

# Lecture 5

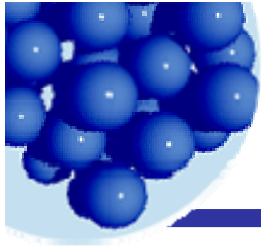
## Foam technology

Jean Siméon Chardin (1699-1779)

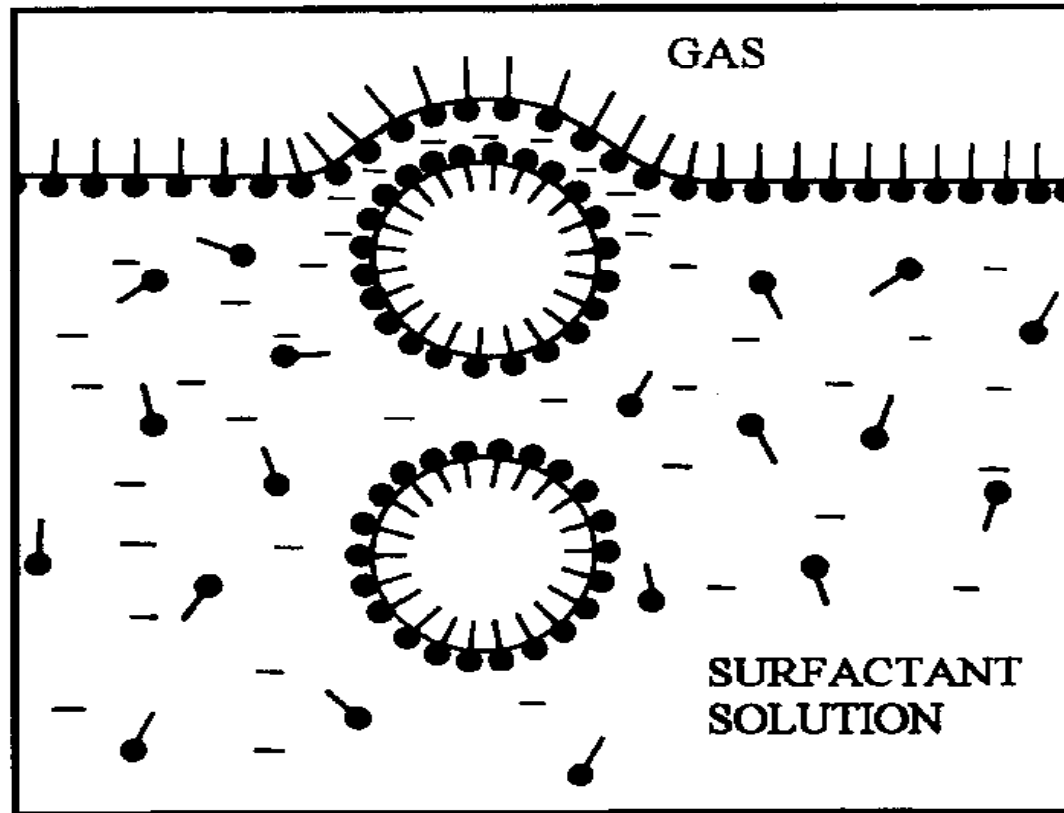




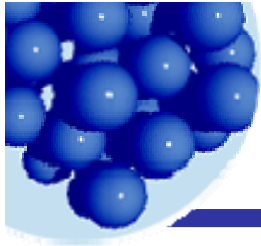




# Formation of bubbles

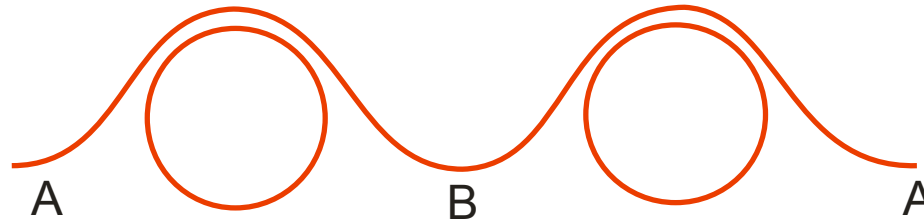


Exerowa and Kruglyakov, p. 2

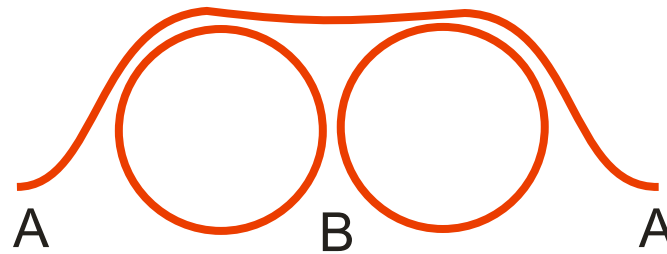


# Formation of foams

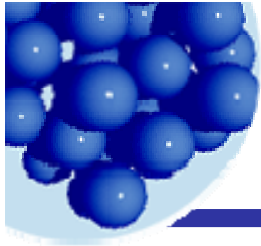
Two bubbles floating at the liquid-air interface:



The Laplace pressure in the liquid at B is less than that at A or A'.  
Which pulls the bubbles together.



