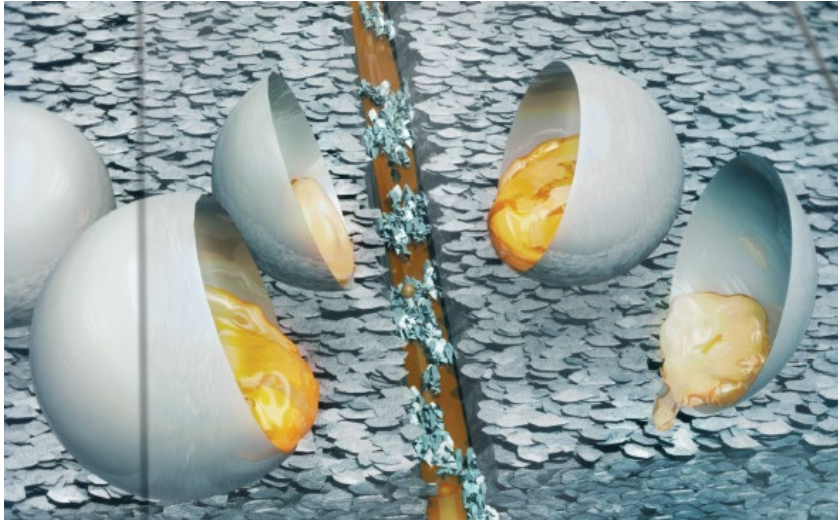
K. M. Manjanna, et al., *Critical Reviews in Therapeutic Drug Carrier Systems*, 2010, **27**, 509-545.



Tirnaksiz, F.; Kalsin, O. *Journal of Pharmacy and Pharmaceutical Sciences* **2005**, *8* (2), 299-315

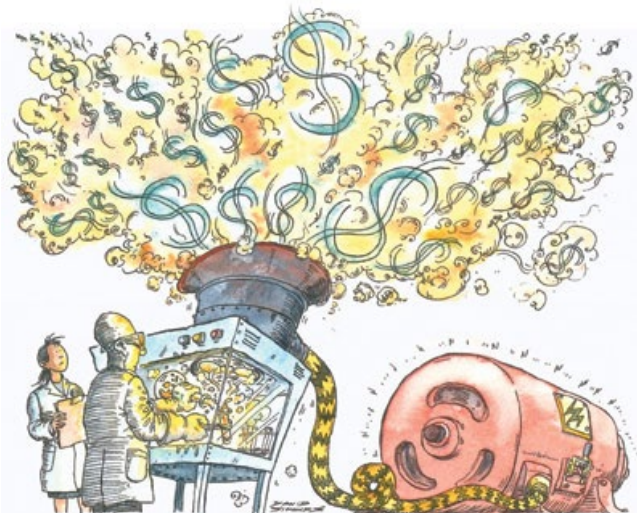
Requirements for carriers

high loading capacity



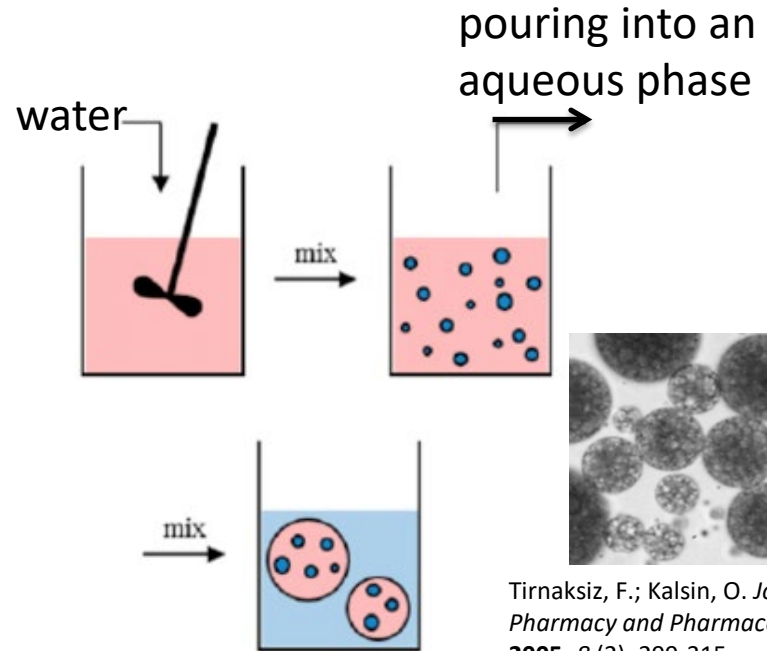
Odom, S. A., et al., 2012, "Advanced Materials 24(19):

high loading efficiency

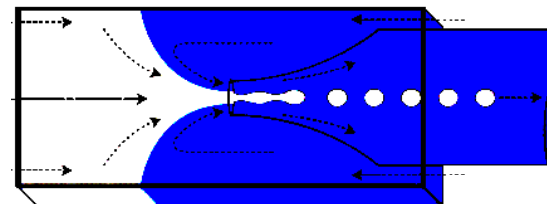


<http://www.nature.com/nature/journal/v445/n7128/images/445590a-i1.0.jpg>

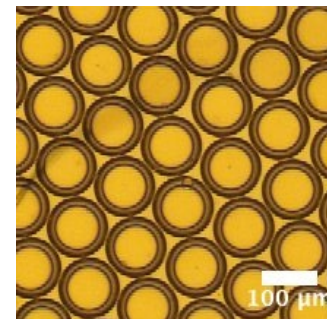
→ Depend on processing



Tirnaksiz, F.; Kalsin, O. *Journal of Pharmacy and Pharmaceutical Sciences* 2005, 8 (2), 299-315

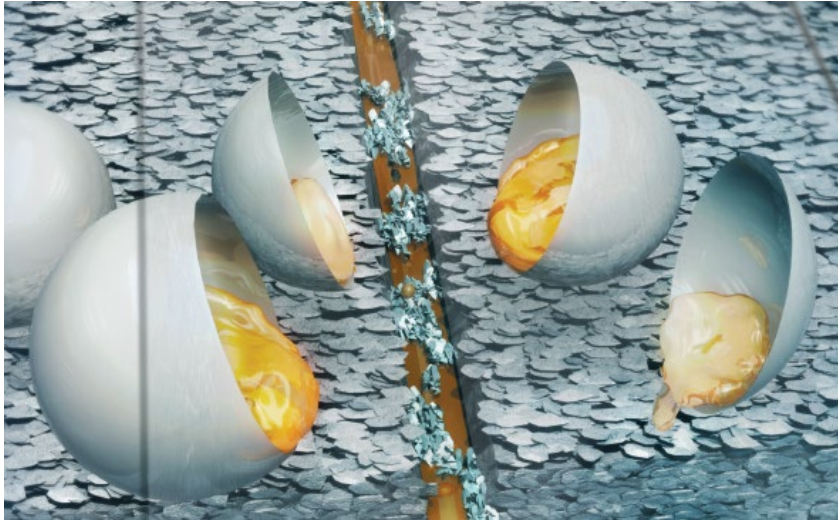


Utada, A.S., et al., *Mrs Bulletin*, 2007. 32(9):



