

THE PHYSICS OF FOAM

- Boulder School for Condensed Matter and Materials Physics**

July 1-26, 2002: Physics of Soft Condensed Matter

1. Introduction

Formation

Microscopics

2. Structure

Experiment

Simulation

3. Stability

Coarsening

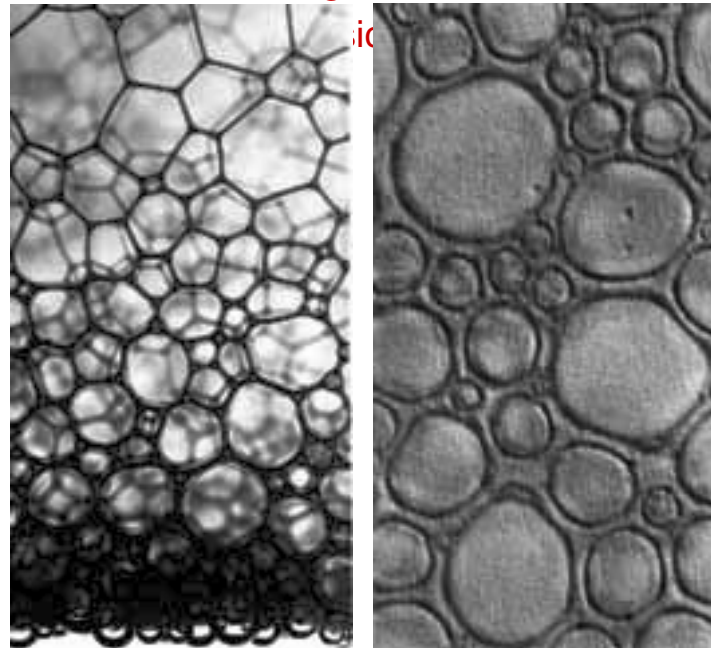
Drainage

4. Rheology

Linear response

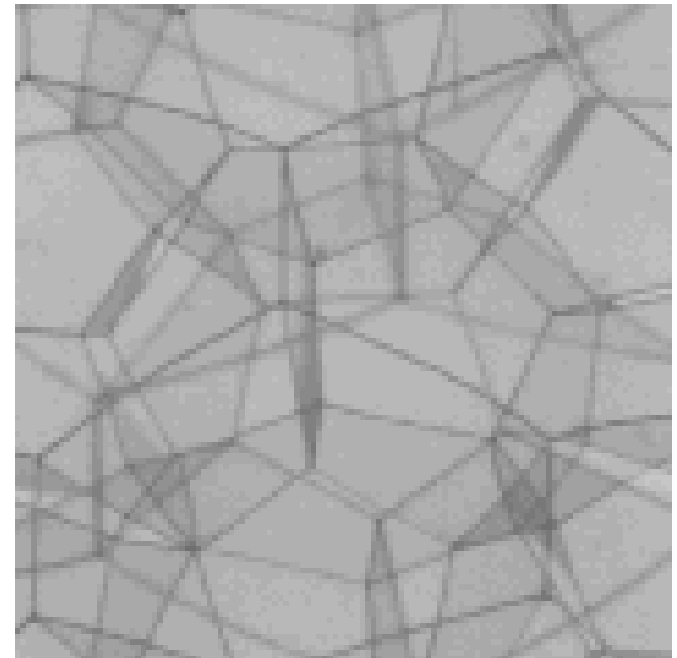
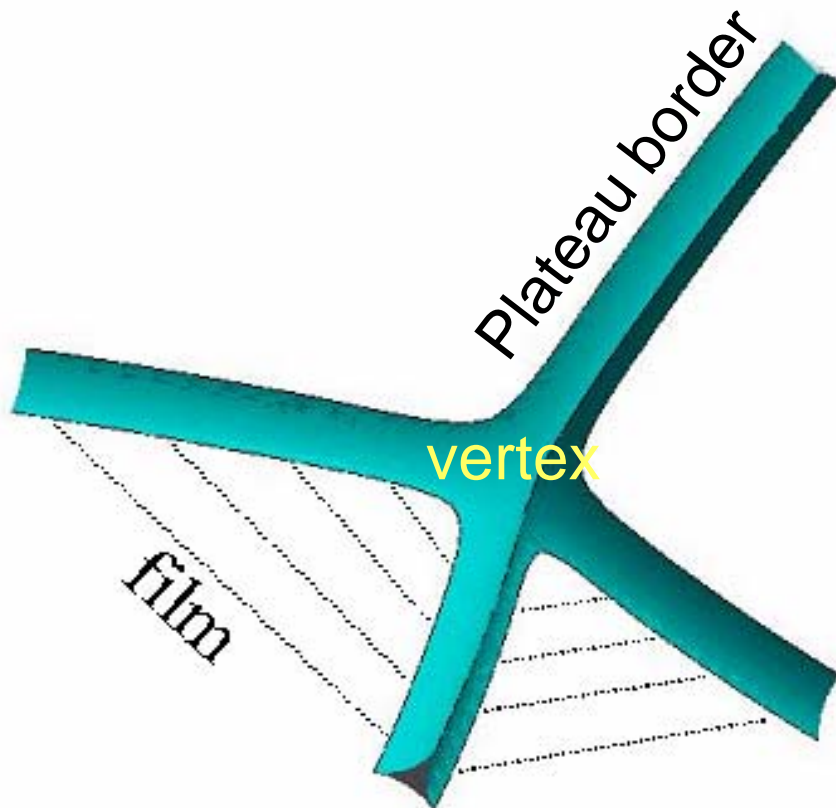
Rearrangement & flow