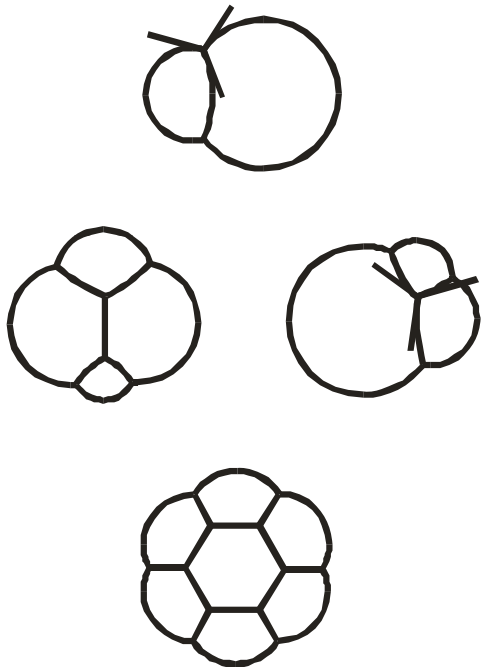
Where the pressures at A and B are equal.



# Bubble geometry

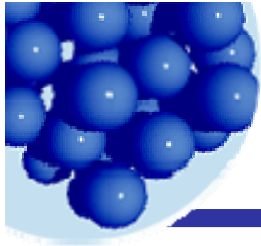
The Laplace equation for bubbles:

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

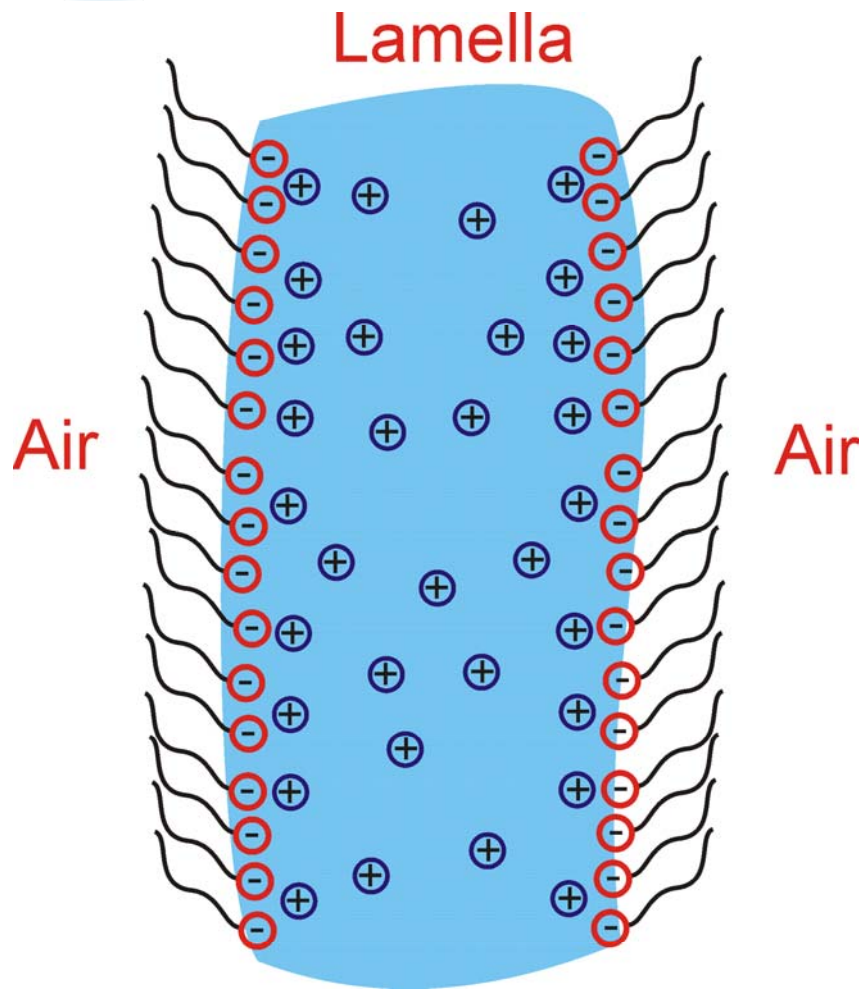


Different curvatures are caused by different pressures.

