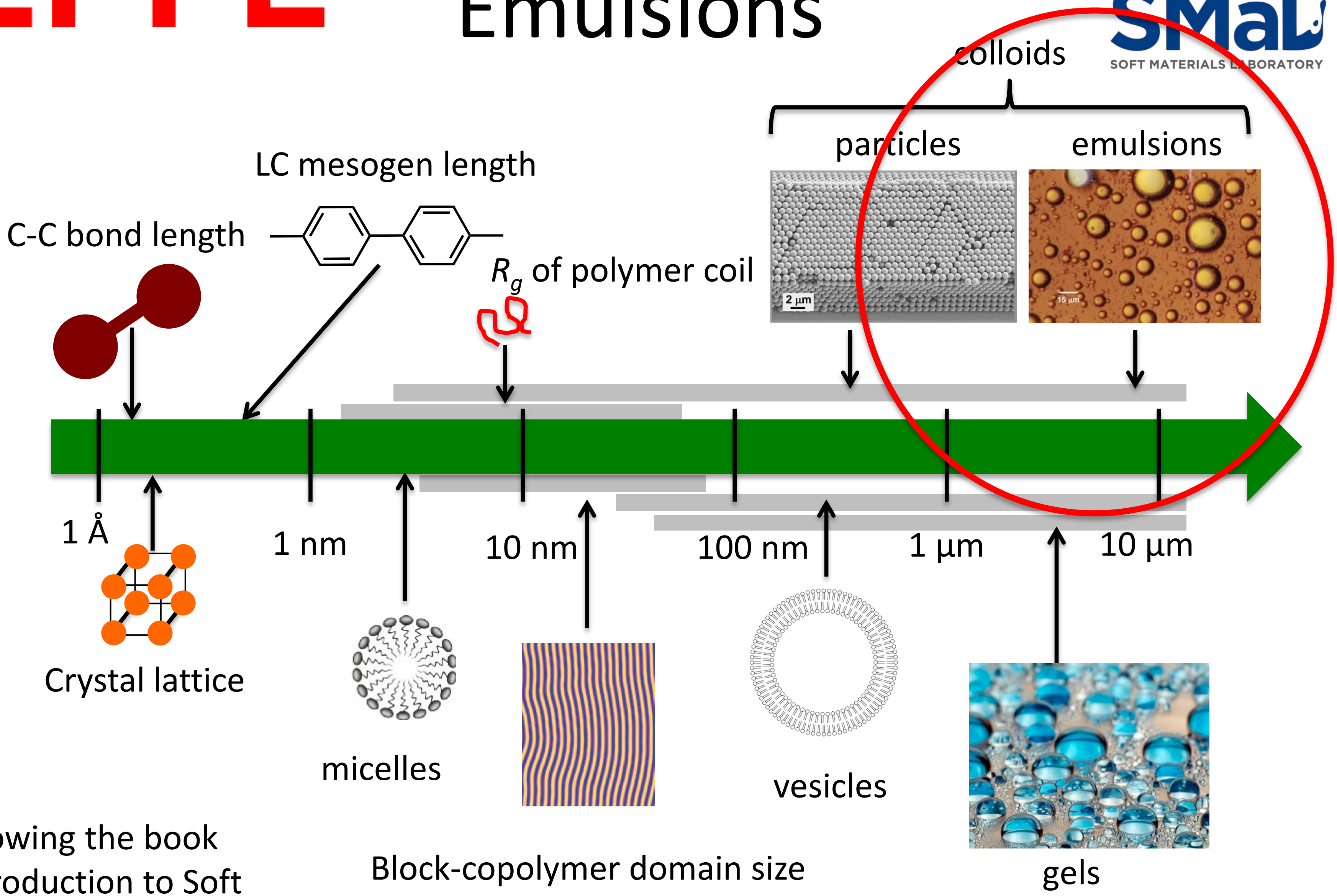
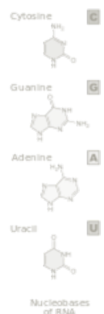
Emulsions

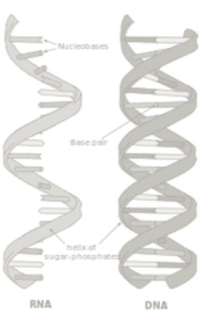


Following the book "Introduction to Soft Matter" by Ian W. Hamley

Course outline

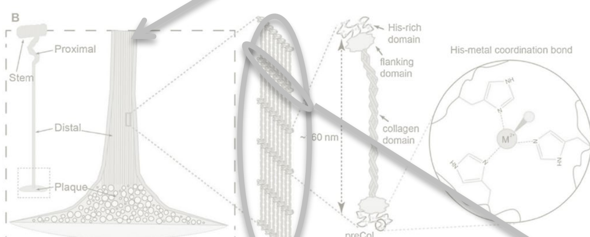
Introduction





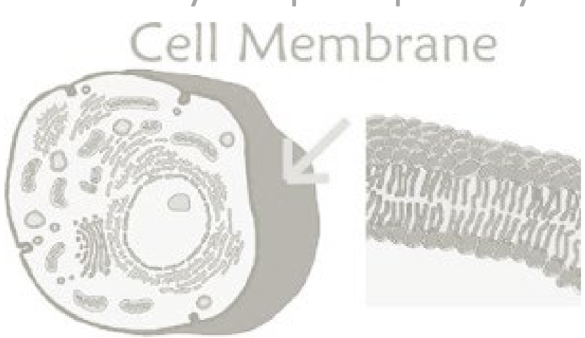
Ordered materials

Thermotropic liquid crystals



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

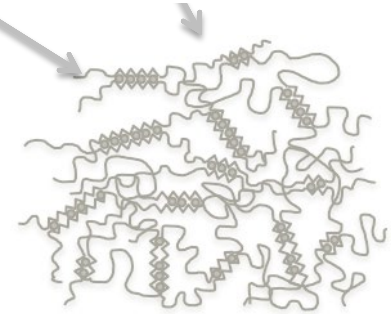
Lyotropic liquid crystals



Disordered materials

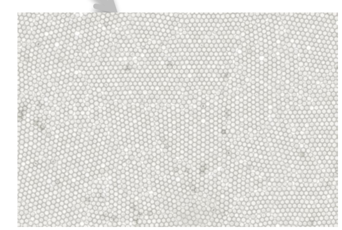
Polymers

Gels



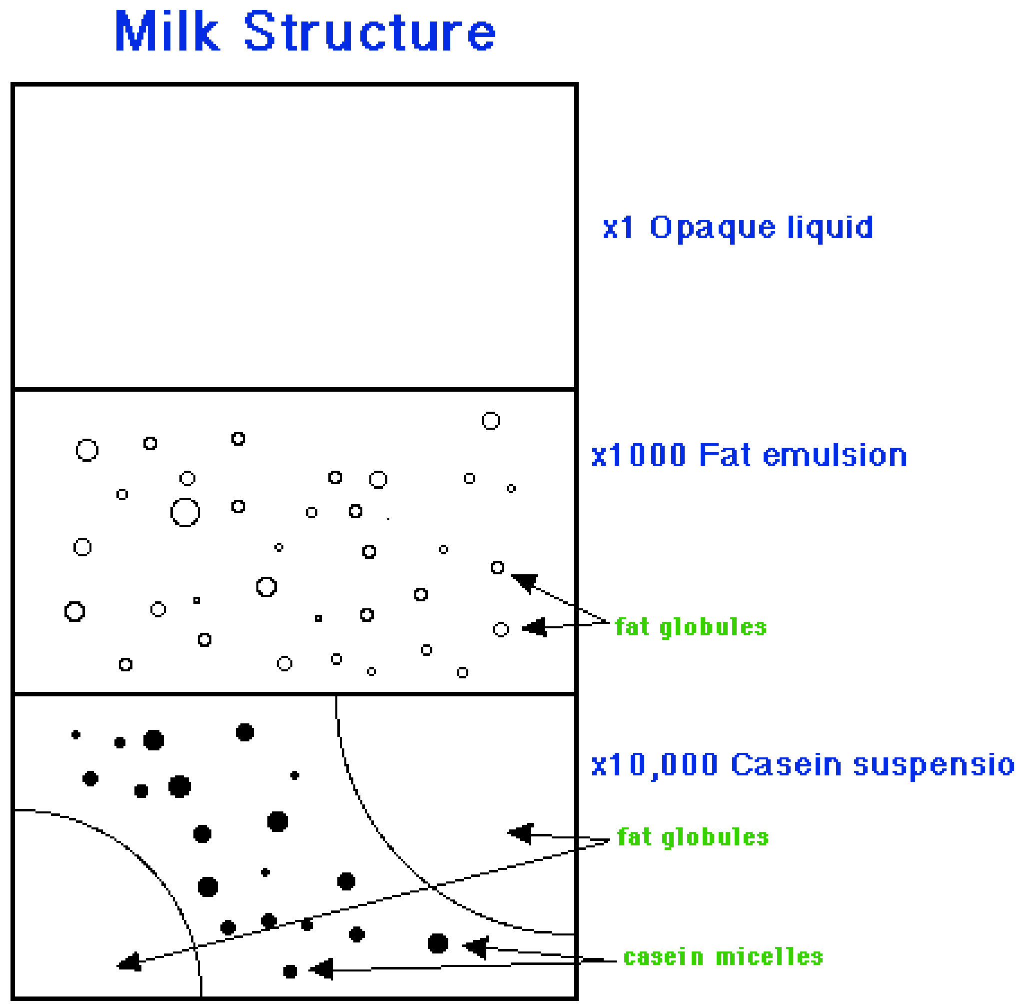
Colloids

Nanoparticles



Emulsions

Milk



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

Outline

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

Outline

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

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 $k_B T$.

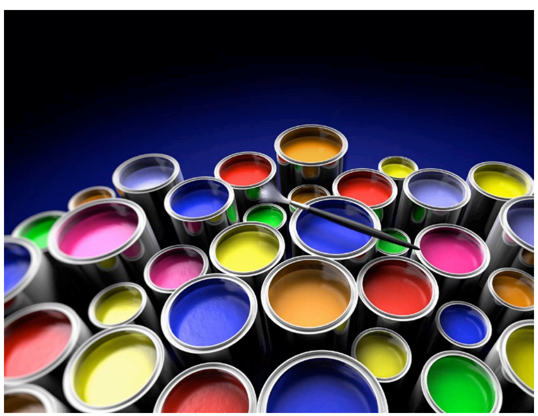
	continuous phase			
dispersed phase		**gas**	**liquid**	**solid**
	gas		soap sud cappuccino froth	pillow foam styrofoam packaging
	liquid	fog hair spray	mayonnaise milk	ice cream
	solid	smoke	paints blood	

Colloids in our daily life

Dispersion: certain sun creams

Emulsion: mayonnaise

Polymer latex dispersion: paint

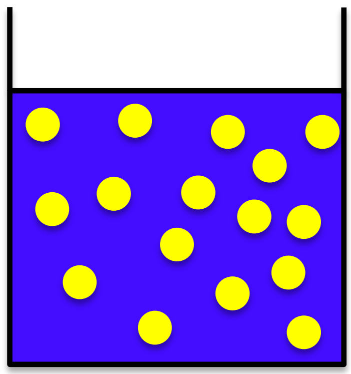


Emulsion: salad dressing

Emulsions

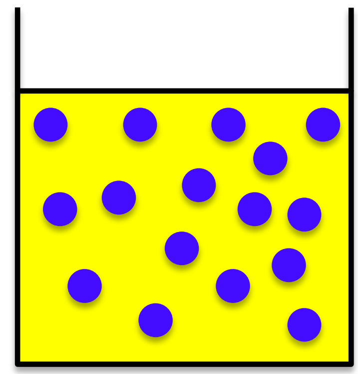
Emulsions are drops of a liquid dispersed in a second, immiscible liquid.

oil in water emulsions



Example: milk

water in oil emulsions



Example: margarine

Examples of emulsions

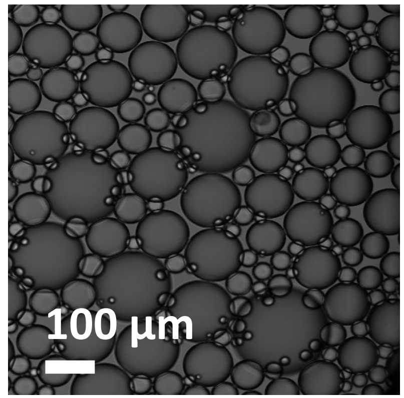
Outline

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

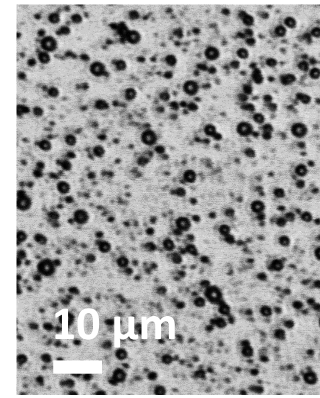
Production of emulsions

mechanical mixing

http://www.csiro.au

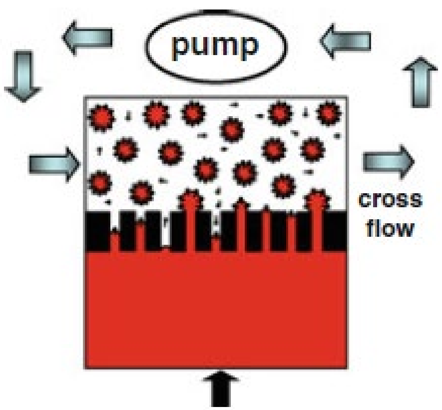


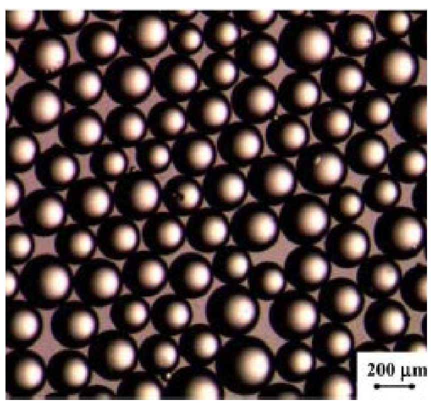
sonication



http://www.hielscher.com

membrane emulsification

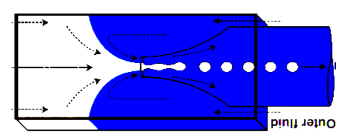


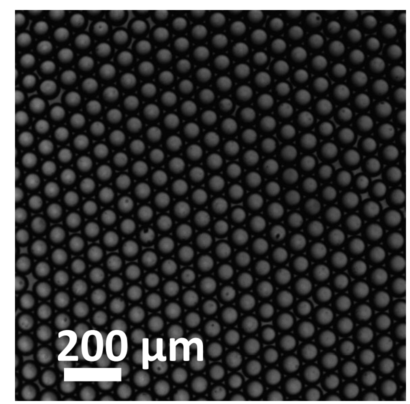


Vladisavljevic, G.T., et al.. Microfluidics and Nanofluidics, 2012. **13**(1)

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

microfluidics



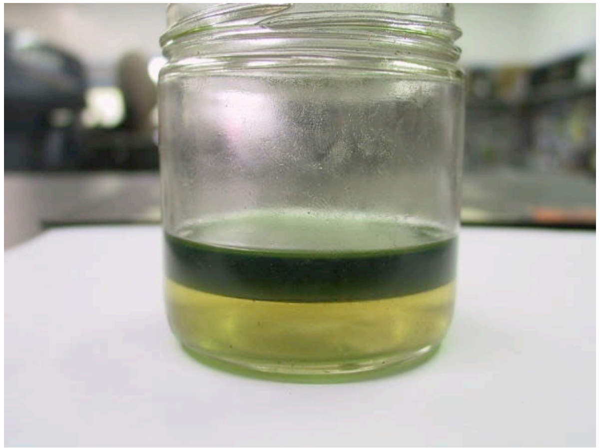


Utada, A.S., et al., Mrs Bulletin, 2007. **32**(9):

Outline

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

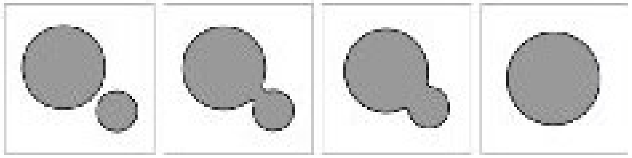
Emulsions



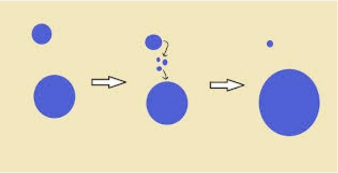
If two immiscible liquids are mixed they usually phase separate.

