THE PHYSICS OF FOAM

- **Boulder School for Condensed Matter and Materials Physics**

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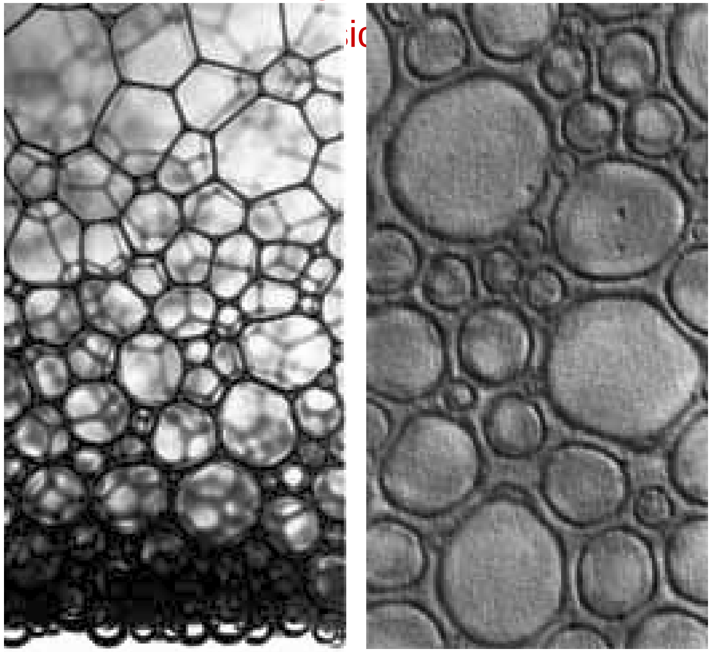
1. Introduction
- Formation
- Microscopics

2. Structure
- Experiment
- Simulation

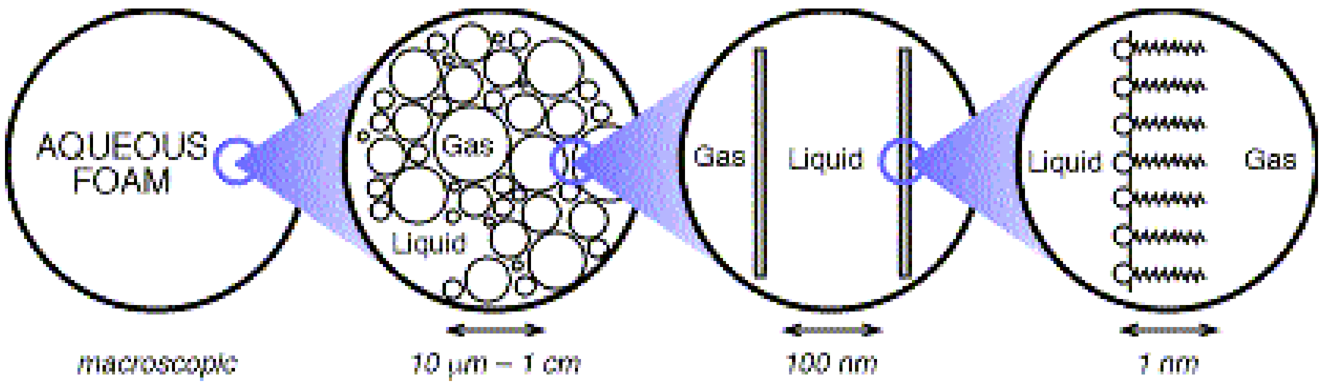
3. Stability
- Coarsening
- Drainage

4. Rheology
- Linear response
- Rearrangement & flow



Foam is…

- …a random packing of bubbles in a relatively small amount of liquid containing surface-active impurities
  - Four levels of structure:



  - Three means of time evolution:
    - Gravitational drainage
    - Film rupture
    - Coarsening (gas diffusion from smaller to larger bubbles)

Foam is…

- …a most unusual form of condensed matter
  - Like a gas:
    - volume ~ temperature / pressure
  - Like a liquid:
    - Flow without breaking
    - Fill any shape vessel
      - Under large force, bubbles rearrange their packing configuration
  - Like a solid:
    - Support small shear forces elastically
      - Under small force, bubbles distort but don’t rearrange

Foam is…

- **Everyday life:**
  - detergents
  - foods (ice cream, meringue, beer, cappuccino, ...)
  - cosmetics (shampoo, mousse, shaving cream, tooth paste, ...)
- **Unique applications:**
  - firefighting
  - isolating toxic materials
  - physical and chemical separations
  - oil recovery
  - cellular solids
- **Undesirable occurrences:**
  - mechanical agitation of multicomponent liquid
  - pulp and paper industry
  - paint and coating industry
  - textile industry
  - leather industry
  - adhesives industry
  - polymer industry
  - food processing (sugar, yeast, potatoes)
  - metal treatment
  - waste water treatment
  - polluted natural waters

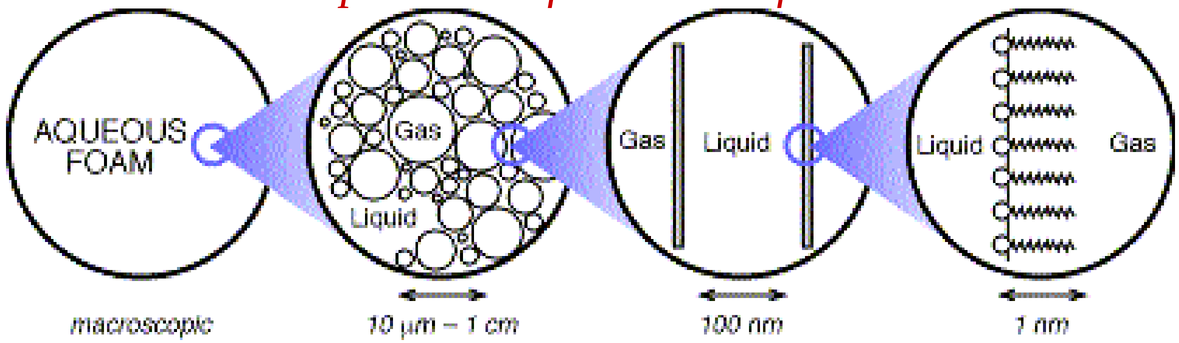
- familiar!
- important!