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

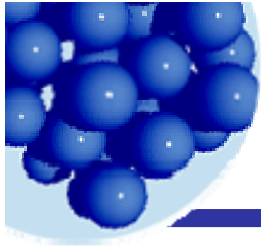


## Electrostatic stabilization of foam films

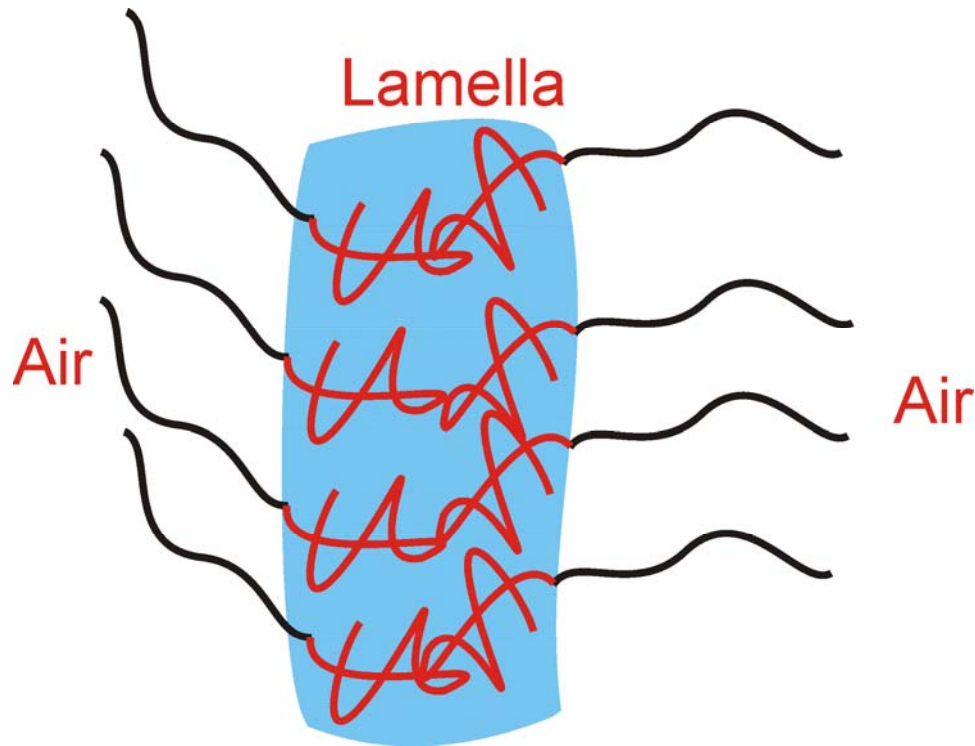


Each interface is electrically charged. As the film thins, electrical double layers overlap and the surface repel each other.

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



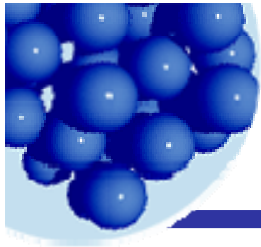
## Steric stabilization of foam films



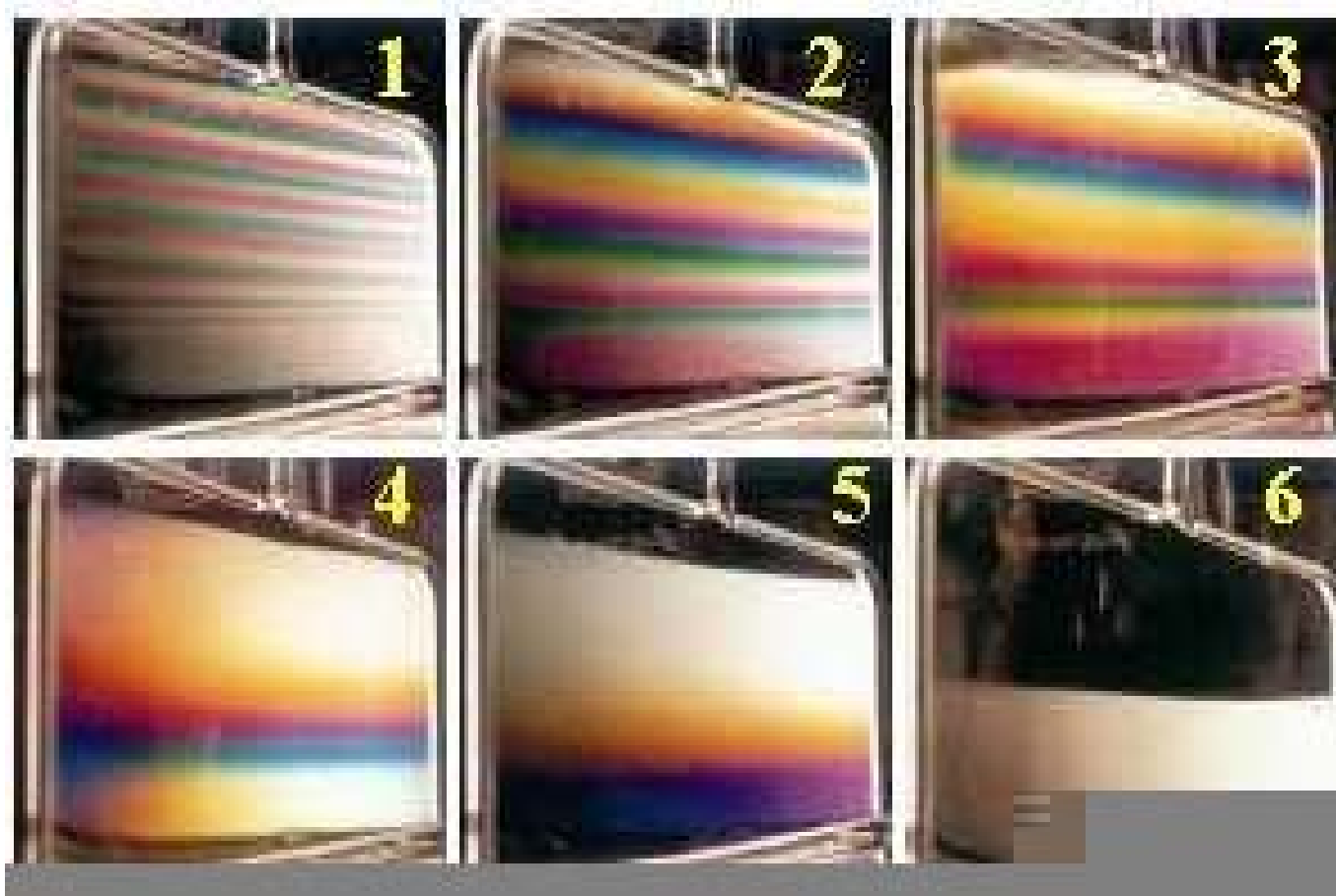
Each interface has adsorbed polymer. As the film thins, polymer molecules overlap and the surfaces repel each other.