Requirements for carriers

high loading capacity



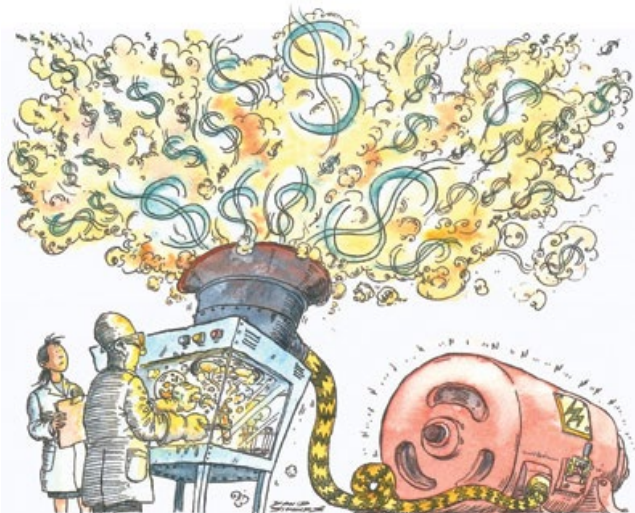
Odom, S. A., et al., 2012, "Advanced Materials 24(19):

low permeability during storage



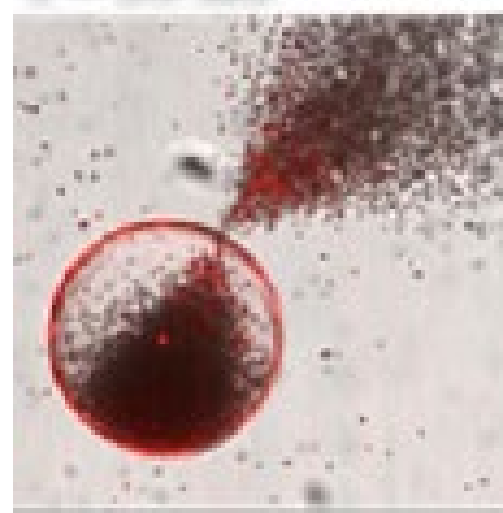
<http://lparhive.org/Mother-3/Update%2034/>

high loading efficiency



<http://www.nature.com/nature/journal/v445/n7128/images/445590a-i1.0.jpg>

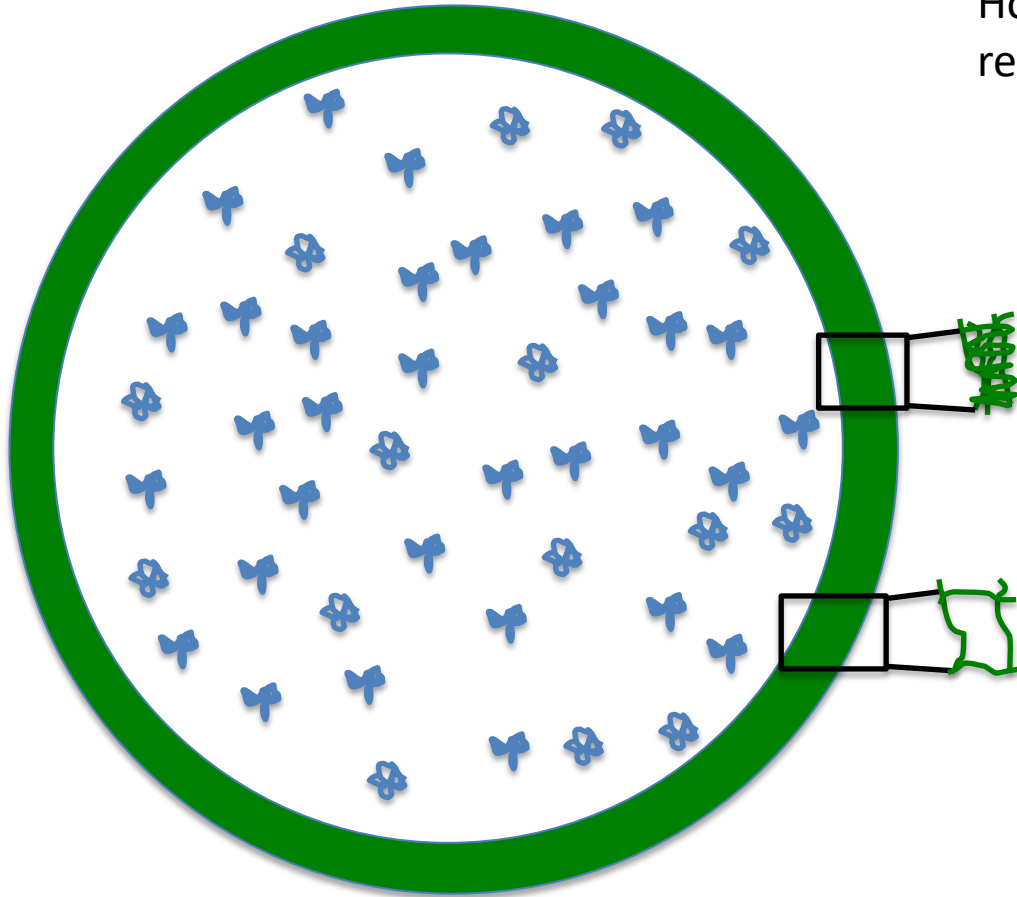
high permeability when applied



Abbaspourrad, A. et al., 2013, Journal of the American Chemical Society 135(20)

Capsules for controlled release

How much time is needed to release 10% of the encapsulants...



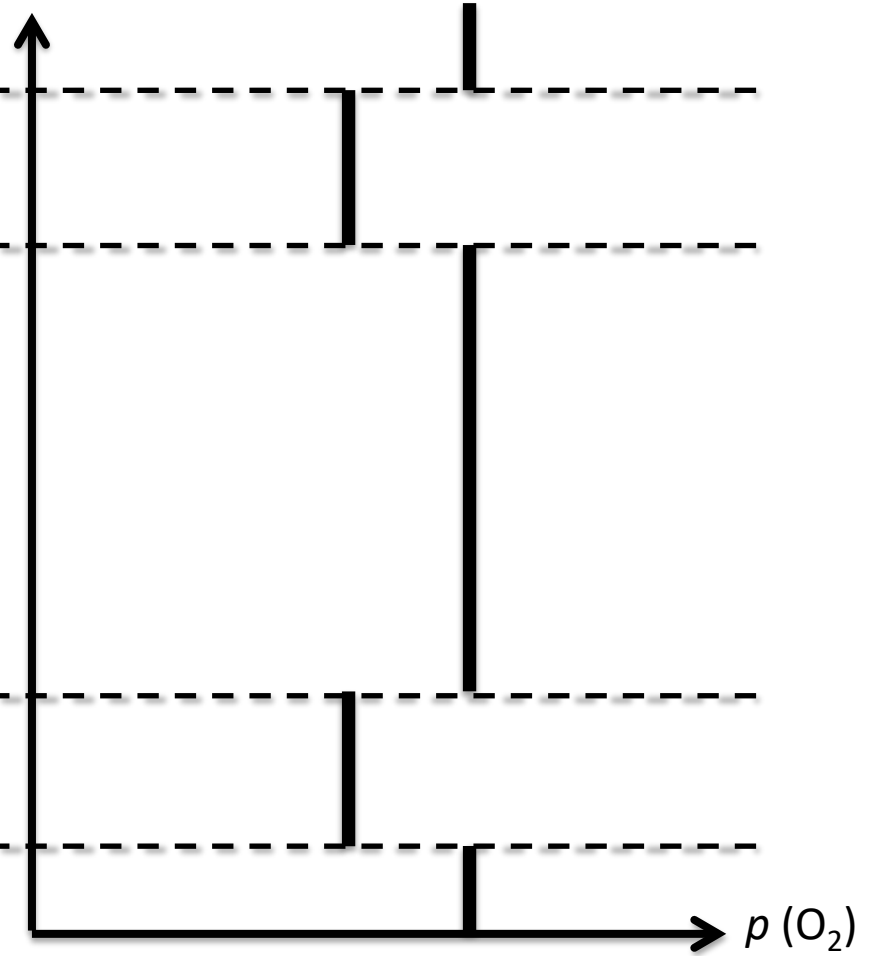
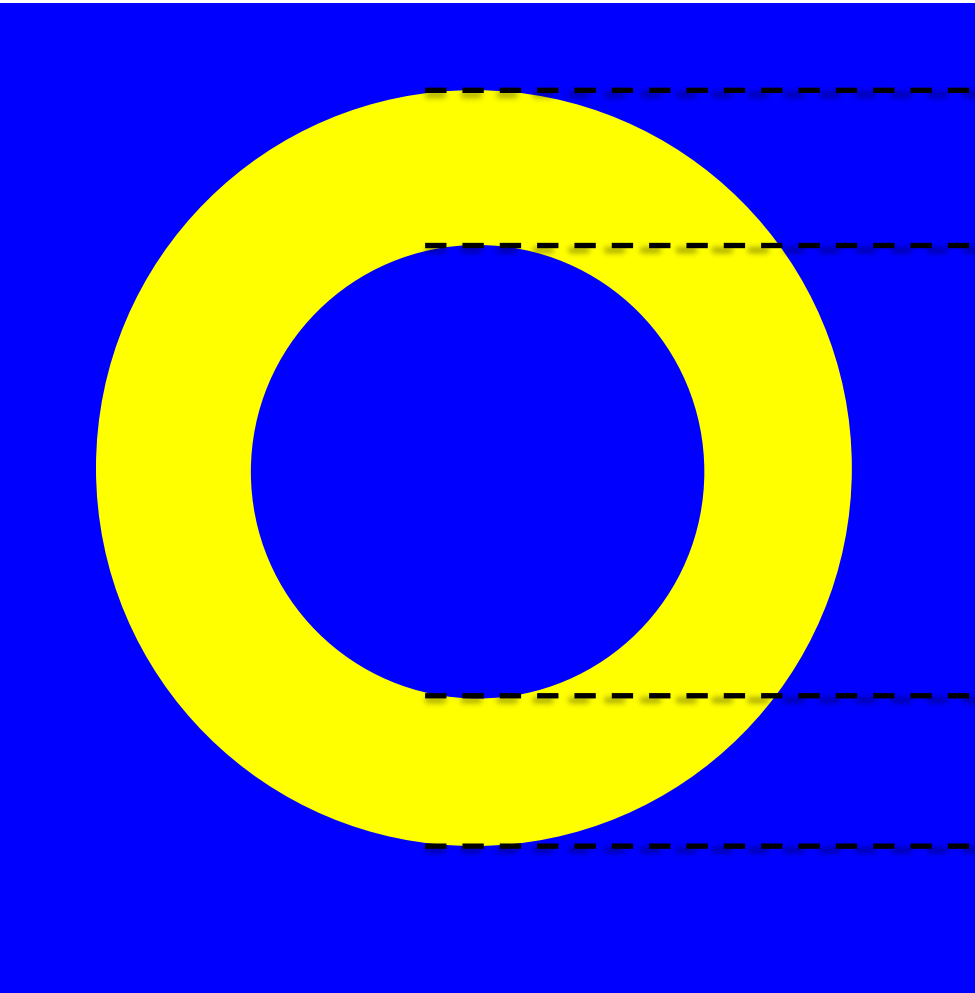
...if the mesh size is smaller than R_g of the encapsulant?