- *need to control stability and mechanics*
- *must first understand microscopic structure and dynamics…*

Condensed-matter challenge

- To understand the stability and mechanics of bulk foams in terms of the behavior at microscopic scales

bubbles are the "particles" from which foams are assembled

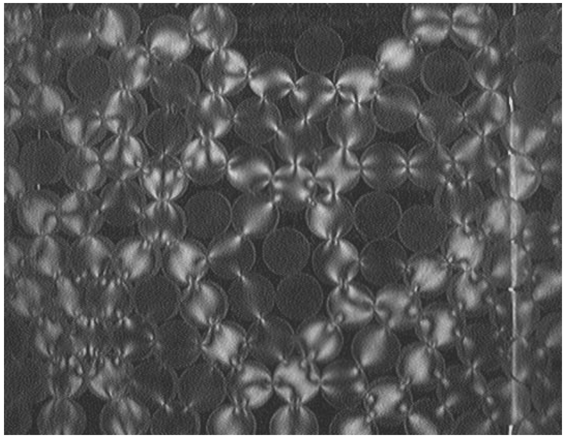


  - Easy to relate surfactant-film and film-bubble behaviors
  - Hard to relate bubble-macro behavior
    - Opaque: *no simple way to image structure*
    - Disordered: *no periodicity*
    - $k_B T$ << interaction energy: *no stat-mech.*
    - Flow beyond threshold: *no linear response*

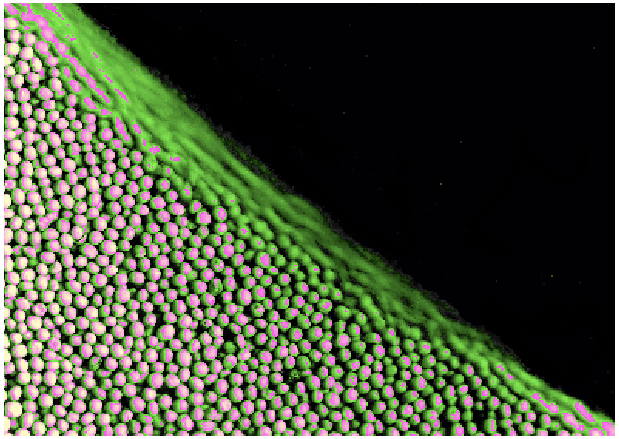
- hard problems!
- new physics!

Jamming

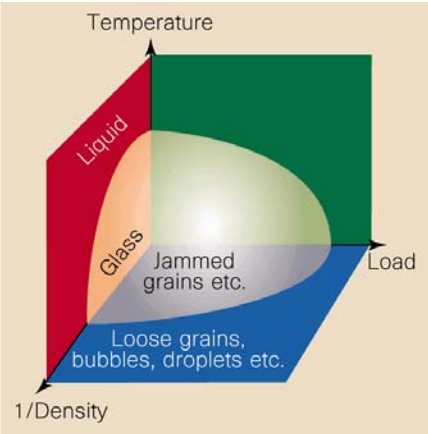
- Similar challenge for seemingly unrelated systems
  - Tightly packed collections of bubbles, droplets, grains, cells, colloids, fuzzy molecules, tectonic plates,….
    - jammed/solid-like: *small-force / low-temperature / high-density*
    - fluid/liquid-like: *large-force / high-temperature / low-density*



force-chains (S. Franklin)



avalanches (S.R. Nagel)



universality?

Foam Physics Today

- visit the websites of these Summer 2002 conferences to see examples of current research on aqueous foams
  - Gordon Research Conference on Complex Fluids
    - Oxford, UK
  - EuroFoam 2002
    - Manchester, UK
  - Foams and Minimal Surfaces
    - Isaac Newton Institute for Mathematical Sciences
  - Geometry and Mechanics of Structured Materials
    - Max Planck Institute for the Physics of Complex Systems

after these lectures, you should be in a good position to understand the issues being addressed & progress being made!

General references

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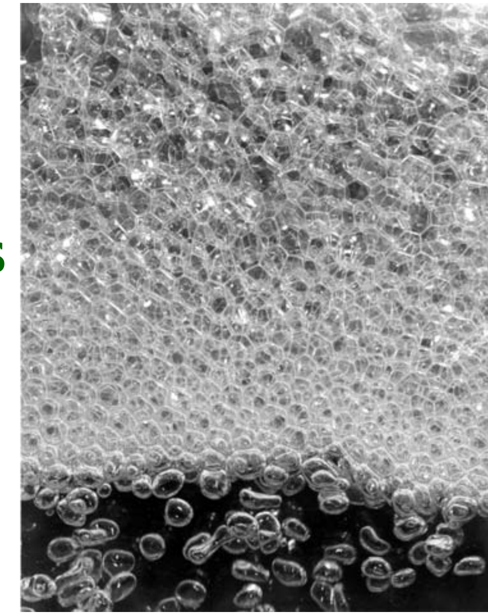
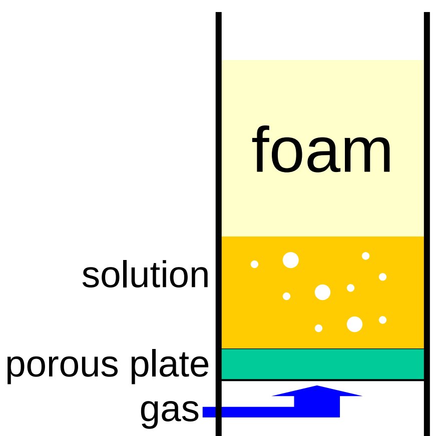
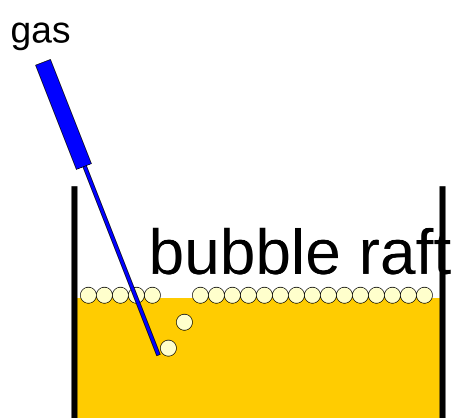
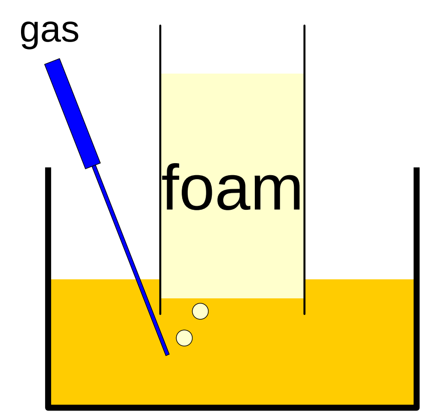
Foam production I.