Phase separation of emulsions can occur through:

coalescence of drops



Ostwald ripening

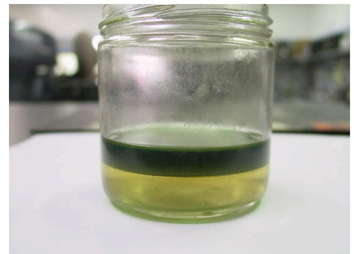


Free energy required to form emulsions

Free energy of undispersed systems:

$$G^{I} = G^{I}_{a} + G^{I}_{b} + G^{I}_{ab}$$

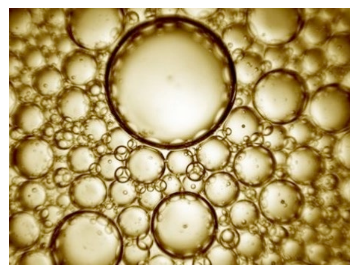
$$G^{I}_{ab} = \gamma_{ab} A^{I}$$



Free energy of emulsified systems:

$$G^{II} = G^{II}_{a} + G^{II}_{b} + G^{II}_{ab} - TS^{II}(config)$$

↑ reflects decrease in the order of the system



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

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

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

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

G^{I}: free energy of undispersed system [J]
G^{I}_{a}: free energy of liquid a [J]
G^{I}_{b}: free energy of liquid b [J]
G^{I}_{ab}: excess free energy associated with liquid-liquid interface [J]
γ: interfacial tension [N/m]
A^{I}: interface area [m^2]
Φ: volume fraction [-]
N: number of drops [-]
ΔA: increase in surface area [m^2]

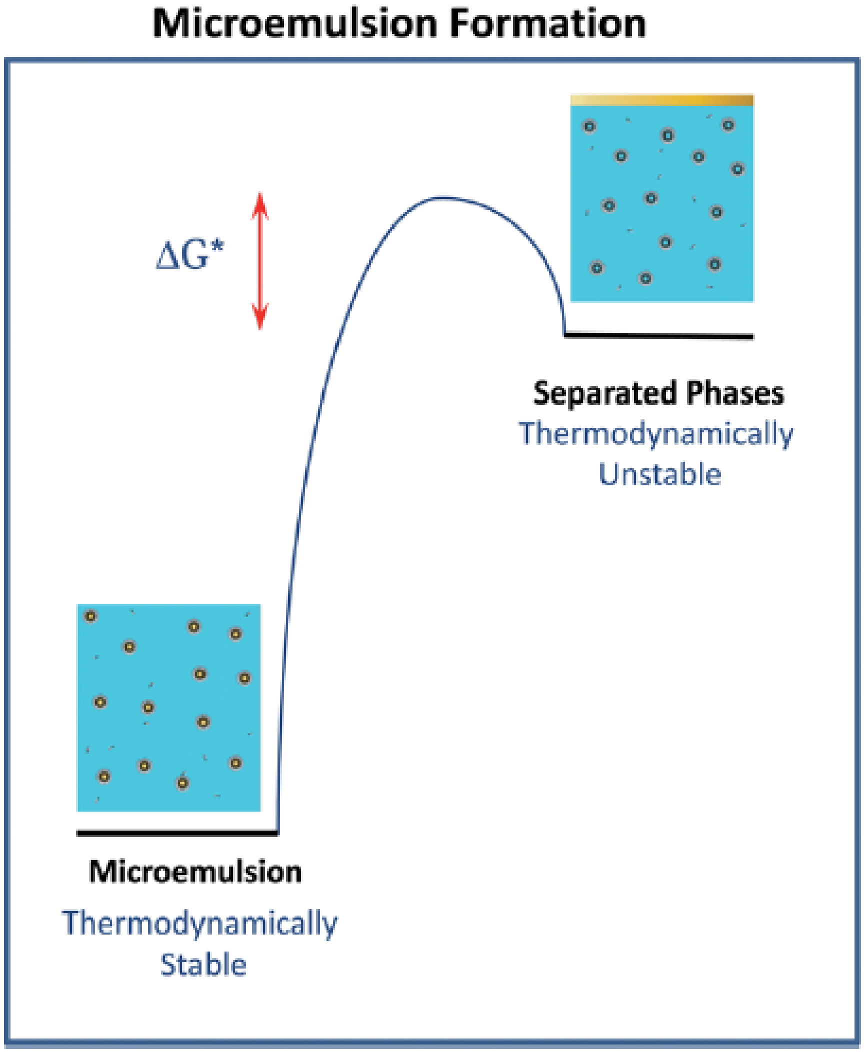
Emulsion formation

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

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

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

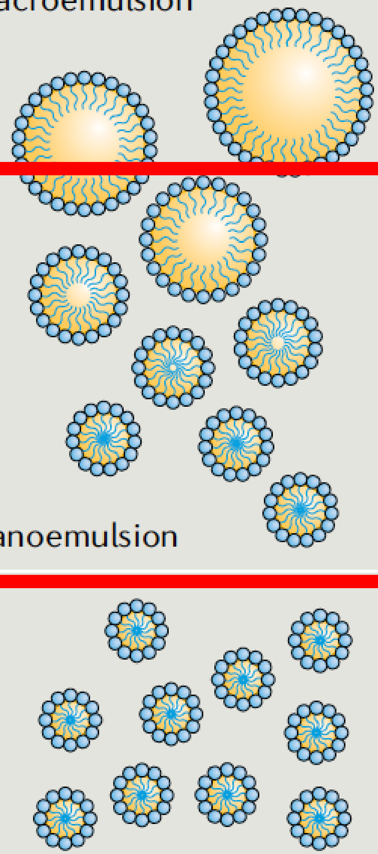
Emulsions



They are thermodynamically stable.

D. J. McClements, *Soft Matter*, 2012, **8**, 1719-1729

Emulsion classes



Decreasing size

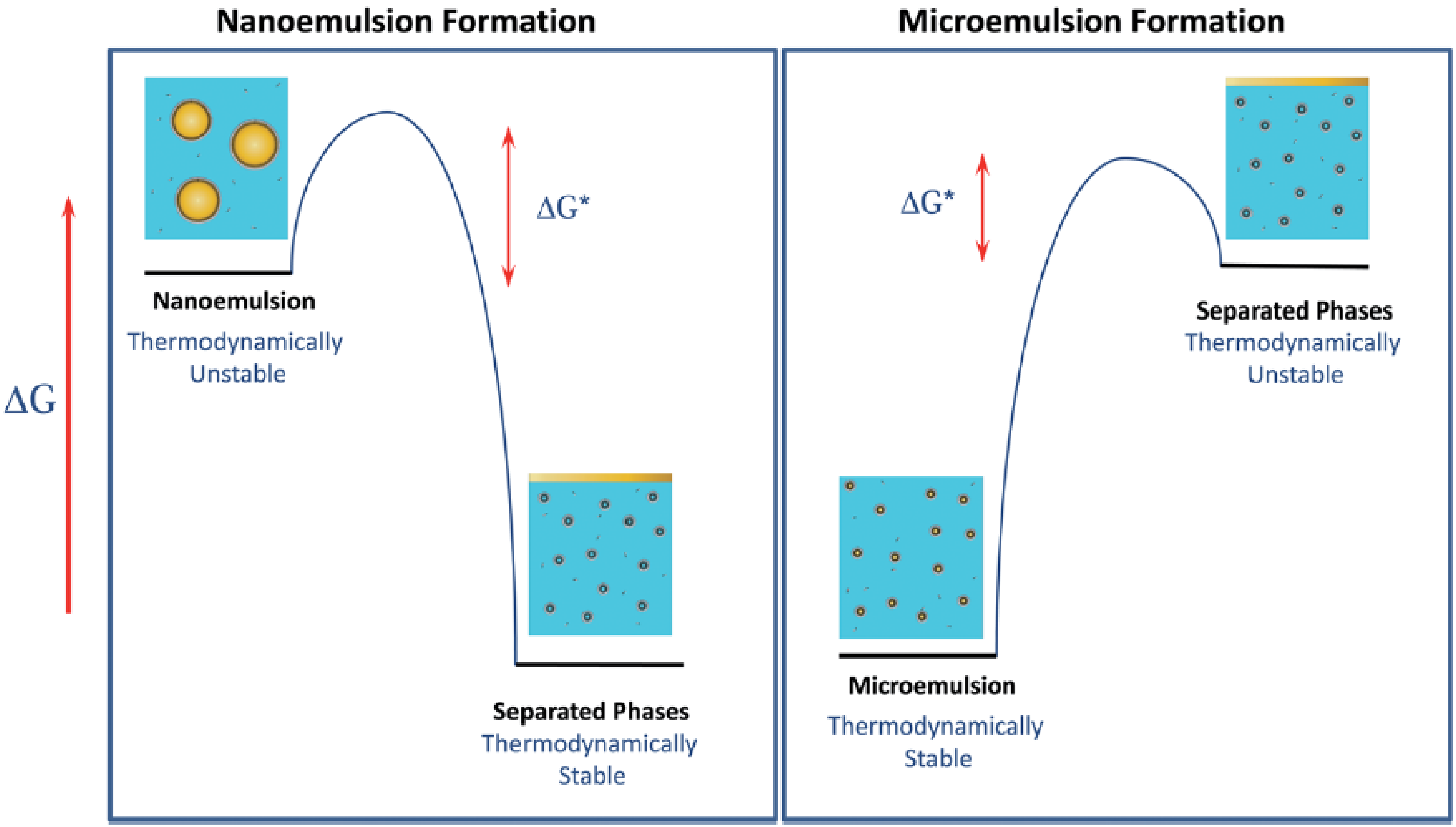
Emulsion type	Size	Stability	Requirements
Macroemulsion	Large (>1 μm), limited by large surface tension. Droplets tend to be polydisperse.	Unstable. Droplets coarsen into phase-separated mixtures in minutes or hours.	Simple to produce through low-energy agitation or, more precisely, using microfluidic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

Sheth, T.; *et al. Nature Reviews Materials* **2020**, *5* (3), 214–228.

Coalescence

http://www.carllegge.com/2012/01/vinaigrette-recipe-salad-dressings-no-1/

Emulsions



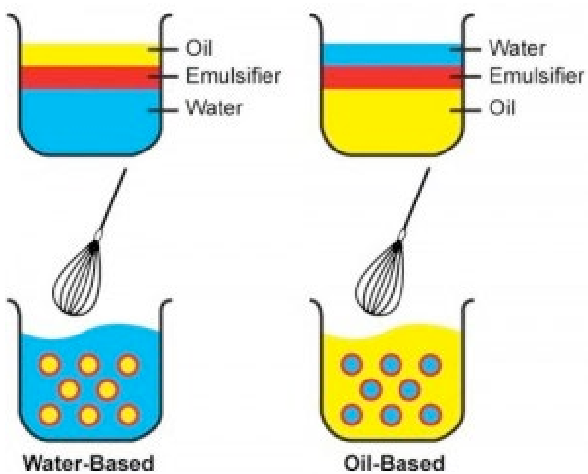
They are thermodynamically unstable. They are thermodynamically stable.

D. J. McClements, *Soft Matter*, 2012, **8**, 1719-1729

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

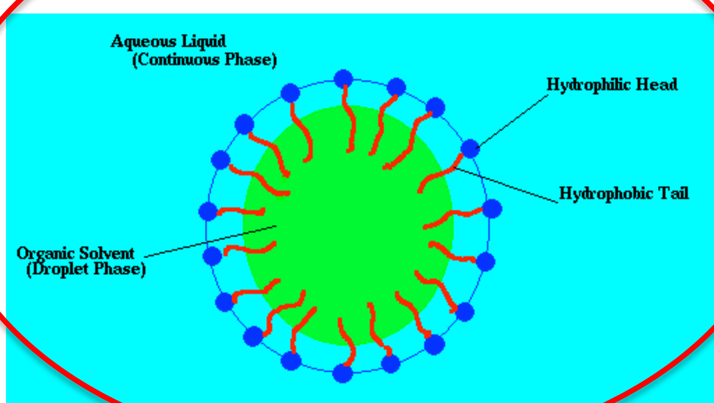
A. decrease the temperature
B. increase the volume fraction of oil
C. lower the interfacial tension
D. stir vigorously

Stabilization of emulsions



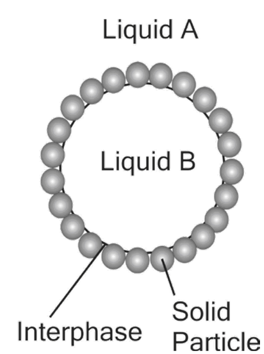
http://www.dermalessence.com.au

Surfactants



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

Nanoparticles
(Pickering emulsions)



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

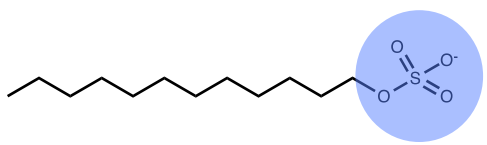
Outline

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

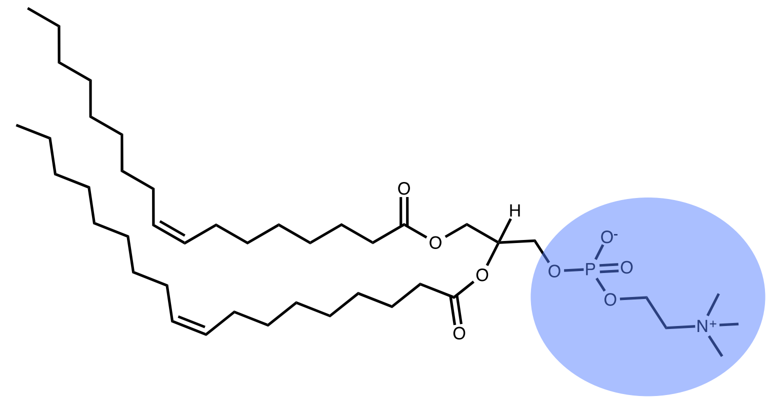
Surfactants

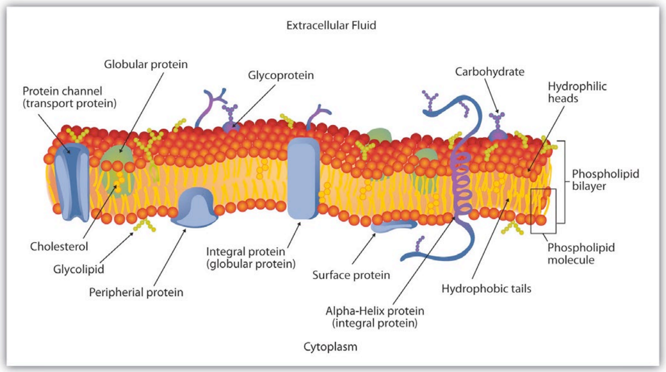
Surfactants are molecules composed of parts that have a chemical preference to one solvent and other parts with a chemical preference to the other solvent.