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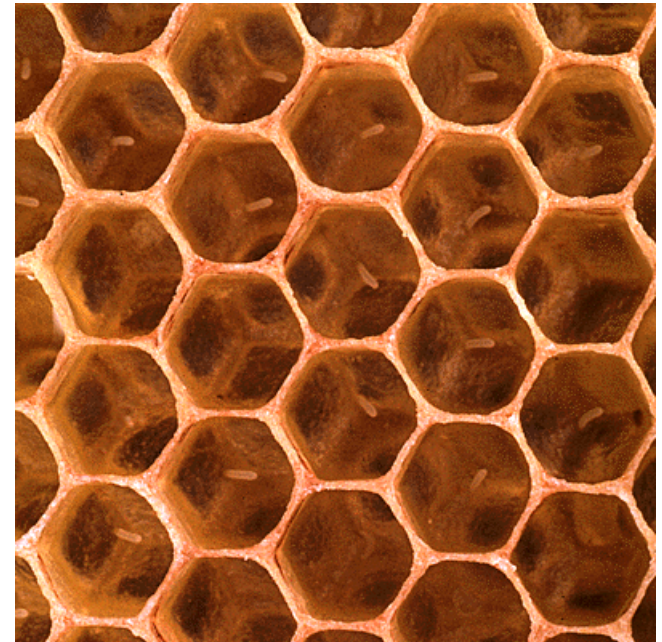
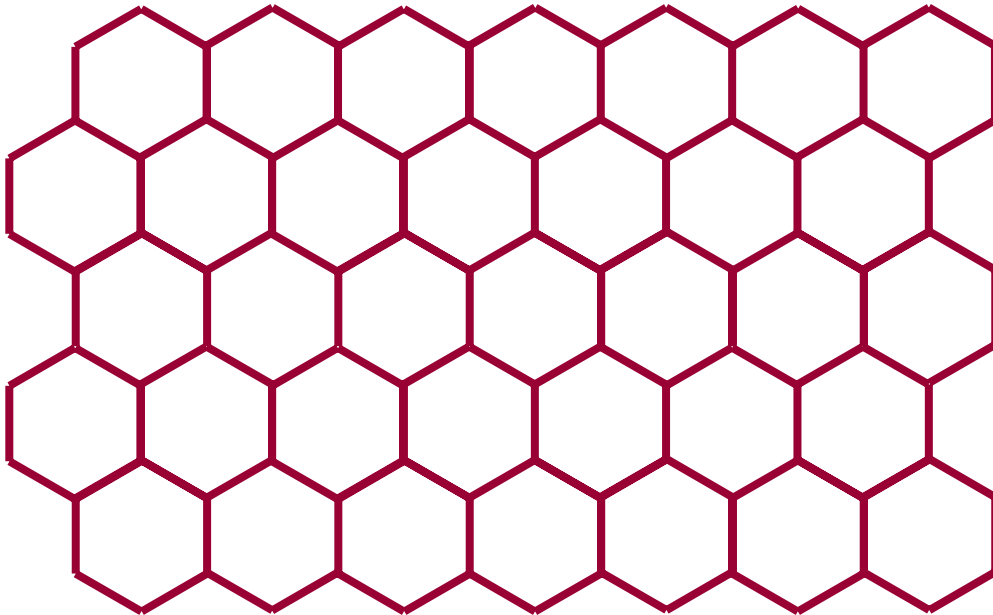
local structure recap

- liquid fraction $\varepsilon \sim [(\text{border radius } r) / (\text{bubble radius } R)]^2$
- Plateau's rules for mechanical equilibrium:
 - (1) films have constant curvature & intersect three at a time at 120°
 - (2) Plateau borders intersect four at a time at $\cos^{-1}(1/3)=109.47^\circ$

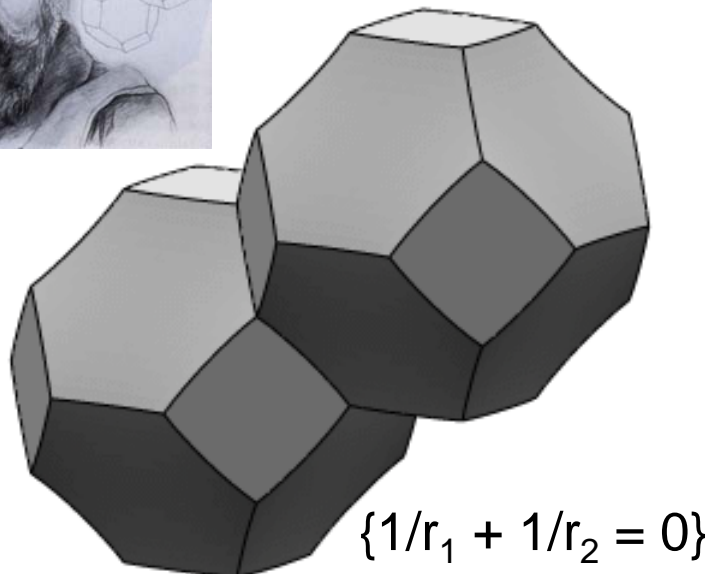


Periodic foams, 2D

- the simplest structure to satisfy Plateau's rules is a honeycomb
 - seems obvious, but only proved in 2001 by T.C. Hales to be the partitioning of 2D space into cells of equal area with the minimum perimeter



- it's not possible to satisfy Plateau's rules with regular solids having flat faces & straight Plateau borders
 - Kelvin foam: like Wigner-Seitz cell for BCC lattice, but with films and Plateau borders curved to satisfy Plateau
 - tetrakaidecahedron (14 sided): 6 quadrilaterals + 8 hexagons



$$\{1/r_1 + 1/r_2 = 0\}$$



Honeycomb for a 4D bee?

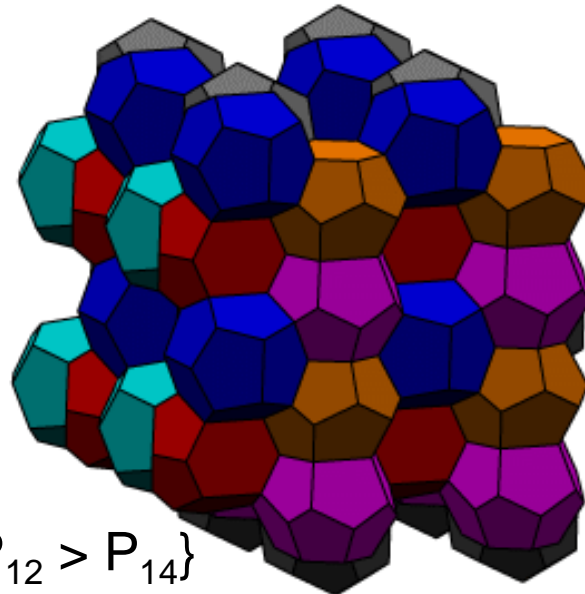
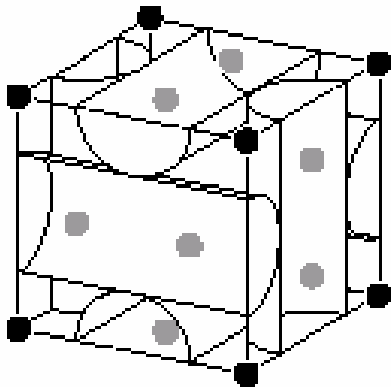
- Bees build a 2D foam that minimizes perimeter/cell
- What foam structure minimizes area at unit cell volume?
 - values for Wigner-Seitz cells curved according to Plateau
 - SC {1x1x1}: 6
 - FCC: 5.34539
 - BCC/Kelvin: 5.30628
 - {sphere: $(36\pi)^{1/3} = 4.83598$ }

Long believed to be the optimal 3D periodic foam

A15/Weaire-Phelan foam

- BCC/Kelvin: 5.30628
- A15/Weaire-Phelan: 5.28834
 - constructed from *two* different cell types
 - tetraikaidecahedron: 12 pentagons and 2 opposing hexagons
 - these stack into three sets of orthogonal columns
 - dodecahedron: 12 pentagons
 - these fit into interstices between columns

A new champion!
(0.3%
improvement)