...if the mesh size is larger than R_g of the encapsulant?



Capsules for protection

Draw the O_2 concentration profile across this capsule assuming it is in equilibrium.

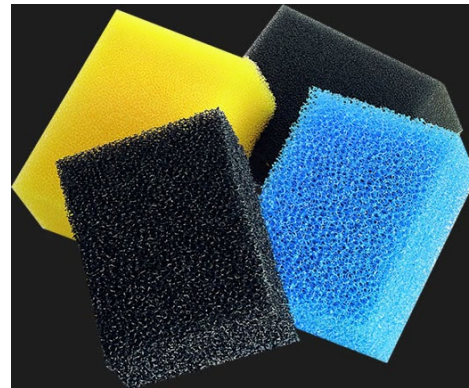
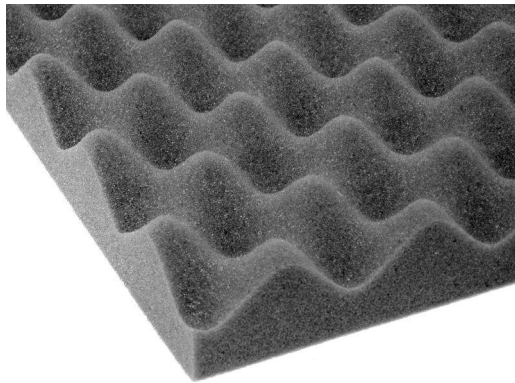


Outline

- Introduction
- Production of emulsions
- Stabilization of emulsions
 - Surfactants
 - Particles
- Applications of emulsions
- **Foams**

Foams

Foams are air bubbles contained in a liquid.



They have a high surface to volume ratio such that they are metastable. The foam formation can be assisted with porogens. To delay the coalescence of the air bubbles, additives, such as surfactants or colloids are needed.

How can one slow down the coalescence of foams?

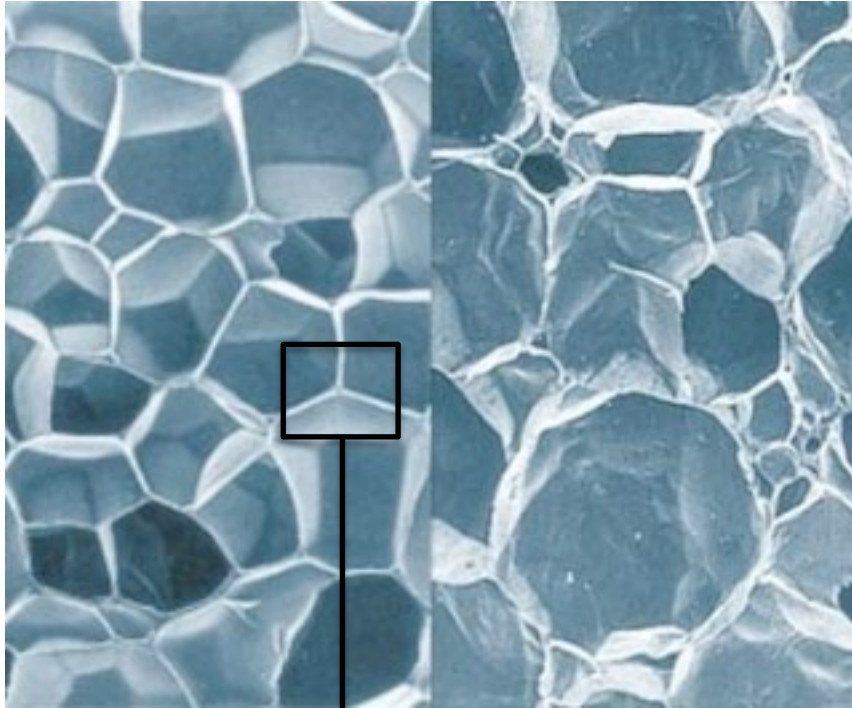
- A. By reducing the interfacial tension.
- B. By increasing the solubility of the gas in the liquid.
- C. By using less volatile liquids.
- D. By increasing the air bubble size.