Example:
sodium dodecyl sulfate (SDS)

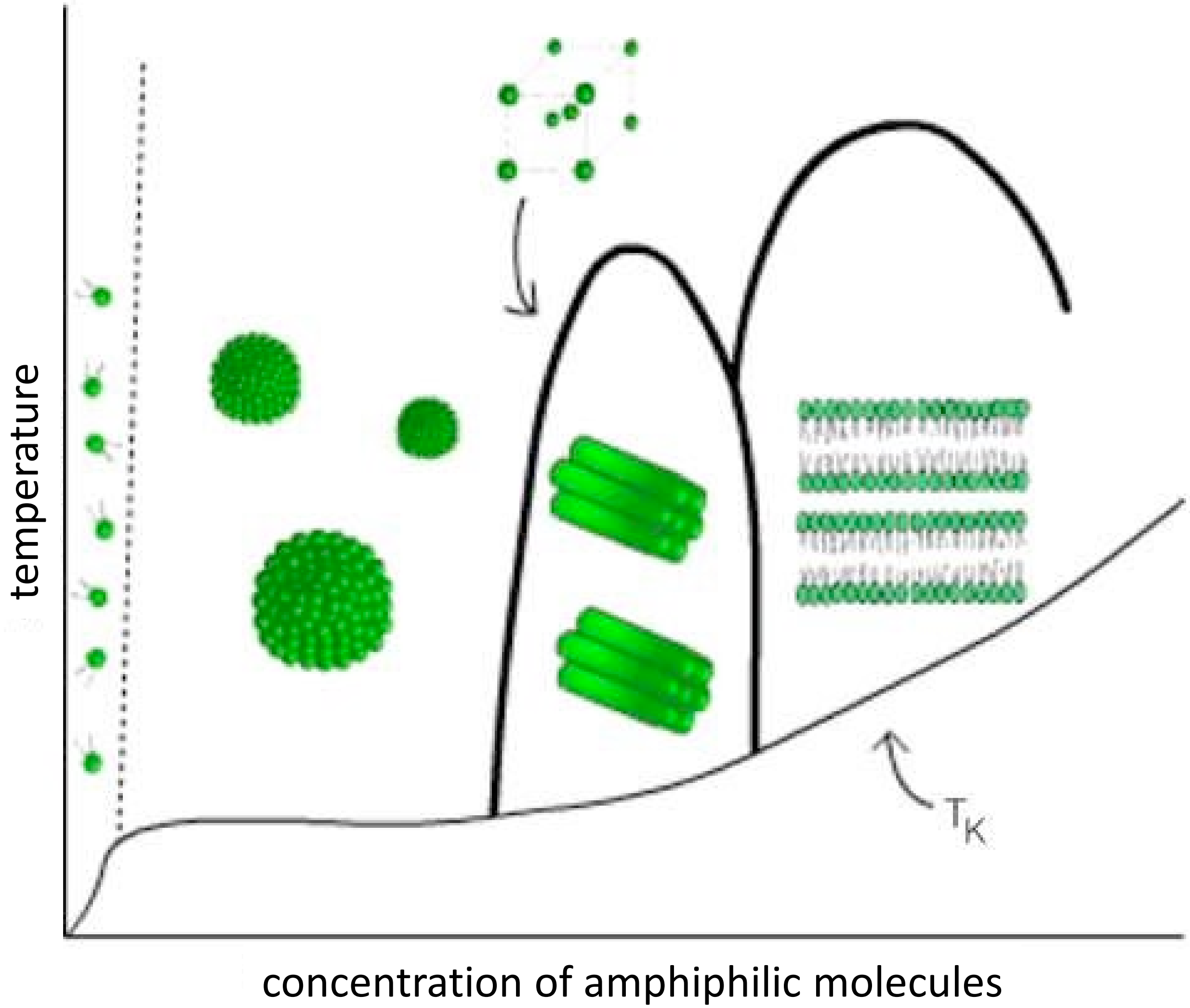


Example:
1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC)





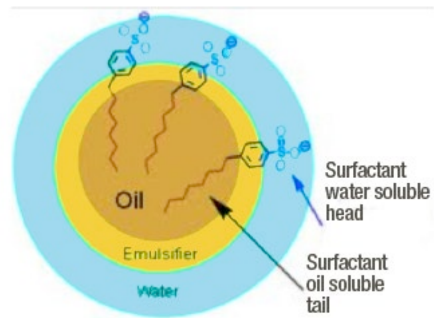
What are surfactants?



Surfactant are usually lyotropic liquid crystals.

http://plc.cwru.edu/tutorial/enhanced/files/llc/phase/phase.htm

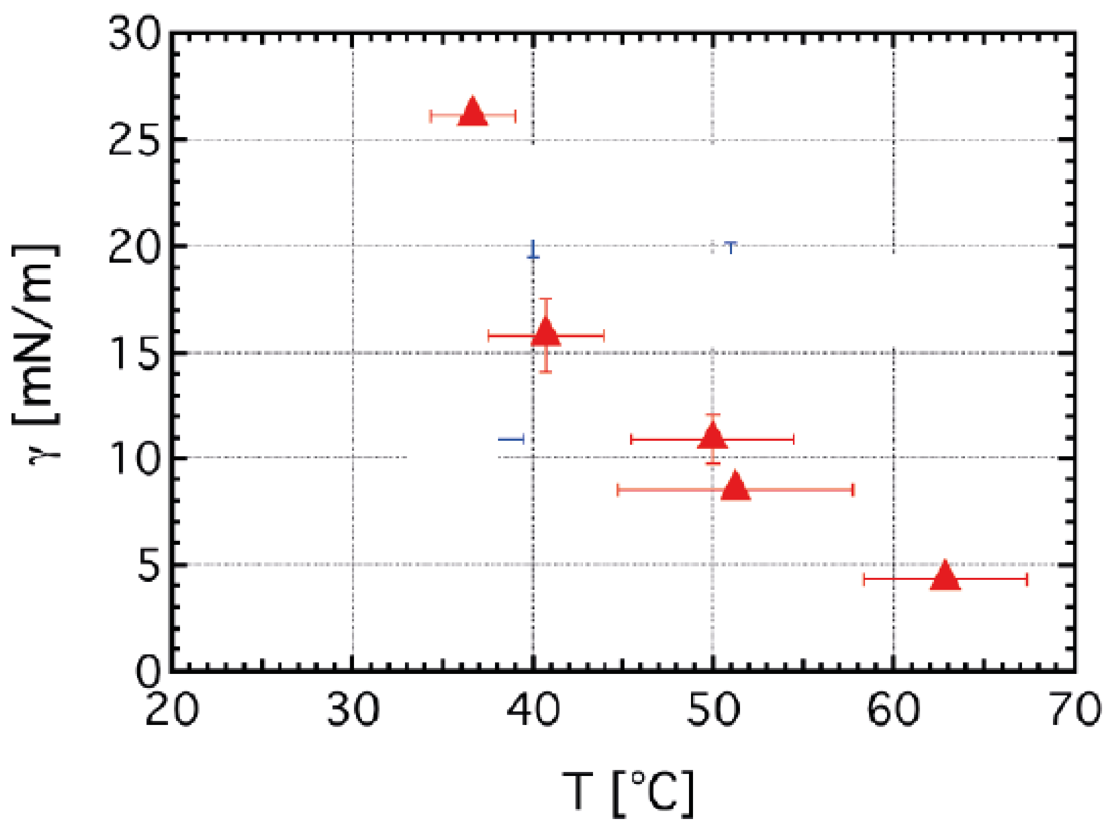
What do surfactants do?



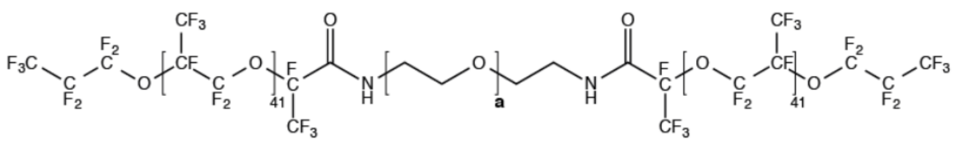
http://www.verutek.com

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

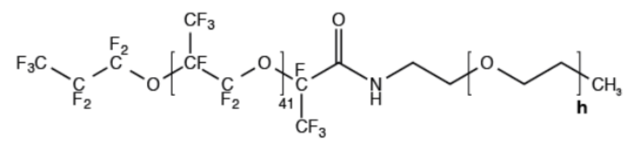
Surfactants



Triblock-copolymers



Diblock-copolymers

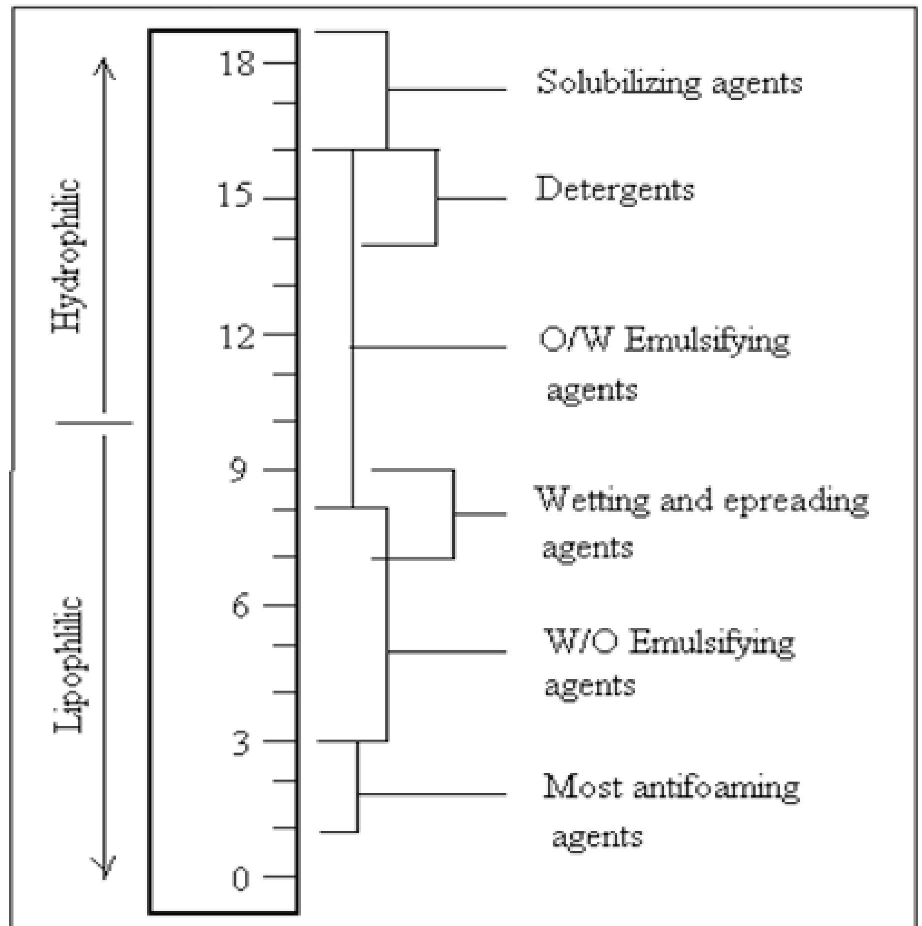


Etienne, G.; Kessler, M.; Amstad, E., *Macromolecular Chemistry and Physics* **2017,** *218* (2)

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).

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

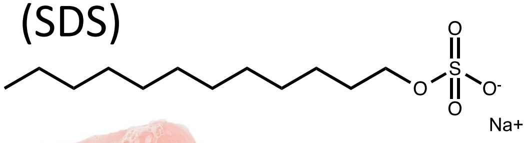


M_h: molecular weight of hydrophilic part [g/mol]
M_{tot}: molecular weight of surfactant [g/mol]

http://www.pharmatutor.org

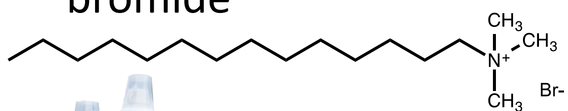
Types of surfactants

Anionic surfactants
Example:
sodium dodecyl sulfate (SDS)



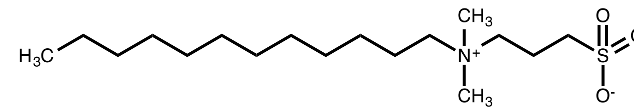
use: soaps, detergents

Cationic surfactants
Example:
alkyl trimethylammonium bromide



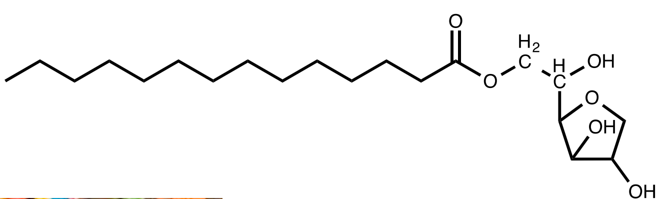
more expensive than anionic surfactants
use: bactericides, to kill bacteria

Zwitterionic surfactants
Example:
sulfobetaine



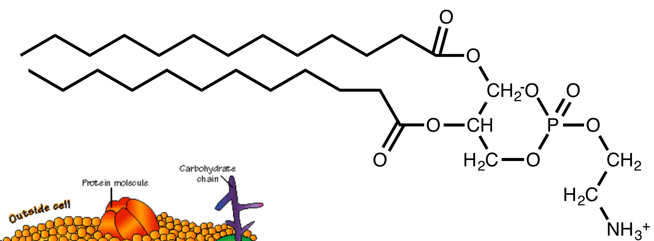
use: cosmetic products, as it is non-irritating to skin and eyes

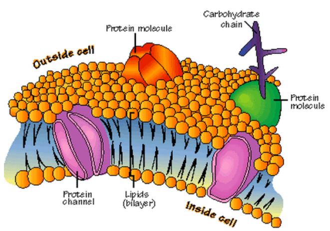
Nonionic surfactants
Example:
sorbitan alkanoate (Span)



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

Lipids
Example:
phosphatidylethanolamine (PE)





abundant in cell membranes

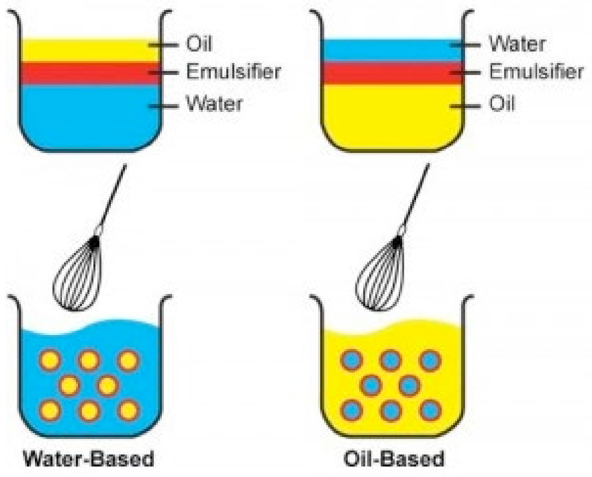
Coalsecence

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

Outline

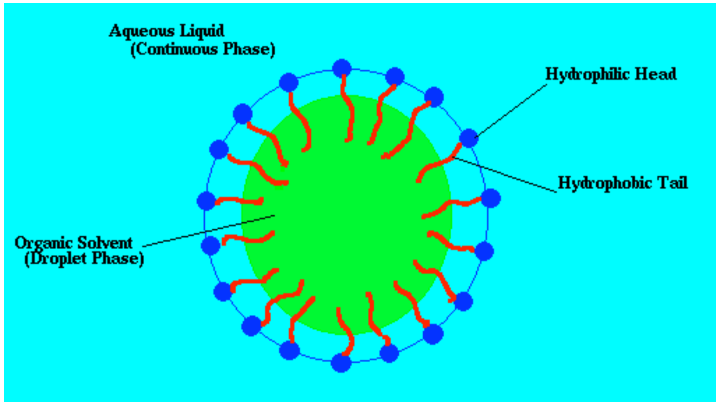
- Introduction
- Production of emulsions
- Stabilization of emulsions
  - Surfactants
  - Particles
- Applications of emulsions
- Foams