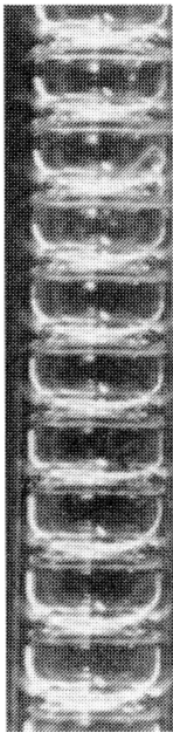


$$\{P_{12} > P_{14}\}$$

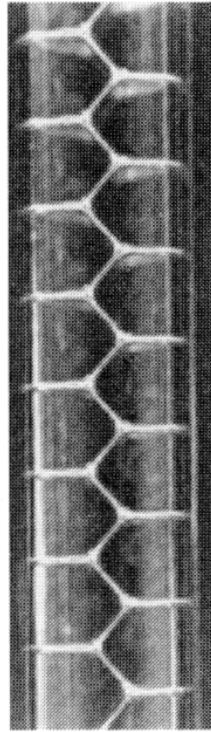


Bubbles in a tube

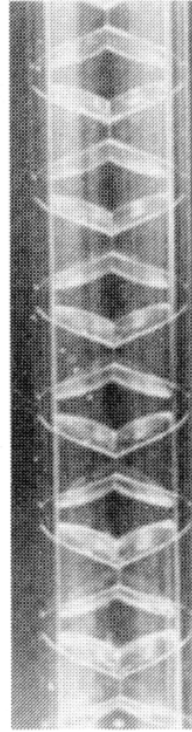
- other ordered structures can readily be produced by blowing monodisperse bubbles into a tall tube:



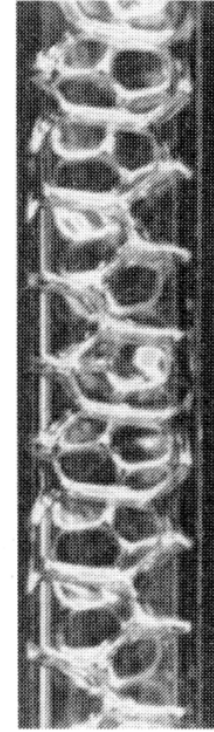
bamboo



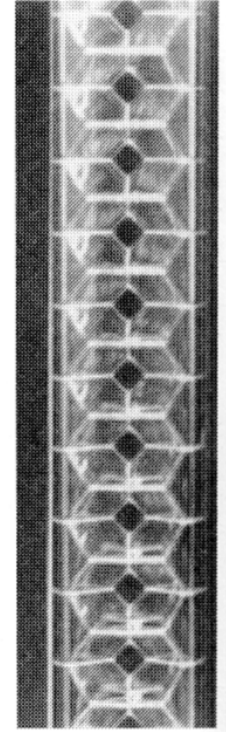
$(2,1,1)$



$(2,2,0)$



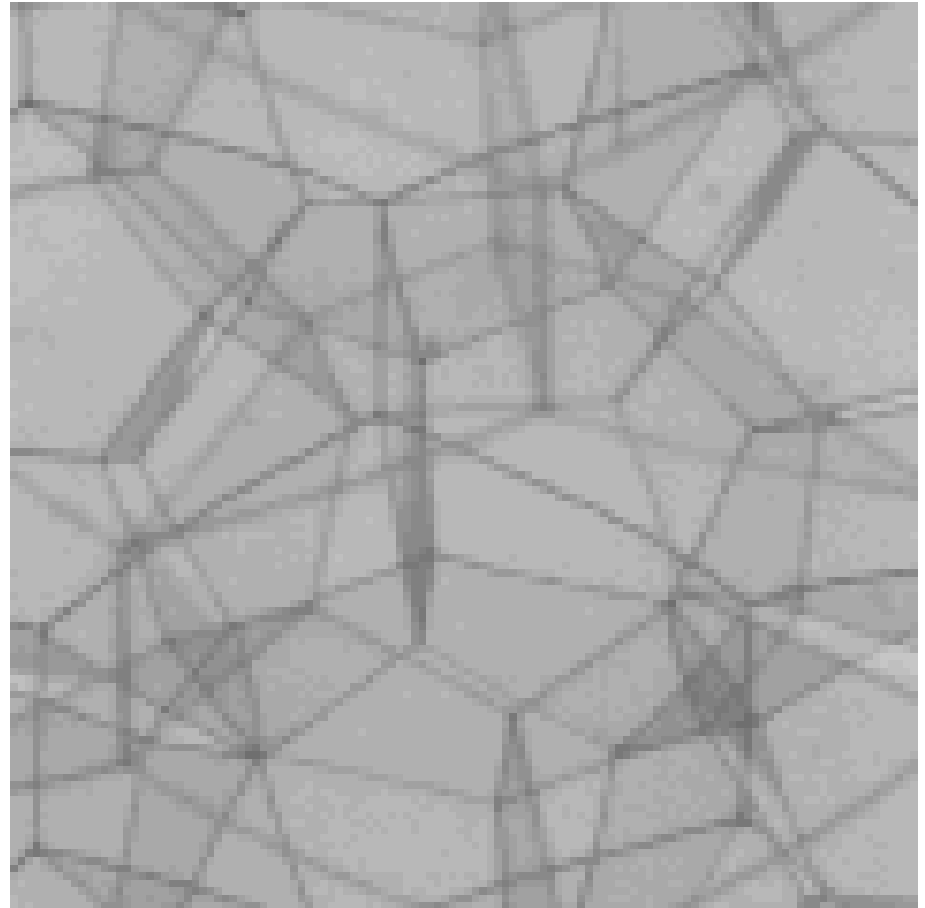
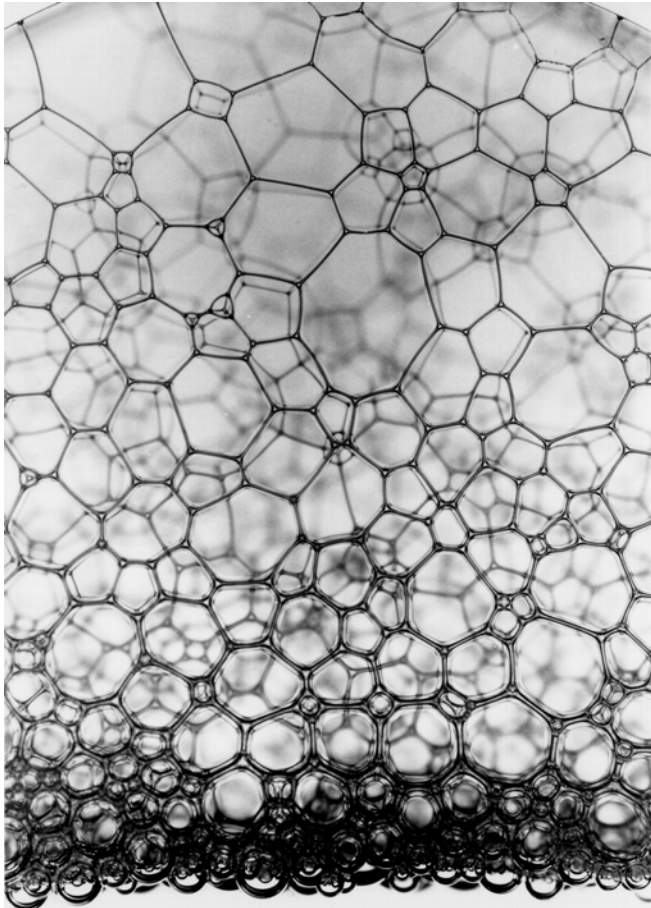
$(3,2,1)$