- Shake, blend, stir, agitate, etc.
  - Uncontrolled / irreproducible
  - Unwanted foaming of multicomponent liquids
- Sparge = blow bubbles
  - Polydisperse or monodisperse
  - Uncontrolled/non-uniform liquid fraction



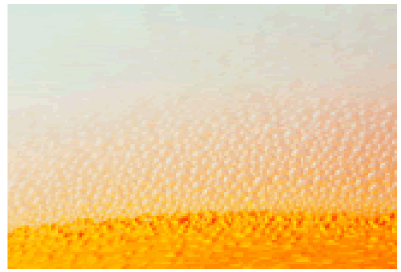




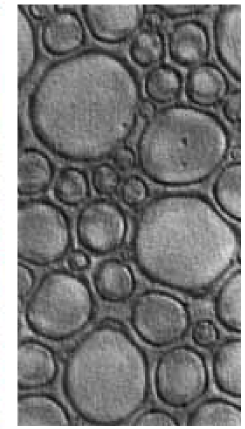


Foam production II.

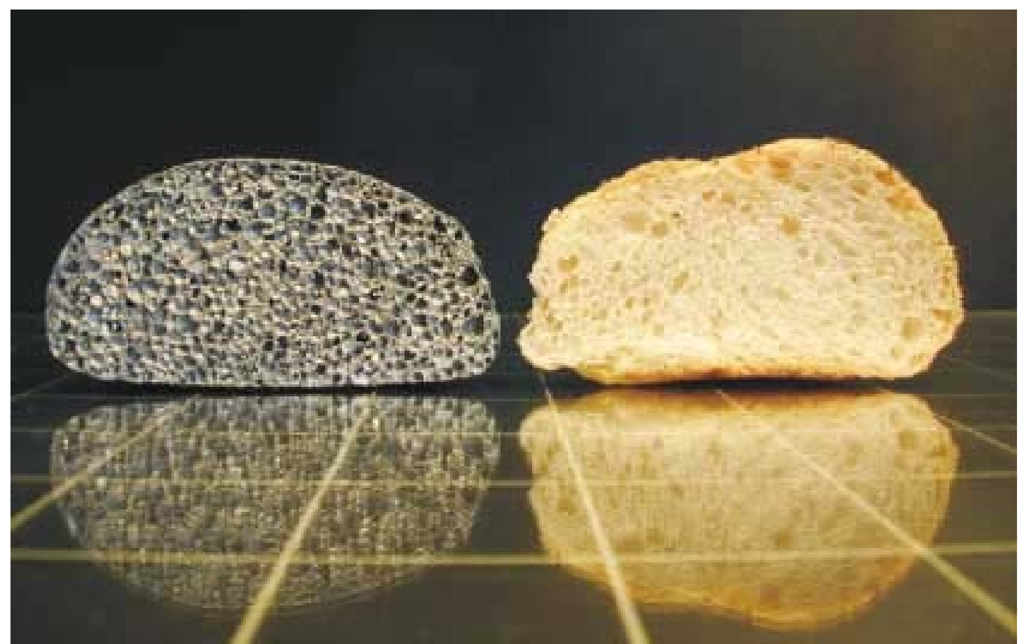
- *in-situ* release / production of gas
  - nucleation
    - eg CO_2 in beer



  - aerosol:
    - eg propane in shaving cream
    - small bubbles!

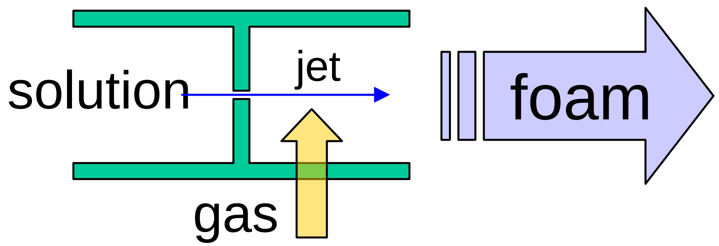


  - active:
    - eg H_2 in molten zinc
    - eg CO_2 from yeast in bread



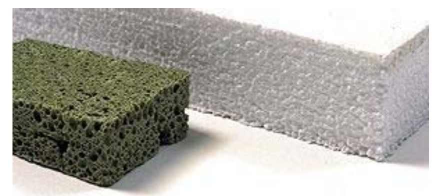
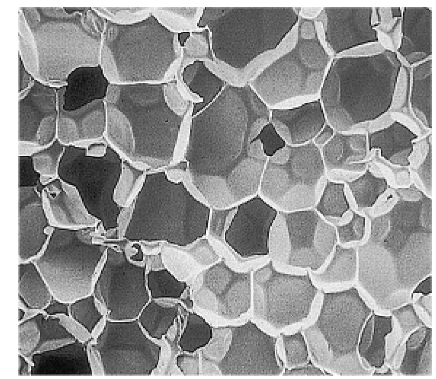
Foam production III.

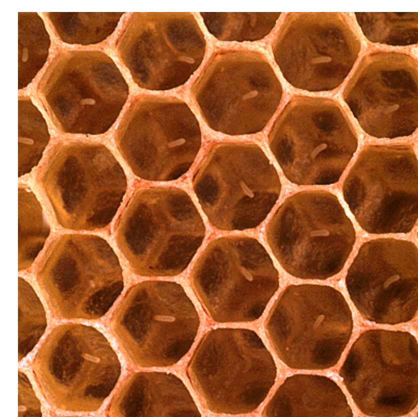
- turbulent mixing of thin liquid jet with gas
  - vast quantities
  - small polydisperse bubbles
  - controlled liquid fraction
    - lab samples
    - firefighting
    - distributing pesticides/dyes/etc.
    - covering landfills
    - supressing dust
    - …



Foam production IV.