Stabilization of foams



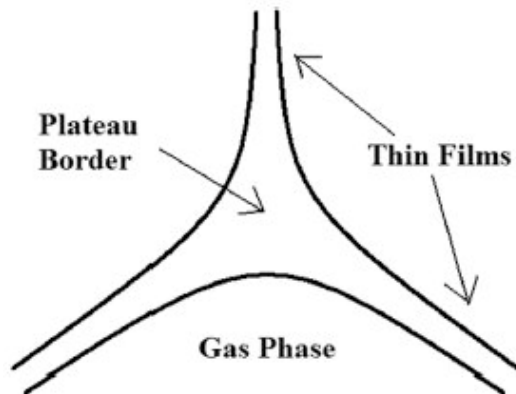
Surfactants

Foam structure



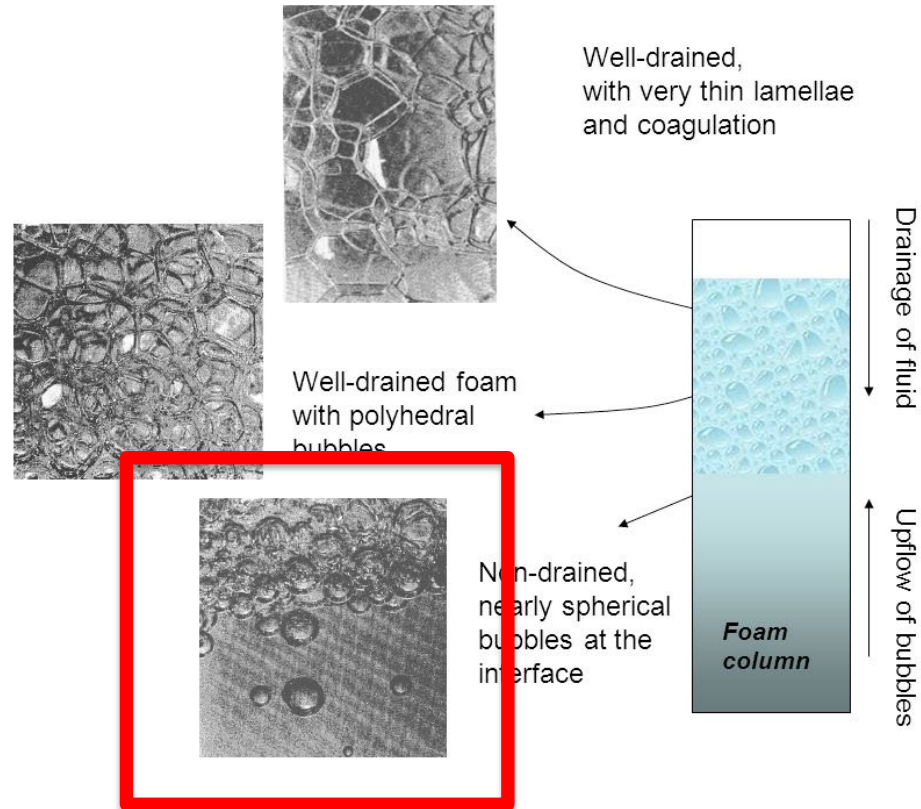
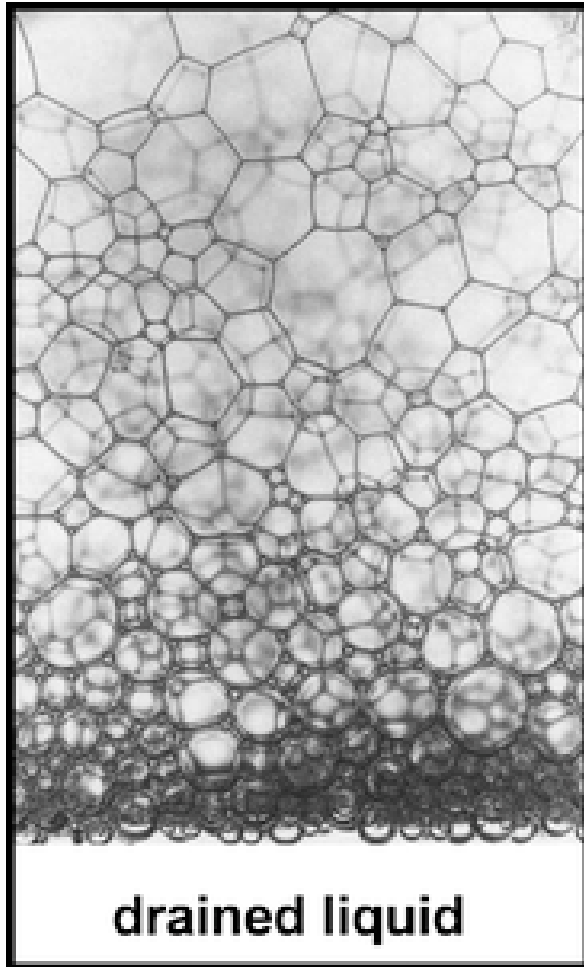
Foam structure:

- Three flat sides of a polyhedra meet at an angle of 120° .
- If four or more sites come together in one line the configuration is unstable.
- If the four edges meet in a tetragonal arrangement at all corners of a polyhedra, the angle between any two edges is 109.5° .



Foam destabilization: drainage

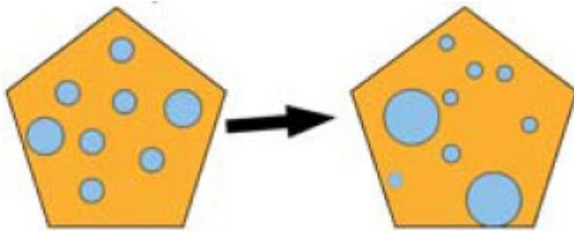
Drainage is the flow of liquids through channels.



Gravity causes liquid to flow to the bottom. This results in a coarsening of the gas bubbles.

Foam destabilization: Ostwald ripening

The larger air bubbles grow on the expense of the smaller ones.



Vincent, R. R. R.; Gillies, G.; Stradner, A. *Soft Matter* **2011**, *7*, 2697.

$$RT \ln \left(\frac{p_r}{p_0} \right) = \frac{2\gamma V_m}{r}$$

p_r : pressure of bubble [Pa]

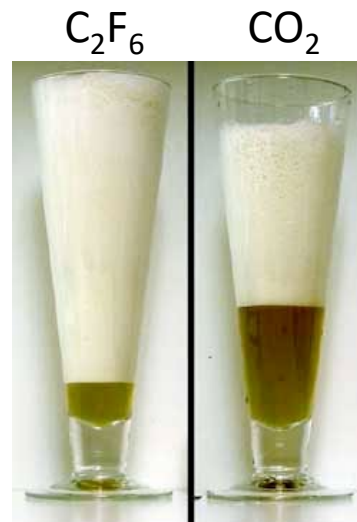
p_0 : pressure of flat surface [Pa]

γ : interfacial tension [N/m]

V_m : molar volume of liquid [m³]

r : radius of bubble [m]

r (m)	p_r/p_0
10^{-7}	1.01
10^{-8}	1.1
10^{-9}	3



Beer foam lasts longer if C₂F₆ is used.

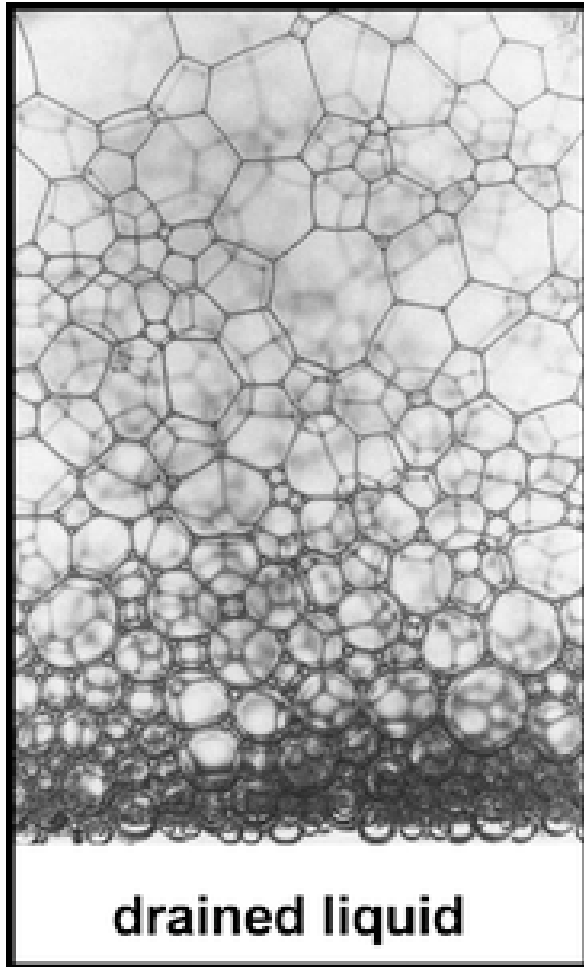
Why?

C₂F₆ has a lower solubility in the aqueous phase than CO₂. This slows down Ostwald ripening such that the drainage is slower.