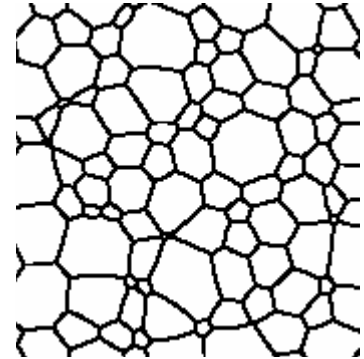
$(4,2,2)$

Random structures

- bulk foams are naturally polydisperse and disordered!
 - (we'll see later that ordered foams are unstable)



- bubbles squashed between glass plates
- bubbles floating at an air/water interface (“raft”)
- domains of phase-separated lipid monolayers



- distribution of edges per bubble, $p(n)$

- average number of edges per bubble: $\langle n \rangle = \Sigma[n p(n)] = 6$
- second moment, $\mu_2 = \Sigma[(n-6)^2 p(n)] = 1.4$
 - hexagons are common, but there is considerable width

- neighbor correlations

- average number of edges of neighbors to n -sided bubbles, $m(n)$
- Aboav law: $m(n) = 5 + 8/n$
 - combined with Lewis “law” ($A_n \sim n+n_0$, which actually doesn’t work so well) big bubbles are surrounded by small bubbles and vice-versa

- Euler equation for total # of cells, faces, edges, vertices:

$$N_F - N_E + N_V = 1 \quad (2D)$$

$$-N_C + N_F - N_E + N_V = 1 \quad (3D)$$

- Combine with Plateau in 2D

$$N_V = 2/3 N_E, \text{ so large } N_F = N_E - N_V = 1/3 N_E$$

$$\text{hence } \langle n \rangle = 2 N_E / N_F = 6$$

– as observed

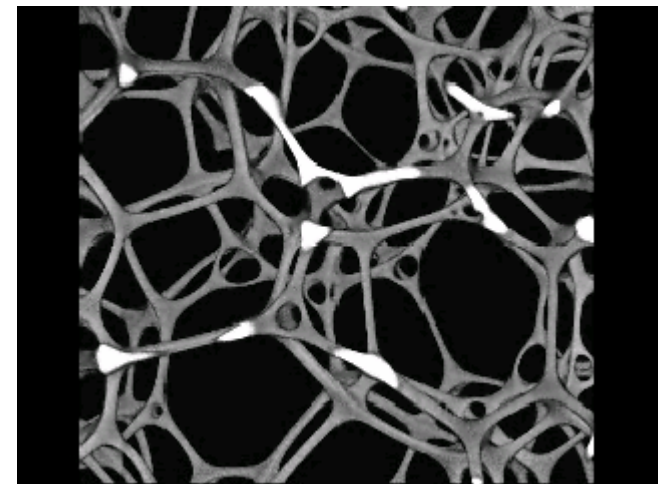
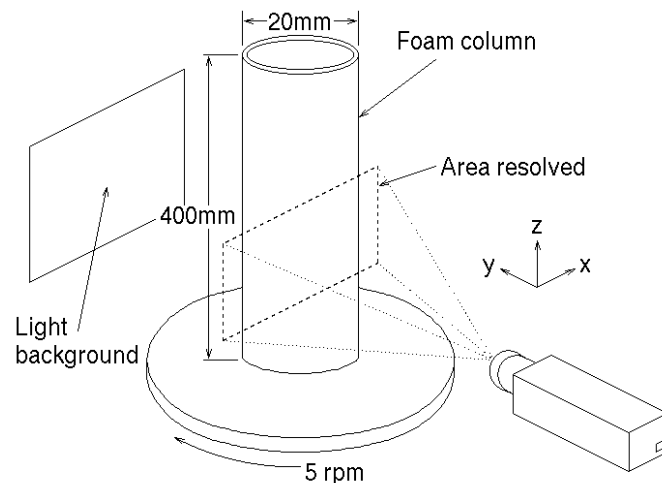


- Combine with Plateau in 3D

$$\langle f \rangle = 12 / (6 - \langle n \rangle)$$

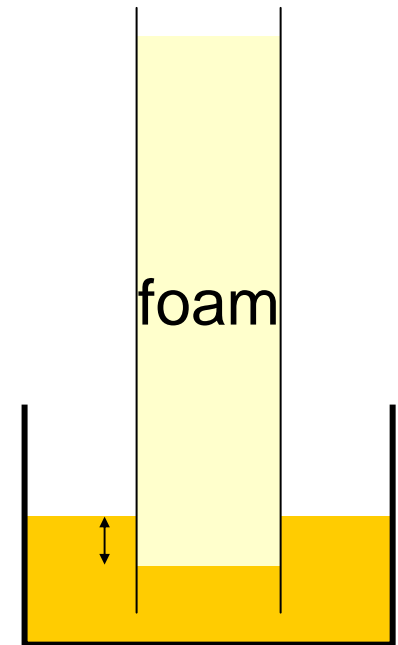
– Matzke result $\langle f \rangle = 13.70$ implies $\langle n \rangle = 5.12$

- ordinary microscopy / photography (eg Matzke)
 - good only for very dry foams a few bubbles across
- large numerical-aperture lens
 - image one 2D slice at a time, but same defect as (1)
- confocal microscopy – reject scattered light
 - *slightly* wetter foams / larger samples
- medical (MRI, tomography)
 - slow



