1. Introduction
   Formation
   Microscopics

2. Structure
   Experiment
   Simulation

3. Stability
   Coarsening
   Drainage

4. Rheology
   Linear response
   Rearrangement & flow
local structure recap

- liquid fraction $\varepsilon \sim \left( \frac{\text{border radius } r}{\text{bubble radius } R} \right)^2$
- Plateau’s rules for mechanical equilibrium:
  1. films have constant curvature & intersect three at a time at $120^\circ$
  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
Periodic foams, 3D

- 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

\[ \frac{1}{r_1} + \frac{1}{r_2} = 0 \]
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
  - tetrakaidecahedron: 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)
Bubbles in a tube

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

- bulk foams are naturally polydisperse and disordered!
  - (we’ll see later that ordered foams are unstable)
A tedious experiment

- Matzke (J. Botany 1946) constructed random monodisperse foams by individually blowing $\sim 10^3$ bubbles and placing them into a container by hand
  - most abundant cell: 13-hedron
    - 1 quadrilateral, 10 pentagons, 2 hexagons
    - Matzke didn’t find even a single Kelvin tetrakaidecahedron!
  - almost all faces were 4, 5, or 6 sided
  - average number of faces per cell $<f>$=13.70
easier for 2D foams

- 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: \( \langle n \rangle = \sum n \, p(n) \) = 6
  - second moment, \( \mu_2 = \sum (n-6)^2 \, p(n) \) = 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: \( m(n) = 5 + \frac{8}{n} \)
    - 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:

\[ N_F - N_E + N_V = 1 \] (2D)
\[ -N_C + N_F - N_E + N_V = 1 \] (3D)

• Combine with Plateau in 2D

\[ N_V = \frac{2}{3} N_E \text{, so large } N_F = N_E - N_V = \frac{1}{3} N_E \]

hence \( \langle n \rangle = \frac{2 N_E}{N_F} = 6 \)

– as observed

• Combine with Plateau in 3D

\[ \langle f \rangle = \frac{12}{6 - \langle n \rangle} \]

– Matzke result \( \langle f \rangle = 13.70 \) implies \( \langle n \rangle = 5.12 \)
Imaging methods

• 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
Photon diffusion

• 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!)

\[ \lambda \ll r \]

• 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
    \[ T_b = \exp[-L/l_s] \] (vanishingly small: \(10^{-5}\) or less)
  - **diffuse** transmission is set by transport mean free path (\(D=cl^*/3\))
    \[ T_d = (z_p+z_e)/(L/l^*+2z_e) \approx l^*/L \] (easily detectable: 0.01 – 0.1)
**Foam optics**

- 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 \( \frac{l_a}{l_{a_{soln}}} = \frac{1}{\varepsilon} \)
  - 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:
Surface Evolver – uses

- discovery of A15/Weaire-Phelan foam
- wet Kelvin foams
Surface Evolver – uses

- random monodisperse foams
- polydisperse foams
Surface Evolver – uses

• 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:

```
1 1 1 1 1 1 1 1 1 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 2 2 2 2 2 2 2
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
1 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3
```

- 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
Bubble model

- 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 (~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
Next time...

{not yet ready foam rheology}

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