Stabilization of emulsions



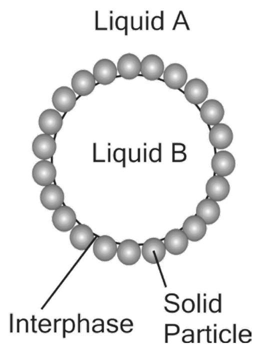
http://www.dermalessence.com.au

Surfactants



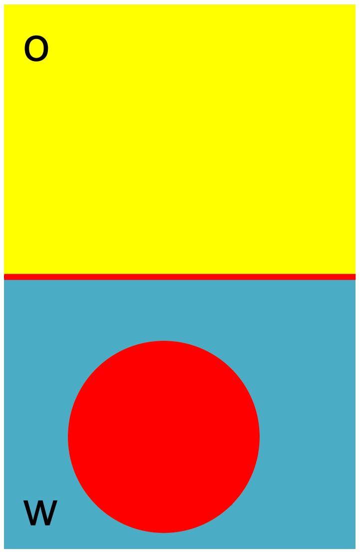
http://www.physics.emory.edu/faculty/weeks//lab/emulsion/

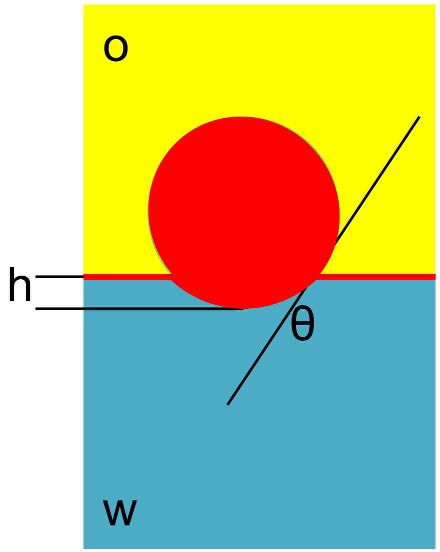
Nanoparticles (Pickering emulsions)



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

Particle adsorption at liquid-liquid interfaces





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

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

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

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

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

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

$\theta < 90°$ hydrophilic

$\theta = 90°$ neutrally-wetting

$\theta > 90°$ hydrophobic

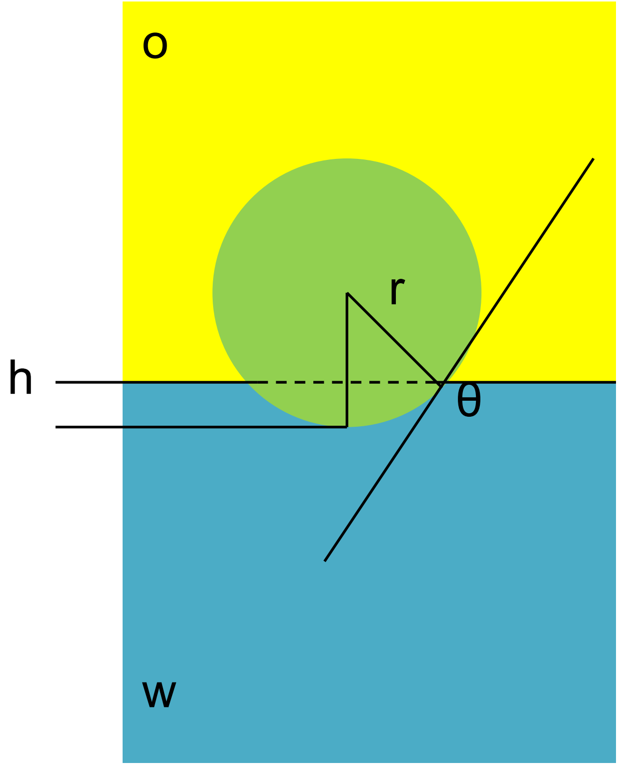
slide adapted from Lucio Isa, ETHZ

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

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



slide adapted from Lucio Isa, ETHZ

What is the energy required to take a particle with a radius of 5 nm away from a water-oil interface with γ_{ow} = 30 mN/m at 25° C if $\theta = 90°$?

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 × 10^{-23} J/K
T = 298 K

What is the energy required to take a particle with a radius of 5 nm away from a liquid-oil interface with γ_{ow} = 30 mN/m at 25° C if θ = 10° ?

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 × 10^{-23} J/K
T = 298 K

What is the energy required to take a particle with a radius of 100 nm away from a liquid-oil interface with γ_{ow} = 30 mN/m at 25° C if $\theta = 10°$?

A. 0.5 $k_B T$

B. 5 $k_B T$

C. 50 $k_B T$

D. 500 $k_B T$

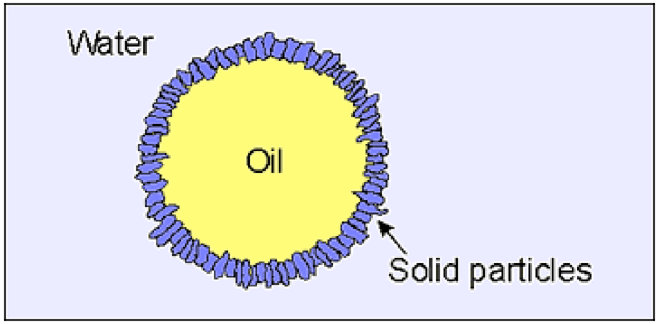
E. 50000 $k_B T$

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

$k_B = 1.38 \times 10^{-23}$ J/K
T = 298 K

Pickering emulsions

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



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

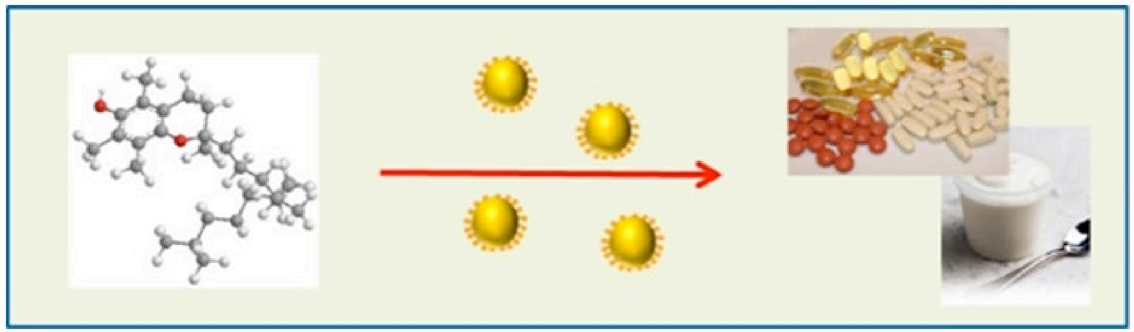
Sunscreens are often Pickering emulsions.

Outline

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

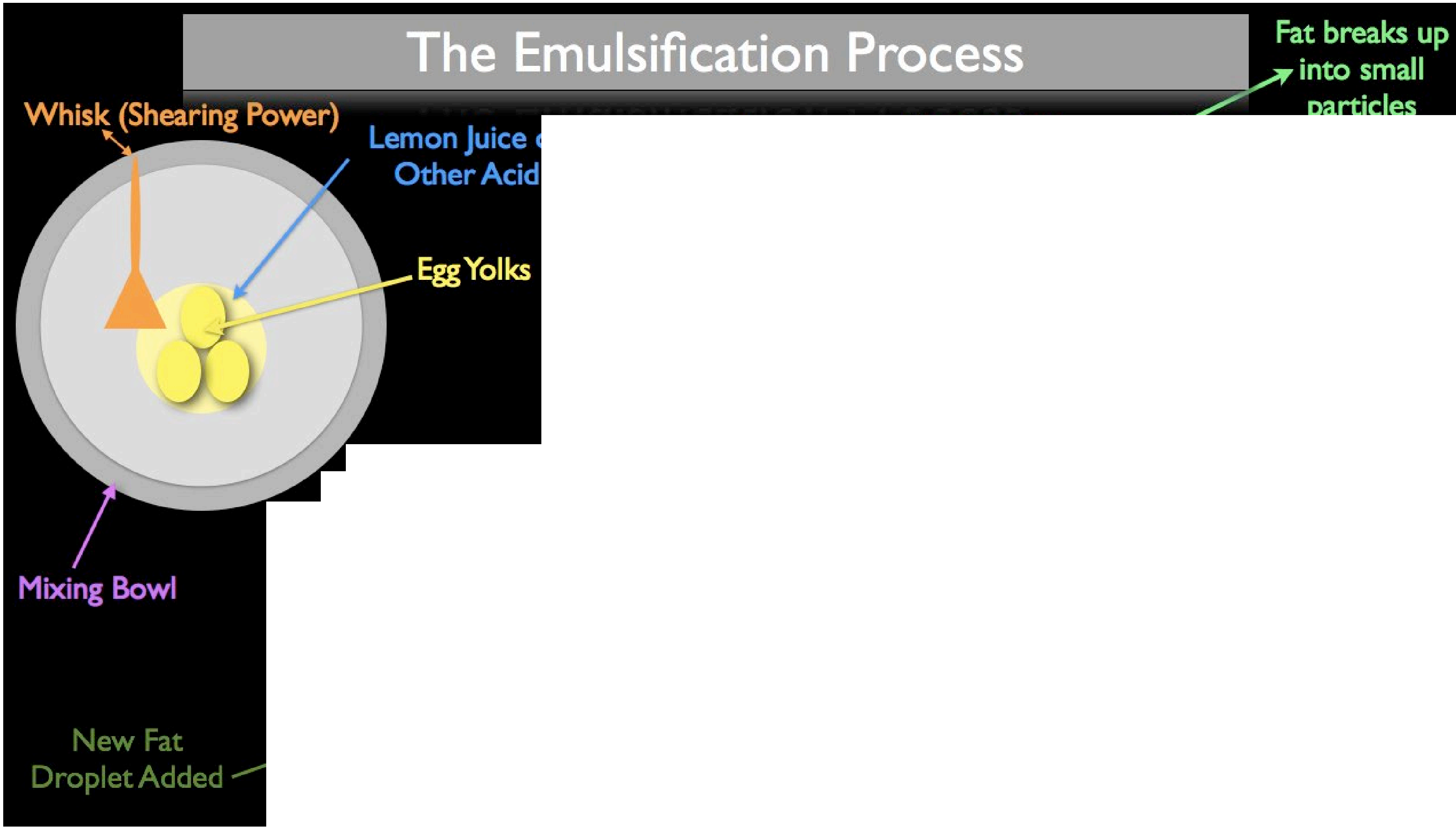
Emulsions in our daily life

Emulsion



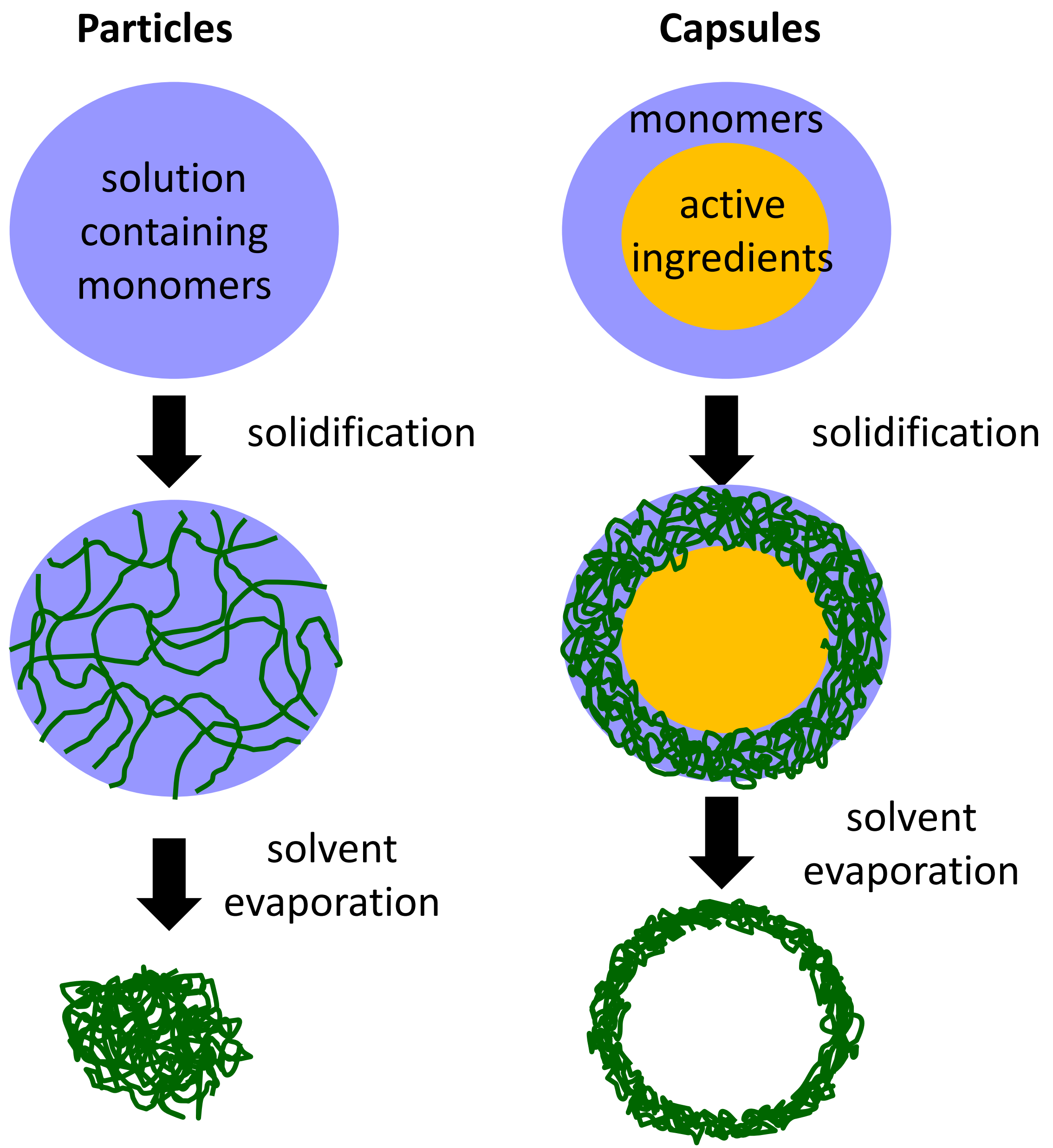
https://www.umass.edu/cbd/emulsion-based-delivery-systems-oil-soluble-vitamins

Mayonnaise



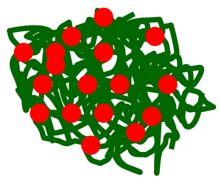
https://stellaculinary.com/cooking-videos/food-science-101/fs-001-what-emulsion-cooks-guide

Drops as templates to produce carriers

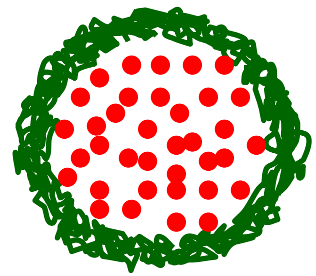


Why do you need to encapsulate substances?