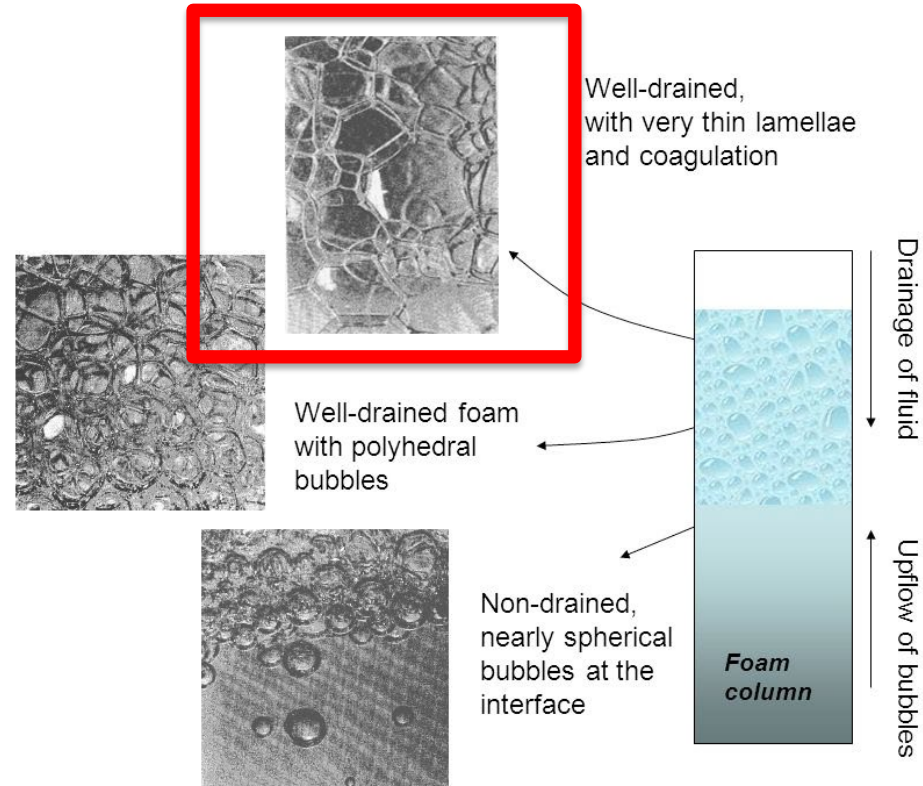
S. Hilgenfeldt, et al., *Phys. Rev. Lett.* **86**, 4704 (2001)

Foam destabilization: drainage

Drainage is the flow of liquids through channels.

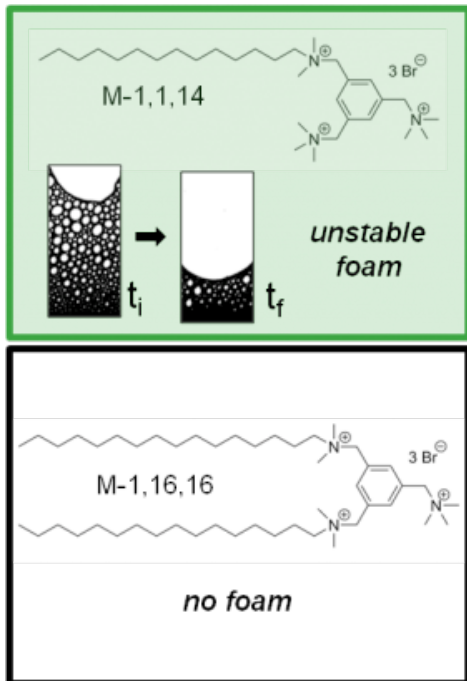


A. Saint-Jalmes, *Soft Matter*, 2006, **2**, 836-849.

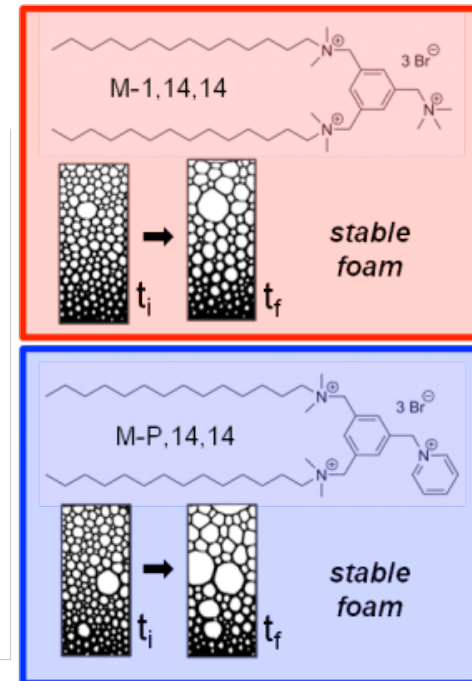
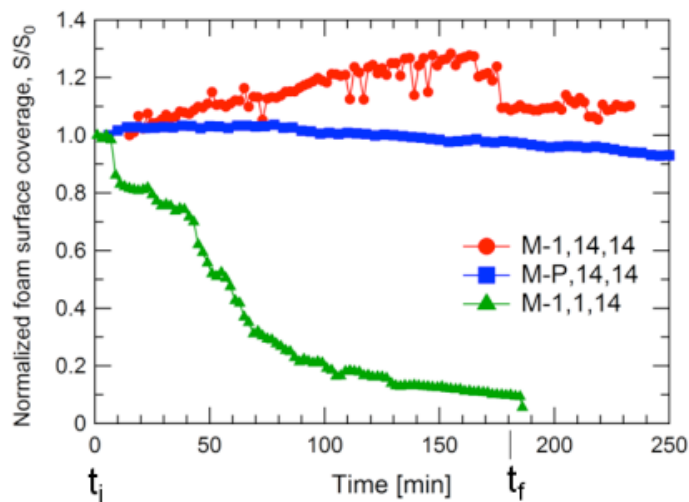


Gravity causes liquid to flow to the bottom. This results in a coarsening of the gas bubbles.

Foam stability



Stability of tricationic surfactant foams



<http://sites.jmu.edu/feitosa/research/>



Ethanol can destabilize foams.

Why?

Ethanol also lowers γ but not to the same extent as surfactants. Because of its high mobility, it quickly adsorbs at the air-liquid interfaces and competes with the adsorption of surfactants.

A foam is most stable when...

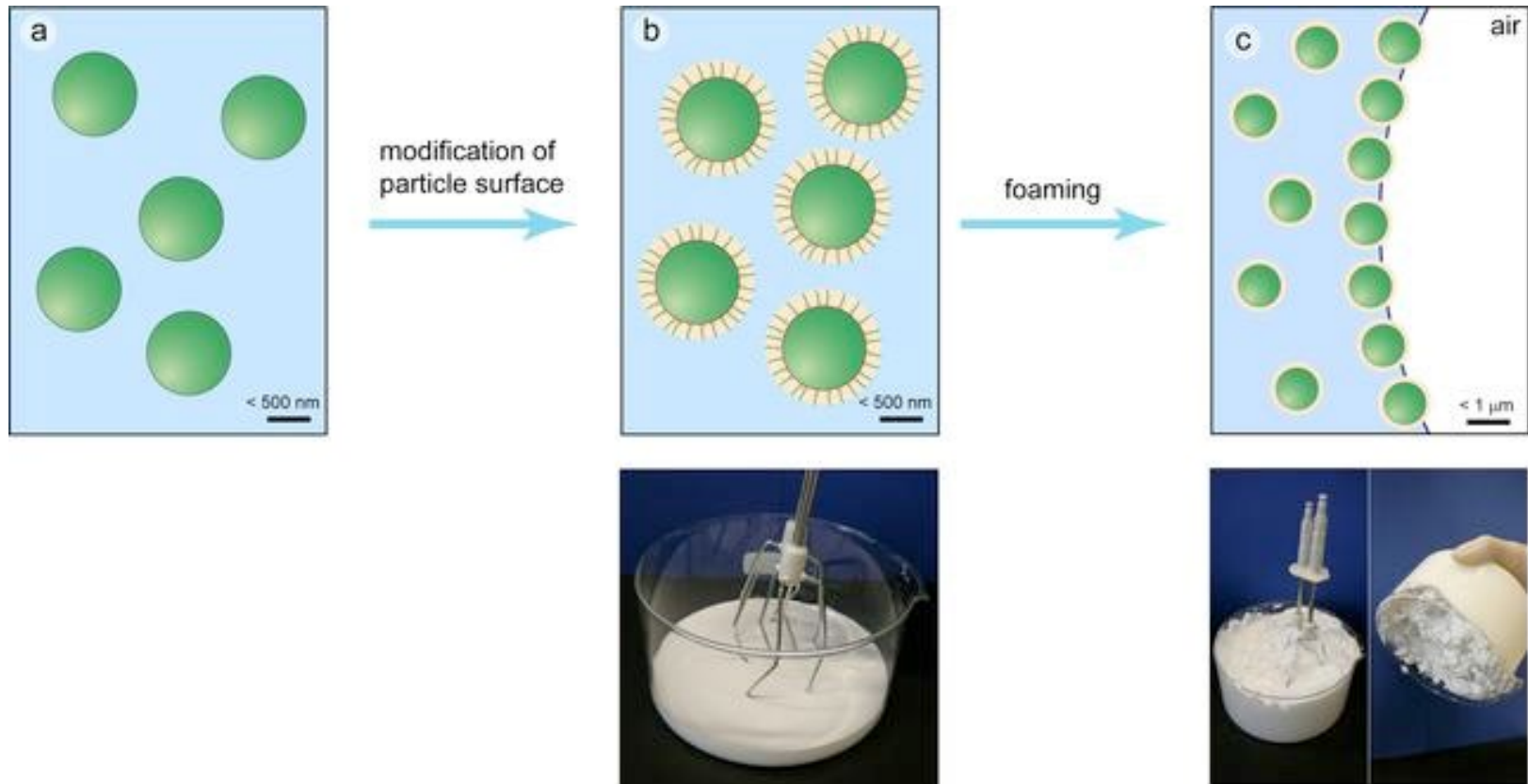
- A. ... it is stabilized with an appropriate surfactant.
- B. ... it is stabilized with appropriate nanoparticles.
- C. ... it is produced using porogens.
- D. ... a solvent is added to reduce the interfacial tension.