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

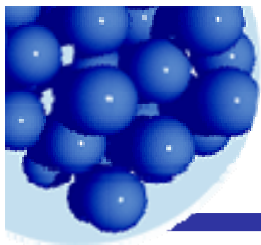




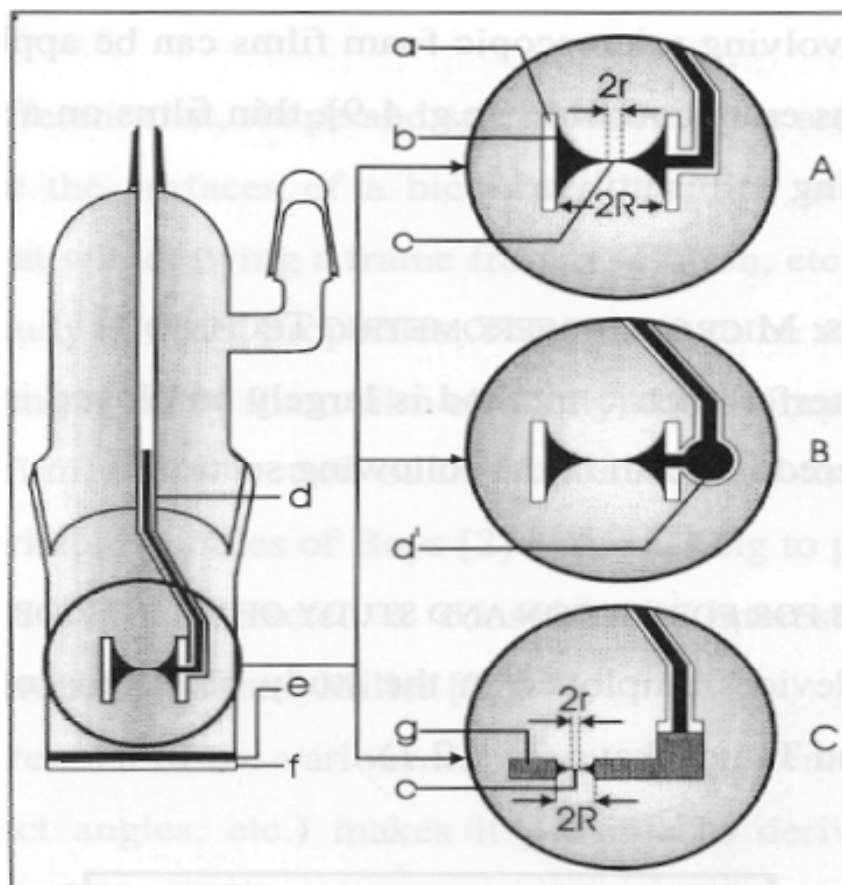
## Draining of foam films



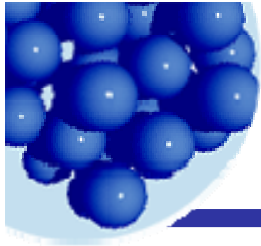
<http://ptcl.chem.ox.ac.uk/~rkt/tutorials/tutimages/foam.jpg>