Other structural probes

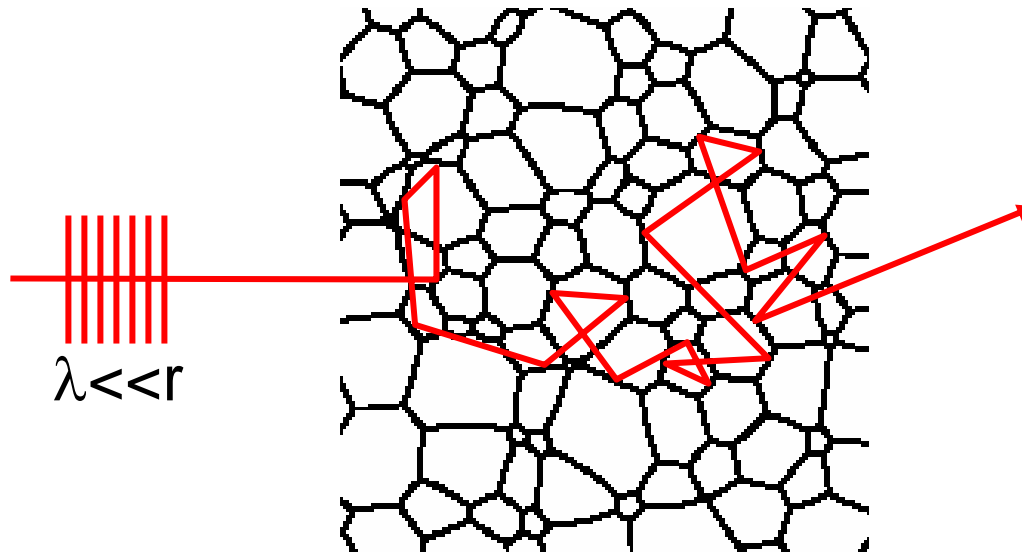
- Moving fiber probe
 - drive optical fiber through a bulk foam: reflection spikes indicate proximity of a film; gives ~cell-size distribution
 - doesn't pop the bubbles!
- Electrical conductance
 - conductivity is proportional to liquid fraction
 - independent of bubble size!
- Archimedes – depth of submerged foam
 - deduce liquid fraction



- 3D foams are white / opaque

clear foams do not exist!

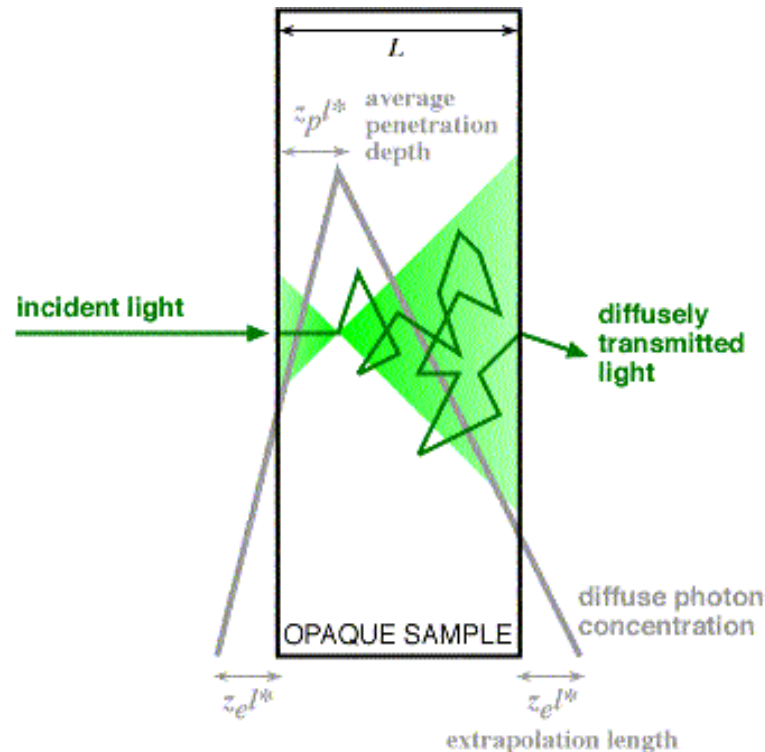
- photons reflect & refract from gas/liquid interfaces
- multiple scattering events amount to a random walk (diffusion!)



- while this limits optical imaging methods, it can also be exploited as a probe of foam structure & dynamics...

Transmission probability

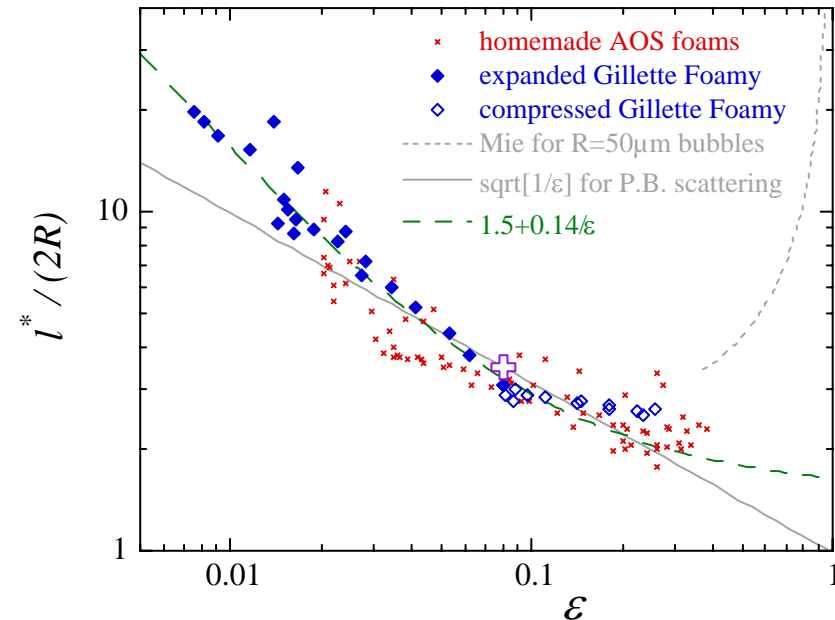
- how much light gets through a sample of thickness L ?
 - *ballistic* transmission is set by scattering length
 $T_b = \text{Exp}[-L/l_s]$ (vanishingly small: 10^{-5} or less)
 - *diffuse* transmission is set by transport mean free path ($D = cl^*/3$)
 $T_d = (z_p + z_e) / (L/l^* + 2z_e) \sim l^*/L$ (easily detectable: 0.01 – 0.1)



- Plateau borders are the primary source of scattering
 - recall liquid fraction $\varepsilon \sim (\text{border radius } r / \text{bubble radius } R)^2$
 - estimate the photon transport mean free path from their number density and geometrical cross section:

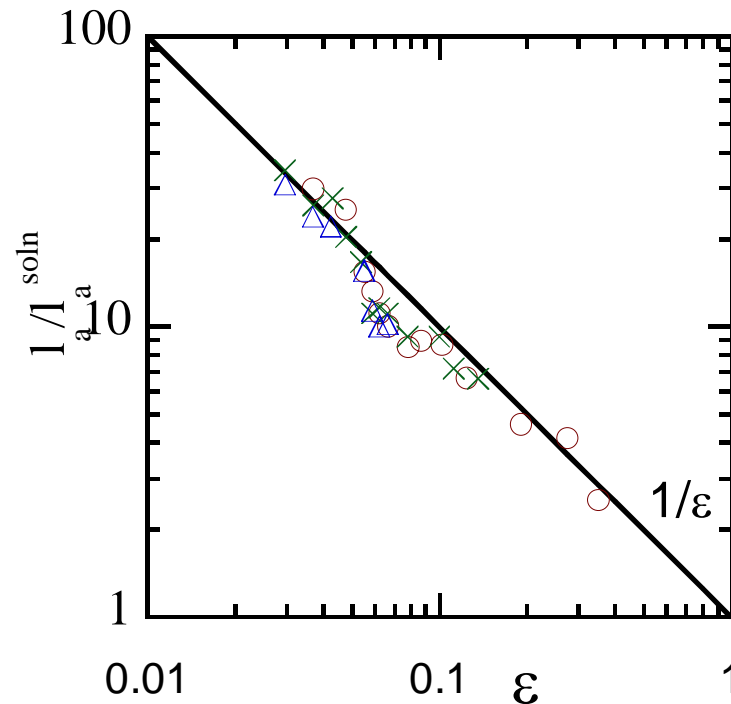
$$l^* = \frac{1}{\rho\sigma^*} \sim \frac{1}{(1/R^3)(rR)} \sim \frac{R}{\sqrt{\varepsilon}}$$