Which of the following contributes to the destabilization of foams?

- A. High viscosity
- B. Ostwald ripening
- C. Low surface-to-volume ratio
- D. Use of surfactants

Stabilization of foams

Colloids

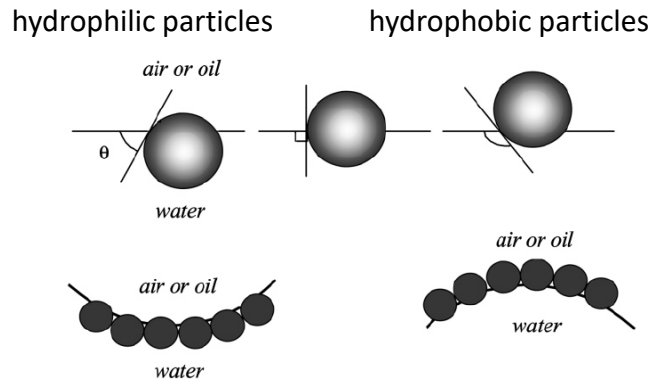


Gonzenbach, U. T.; Studart, A. R.; Tervoort, E.; Gauckler, L. J. *Angewandte Chemie-International Edition* **2006**, *45*, 3526.

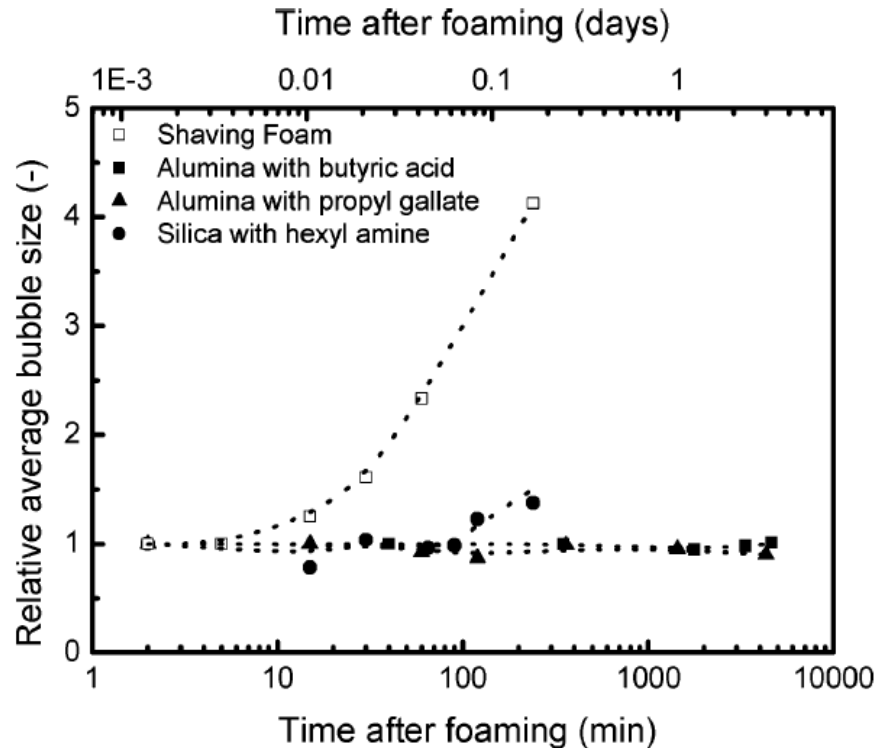
Foam stability

Foams that are stabilized with nanoparticles are more stable than those stabilized with surfactants.

$$\Delta E = -\gamma_{ow}\pi r^2(1 - |\cos \theta|)^2$$

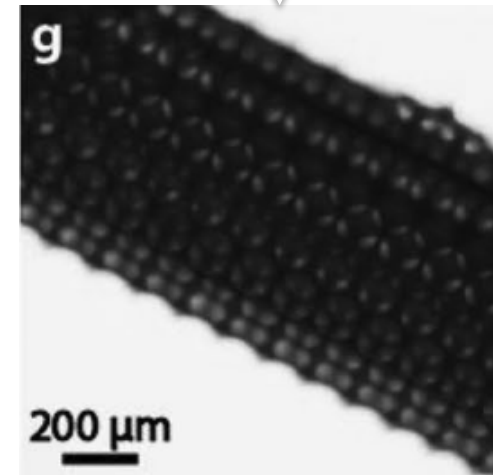
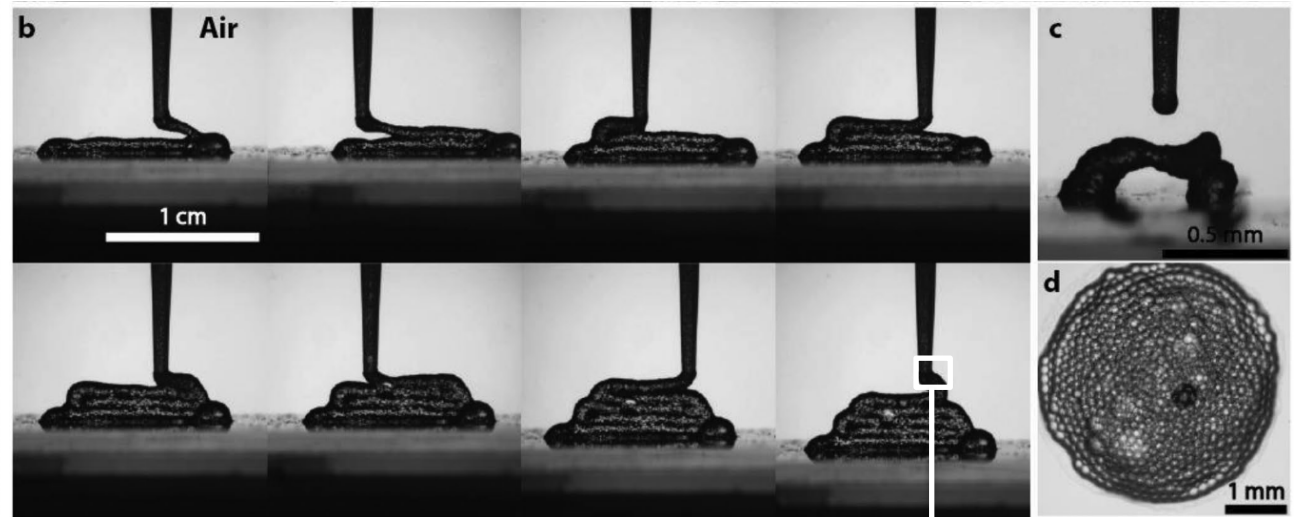
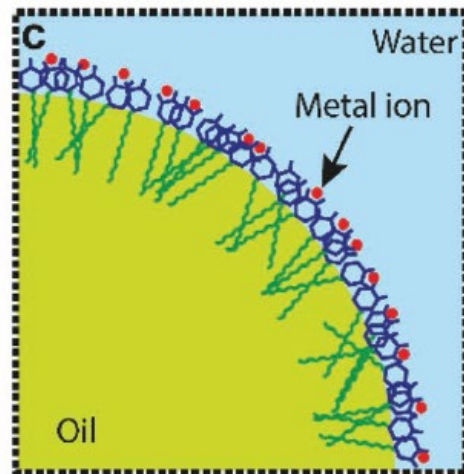
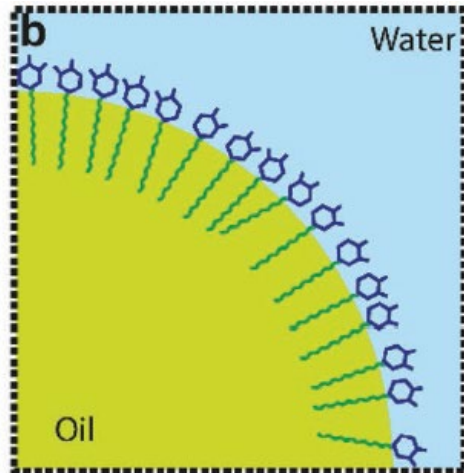