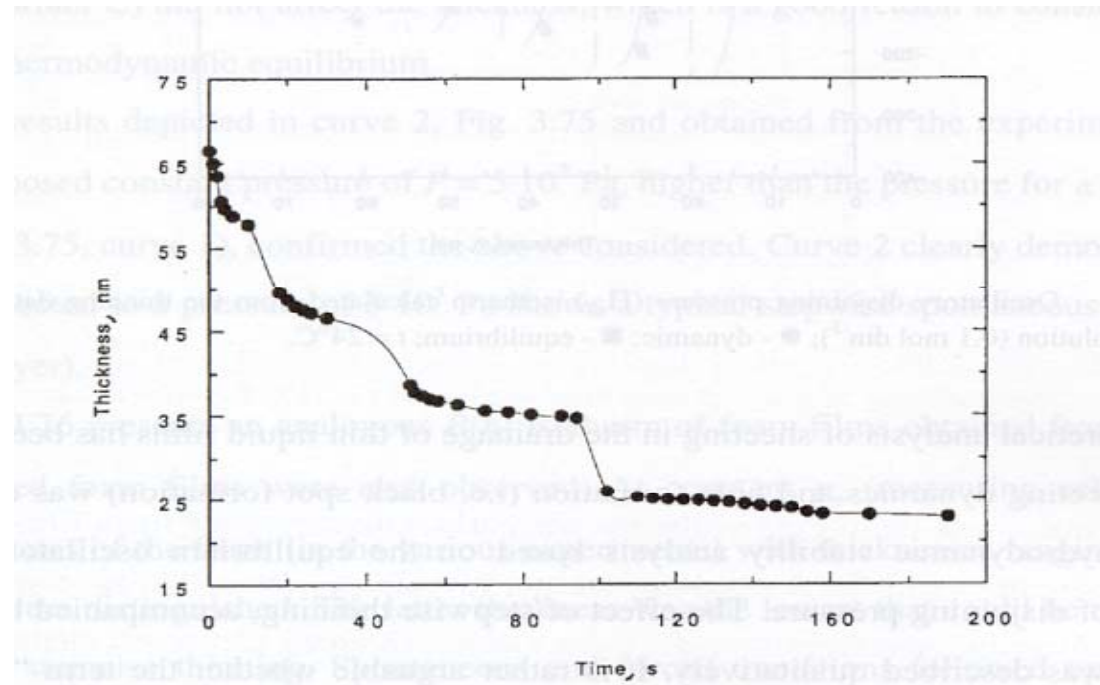
# Measuring film stability



Exerowa and Kruglyakov, p. 44

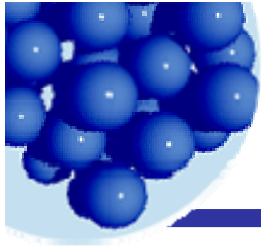


# Uneven film drainage

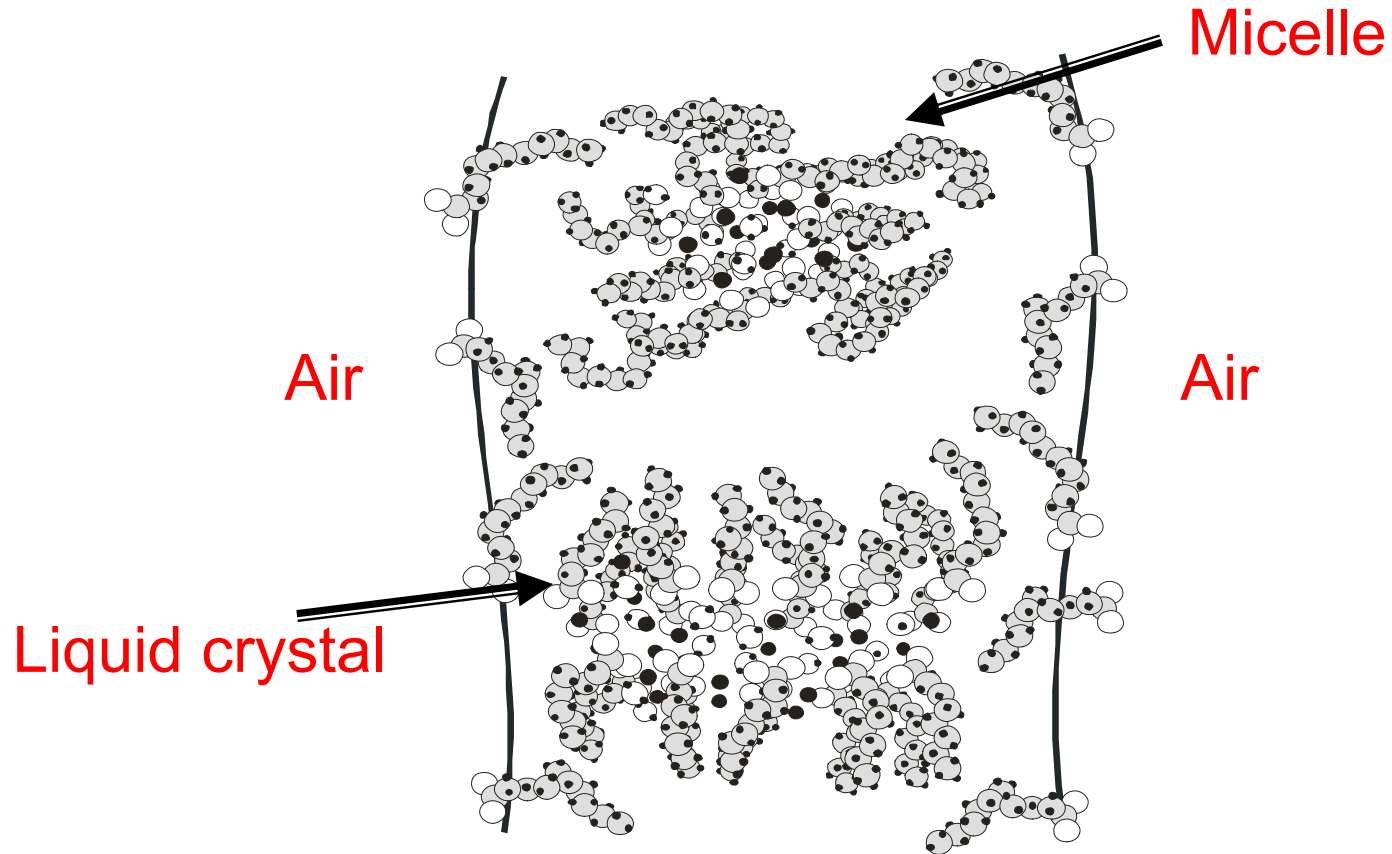


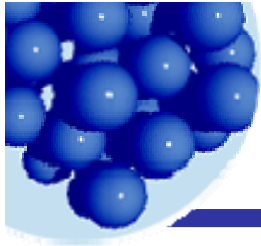
Wasan et al. discovered the stepwise thinning of thin films.  
The stable thicknesses are layers of close-packed micelles.

