

Foam Technology

Dispersions in liquids:
suspensions, emulsions,
and foams

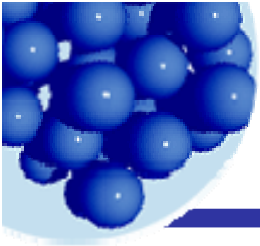
ACS National Meeting

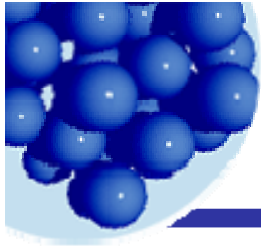
March 21 – 22, 2009

Salt Lake City

Jean Siméon Chardin (1699-1779)







Foams in industry

Marshmallow - foam formed from egg white, gelatin, and sugar.

Ice cream - refrigerated and aerated at the same time. Ice crystals and fat crystals form the matrix.

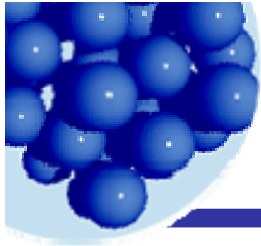
Dynamic foams: cakes, sponges, bread, meringes, soufflés. Bubbles change at various stages of preparation.

Foams on drying or stripping, especially in distillation columns. A foam blanket at the surface acts as an insulating layer - causing overheating.

Metallic slags foam probably because of the high viscosity. Cooling stabilizes the foam.

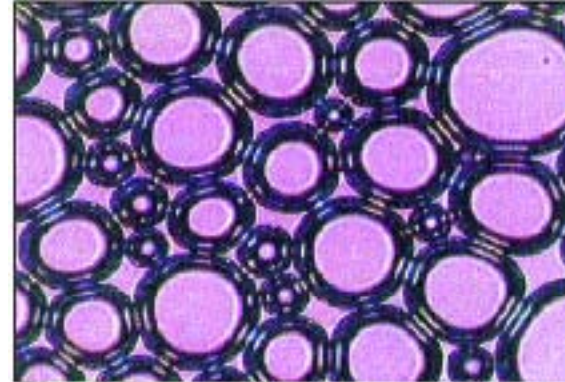
Paper making - Caused by lignin, resin, and fatty acids in wood, sulfate soaps from pitch. Also, sizing materials, dyes, fillers, oxidized starch, proteins, etc act as profoamers.

Beer - foam should not affect taste, but it remains important. Too little, beer looks "flat". Sources of foam: entrained air in the pouring, in the pressurizing, and from dissolved carbon dioxide. Mostly stabilized by proteins. Protein-polysaccharide complexes are especially stabilizing.

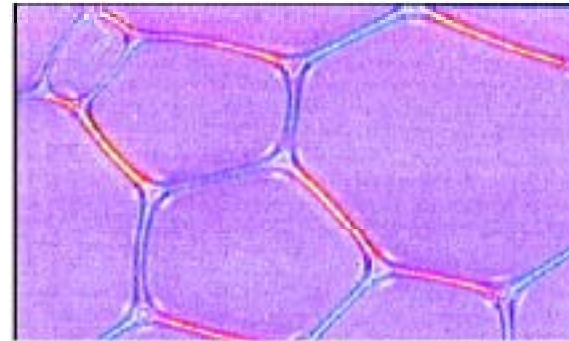


Foam structures

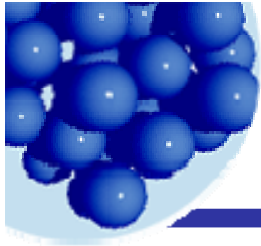
Foam structure of a wet spherical foam made with Sodium Caproyl Lactylate at 400X magnification



Foam structure of dry hexagonal foam from cocoamidopropyl betaine at 400X magnification

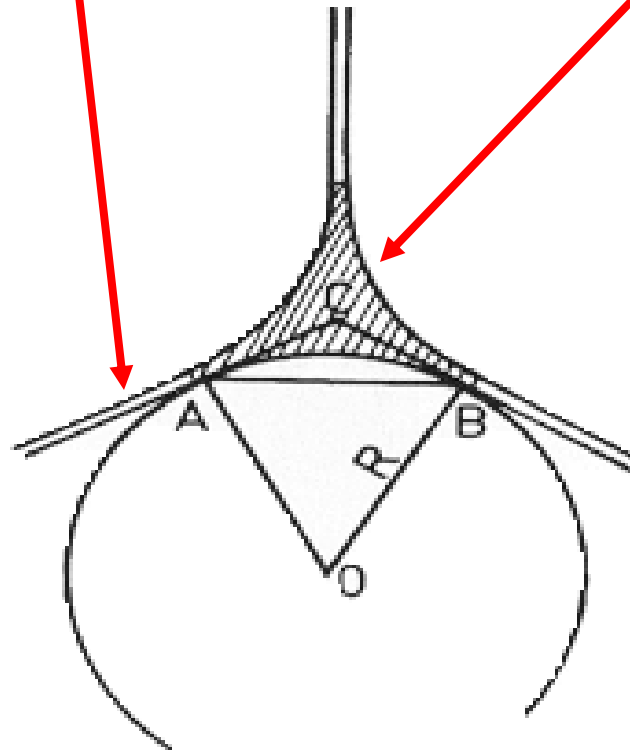


[/www.ctmw.com/articles/Rita/2.htm](http://www.ctmw.com/articles/Rita/2.htm)



Plateau borders and Gibbs angles

The pressure is least in the Gibbs angles.

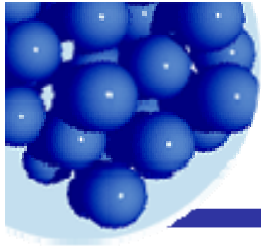


And gravity pulls the liquid down.

Exerowa and Kruglyakov, p. 15

Ian Morrison© 2009

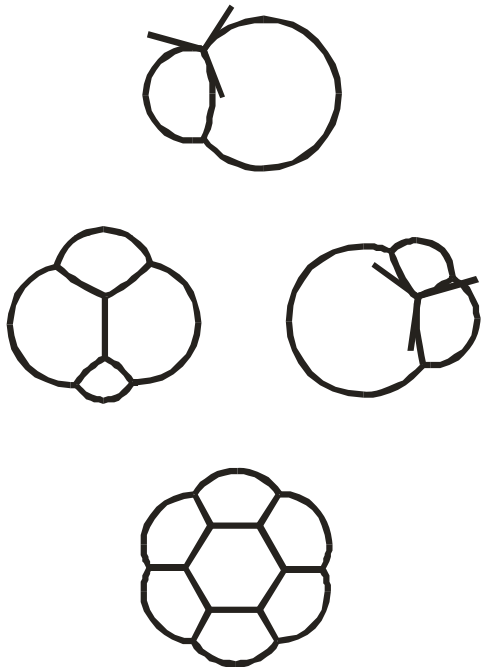
Lecture 7 - Foam technology



Bubble geometry

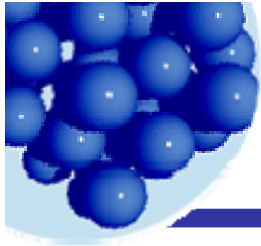
The Laplace equation for bubbles:

$$\Delta p = \frac{4\sigma}{r}$$



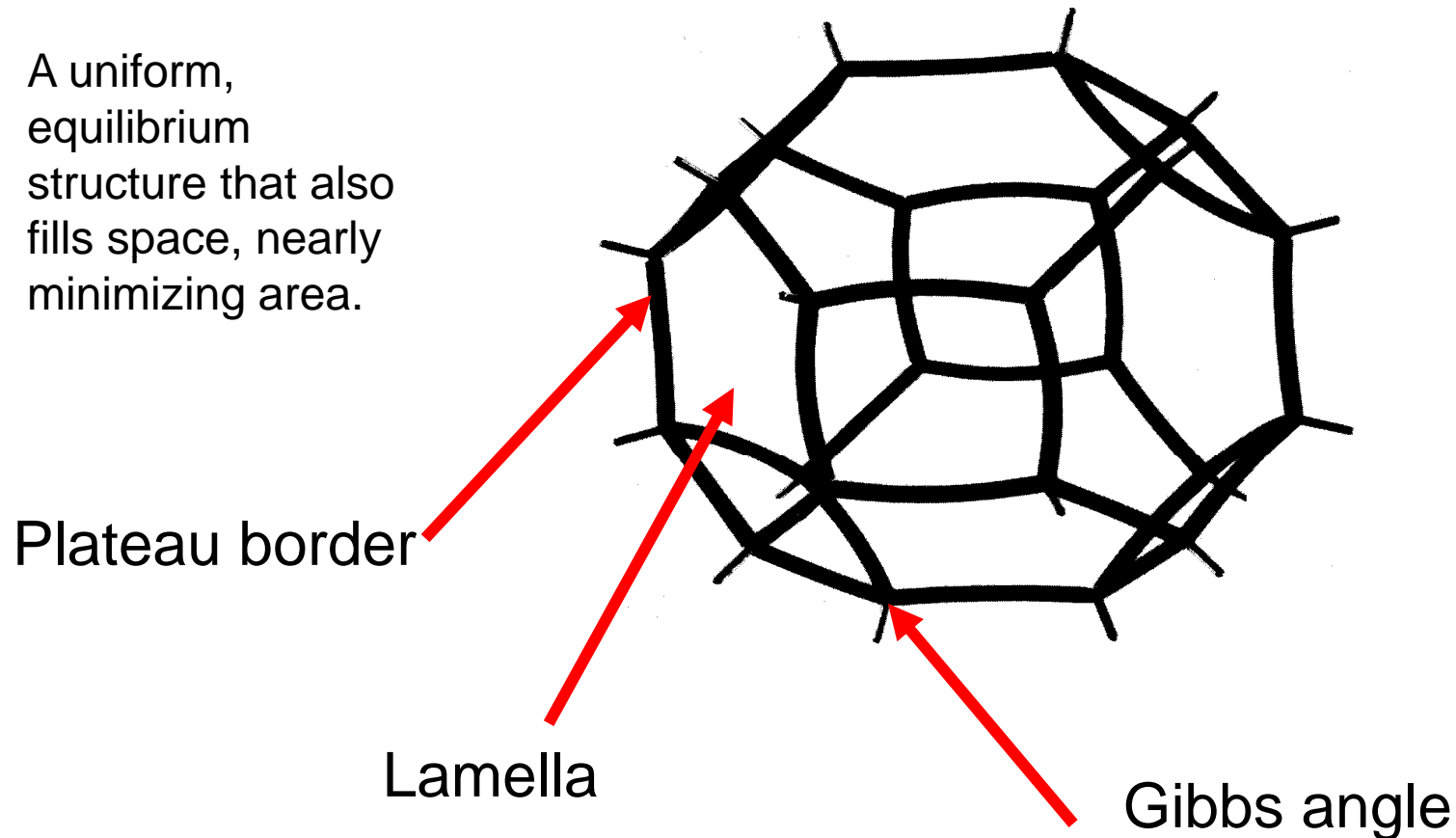
Different curvatures are caused by different pressures.

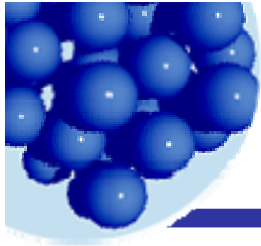
But the uniformity of surface tension creates (some) uniformity in structure.



The Kelvin tetrakaidcahedron

A uniform, equilibrium structure that also fills space, nearly minimizing area.

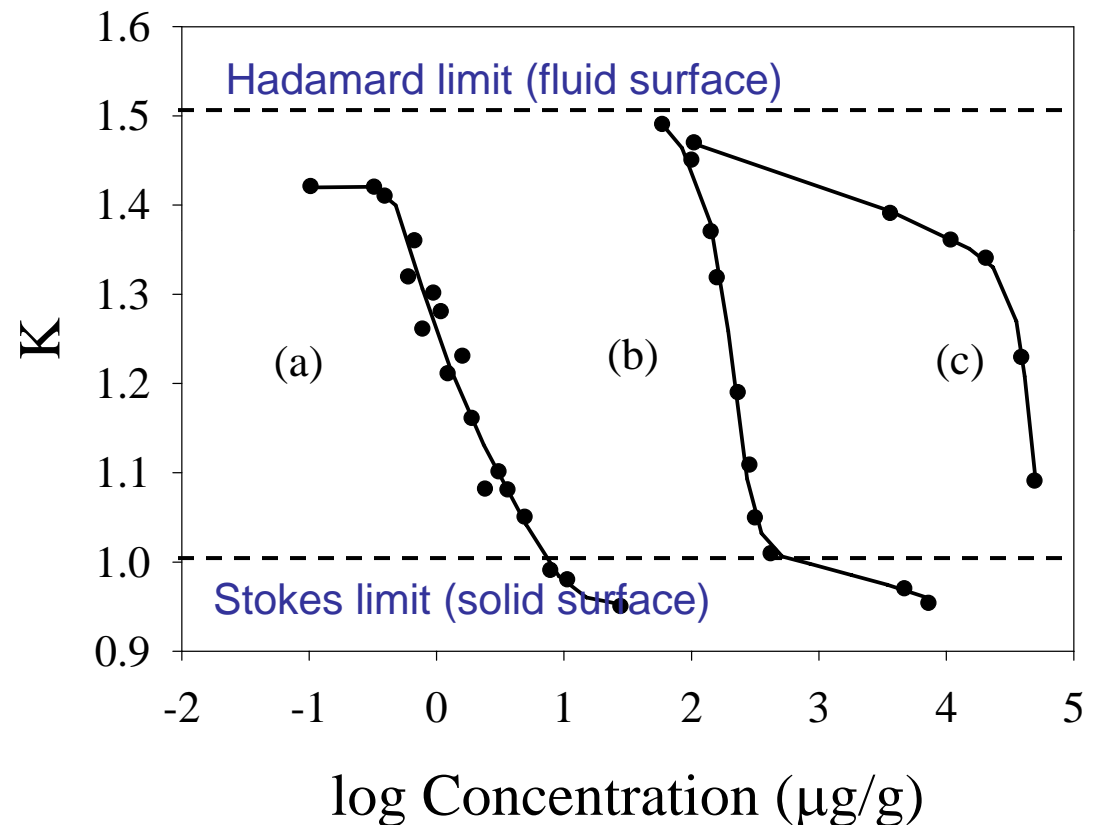


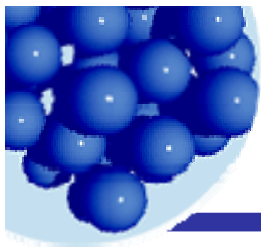


Adsorption on bubbles – bubble rise

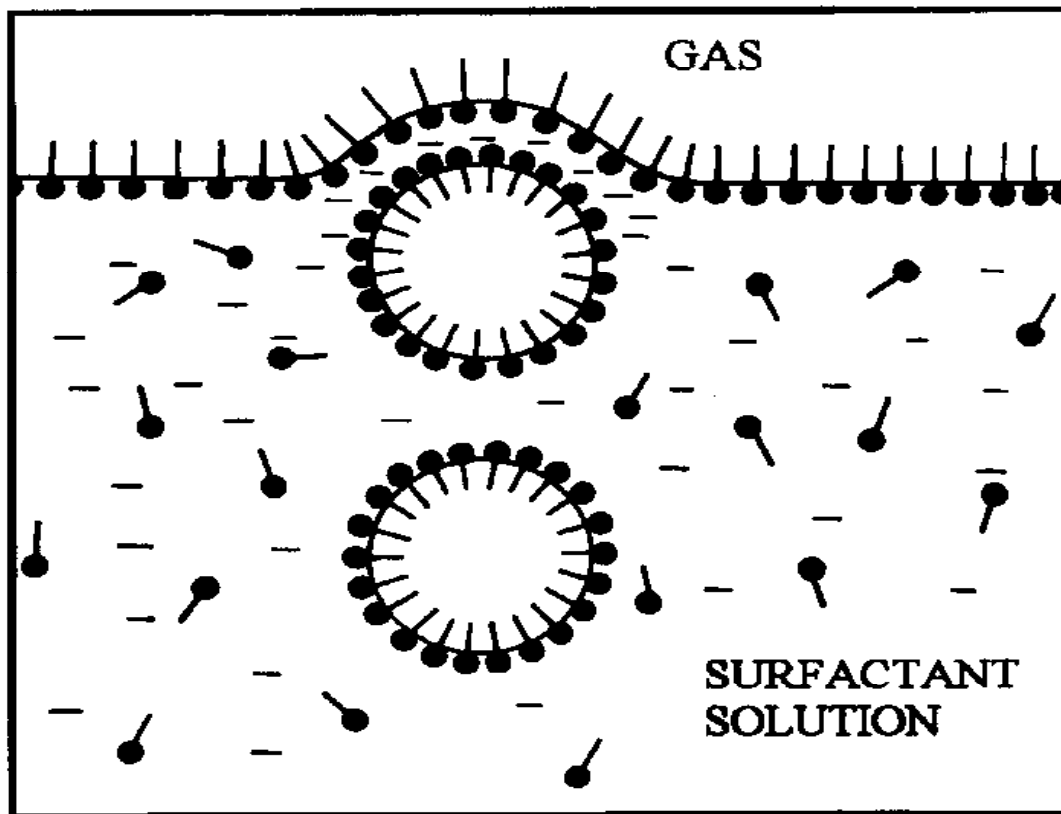
Ratio of the observed velocity of ascent of a bubble to the calculated Stokes' velocity in solutions of various concentrations of (a) polydimethylsiloxane in trimethylolpropane–heptanoate; (b) polydimethylsiloxane in mineral oil; (c) *N*-phenyl-1-naphthylamine in trimethylolpropane–heptanoate.¹ Each figure shows the transition from the Hadamard to the Stokes regime.