- many materials can be similarly foamed
  - nonaqueous liquids (oil, ferrofluids,…)
  - polymers (styrofoam, polyurethane,…)
  - metals
  - glass
  - concrete
- variants found in nature
  - cork
  - bone
  - sponge
  - honeycomb



Foams produced by animals

- spittle bug:

- cuckoo spit / froghoppers:

- stickleback-fish’s nest

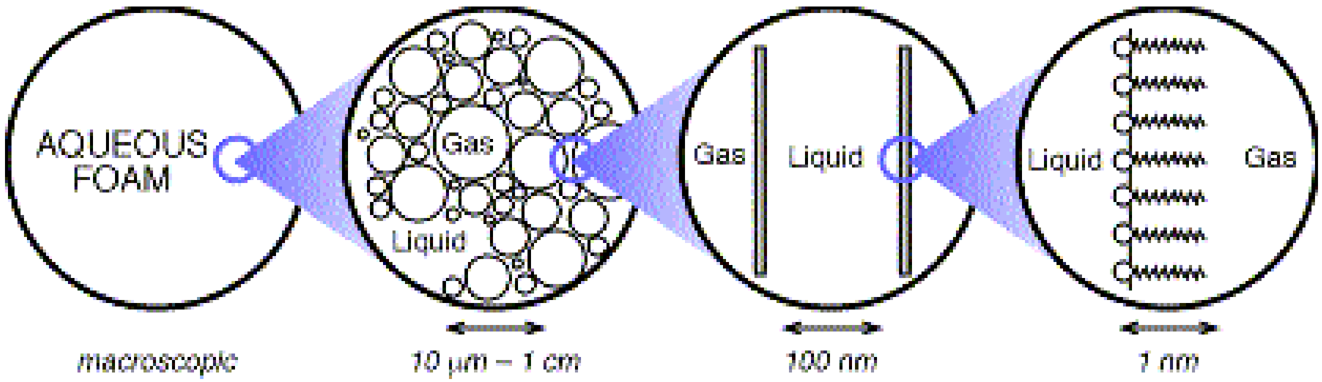
Foam production V.

- antifoaming agents
  - prevent foaming or break an existing foam

- mysterious combination of surfactants, oils, particles,…

Microscopic behavior

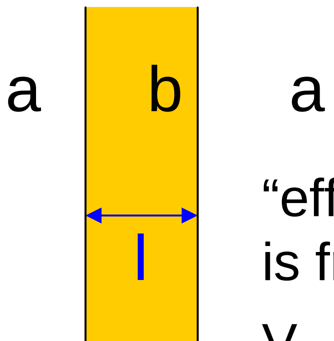
- look at progressively larger length scales…



  - surfactant solutions
  - soap films
  - local equilibrium & topology

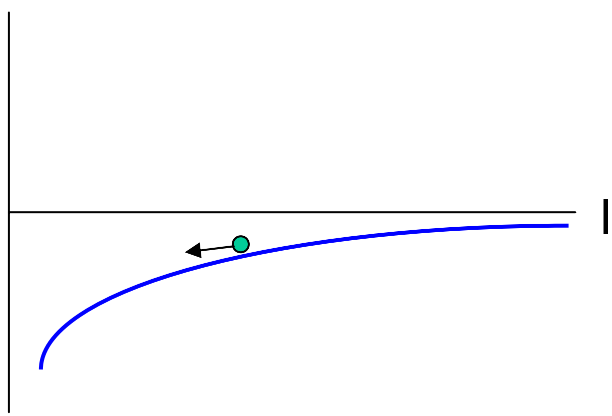
Pure liquid

- bubbles quickly coalesce – no foam
  - van der Waals force prefers monotonic dielectric profile; therefore, bubbles attract:



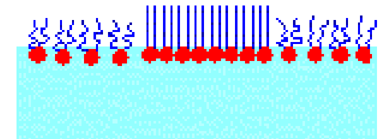
"effective interface potential"
is free energy cost per unit area:

$V_{vdw}(l) = -A/12\pi l^2$, A=Hamaker constant

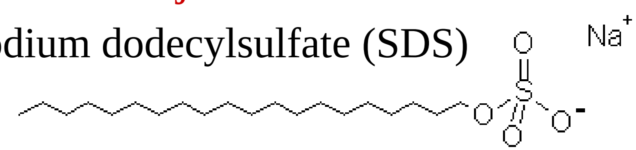


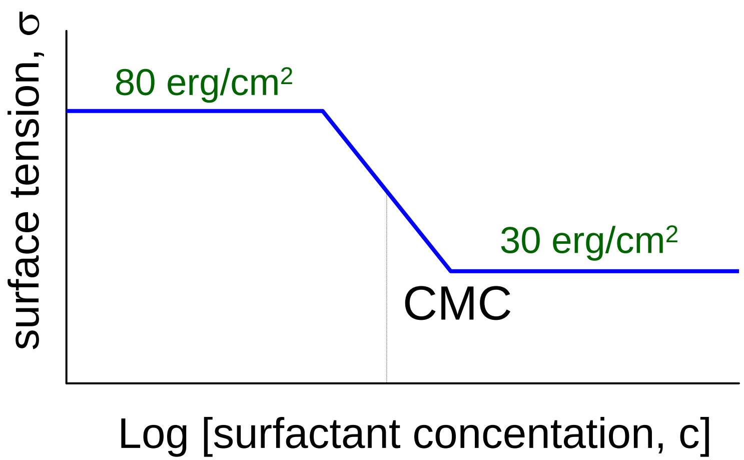
Surfactant solution

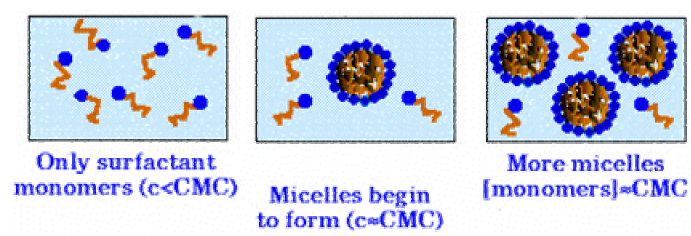
- **<u>surf</u>**ace **<u>act</u>**ive agent – adsorbs at air/water interface
  - head: hydrophilic (eg salt)
  - tail: hydrophobic (eg hydrocarbon chain)
    - lore for good foams…
      - chain length: short enough that the surfactant is soluble
      - concentration: just above the "critical micelle concentration"



eg sodium dodecylsulfate (SDS)



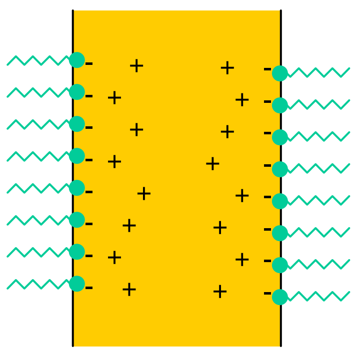




{NB: lower σ doesn't stabilize the foam…

Electrostatic “double-layer”

- adsorbed surfactants dissociate, cause repulsion necessary to overcome van der Waals and hence stabilize the foam
  - electrostatic
  - entropic (dominant!)



free energy cost per unit area:

$V_{DL}(l) = (64 k_B T \rho / K_D) \mathrm{Exp}[-K_D l]$,

ρ = electrolyte concentration

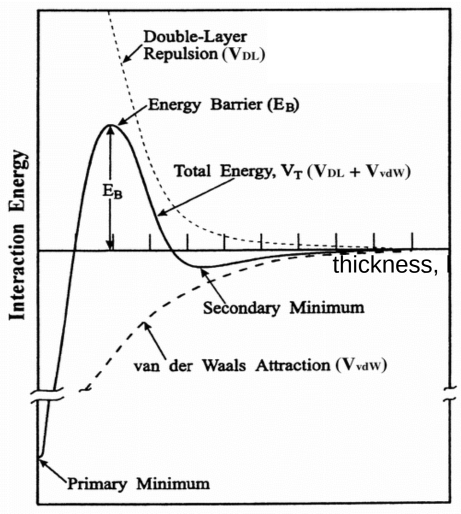
$K_D^{-1} \sim \rho^{-1/2}$ = Debye screening length

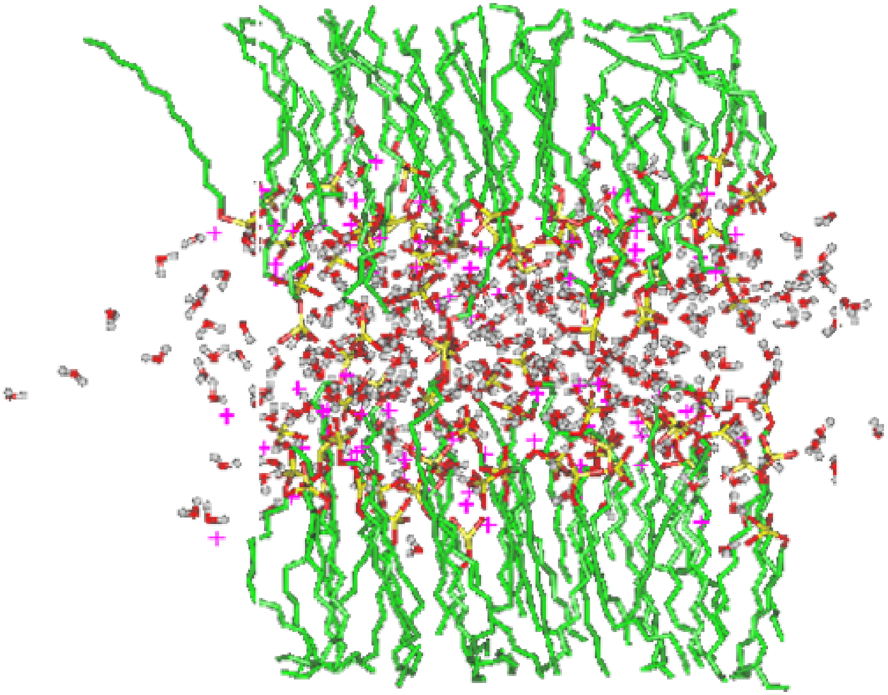
  - NB: This is similar to the electrostatic stabilization of colloids

Soap film tension

- film tension / interface potential / free energy per area:

  $\gamma(l) = 2\sigma + V_{VDW}(l) + V_{DL}(l) \;\; \sim \;\; 2\sigma$

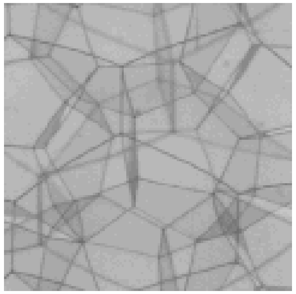


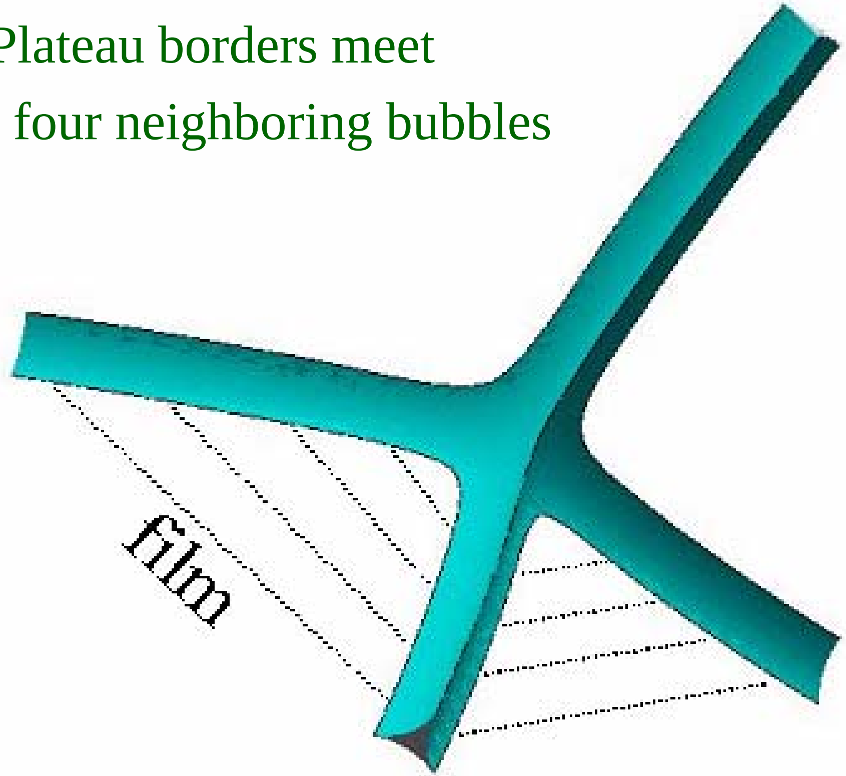


- disjoining pressure: $\Pi(l) = -d\gamma/dl$
  - vanishes at equilibrium thickness, $l_{eq} \sim K_D^{-1}$ (30-3000Å)

Film junctions

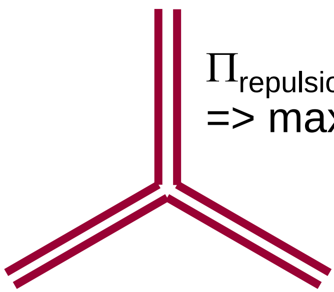
- Plateau border
  - scalloped-triangular channel where three films meet
  - the edge shared by three neighboring bubbles
- Vertex
  - region where four Plateau borders meet
  - the point shared by four neighboring bubbles