FAST & NON-INVASIVE PROBE:
 diffuse transmission gives l^*
 l^* gives bubble size or liquid fraction



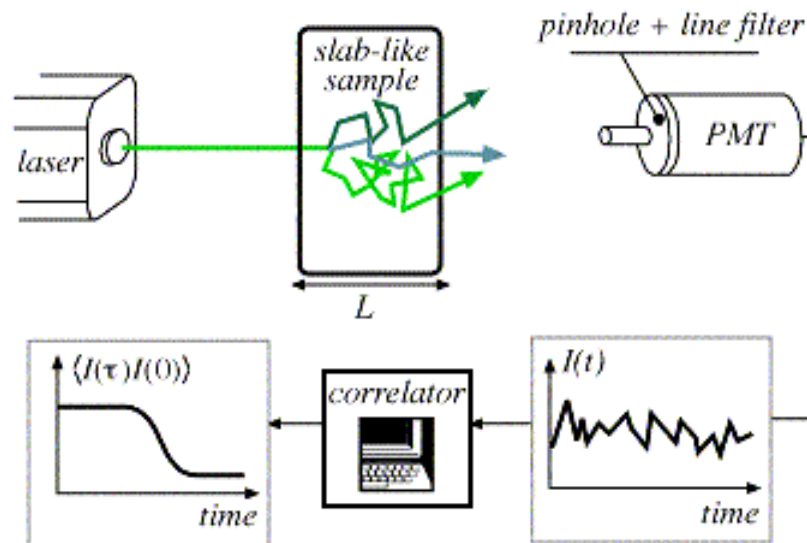
How random is the walk?

- the foam absorbs more light than expected based on the volume fraction of liquid $\{l_a/l_a^{\text{soln}} = 1/\varepsilon\}$
 - Plateau borders act like a random network of optical fibers
 - effect vanishes for very wet foams: Plateau border length vanishes
 - effect vanishes for very dry foams: photons exit at vertices



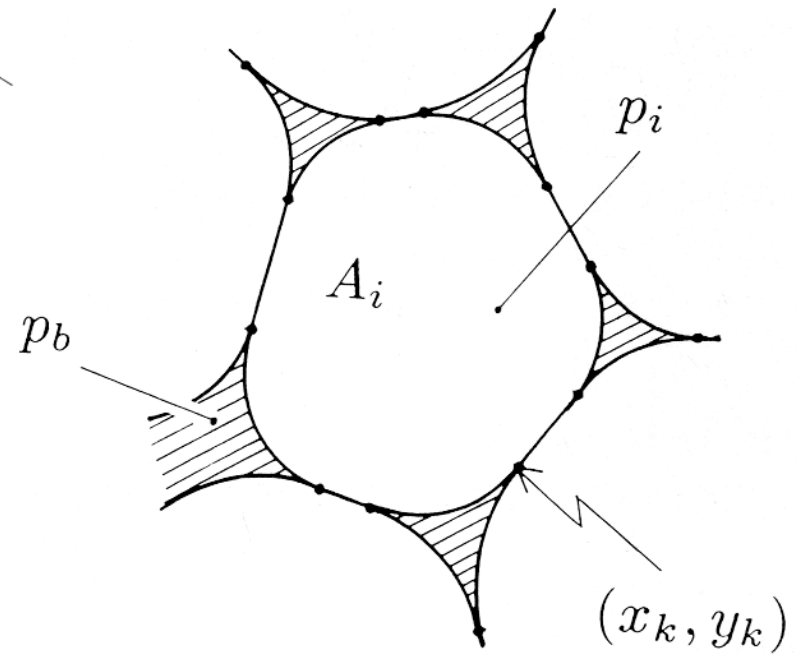
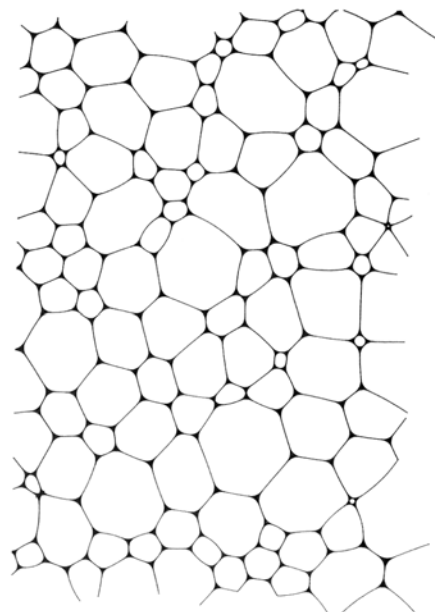
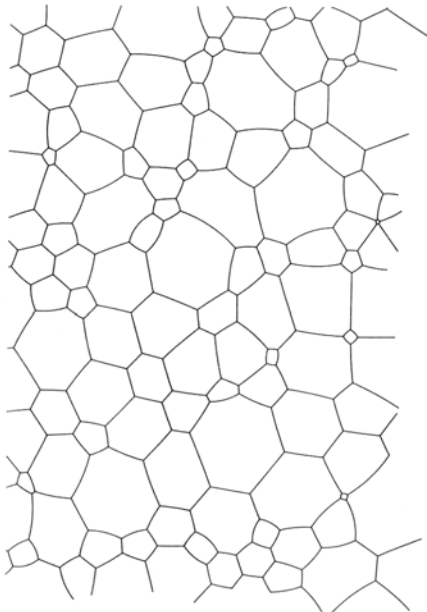
Diffusing-wave spectroscopy

- Form a speckle pattern at plane of detector
- As scattering sites move, the speckle pattern fluctuates
 - for maximum intensity variation: detection spot = speckle size
 - measure $\langle I(0)I(t) \rangle$ to deduce nature & rate of motion