Binks, B. P. *Current Opinion in Colloid & Interface Science* **2002**, 7 (1–2), 21-41



Gonzenbach, U. T.; et al., *Langmuir* **2006**, 22 (26), 10983-10988

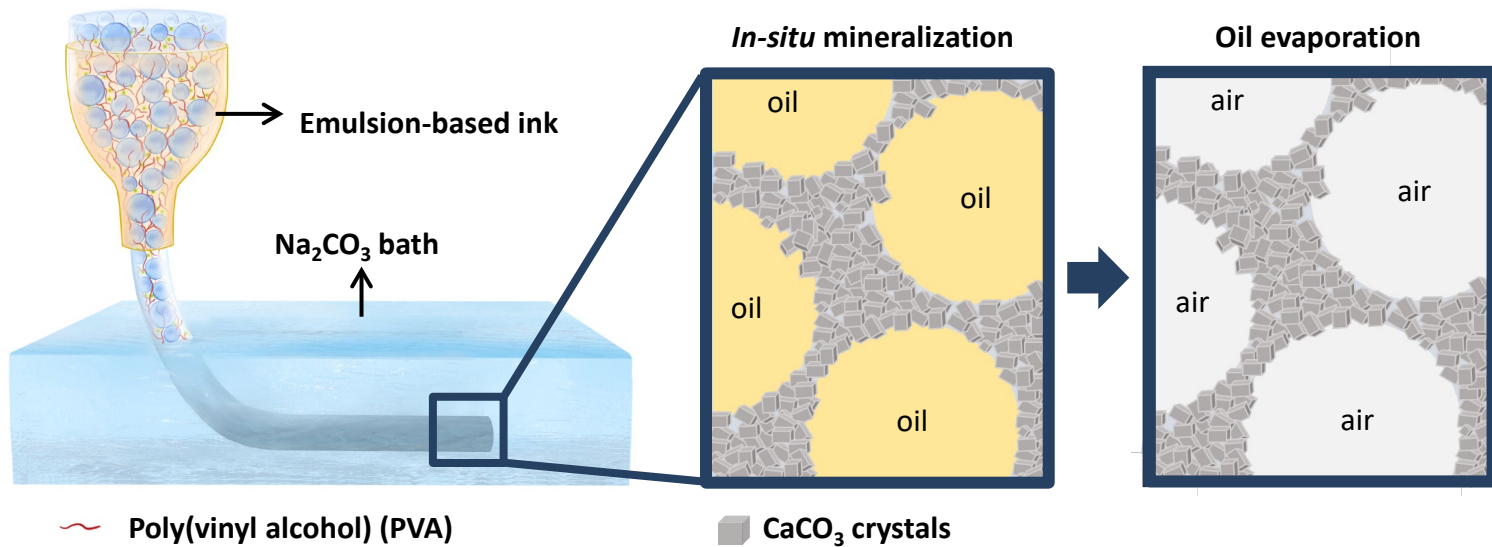
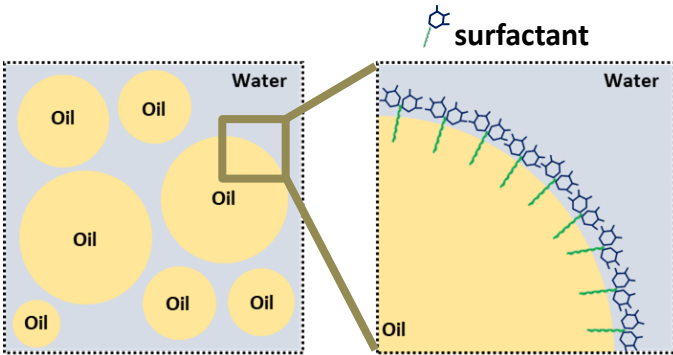
Application: 3D printing of viscoelastic capsules formed from emulsions



Mineralization of emulsion drops



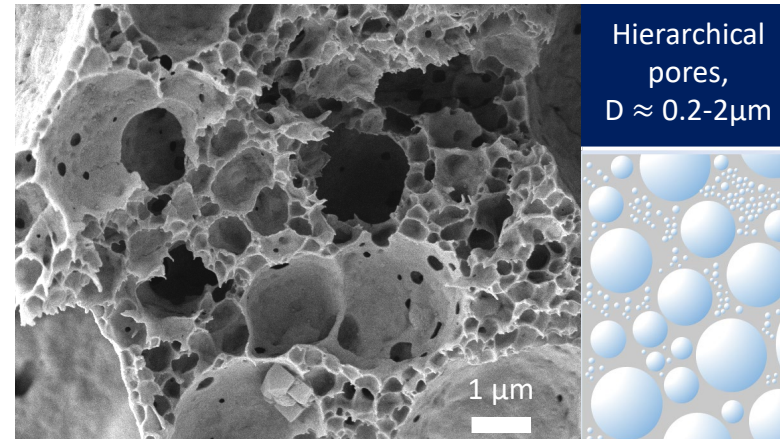
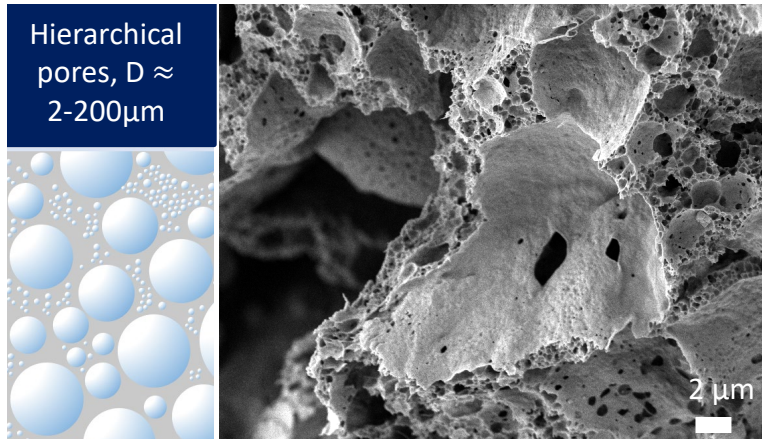
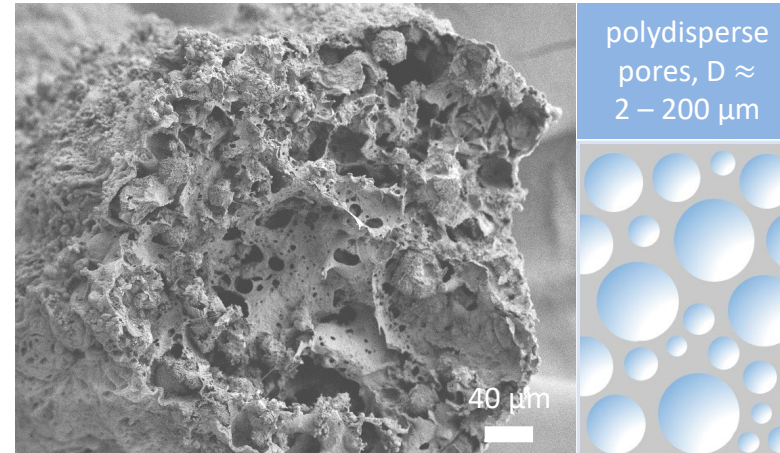
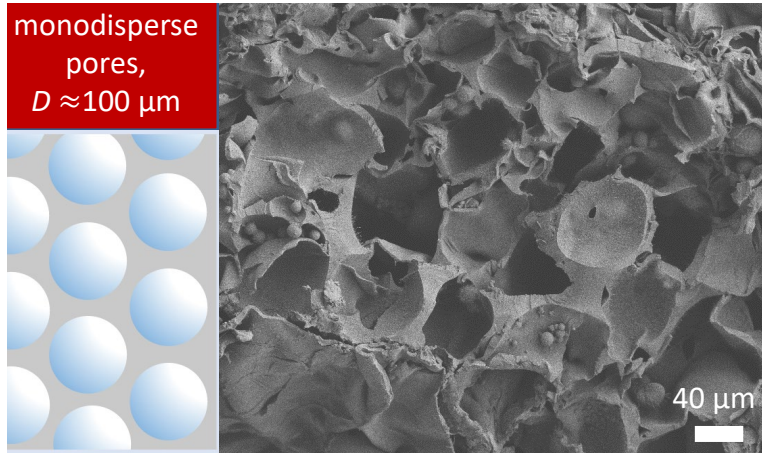
Ran Zhao