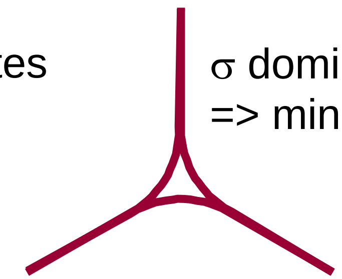


Liquid distribution

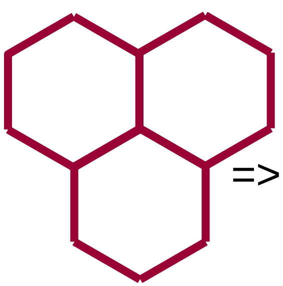
- division of liquid between films-borders-vertices
  - repulsion vs surface tension
  - wet vs dry



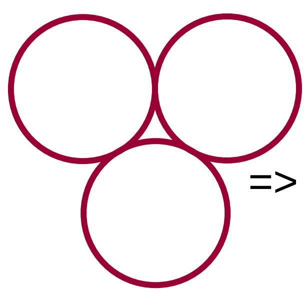
$\Pi_{repulsion}$ dominates
=> maximize l



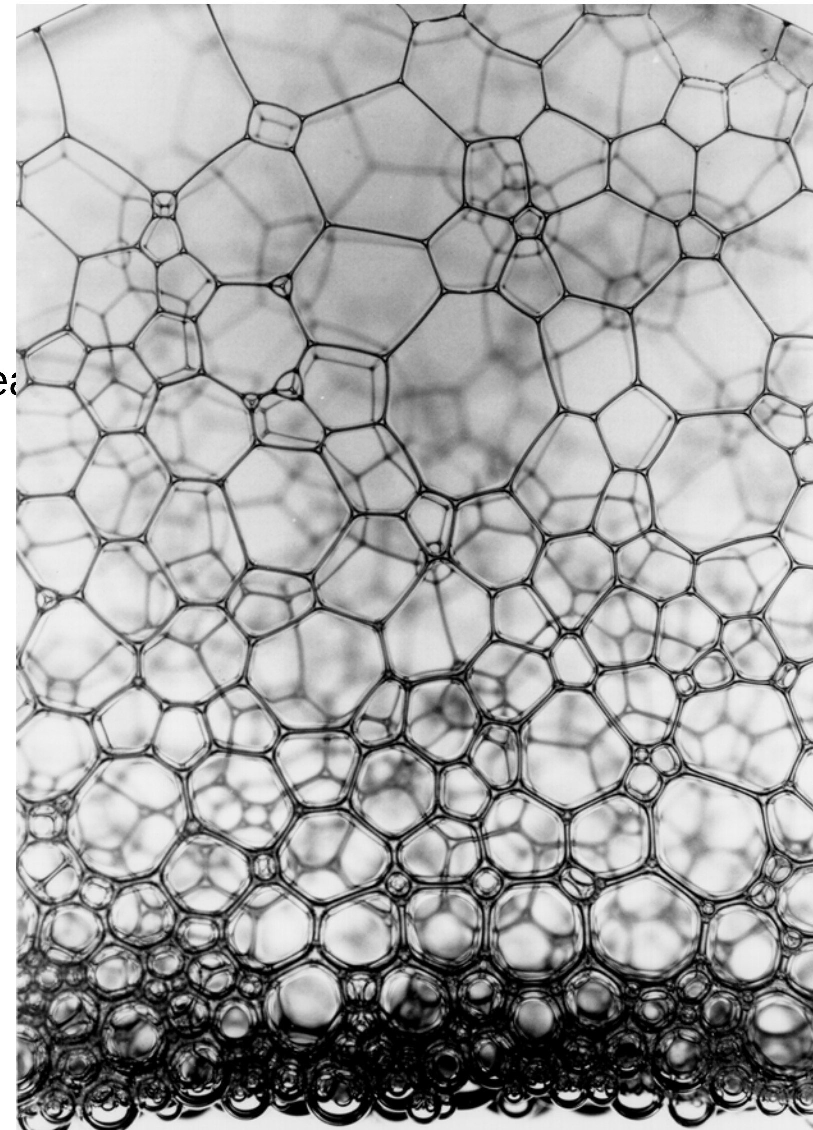
σ dominates
=> minimize area



dry
=> polyhedral



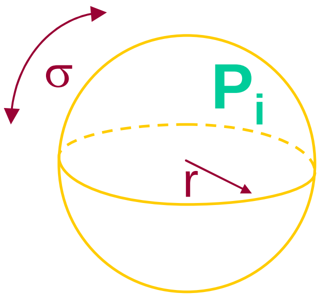
wet
=> spherical



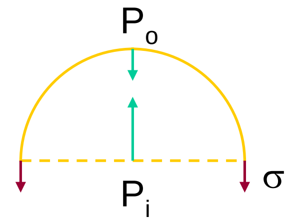
Laplace's law

- the pressure is greater on the inside a curved interface

due to surface tension, σ = energy / area = force / length



$P_i = P_o + 2\sigma/r$ {in general, $\Delta P = \sigma(1/r_1 + 1/r_2)$}

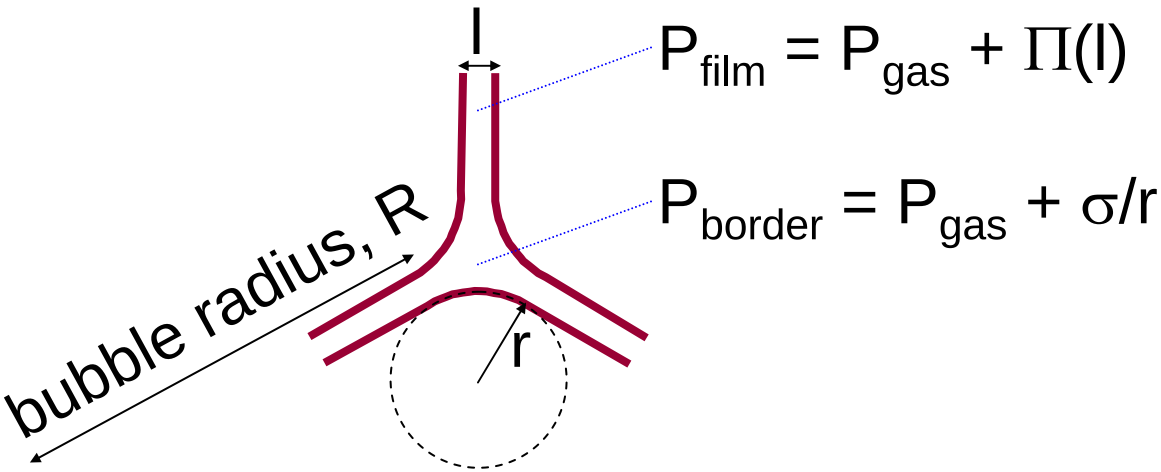


- forces on half-sphere:
  - $\Sigma F_{up} = P_i\pi r^2 - P_o\pi r^2 - 2\pi\sigma r = 0$