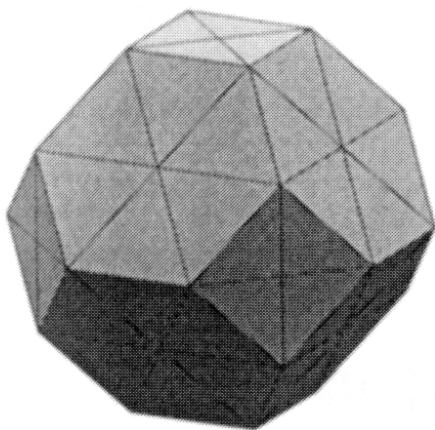


Simulation of structure

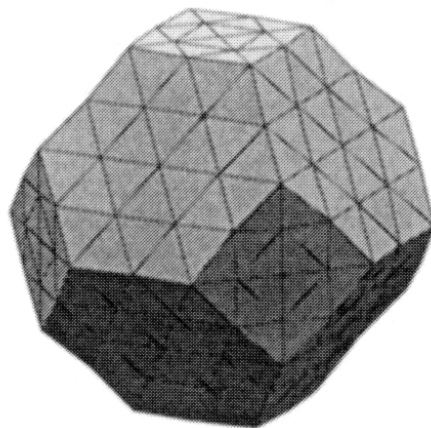
- in 2D the elements are all circular arcs (wet or dry)
 - otherwise the gas pressure wouldn't be constant across the cell
- adjust endpoints and curvature, while maintaining constant area, until Plateau is satisfied everywhere
 - iteratively or all at once



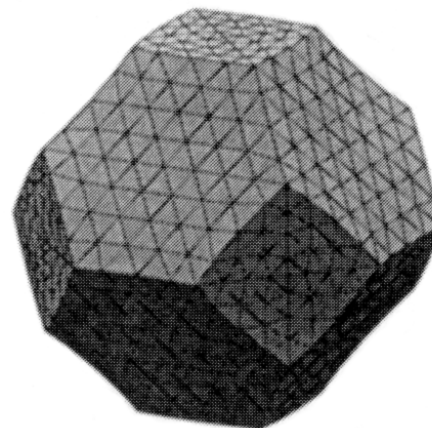
- in 3D it's much harder...
 - films have constant curvature but are not spherical
 - Plateau borders have arbitrary shape
- The “Surface Evolver” program by Ken Brakke minimizes film area at fixed topology
 - approximate surfaces by flat triangular plaquets
 - eg successive refinement of Kelvin cell:



(a) R0



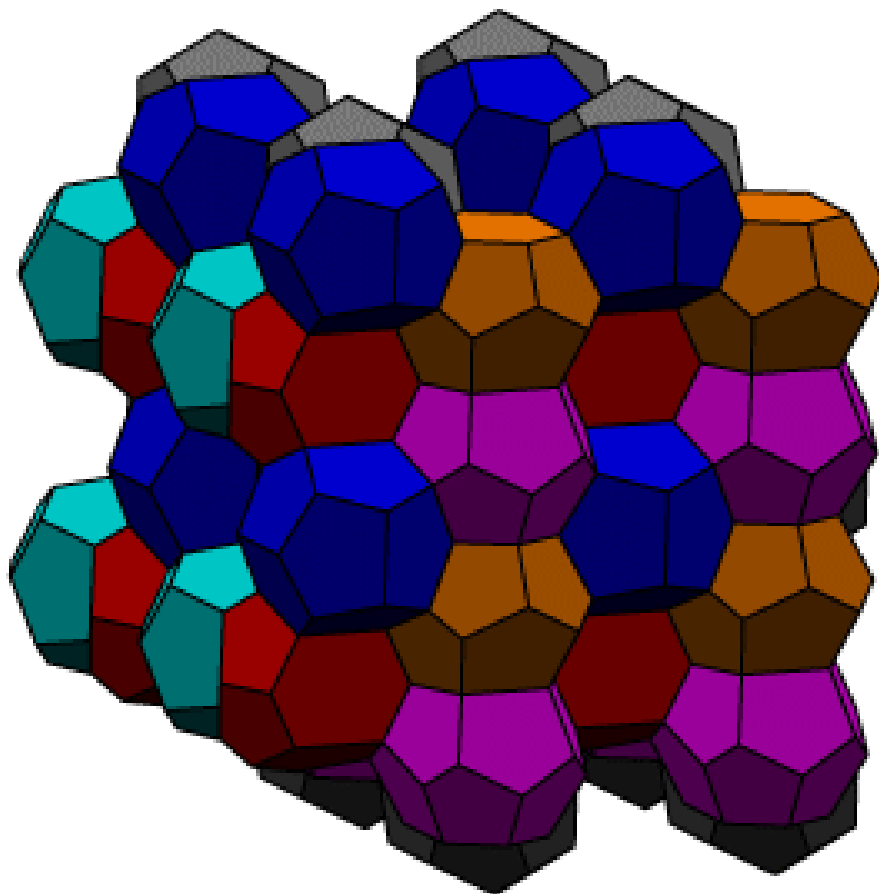
(b) R1



(c) R2

Surface Evolver – uses

- discovery of A15/Weaire-Phelan foam
- wet Kelvin foams



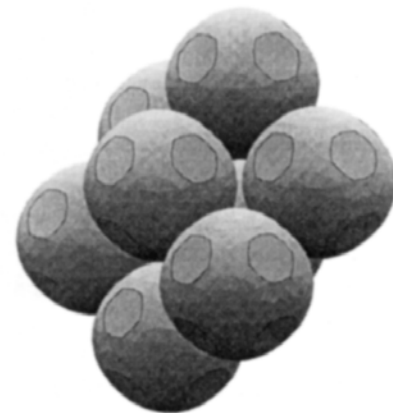
(a)



(b)