¹ Suzin, Y.; Ross, S. Retardation of the ascent of gas bubbles by surface-active solutes in nonaqueous solutions, *J. Colloid Interface Sci.* **1985**, *103*, 578 – 585.

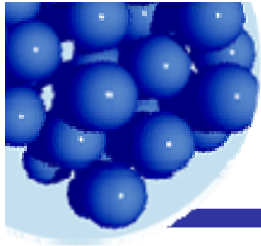




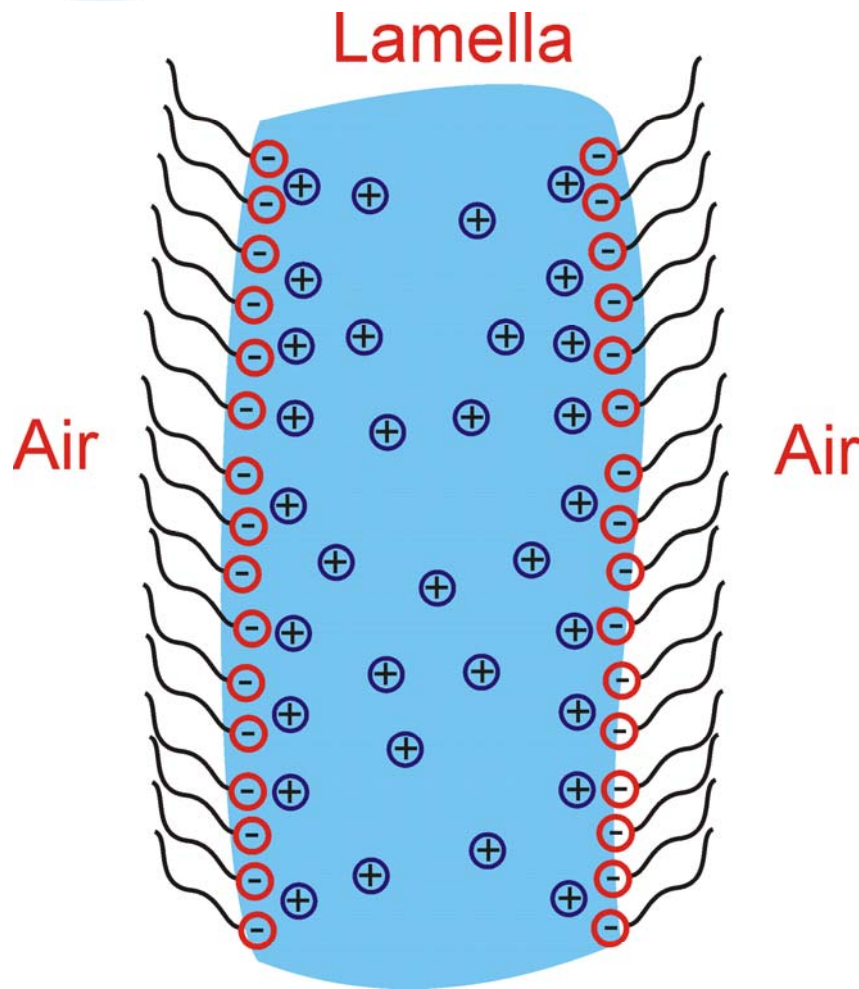
Formation of bubbles



Exerowa and Kruglyakov, p. 2

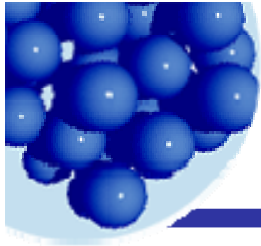


Electrostatic stabilization of foam films

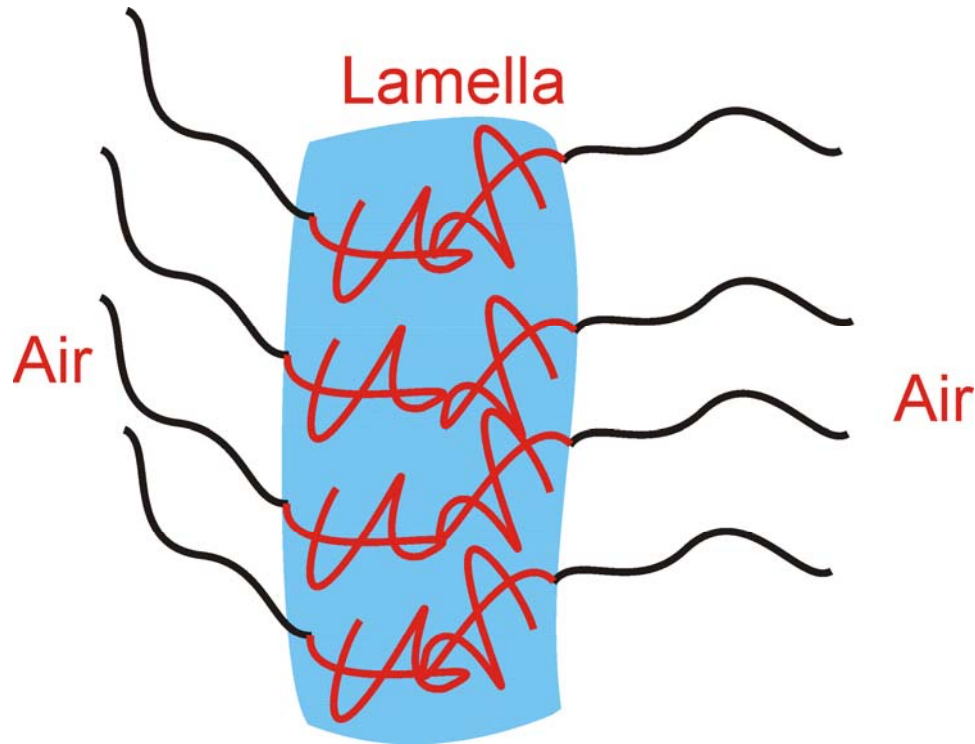


Each interface is electrically charged. As the film thins, electrical double layers overlap and the surface repel each other.

The same factors that reduce electrostatic dispersion stability reduces the stability of these lamellae.