- energy change = pressure x volume change:
  - $dU = (\Delta P)4\pi r^2 dr$, where $U(r) = 4\pi r^2\sigma$

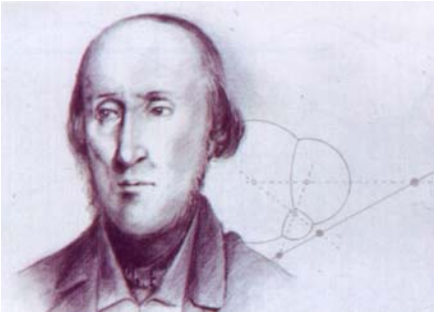
Liquid volume fraction

- liquid redistributes until liquid pressure is same everywhere



- typically: film thickness l << border radius r << bubble radius R
  - liquid volume fraction scales as $\varepsilon \sim (lR^2 + r^2R + r^3)/R^3 \sim (r/R)^2$
  - most of the liquid resides in the Plateau borders
    - PB's scatter light…
    - PB's provide channel for drainage…

Plateau's rules for dry foams

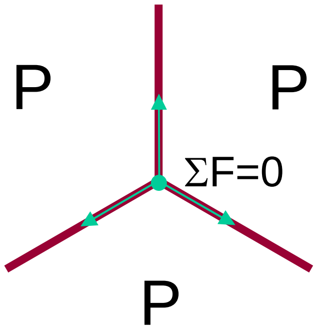


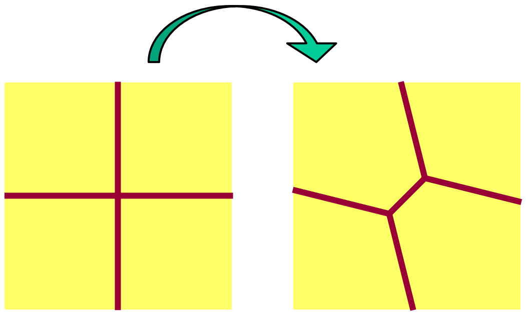
- for mechanical equilibrium:
  - i.e. for zero net force on a Plateau border,
  - zero net force on a vertex,
  - and $\Sigma\Delta P=0$ going around a closed loop:

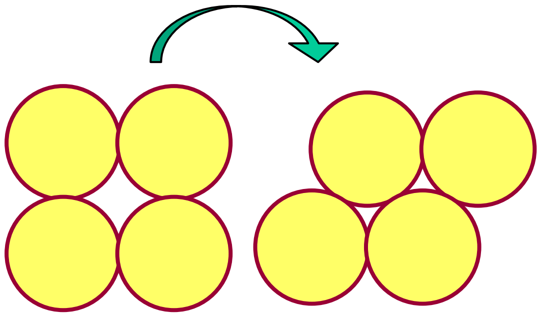
(1) films have constant curvature & intersect three at a time at 120^o

(2) borders intersect four at a time at $\cos^{-1}(1/3)=109.47^o$

- rule #2 follows from rule #1
- both are obviously correct if the films and borders are straight:

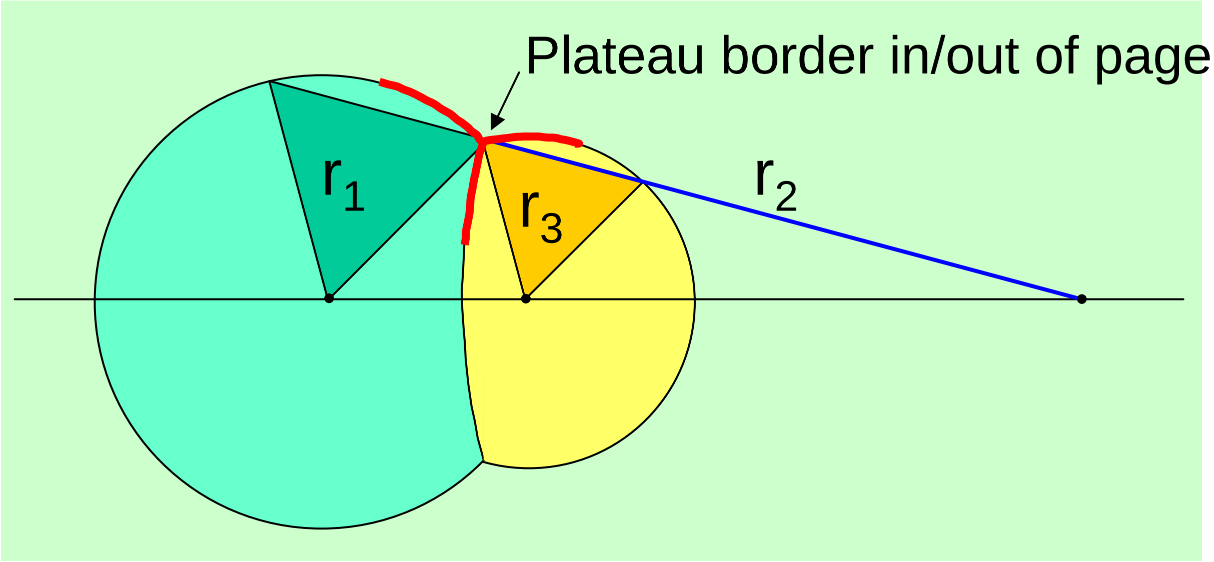






Rule #1 for straight borders

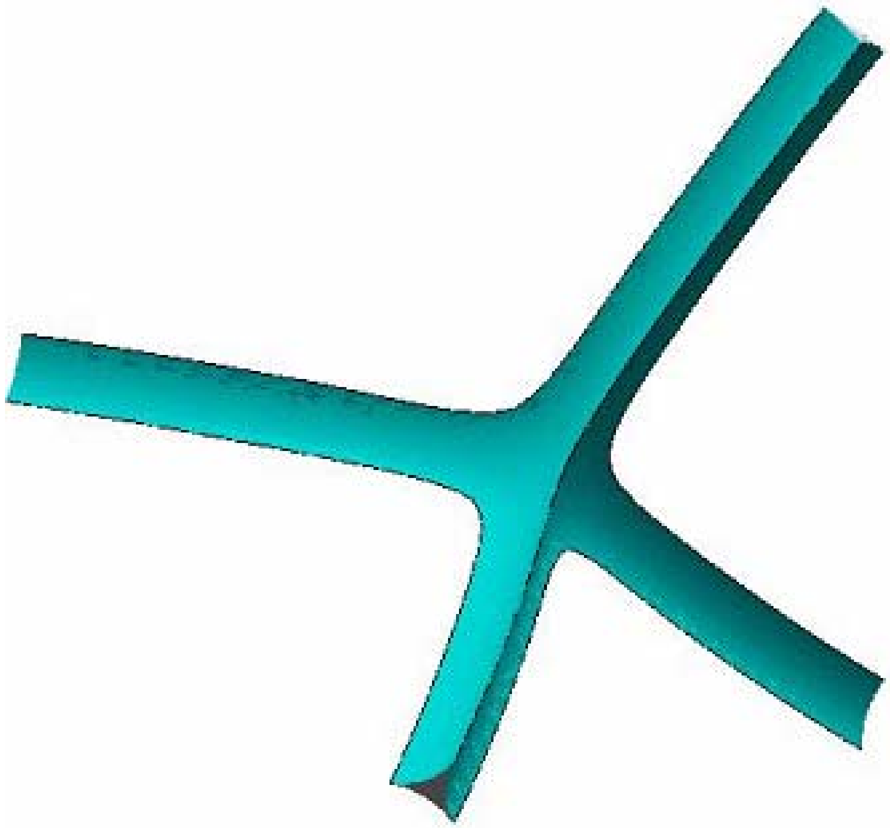
- choose r_1 and orientation of equilateral triangle
- construct r_2 from extension down to axis
- construct r_3 from inscribed equilateral triangle
    - NB: centers are on a line



- films meet at 120° (triangles meet at 60°-60°-60°, and are normal to PB's)
- similar triangles give $(r_1+r_2)/r_1 = r_2/r_3$, i.e. $1/r_1 + 1/r_2 = 1/r_3$ and so $\Sigma P=0$

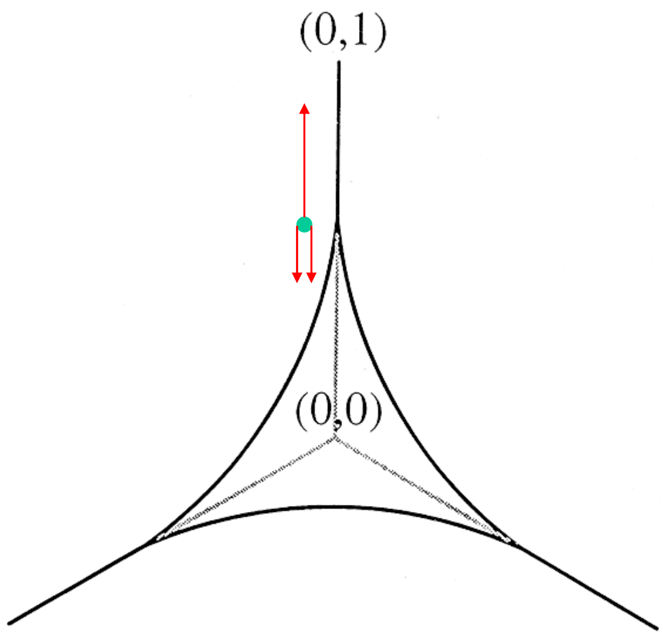
Curved Plateau borders

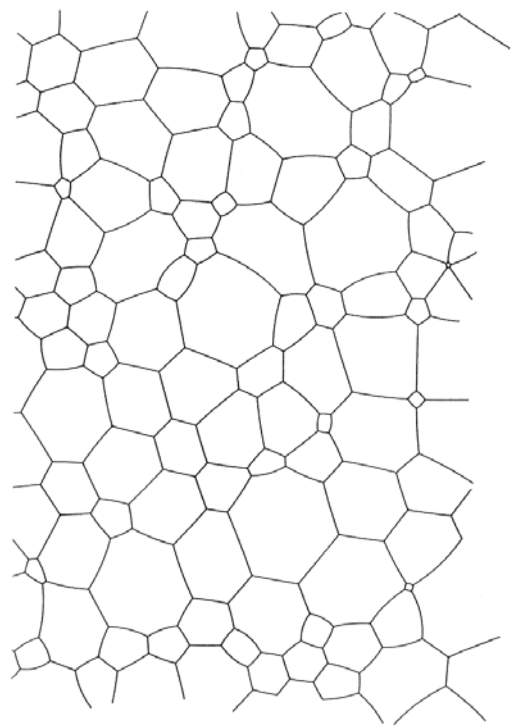
- proof of Plateau’s rules is not obvious!
  - established in 1976 by Jean Taylor

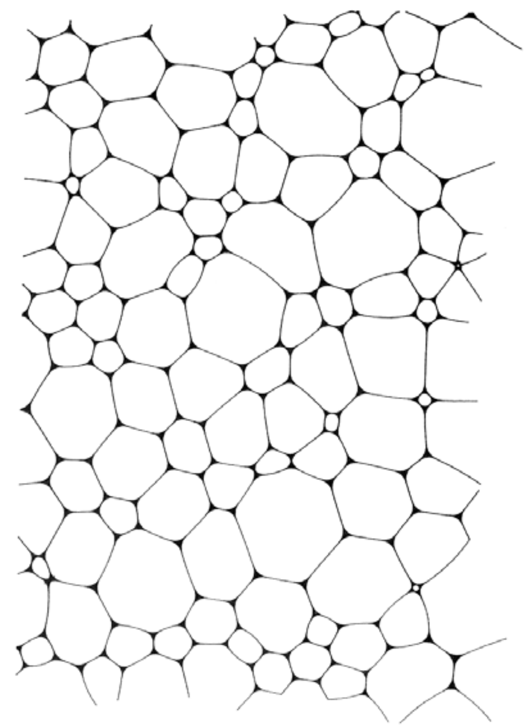


Decoration theorem for wet foams

- for d=2 dimensions, an equilibrium wet foam can be constructed by *decorating* an equilibrium dry foam
    - – can you construct an elementary proof?
        - PB's are circular arcs that join tangentially to film
        - theorem fails in d=3 due to PB curvature







Next time…

- periodic foam structures
- disordered foam structures
  - experiment
  - simulation