Microparticles



Microparticles



Protection

- Degradation
- Consumption prior to use

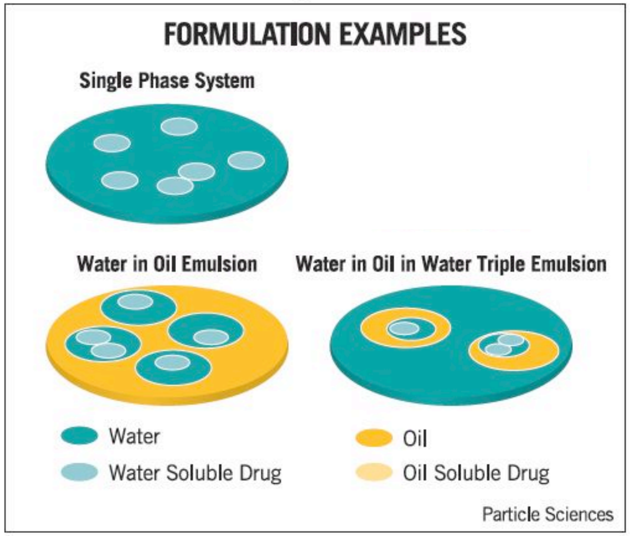
http://entitledtorevelation.com

Localized release

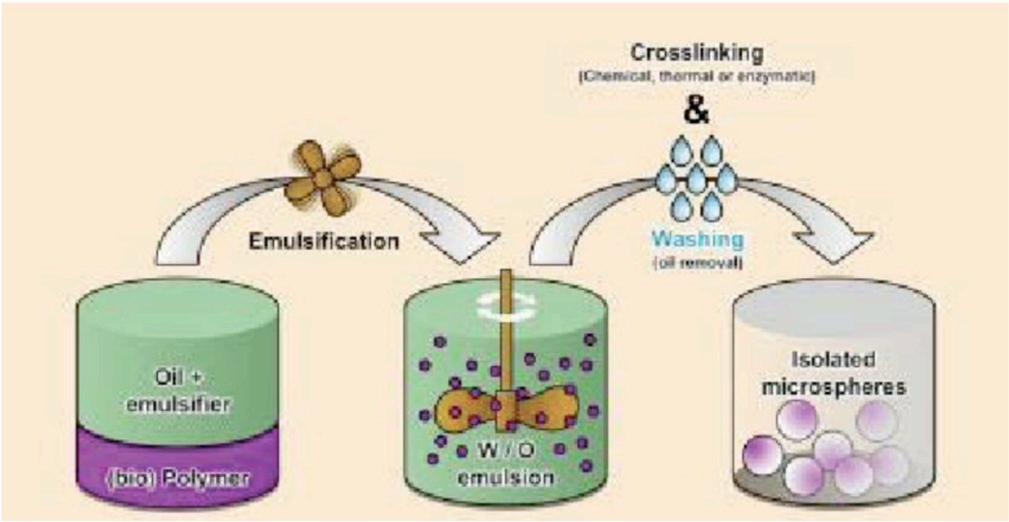
- Minimize the dose of actives
- Minimize side-reactions

http://www.indiamart.com

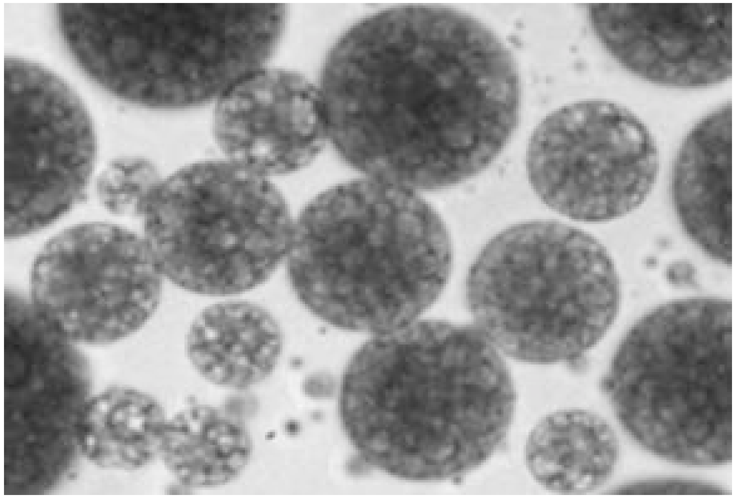
Production of double emulsions



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.

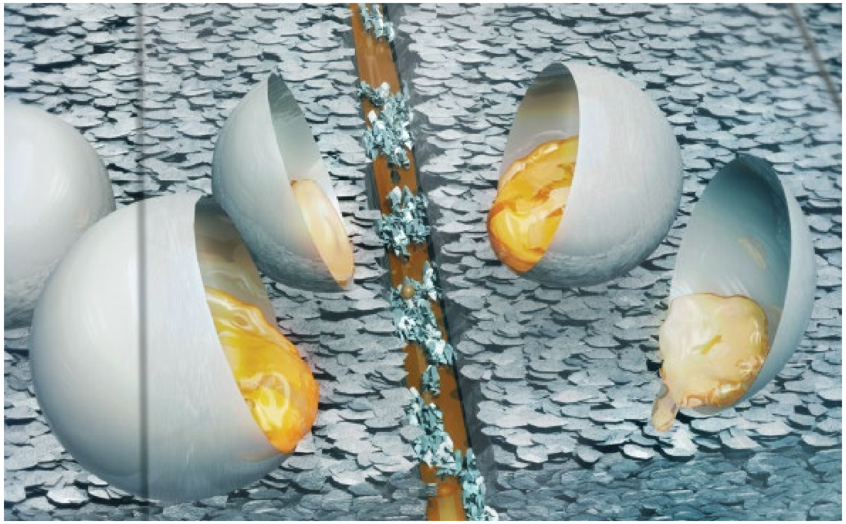


Tirnaksiz, F.; Kalsin, O. *Journal of Pharmacy and Pharmaceutical Sciences* **2005,** *8* (2), 299-315

Requirements for carriers

high loading capacity

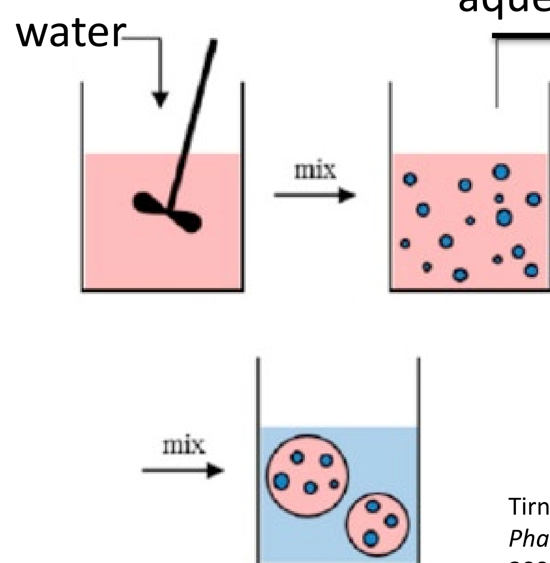
➔ Depend on processing

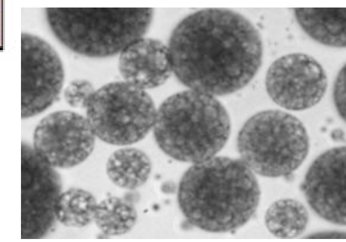


Odom, S. A., et al., 2012, "Advanced Materials **24**(19):

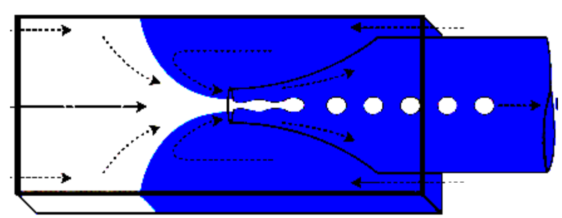
high loading efficiency

pouring into an aqueous phase

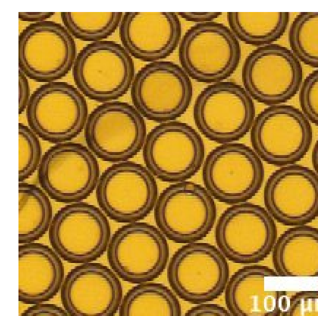




Tirnaksiz, F.; Kalsin, O. *Journal of Pharmacy and Pharmaceutical Sciences* **2005,** *8* (2), 299-315



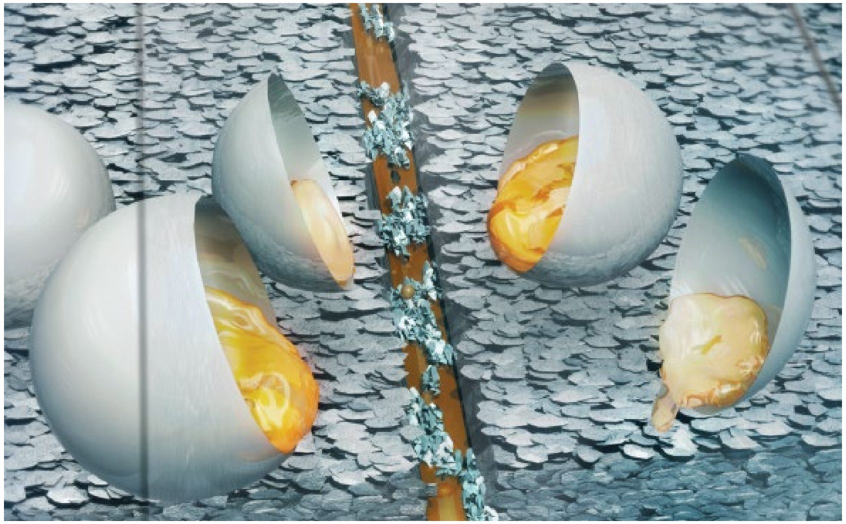
Utada, A.S., et al., Mrs Bulletin, 2007. **32**(9):



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

Requirements for carriers

high loading capacity

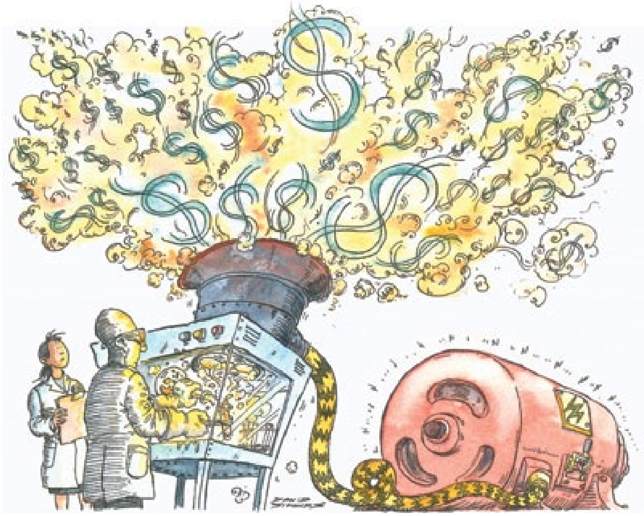


Odom, S. A., et al., 2012, "Advanced Materials **24**(19):

low permeability during storage

http://lparchive.org/Mother-3/Update%2034/

high loading efficiency

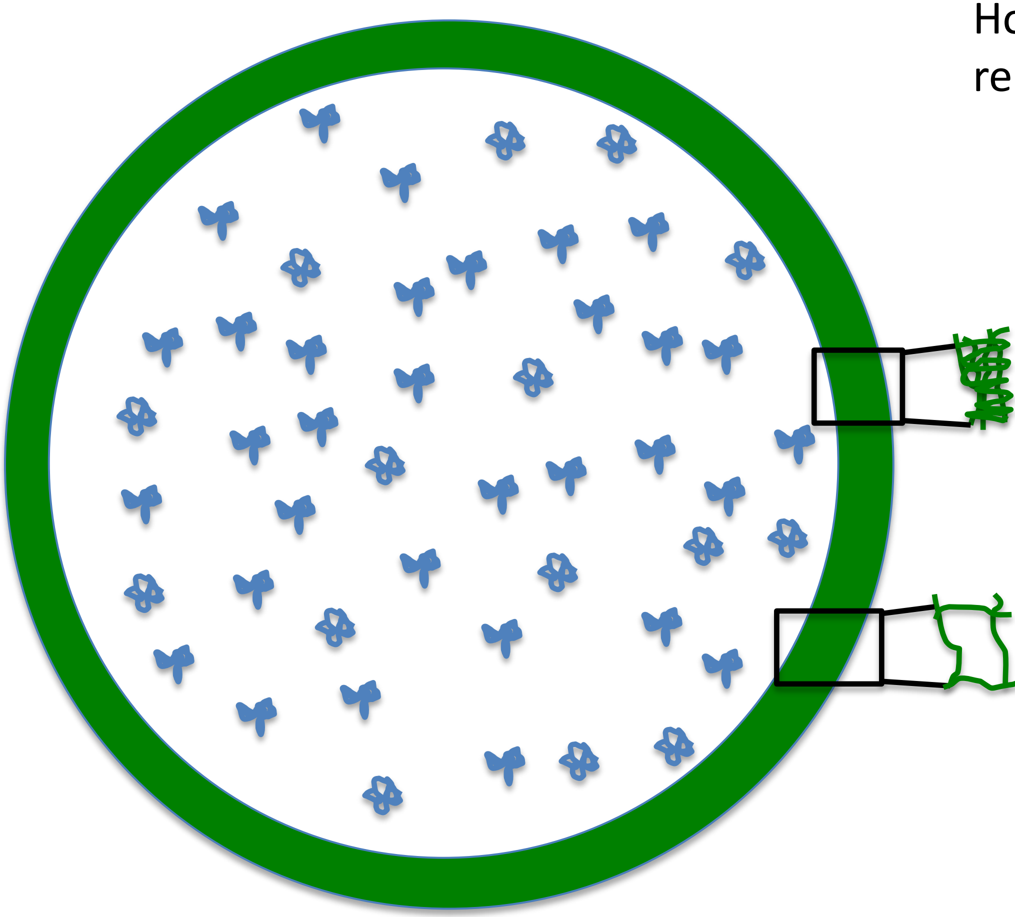


http://www.nature.com/nature/journal/v445/n7128/images/445590a-i1.0.jpg

high permeability when applied

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

Capsules for controlled release



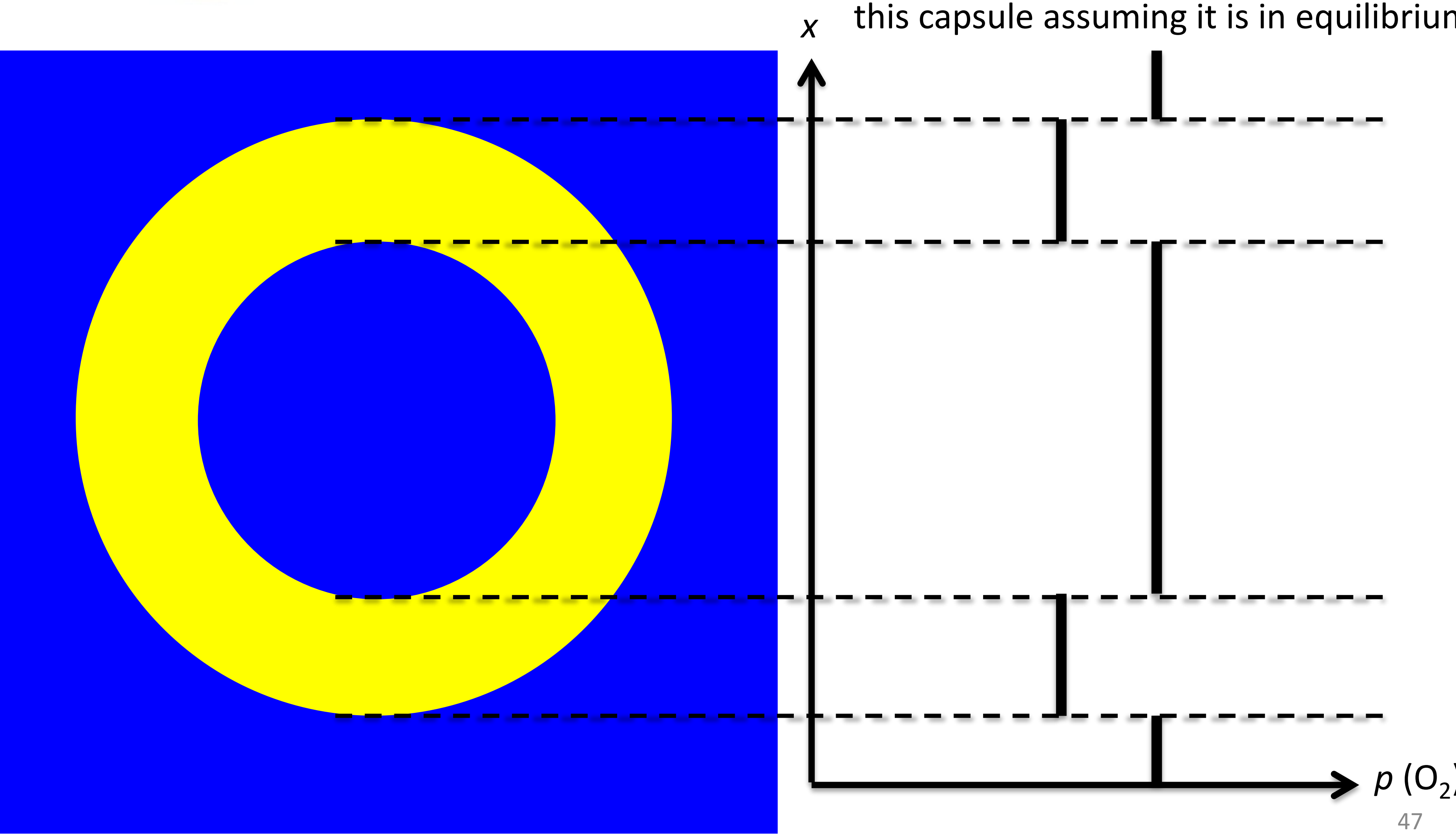
How much time is needed to release 10% of the encapsulants…

…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.