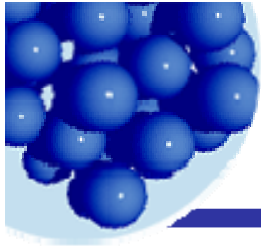


Steric stabilization of foam films



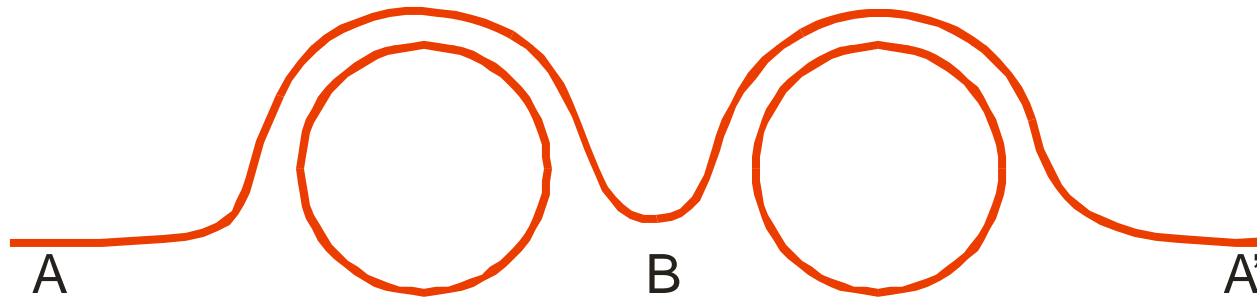
Each interface has adsorbed polymer. As the film thins, polymer molecules overlap and the surfaces repel each other.

The same factors that reduce steric dispersion stability reduces the stability of these lamellae.

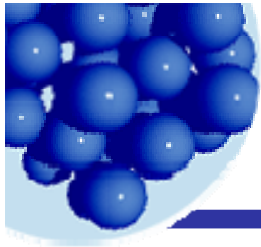


Formation of foams

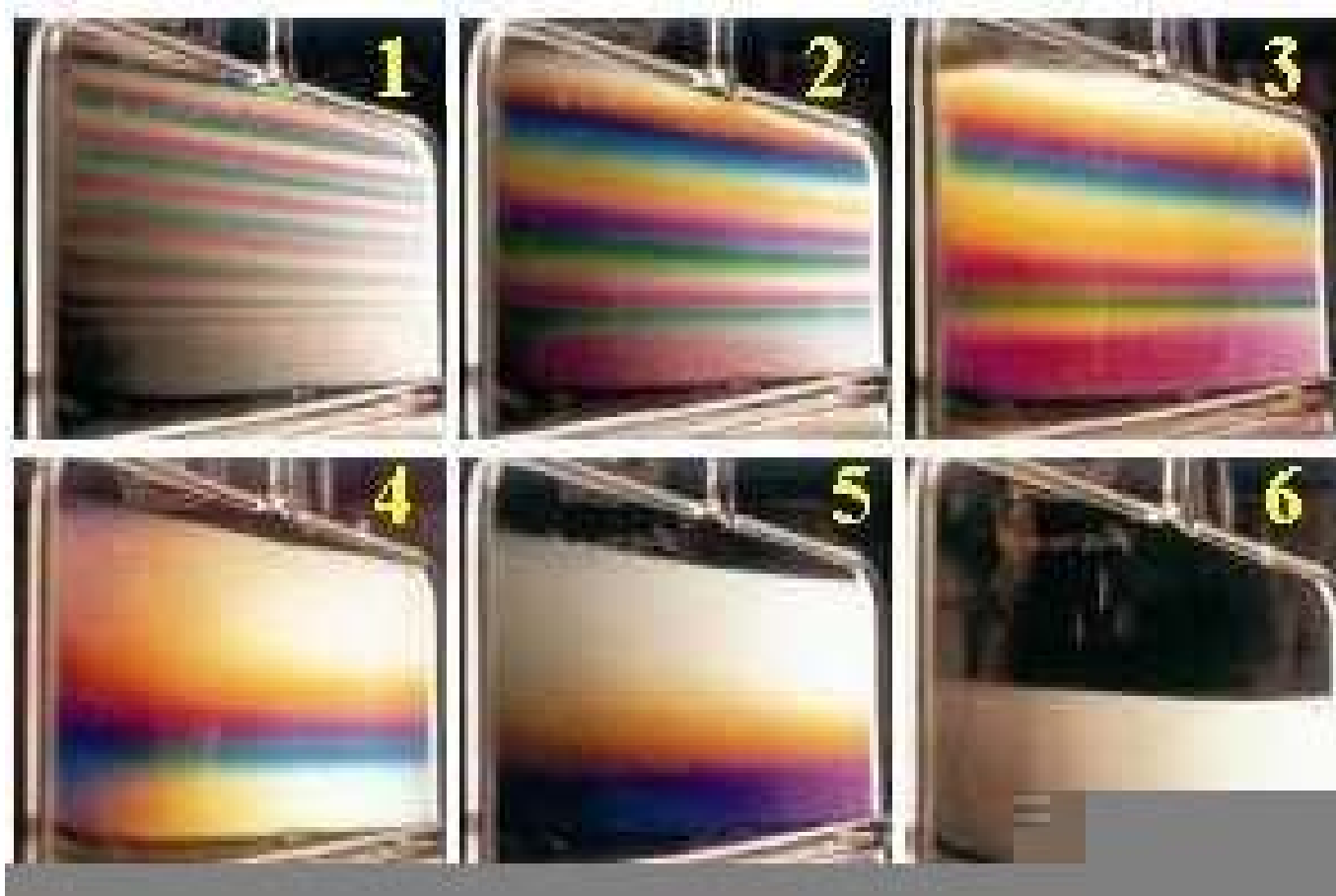
Two bubbles floating at the liquid-air interface:



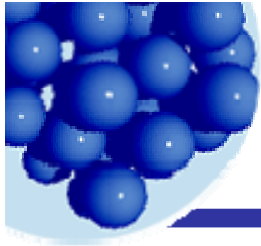
The pressure in the liquid at B is less than that at A or A'.



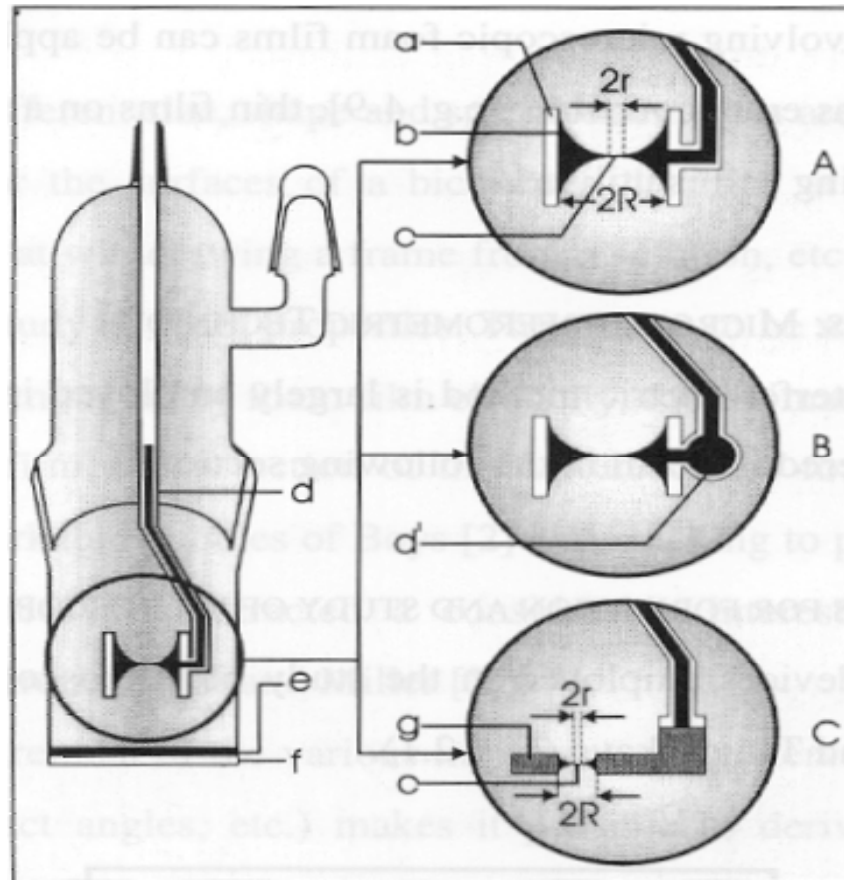
Draining of foam films



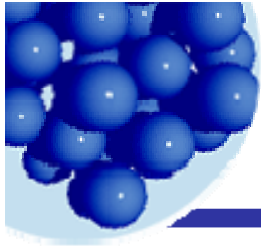
<http://ptcl.chem.ox.ac.uk/~rkt/tutorials/tutimages/foam.jpg>