Exerowa and Kruglyakov, p. 221

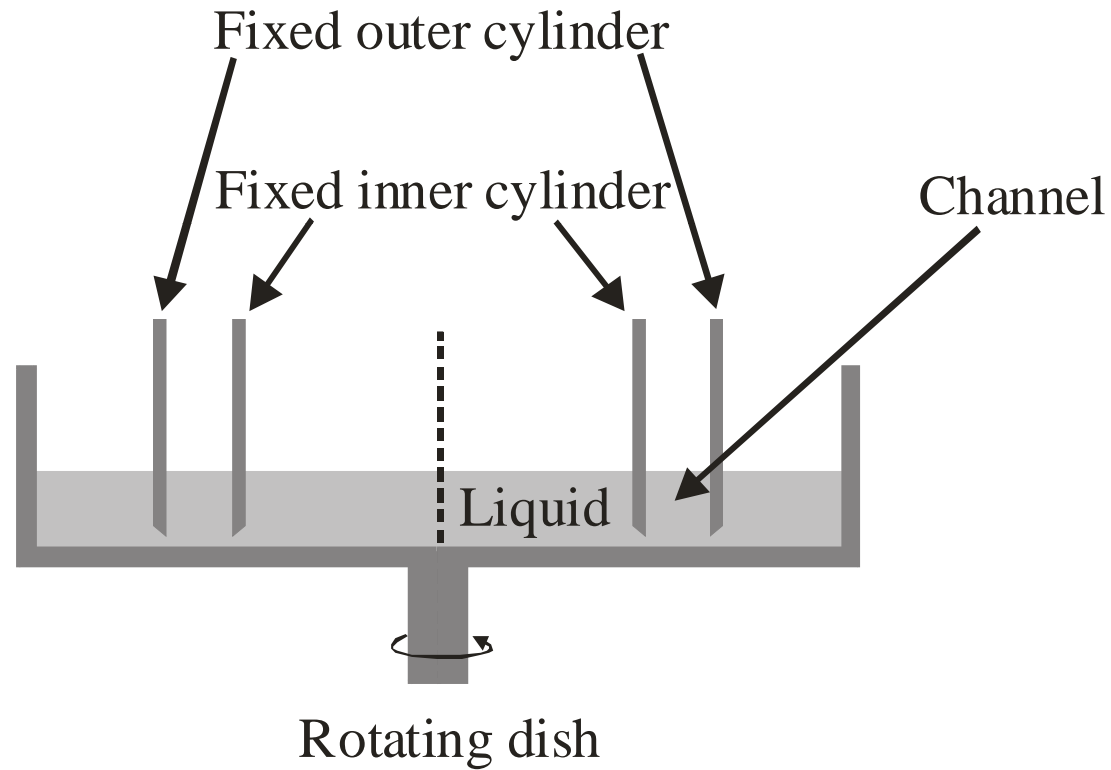


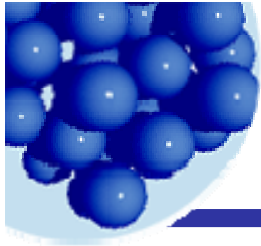
# Liquid crystals stabilize foams





# Deep-channel surface viscosimeter





## Elasticity of surface and thin films

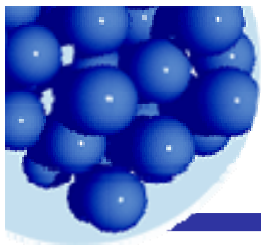
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**ADSORPTION IS SLOW !!!  
IN THIN FILMS EVEN SLOWER !!**

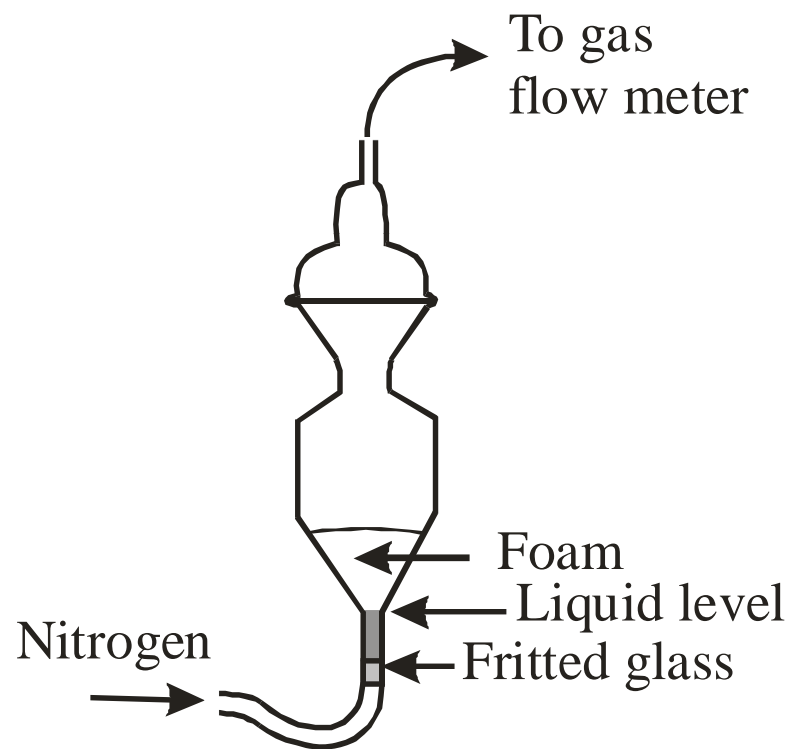
Elasticity is the ratio of the increase in surface tension from a relative increase in surface area. (For a foam film.)

$$E = \frac{2d\sigma}{d \ln A}$$

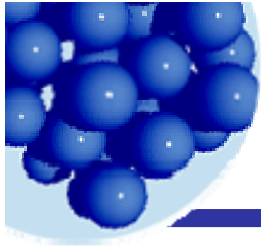
When the surface is not in equilibrium (the common case) with the bulk, this is a Marangoni effect.