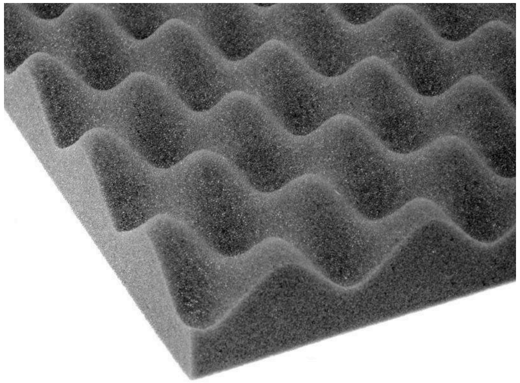


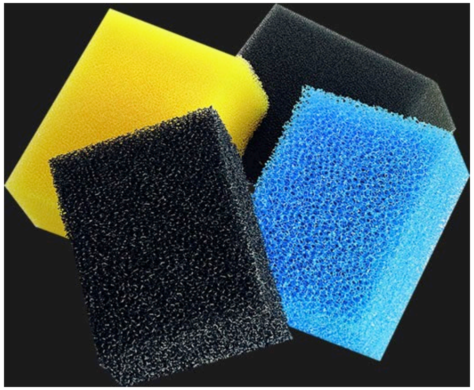
Outline

- 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.

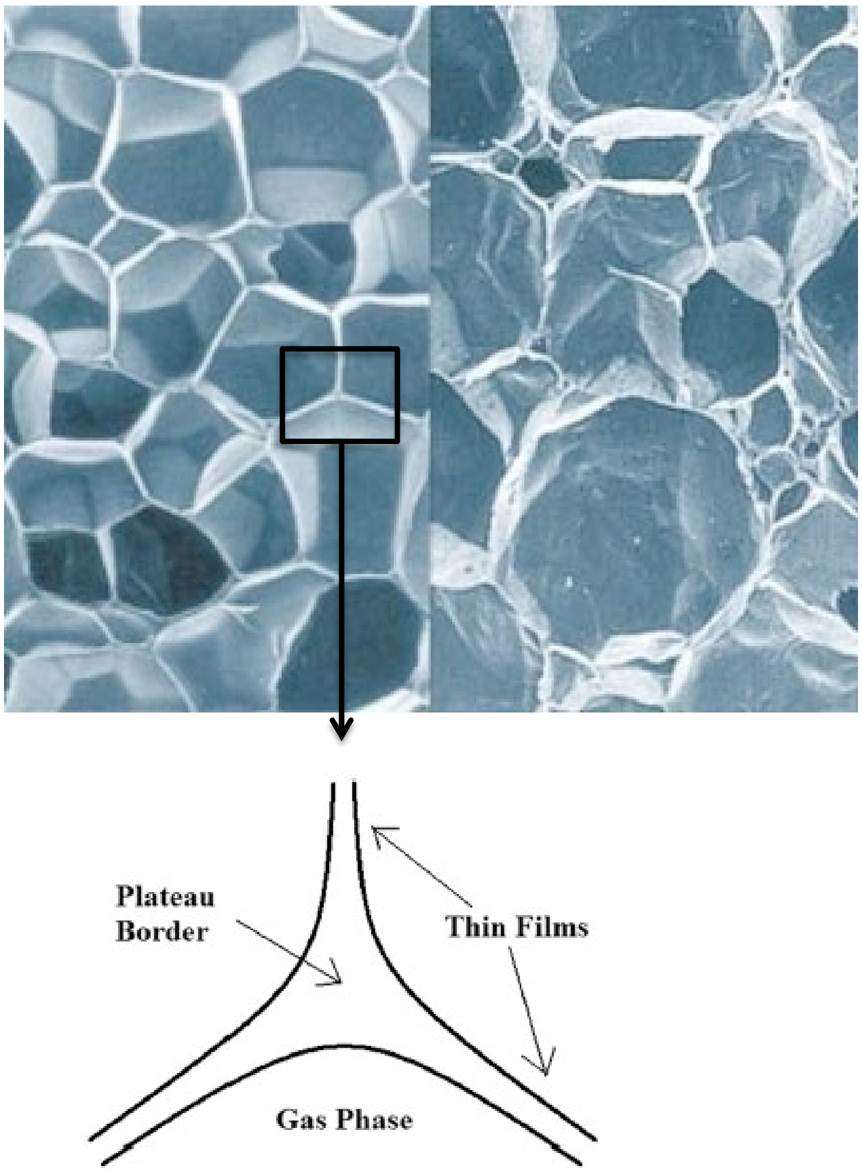
How can one slow down the coalescence of foams?

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

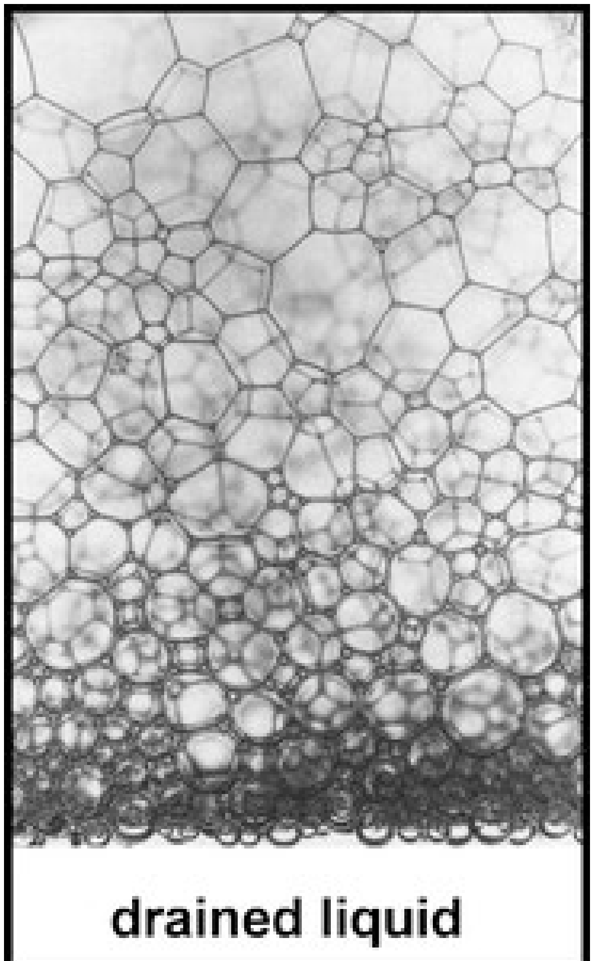


Foam structure:

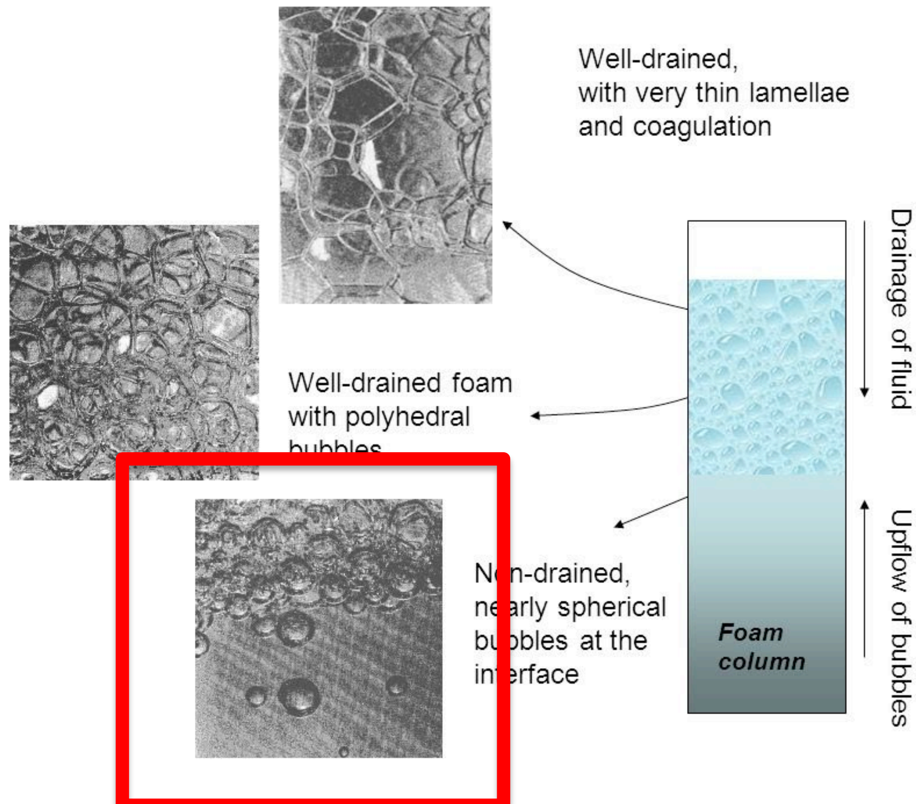
- Three flat sides of a polyhedra meet at an angle of 120°.
- If four or more sites come together in one line the configuration is unstable.
- If the four edges meet in a tetragonal arrangement at all corners of a polyhedra, the angle between any two edges is 109.5°.

Foam destabilization: drainage

Drainage is the flow of liquids through channels.



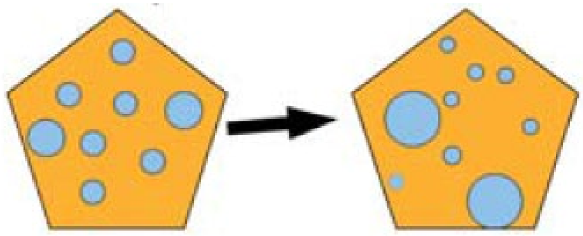
A. Saint-Jalmes, *Soft Matter*, 2006, **2**, 836-849.



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

Foam destabilization: Ostwald ripening

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



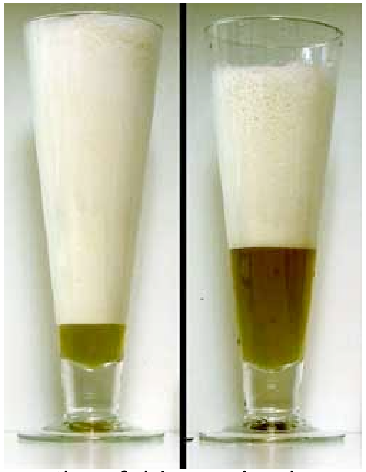
Vincent, R. R. R.; Gillies, G.; Stradner, A. *Soft Matter* **2011**, *7*, 2697.

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

p_r: pressure of bubble [Pa]
p_0: pressure of flat surface [Pa]
γ: interfacial tension [N/m]
V_m: molar volume of liquid [m^3]
r: radius of bubble [m]

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

C_2F_6 CO_2



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

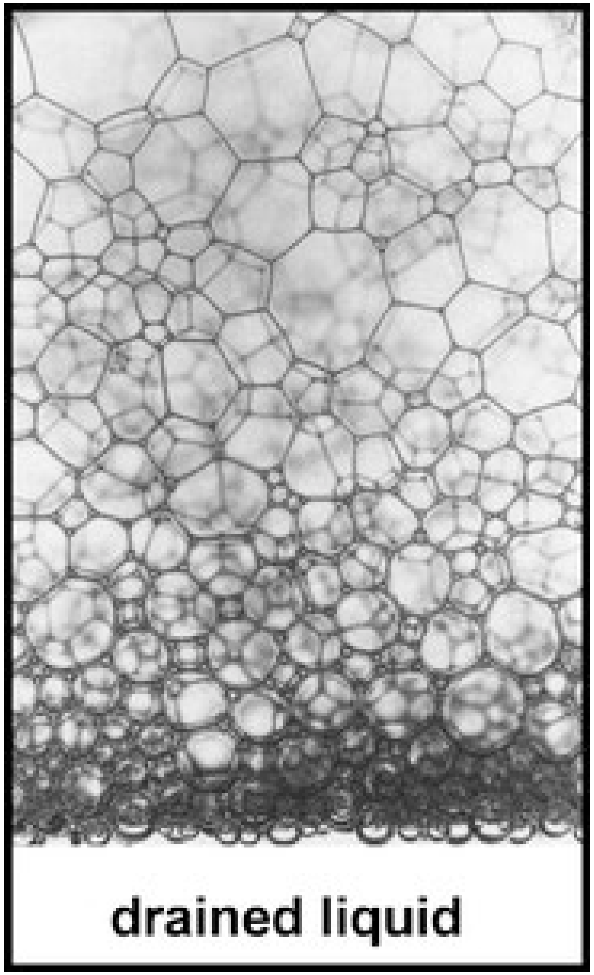
Beer foam lasts longer if C_2F_6 is used.

Why?