Measuring film stability



Exerowa and Kruglyakov, p. 44



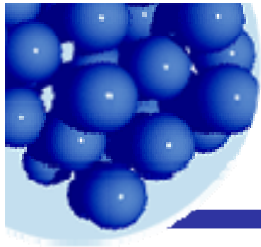
Foam Drainage – “Syneresis”

Drainage is through lamellae (initially) and then through the Plateau borders. Empirical equations can be used to fit the data:

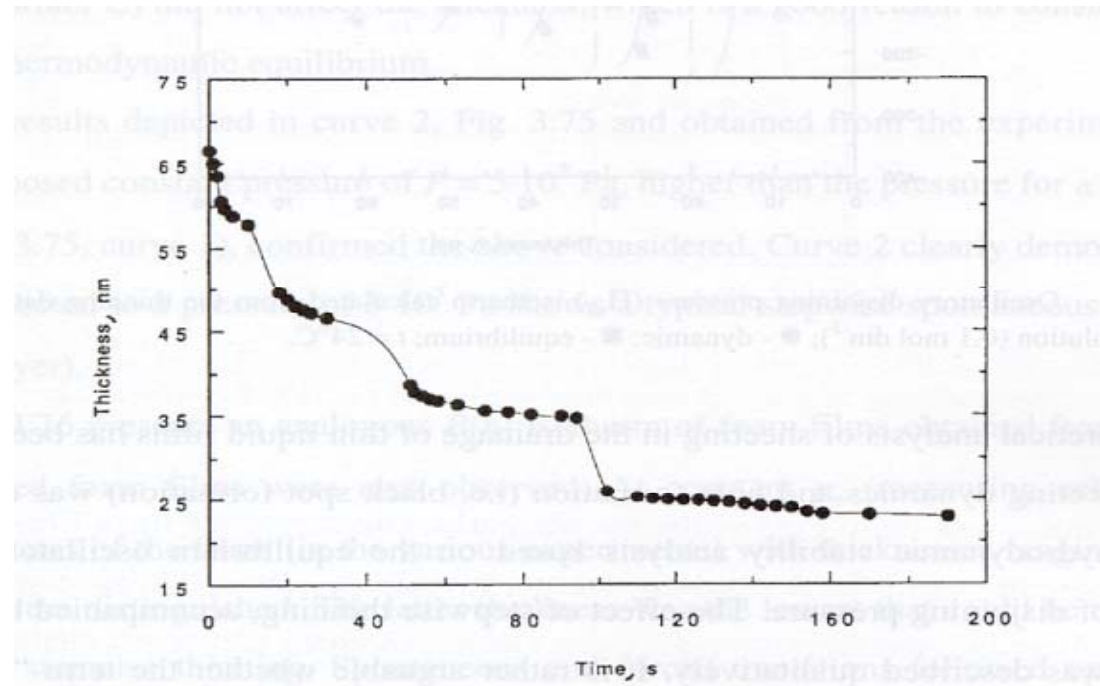
$$V = V_0 (1 - e^{-kt}) \quad \text{or} \quad V = \frac{V_0^2 kt}{1 + V_0 kt}$$

where V is the volume of liquid.

It is sometimes possible to add liquid to the top of the foam and measure drainage through the foam.

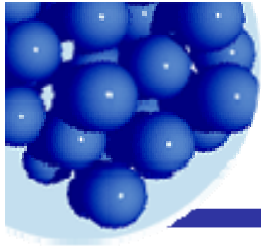


Uneven film drainage

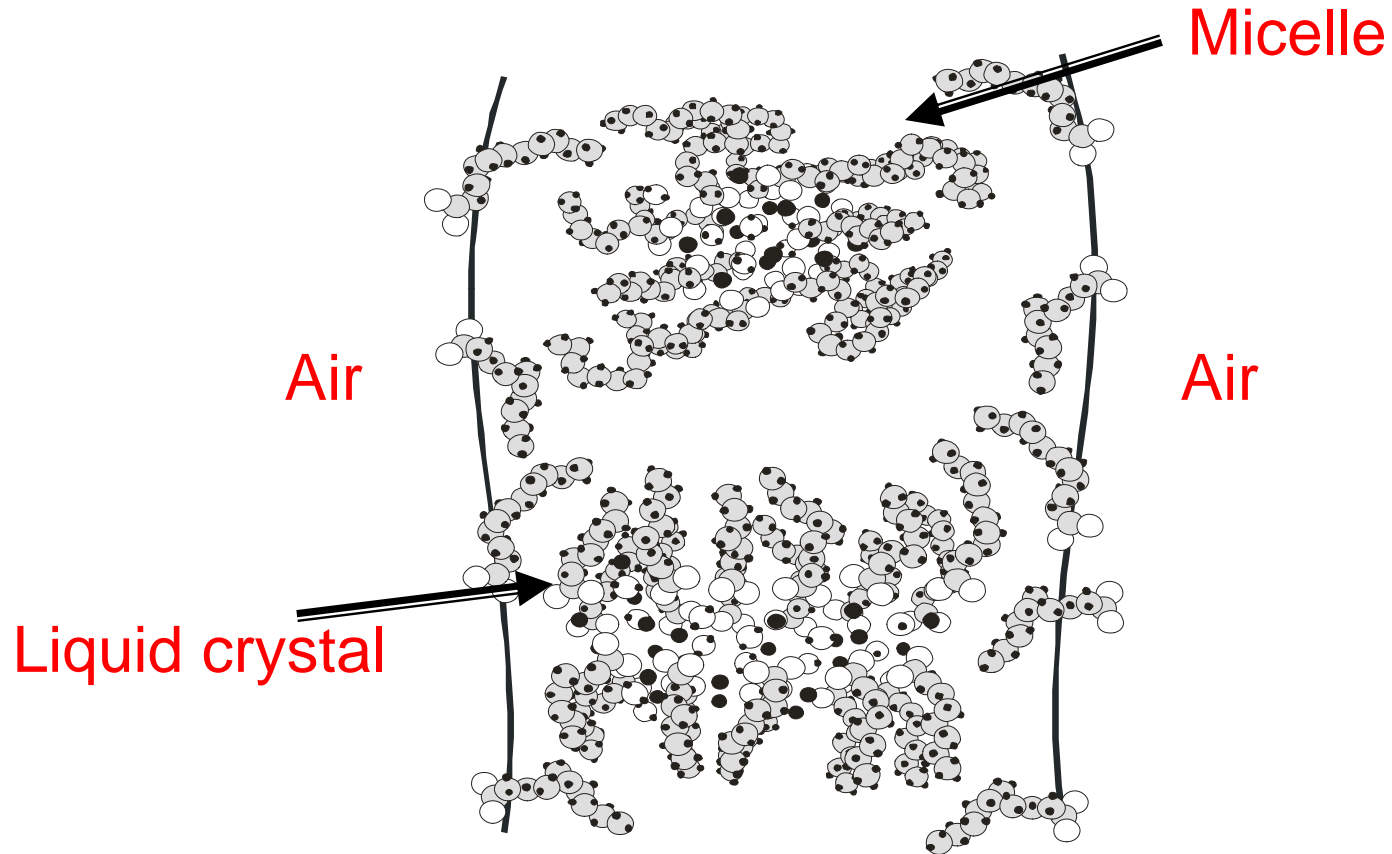


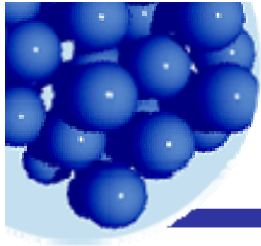
Wasan et al. discovered the stepwise thinning of thin films.
The stable thicknesses are layers of close-packed micelles.