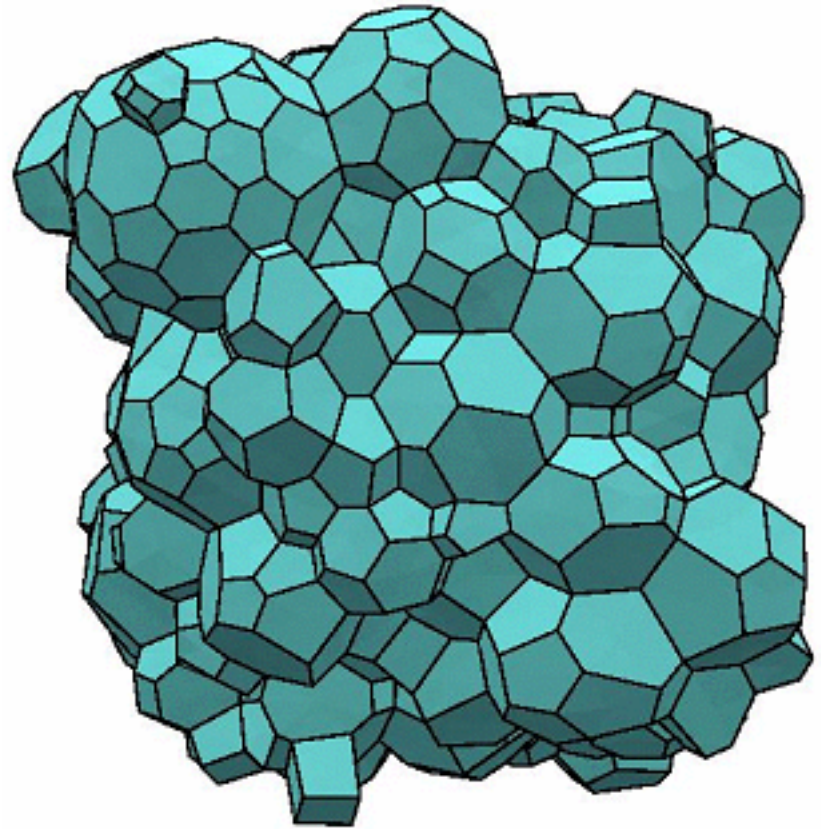
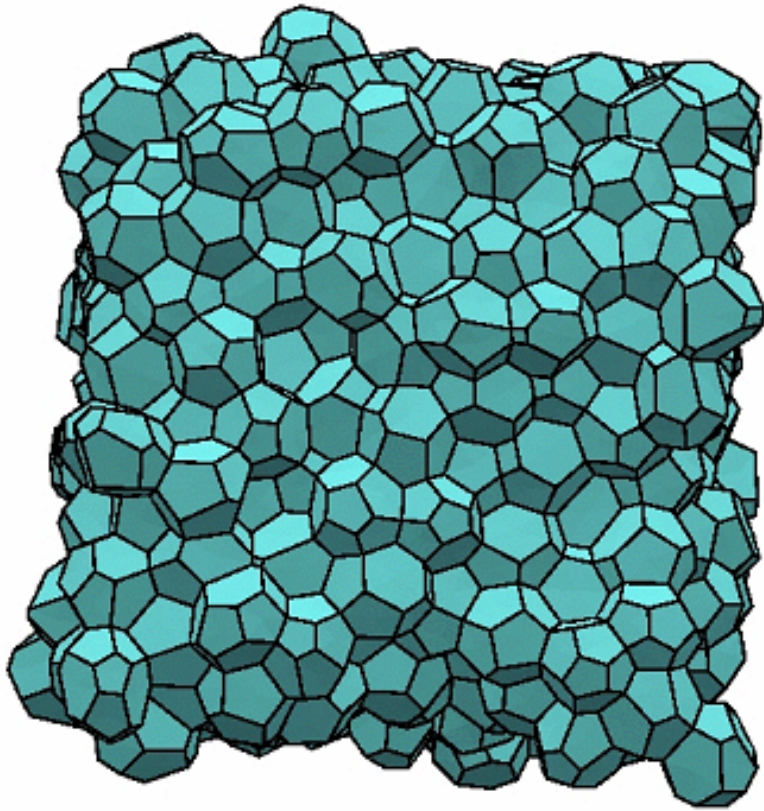
(c)



(d)

Surface Evolver – uses

- random monodisperse foams
- polydisperse foams



- Apply shear to any of the above
- Reconstruct full structure from partial tomographic data
 - eg finding films and volumes knowing only Plateau borders
- In general: statistics of dry foams in static equilibrium
- Drawbacks
 - fixed topology (must be reset by hand during equilibration / flow / evolution)
 - progressively slower for wetter foams
 - no true dynamics (film-level dissipation mechanisms cannot be included)

Q-state Potts model

- each lattice site has a spin, with a value that depends on the cell to which it belongs; eg:

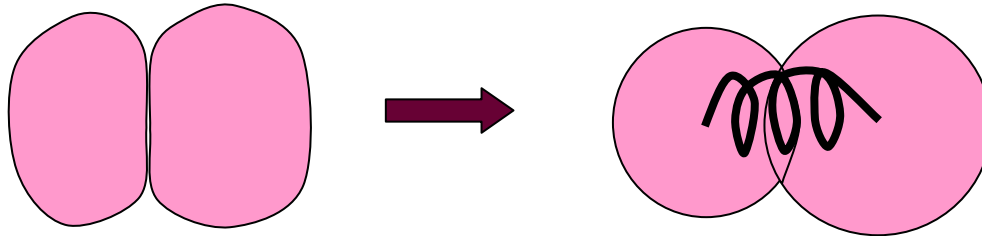
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1 1 1 1 1 1 1 1 1 1 | 2 2 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 1 | 2 2 2 2 2 2 2 2 2
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1 1 1 1 1 1 1 1 1 1 | 2 2 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 1 | 2 2 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 3 | 2 2 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 3 3 | 2 2 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 3 3 3 | 2 2 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 3 3 3 3 | 2 2 2 2 2 2 2 2 2
1 1 1 1 1 3 3 3 3 3 3 3 3 3 | 2 2 2 2 2 2 2 2 2
1 1 1 3 3 3 3 3 3 3 3 3 3 3 3 | 2 2 2 2 2 2 2 2 2
1 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 | 2 2 2 2 2 2 2 2 2

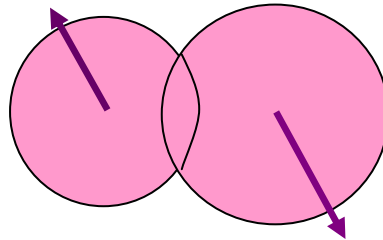
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- energy penalty for neighbors of different spin
- flip spins at interface by Monte-Carlo
 - minimizes interfacial area, like Surface Evolver, but slower
 - avoids the issue of setting topology by hand
 - but no true dynamics

- Consider bubbles, not films, as the structural elements
 - ignore shape degrees of freedom
 - move bubbles according to pairwise interactions:
 1. Spring force for overlapping bubbles (strictly repulsive)
{exact in 2D, good approximation in 3D}

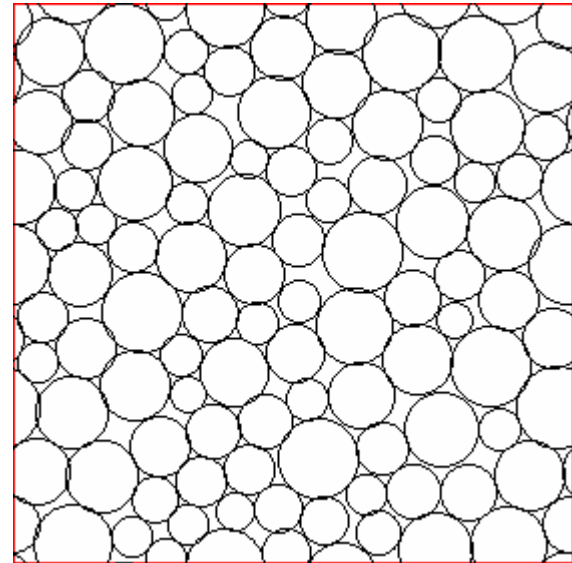


2. Dynamic friction for neighboring bubbles (\sim velocity difference)



Bubble model – uses

- rough caricature of essential microscopic physics
 - exact for wet foam limit of close-packed spheres
- no need to keep track of topology by hand
- true dynamics, and computationally cheap
 - not useful for topology statistics
 - good for evolution and flow



{not yet ready foam rheology}

- evolution of aqueous foams
 - coarsening, in response to gas diffusion
 - drainage, in response to gravity