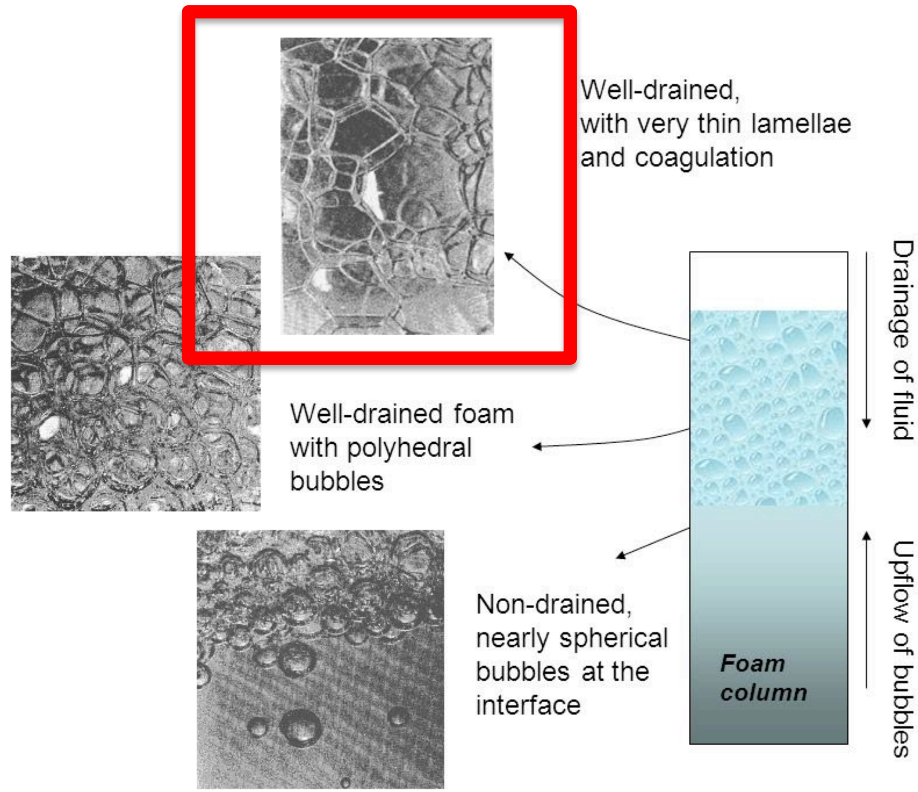
C_2F_6 has a lower solubility in the aqueous phase than CO_2. This slows down Ostwald ripening such that the drainage is slower.

Foam destabilization: drainage

Drainage is the flow of liquids through channels.

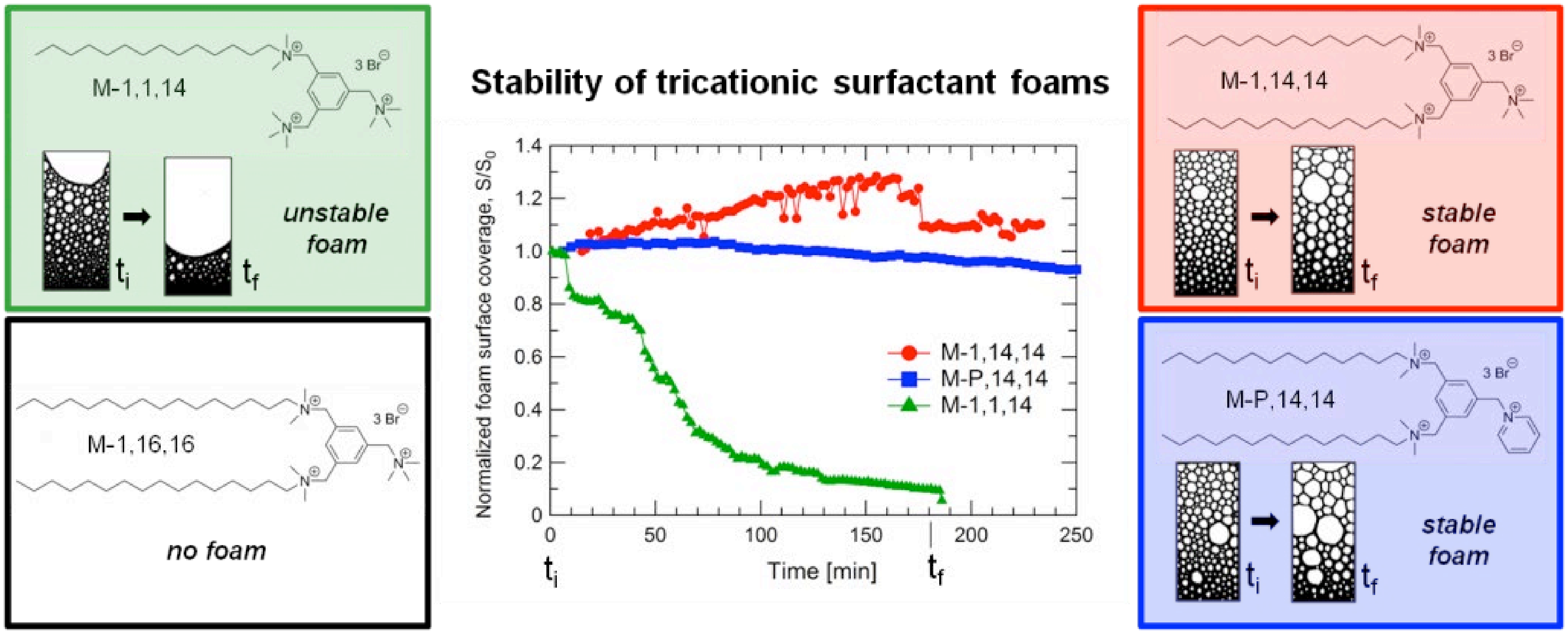


A. Saint-Jalmes, *Soft Matter*, 2006, **2**, 836-849.



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

Foam stability



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

Ethanol can destabilize foams.

Why?

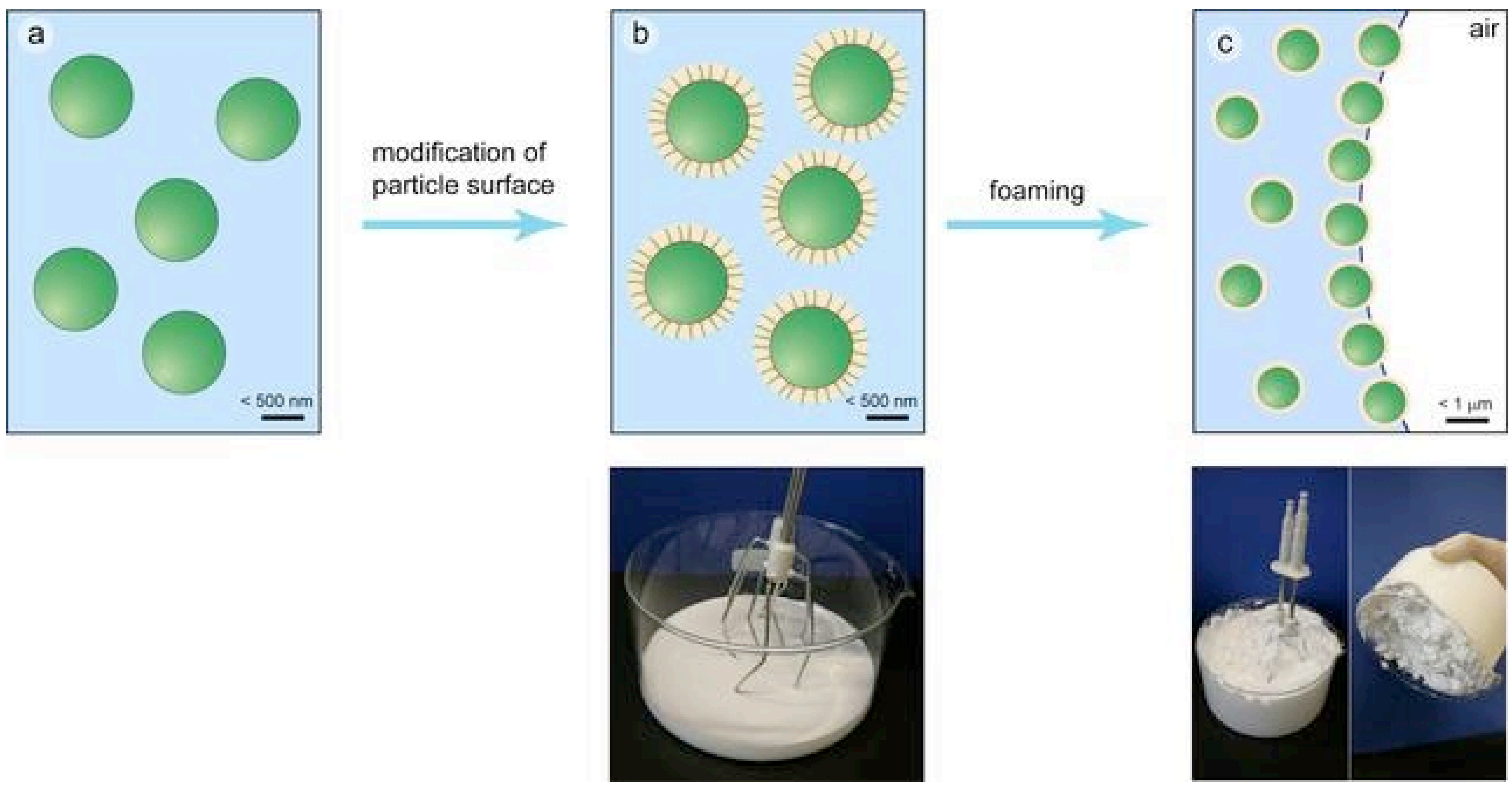
Ethanol also lowers γ but not to the same extent as surfactants. Because of its high mobility, it quickly adsorbs at the air-liquid interfaces and competes with the adsorption of surfactants.

A foam is most stable if…

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.

Stabilization of foams

Colloids



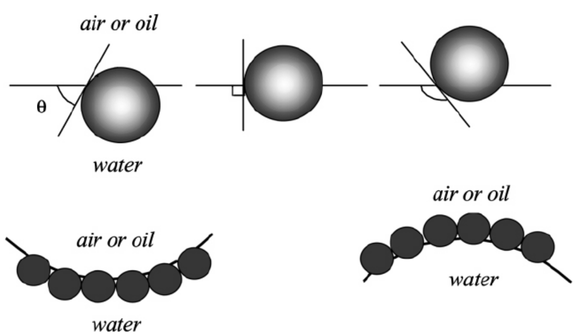
Gonzenbach, U. T.; Studart, A. R.; Tervoort, E.; Gauckler, L. J. *Angewandte Chemie-International Edition* **2006**, *45*, 3526.

Foam stability

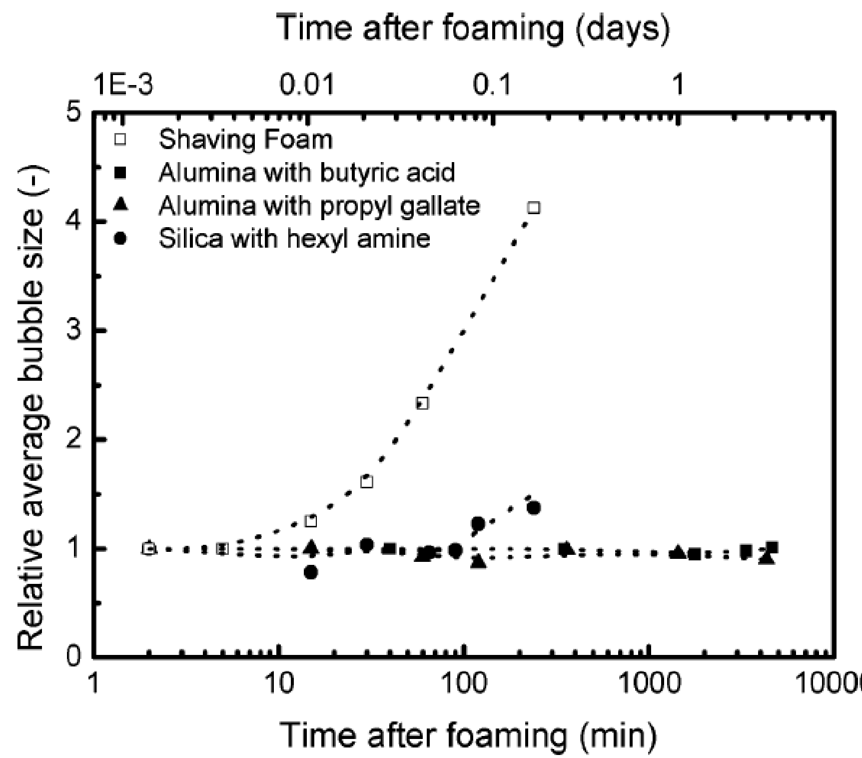
Foams that are stabilized with nanoparticles are more stable than those stabilized with surfactants.

$$E = \Pi r^2 \gamma_{ow} \left(1 - \left|\cos\Theta\right|\right)^2$$

hydrophilic particles hydrophobic particles

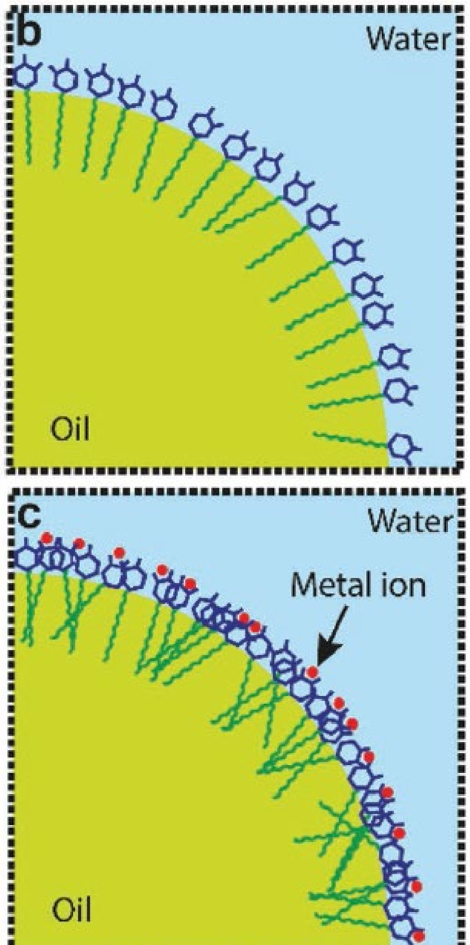


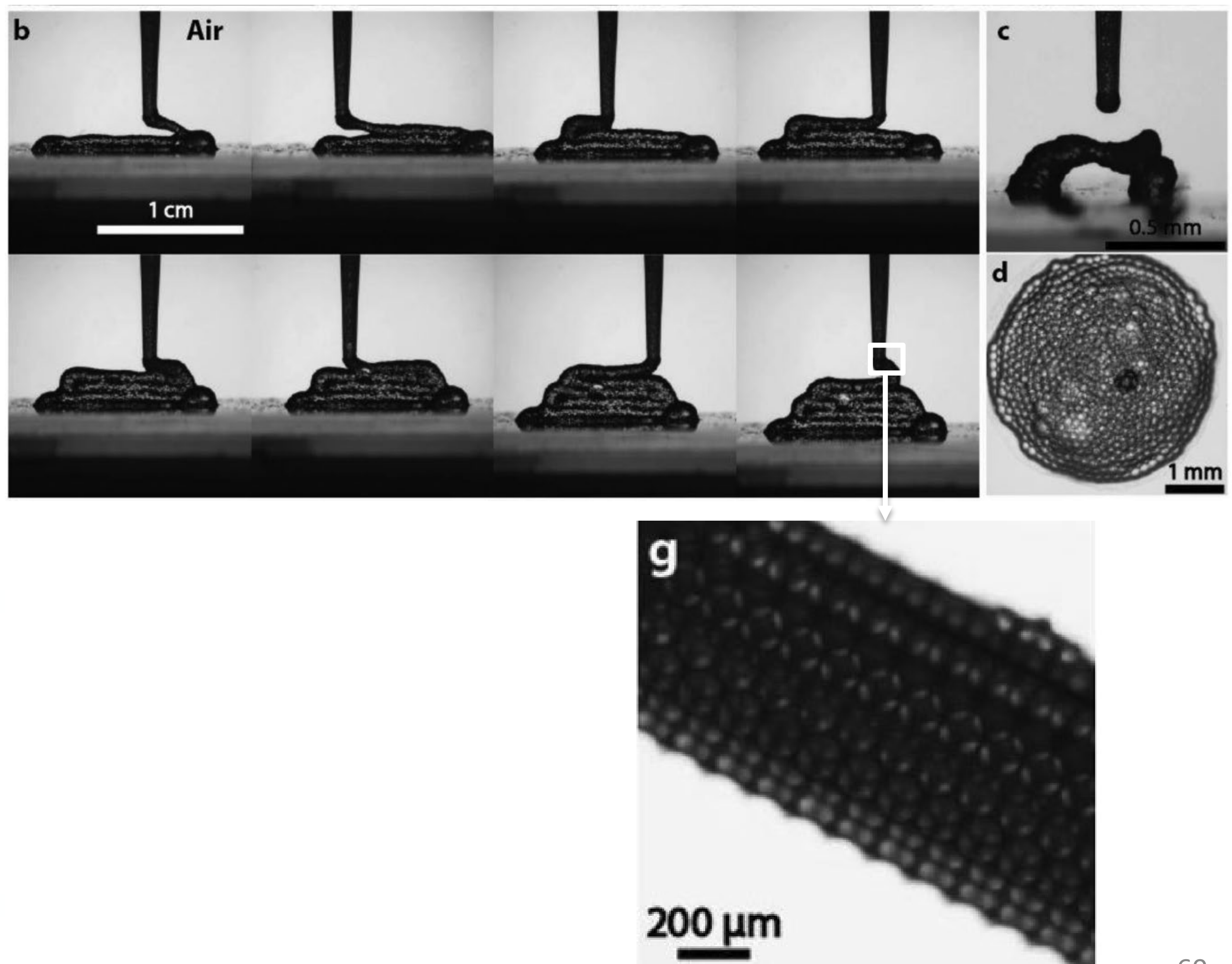
Binks, B. P. *Current Opinion in Colloid & Interface Science* **2002,** *7* (1–2), 21-41