Exerowa and Kruglyakov, p. 221

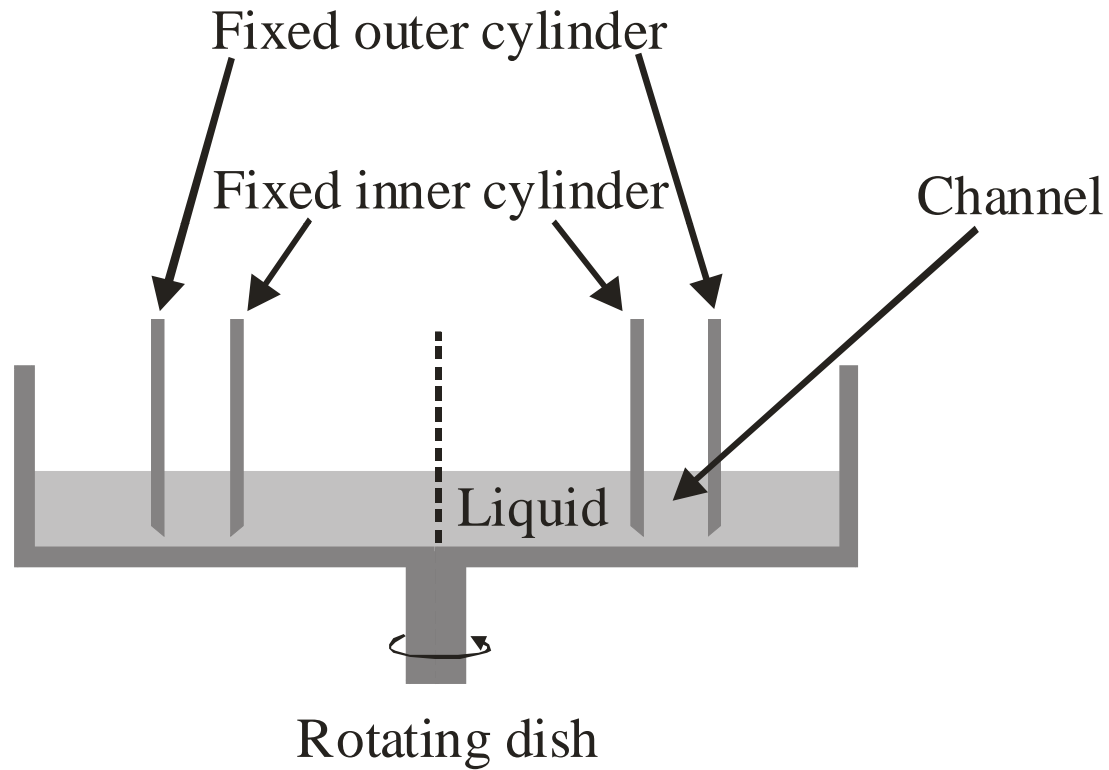


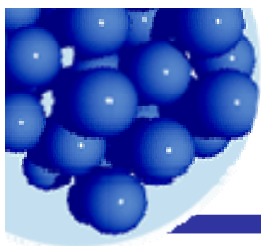
Liquid crystals stabilize foams



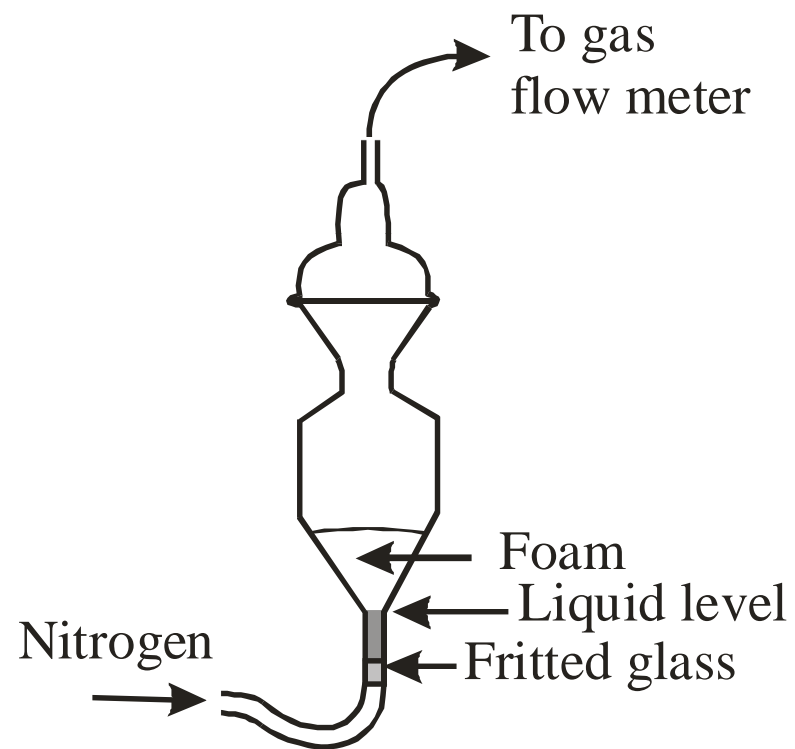


Deep-channel surface viscosimeter

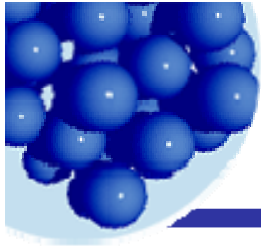




Dynamic foam stability



Ross & Suzin, *Langmuir*,
1985, 1, 145-9.



Equation of state for foam

Consider a single bubble:

$$p - P = \frac{4\sigma}{r}$$

For a sphere:

$$\frac{V}{A} = \frac{r}{6}$$

For an ideal gas:

$$pV = nRT$$

Combining gives:

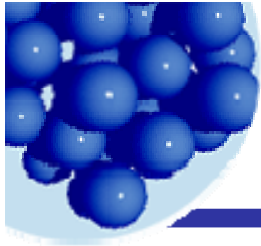
$$pV + \frac{2}{3}\sigma A = nRT$$

Assume this is true for a foam (only proved for a few geometries).

The differential form is:

$$dA = -\frac{3V}{2\sigma} dP$$

Text p. 297

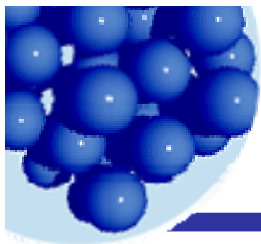


Theories of foam stability

Why don't foam films fall fast?

- Mutual repulsion of electrical double layers.
- Formation of layers of micelles "spacing" the surface apart.
- Formation of liquid crystalline phases in the thin films (originally associated with black films.)
- High fluid viscosity. Especially when high MW materials are present, e.g. gelatin or proteins.
- High surface viscosity. Surfactants are dense in the surface.
- Marangoni effects. Slow diffusion of surfactant to stretched surface. Marangoni effects are important in spontaneous healing of thin spots and in foam destruction by antifoaming agents.*

*Explains why foam stability near saturation is often diminished.
Above the CMC, the micelles serve as reservoirs for the surfactant.

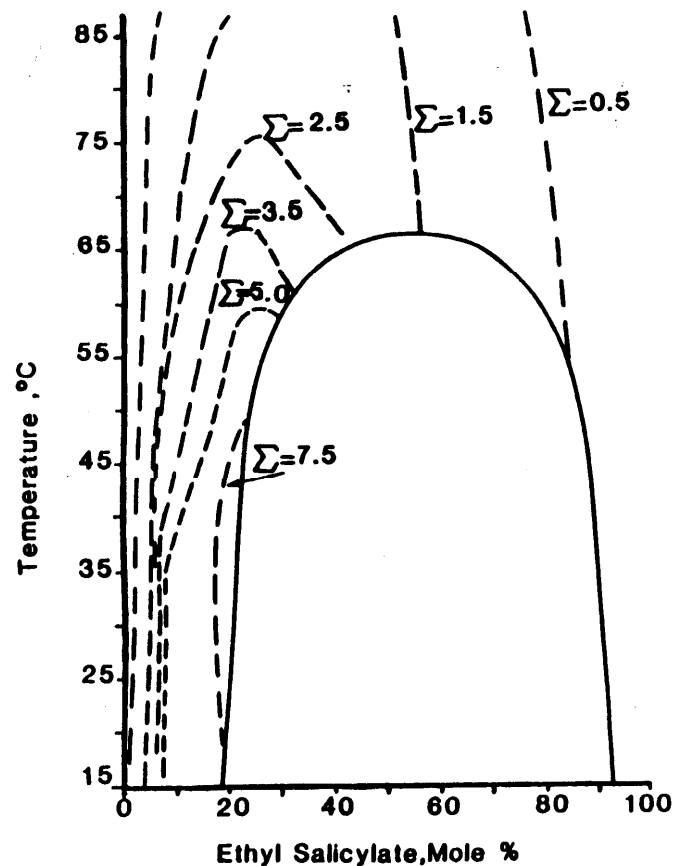


Foaminess and the phase diagram

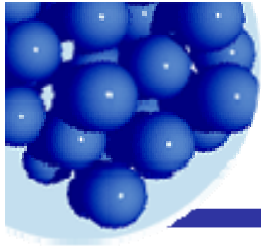
Not just solutions of "surfactants" foam.