# Dynamic foam stability



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



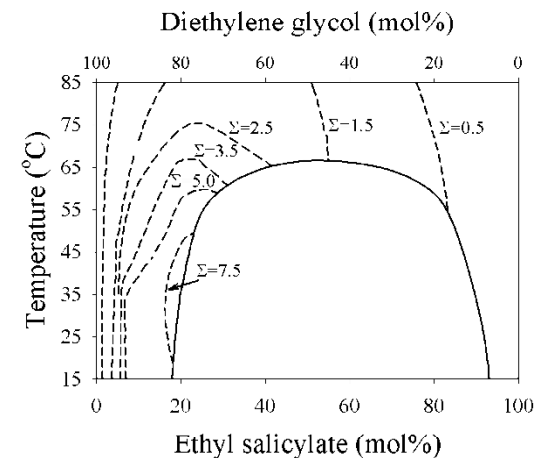
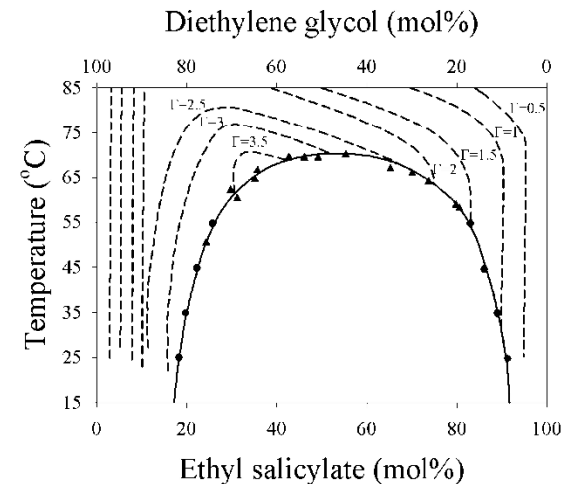
# Foaminess and the phase diagram

Not just solutions of "surfactants" foam.

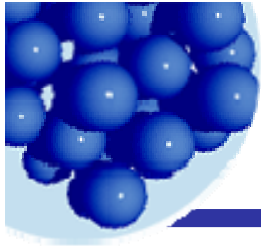
Partially miscible liquids in multiple components foam near the critical point (two components) or plait point (three or more components.)

Surface activity precedes phase separation. The "excess" at the interface stabilizes foam. If the separated phase has a lower surface tension, it will be a defoamer.

Morrison and Ross, p. 311

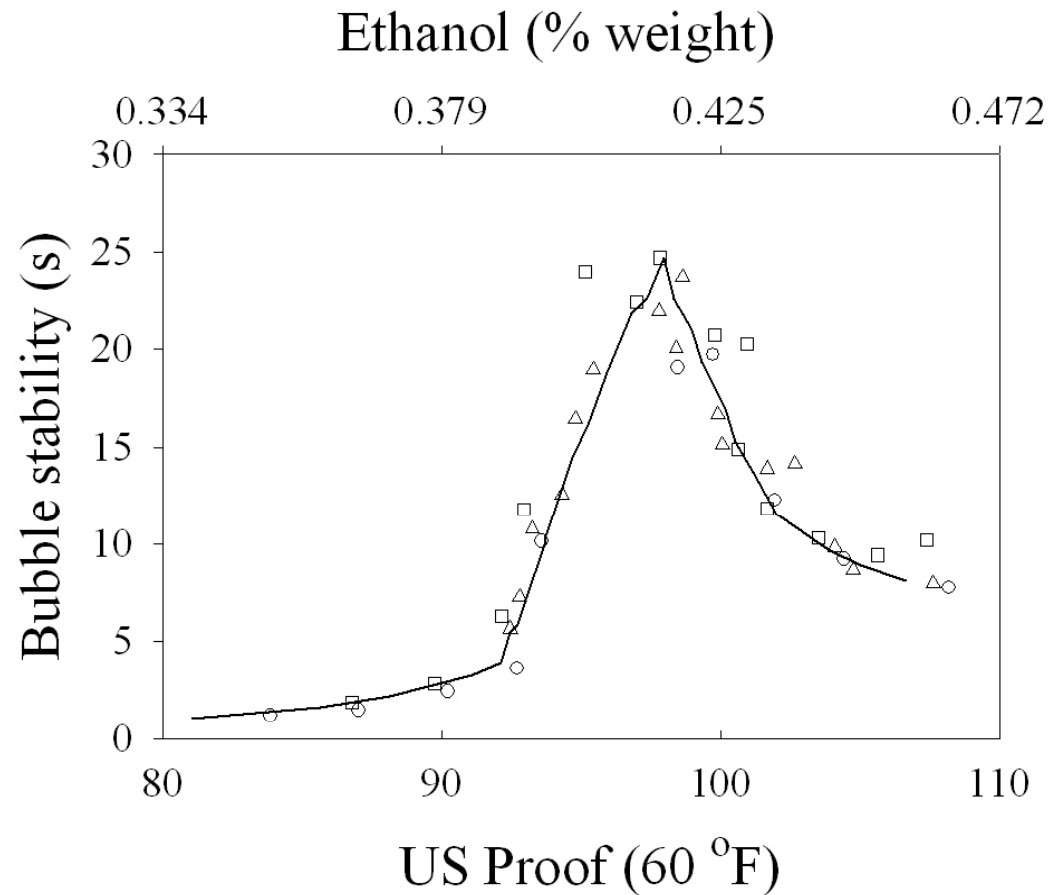


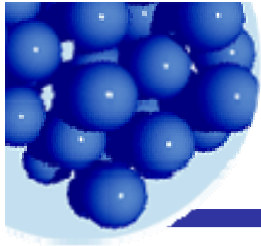




# Whiskey, proof, and foam?!

The Ross-Nishioka effect in fortified bourbon whiskey on dilution with water. Reading from right to left, as the solutions approach a phase boundary, bubble stability increases until phase separation creates a foam inhibitor.



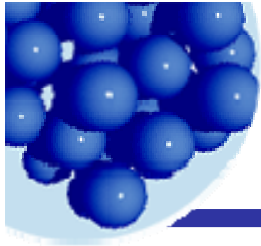


## Ross' Rule – Capillary effects appear near phase boundaries

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- 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.