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

Application: 3D printing of viscoelastic capsules formed from emulsions

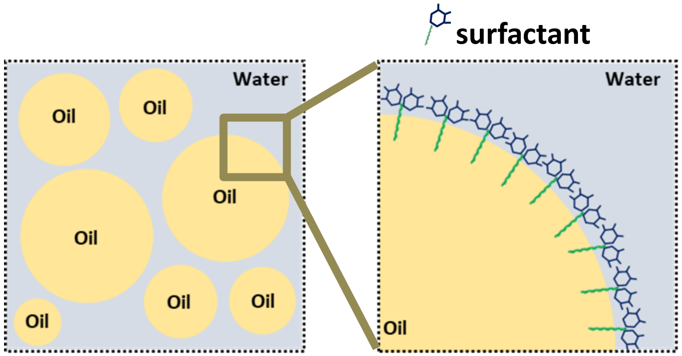


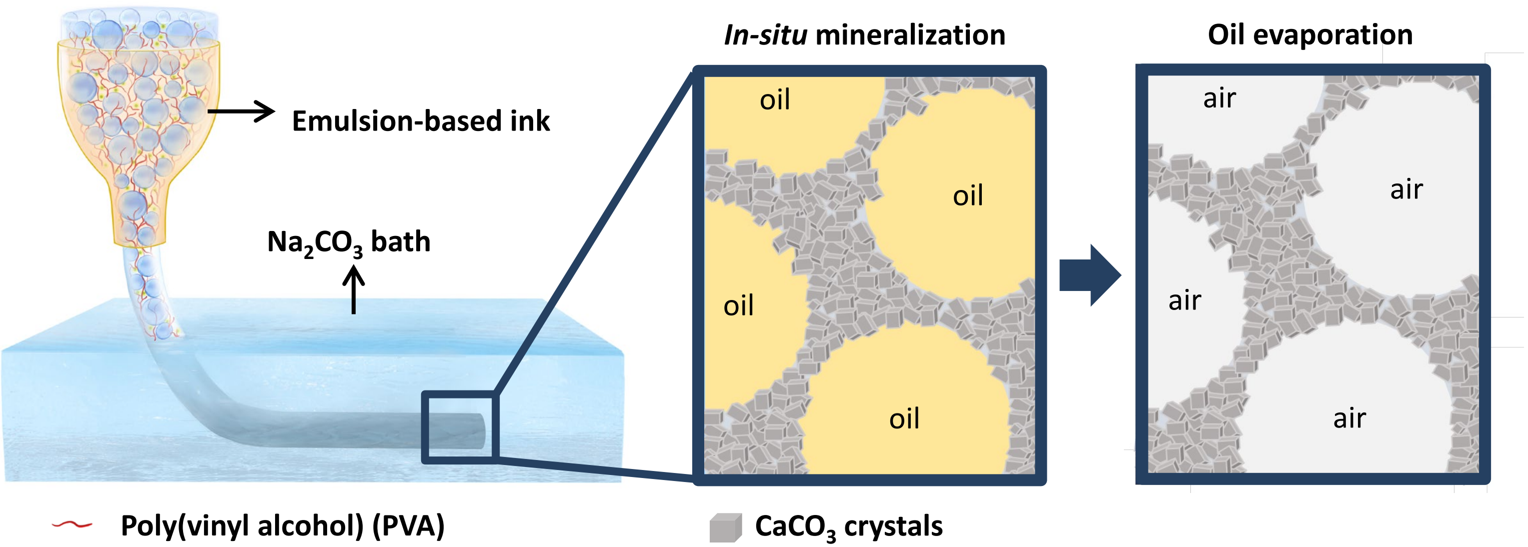


Etienne, G.; *et al.*. *Advanced Materials* **2019**, *31* (27), 1808233

Mineralization of emulsion drops

Ran Zhao

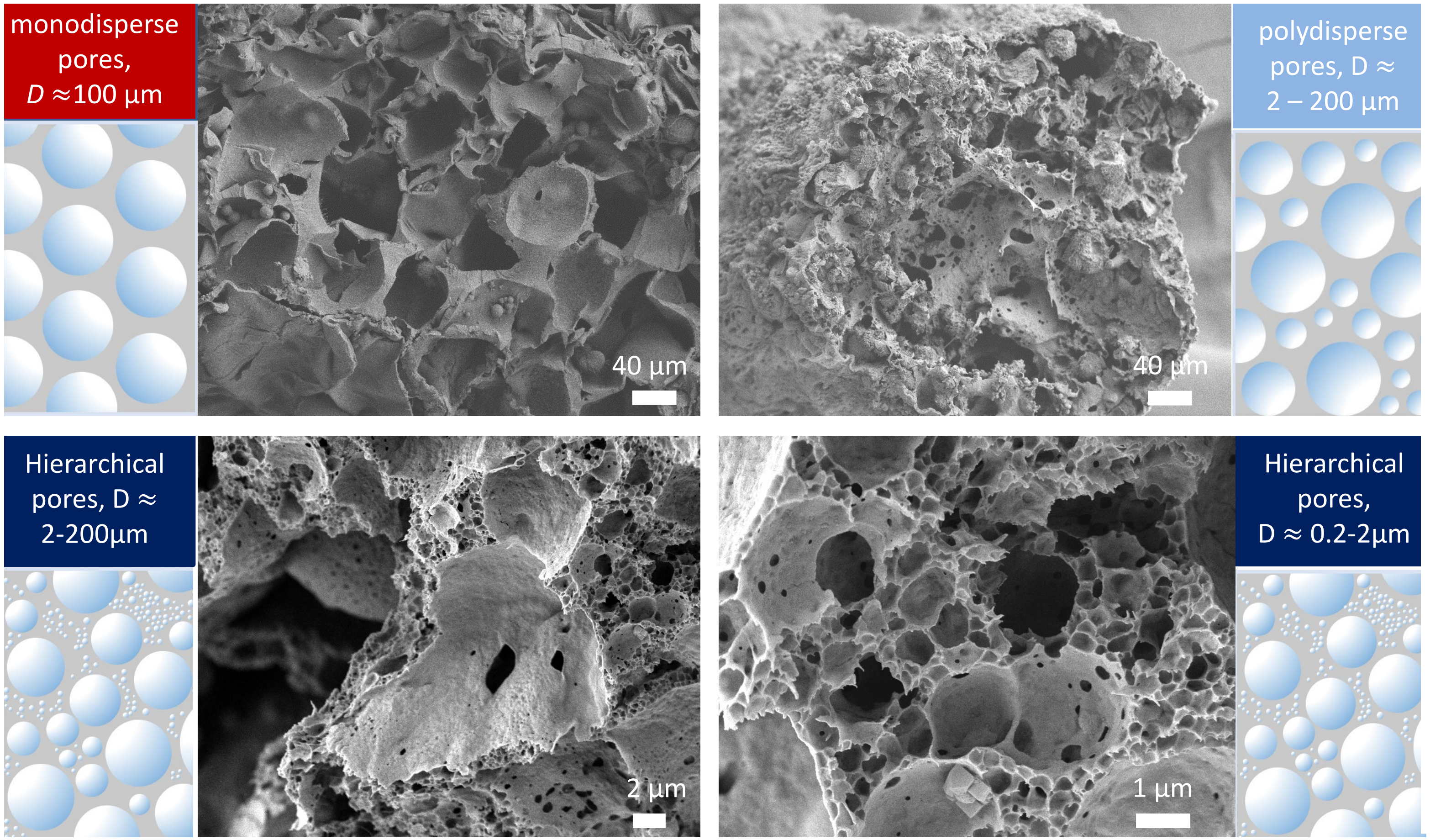




Zhao, R., *et al.*, (2023). Advanced Functional Materials *33*, 2300950. 10.1002/adfm.202300950

Microstructure of 3D printed $CaCO_3$

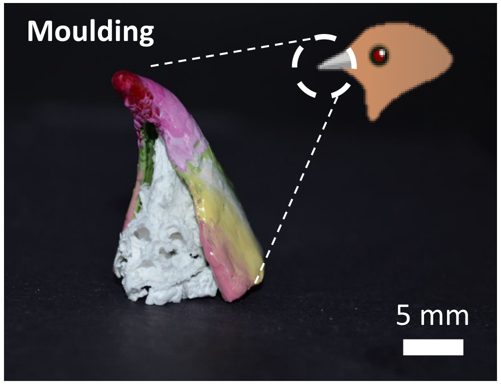
Ran Zhao

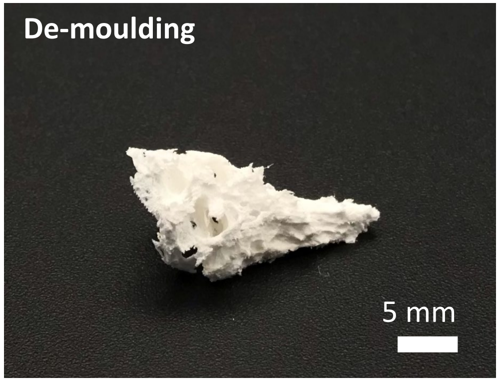


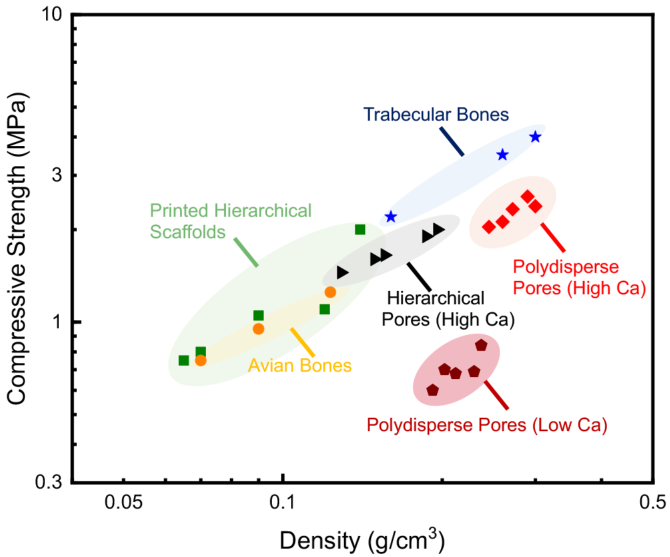
Zhao, R., *et al.,* (2023). Advanced Functional Materials *33*, 2300950. 10.1002/adfm.202300950

Casting toucan beaks

Ran Zhao





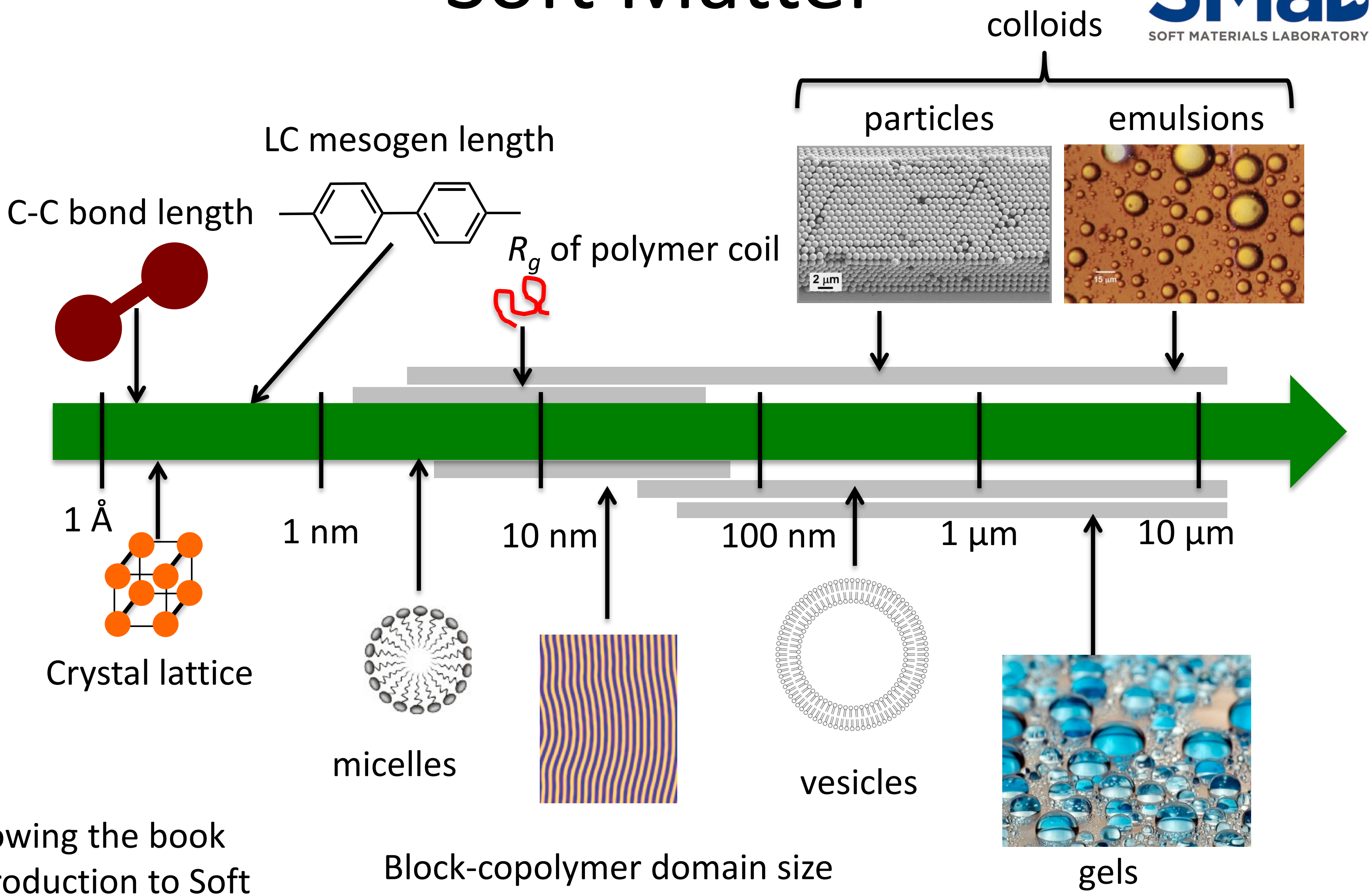


Zhao, R., *et al.,* (2023). Advanced Functional Materials *33*, 2300950. 10.1002/adfm.202300950

EPFL

Soft Matter

SMaL SOFT MATERIALS LABORATORY



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