Partially miscible liquids in multiple components foam near the critical point (two components) or plait point (three or more components.) Surface activity precedes phase separation.

If the separated phase has a lower surface tension, it will be a defoamer.

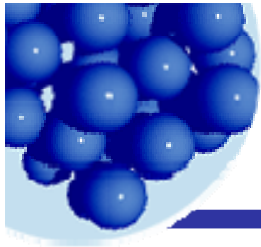


Text p. 311

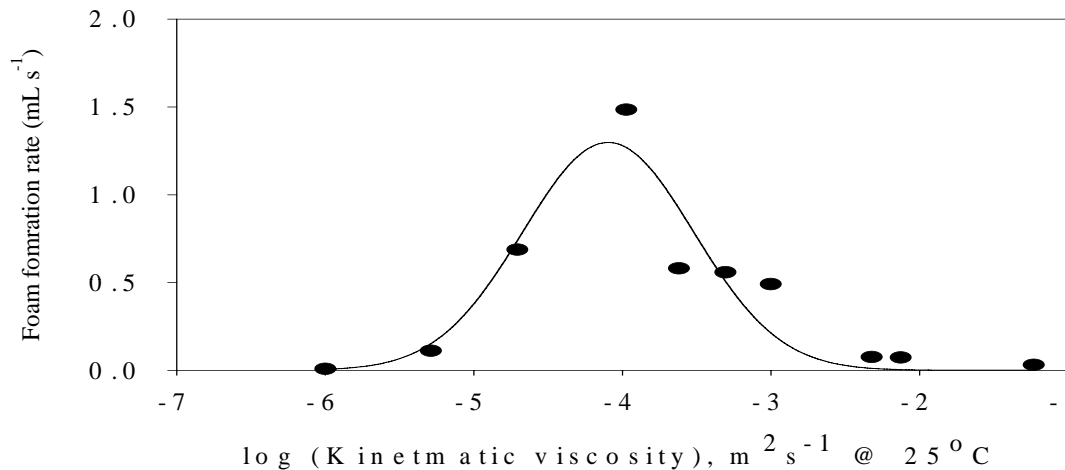


Ross' Rule – Capillary effects appear near phase boundaries

- Adsorption precedes precipitation.
- Foaming can suddenly increase or disappear.
- Dispersion stability suddenly changes.
- Surface and interfacial tensions change abruptly near phase boundaries.
- The number and size of precipitates depend strongly on the position in the phase diagram.
- Sudden changes in product behavior may indicate some component is near its solubility limit.
- Foaming is an indication of some component ready to precipitate.



Effect of PDMS viscosity on foaming

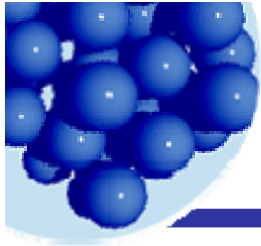


Centers, *Tribology Trans.*,
1993, 36(3), 381.

At low molecular weight (<250) the polymer is too soluble in the ester to be surface active.

At intermediate molecular weights (ca. 6000) the polymer is less soluble and is surface active and is a profoamer.

At higher molecular weights (>60,000) the polymer is insoluble but spreads on the bubble surface and acts as a foam inhibitor.



Froth flotation

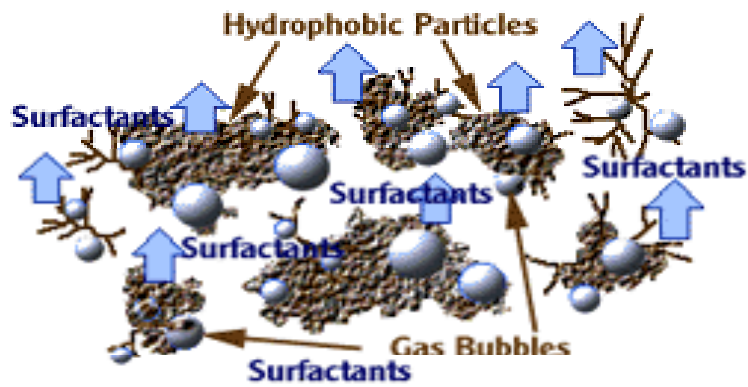
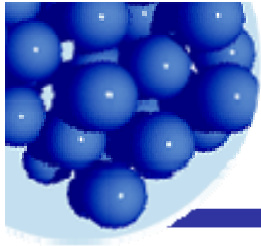


Figure 2. How does foam form?



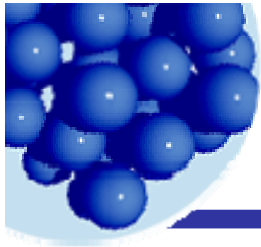
Figure 1. Foaming in two Australian activated sludge plants. Plant on right is an oxidation ditch with foam covering the dividing wall.

From the "Activated Sludge Pages"
<http://www.scitrav.com/wwater/asp/>



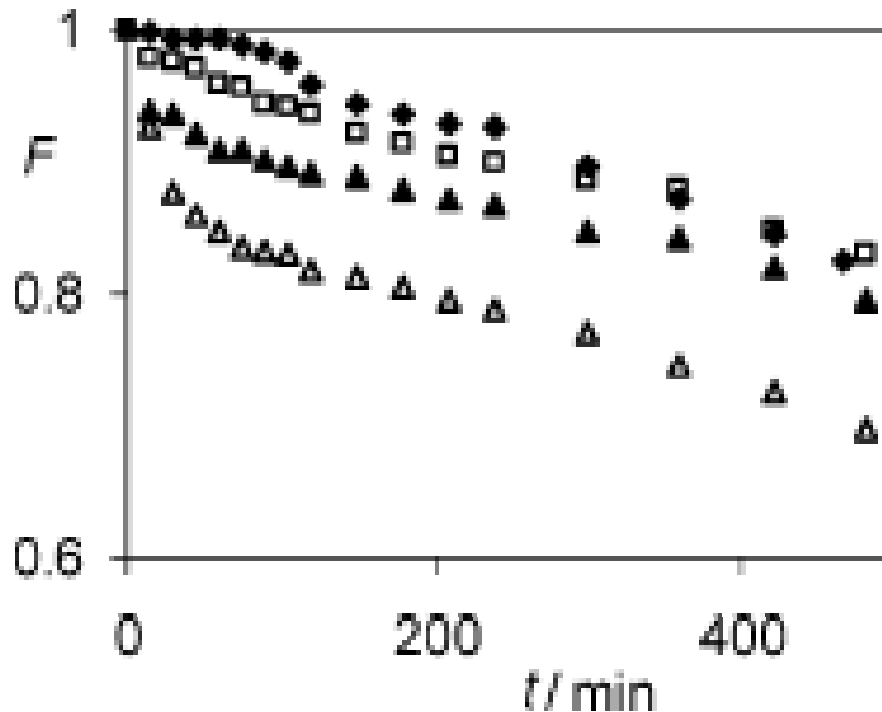
Three Phase Foams

- Powders with finite (receding) contact angles sit at the air/liquid surface.
 - "Collectors" are sometimes added to aid this dewetting of particles.
 - The particles move with the bubble - flotation.
- Particles may stabilize thin films if they have low contact angles, holding the two interfaces apart.
- The finer the particles, the better the stability; lead, silica, ferric oxide are examples.



Bubbles stabilized with fumed silica

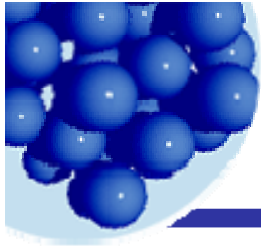
Hydrophobic silica stabilizing a foam in water with added salt.



Fraction (F) of bubbles remaining as a function of time (t) formed in dispersions of 1wt% of 33% SiOR particles at different NaCl concentrations:
3 mol dm⁻³,
2 mol dm⁻³,
1 mol dm⁻³,
0.5 mol dm⁻³.