Morrison and Ross, p.126



# Froth flotation

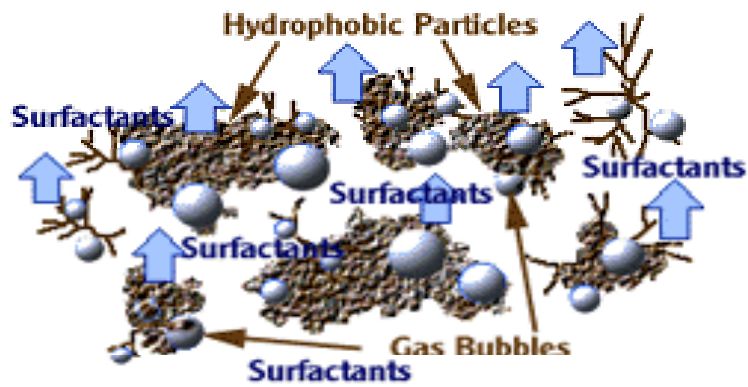
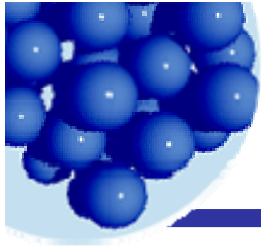


Figure 2. How does foam form?



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

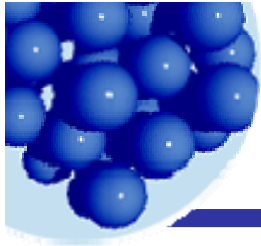
From the "Activated Sludge Pages"  
<http://www.scitrav.com/wwater/asp/>



# Three phase foams

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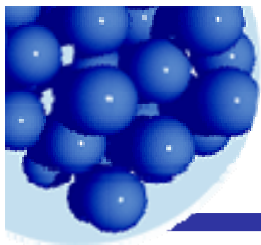
- Powders with finite (receding) contact angles sit at the air/liquid surface.
  - "Collectors" are sometimes added to aid this dewetting of particles.
  - The particles move with the bubble - flotation.
- Particles may stabilize thin films if they have low contact angles, holding the two interfaces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



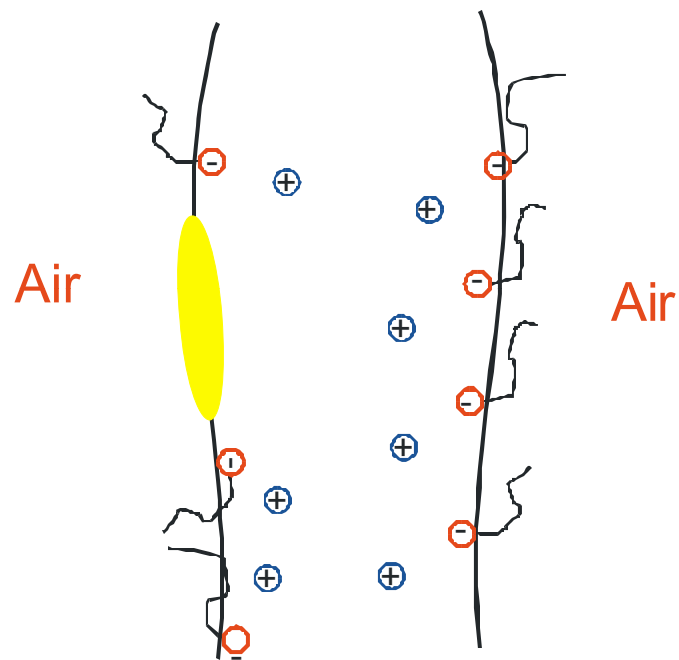
# Mechanisms of antifoaming

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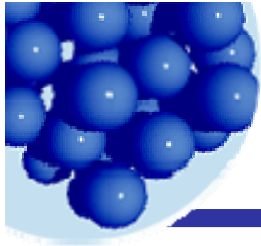
- Contact with a hydrophobic interface, such as Teflon/water, siliconized solid/water.
- Addition of an insoluble, low-surface-tension liquid to a standing foam. Typically, naturally occurring, oils, lard, fatty acids and alcohols, silicone oils,
- Presence of vapor of a volatile liquid.
- Contact with 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.



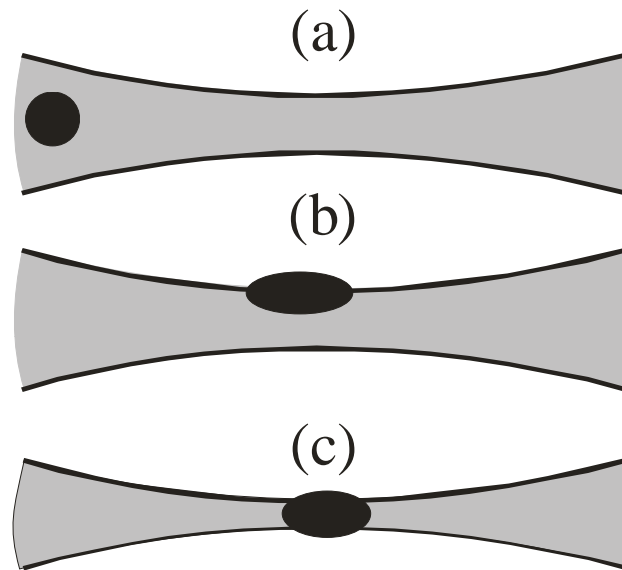
# Antifoams



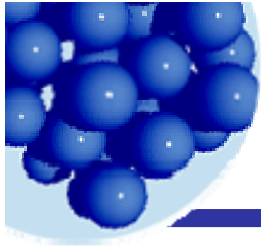
With an antifoam on one surface, electrostatic stabilization is lost.



# Antifoams



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



# Silicone antifoams

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- 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.