Microstructure of 3D printed CaCO_3



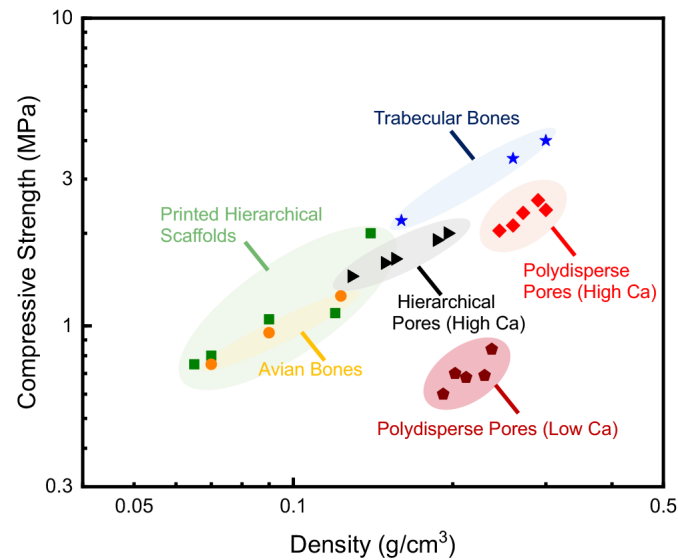
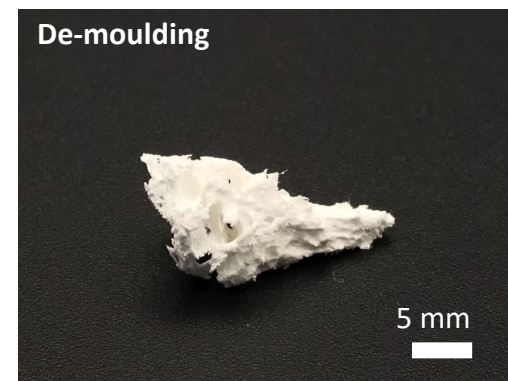
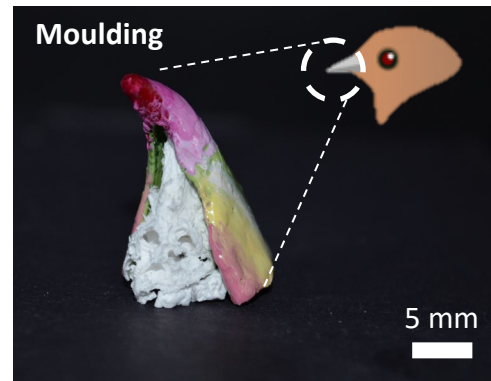
Ran Zhao

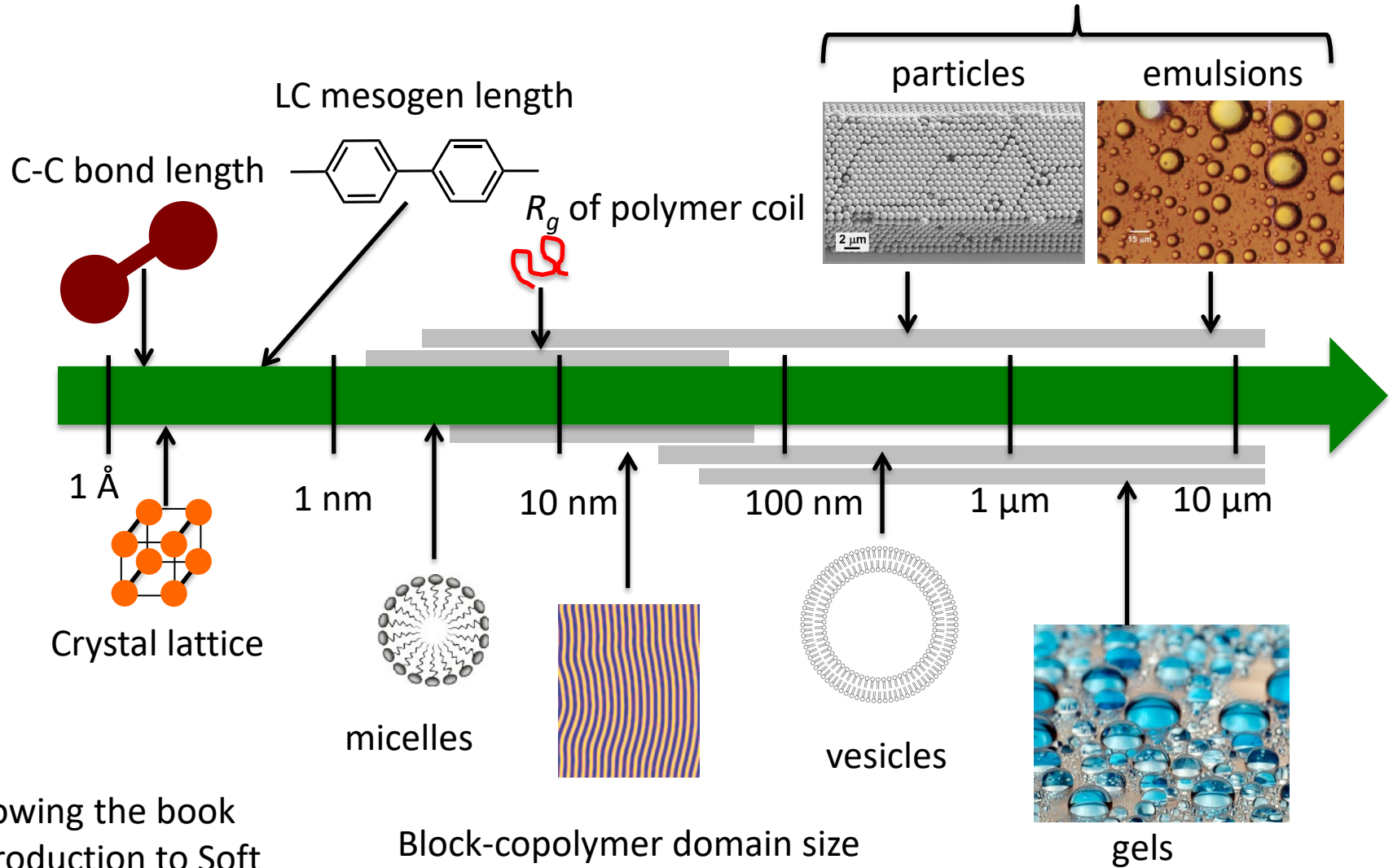


Casting toucan beaks



Ran Zhao





Following the book
 "Introduction to Soft
 Matter" by Ian W. Hamley