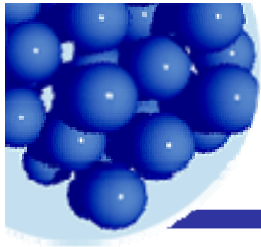
Thomas Kostakis, Rammile Ettelaie, and Brent S. Murray

Langmuir **2006**, *22*, 1273-1280

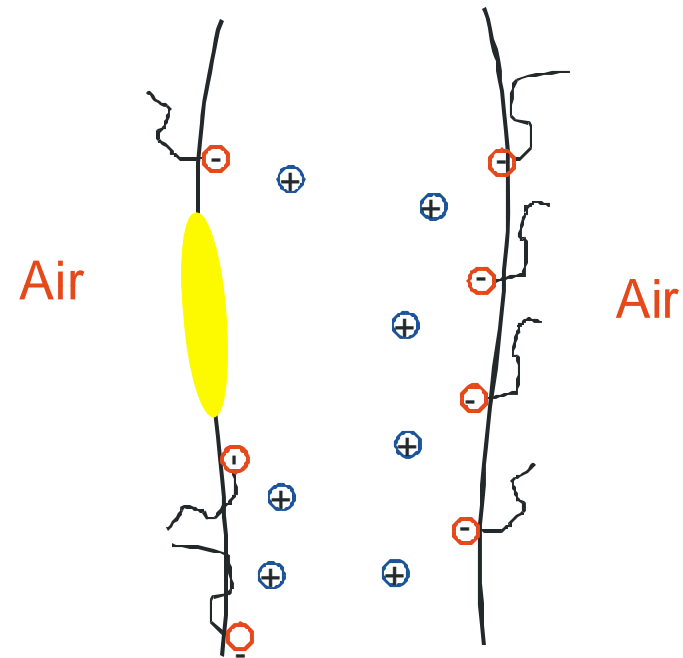


Foams to immobilize

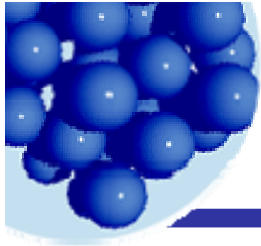
- To retard evaporation. Improve insulation.
- For fumigants(toxic to fungi), insecticides, contraceptives, to keep them in place.
- Applying thin layers, such as adhesives or etching formulations, dyes or bleaches
- Capture of aerosols.
- Aqueous foam is an excellent suspending medium for paper fibers. Pseudoplasticity enables dispersion of long fibers. At low shear stress the fibers are "frozen" in position. Enables the use of long fibers which otherwise orient on coating.
- Shaving lather - no known use!



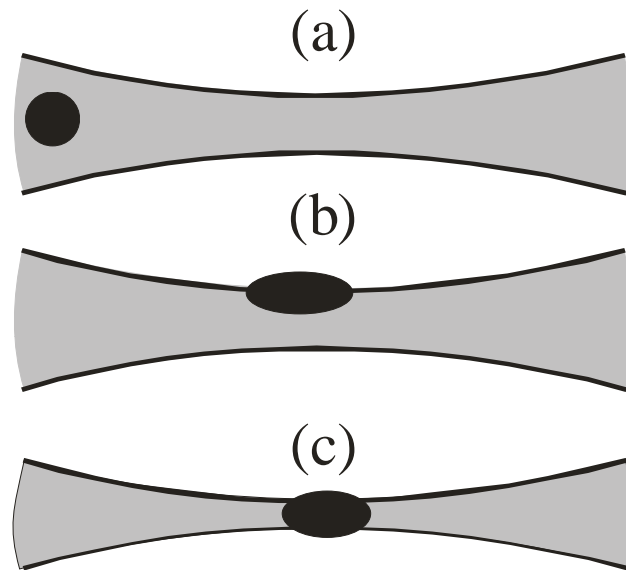
Antifoams



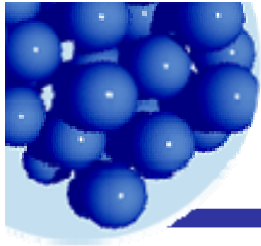
With an antifoam on one surface, electrostatic stabilization is lost.



Antifoams



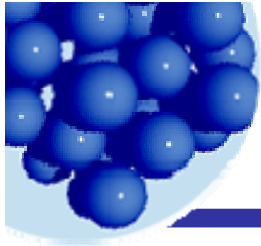
- (a) Antifoam drop
- (b) Entering the surface
- (c) Leading to rupture of the film.



Silicone antifoams

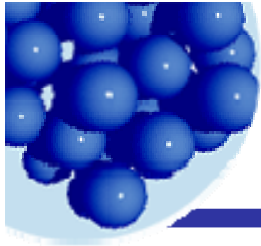
- Silicone oil is emulsified into water with about HLB = 8 dispersant. Silicones are "activated" by the addition of 3-4% silica. Hydrophilic silica is heated in the oil.
- The PDMS spreads, but is retarded by the silica leading to a reasonable sized weakness in the lamella.
- Hypothesis: it is the silica particle that is the defoamer! The silicone oil is only the carrier.

“Silicone antifoams” by Kulkarni et al. in Prud'homme and Khan, Chapter 14.

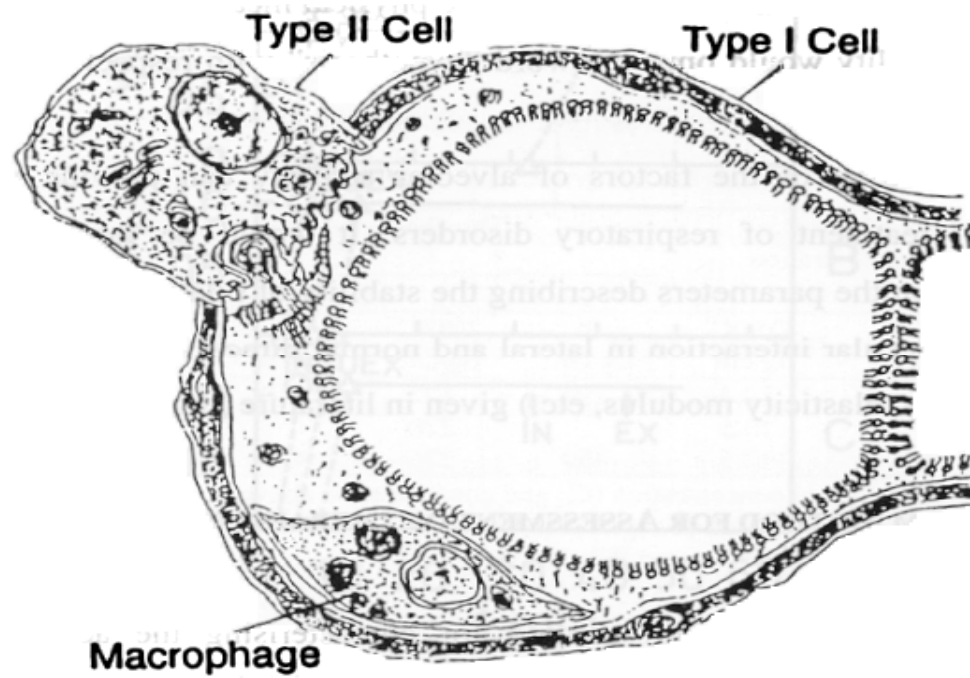


Mechanisms of antifoaming

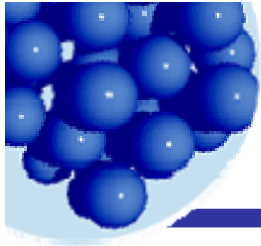
- Contact with a hydrophobic interface, such as Teflon/water, siliconized solid/water.
- Addition of an insoluble, low-surface-tension liquid to a standing foam. Typically, naturally occurring, oils, lard, fatty acids and alcohols, silicone oils,
- Presence of vapor of a volatile liquid.
- Contact with a hot source, such as an electrically heated wire.
- Destruction of a foaming agent by precipitation or heat. *e.g.* Soap added to a protein (as in distillation of whiskey, etc.) or acid added to a soap solution or cationic agent added to an anionic agent.
- Combating the Marangoni effect by a rapid attainment of static surface tension on addition of low molecular weight amphipaths.



The alveolar surface in the lung

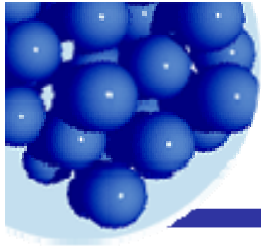


Exerowa and Kruglyakov, p. 753



Foam Technology





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