

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





Gas diffusion

- bubble volumes can change by the diffusion of gas across films
 - gas flux goes from high to low pressure bubbles, as set by Laplace's law {generally, from smaller to larger bubbles}



- monodisperse foams are unstable: fluctuations are magnified...





Coarsening

• small bubbles shrink...large bubbles grow...the texture *coarsens*



- interfacial area decreases with time (driven by surface tension)
- similar behavior in other phase-separating systems
 - eg called Ostwald ripening for grain growth in metal alloys



Coarsening alters the topology

• number of bubbles decreases as small bubbles evaporate



- this is called at "T2" process

{topology change of the second kind}



Other topology changes

- in 2D, neighbor switching happens only one way:
 - the so-called "T1" process



• in 3D, there is more than one type of neighbor-switching process:





Rearrangement dynamics

• these events can be sudden / avalanche-like:



- surface of a bulk foam
- 30 μ m diameter bubbles

- similar rearrangements occur during flow... (next time)



self-similarity

- bubble-size distribution scales with the average
 - $p(R,t) = F(R/\langle R(t) \rangle)$ where all t-dependence is in $\langle R(t) \rangle$
 - arbitrary initial distribution evolves to this distribution
 - time sequence looks like an increase in magnification





this property makes it simple to compute the rate of coarsening...



- The bubbles in a foam are polydisperse
 - smaller bubbles have higher pressures (Laplace)

$$P_{inside} = P_{outside} + \gamma/r$$

 – concentration of disolved gas is therefore higher just outside smaller bubbles (Henry)

 hence there is a diffusive flux of disolved gas down the concentration gradient from smaller to larger bubbles (Fick)





- mean-field argument: $dV/dt \sim -A (P-P_c)$
 - $V = average \ bubble \ volume, \ A = average \ bubble \ area$ ${dV/dt = A \ dR/dt, so \ dR/dt ~ -(P-P_c) \ in \ any \ dimension}$ ${proportionality \ constant \ scales \ as \ diffusivity \ x \ solubility \ / \ film \ thickness}$

 $(P-P_c)$ = pressure difference of average bubble with neighboring 'crossover' bubbles that neither grow nor shrink:



Rate of coarsening III.

• $(P_c-P)=(\gamma/r_c-\gamma/r)$, difference of Plateau border curvatures



- two steps to connect to bubble size:
 - self-similarity of the bubble-size distribution implies that R is *exactly* proportional to R_c
 - $\epsilon \sim (r/R)^2 = (r_c/R_c)^2$
- Altogether: $dR/dt \sim (P_c P) = (\gamma/r_c \gamma/r) \sim 1/(Sqrt[\varepsilon]R)$
 - therefore, $R \sim t^{1/2}$ {in both 2D and 3D}



Lifshitz & Slyozov (1961)

- considered coarsening of metal alloys
 - droplets separated by a distance >> droplet size
 - full distribution size distribution f(R,t), with $\langle R(t) \rangle \sim t^{1/3}$



- sum rule for change in tangent angles going around an n-sided bubble with arclengths l_i and radii r_i is $2\pi = \sum_{i=1}^n \frac{l_i}{r_i} + n \cdot \pi/3$
- flux across each arc scales as l_i / r_i
- rate of change of area thus scales as

$$\frac{dA_n}{dt} \sim \left(-\sum_{i=1}^n \frac{l_i}{r_i}\right) \sim (n-6)$$

- the crossover bubble is six-sided
- the average bubble area grows as A~t {consistent with $r \sim t^{1/2}$ }
- cannot be carried into 3D, but approximations have been proposed
 - $RdR/dt \sim (F-F_o)$ with $F_o \sim 14$ {Glazier}
 - $RdR/dt \sim F^{1/2}\text{-}F_o^{-1/2} \ \{Hilgenfeldt\}$





• soap bubbles squashed between glass plates:







• Gillette Foamy, from multiple light scattering



FIG. 3. Average bubble diameter vs foam age as determined from static (---) and dynamic (\circ) multiple light-scattering measurements. The dashed line has slope $\frac{1}{2}$ and shows that the growth of d is nearly consistent with the scaling prediction for densely packed bubbles.



- custom made foams of uniform liquid fraction (large symbols)
- a single foam sample that is draining and coarsening (small dots)
- liquid-fraction dependence: dR/dt ~ 1/(Sqrt[ε]R) {cf competing arguments where liquid-filled Plateau borders completely block the flux of gas: dR/dt ~ (1-Sqrt[ε/0.44])² (dash)}





Coarsening can't be stopped

- but it can be slowed down:
 - make the bubbles monodisperse
 - choose gas with low solubility and low diffusivity in water
 - add trace amount of "insoluble" gas
 - works great for liquid-liquid foams (ie emulsions)
 - composition difference & osmotic pressure develop that oppose Laplace





- Under influence of earth's gravity, the liquid drains downwards in between the bubbles primarily through the Plateau borders
 - some debate about role of films in liquid transport...
 - unlike coarsening, this mechanism can be turned off (microgravity)
 - drainage and/or evaporation are often a prelude to film rupture



different from ordinary porous medium: the pore (i.e. Plateau borders) shrink as drainage proceeds: $\varepsilon \sim (r/R)2$



Forces?

- drainage is driven by gravity, but opposed by two other forces
 - viscous dissipation
 - if the monolayer are rigid:
 - no-slip boundary, so Shear Flow in Plateau borders
 - if the monolayers are mobile:

- slip boundary, so Plug Flow in Plateau borders and shear flow only in vertices

capillarity





• estimate ΔE /time in volume r²L for all three three forces:



• use $r \sim \epsilon^{1/2} R$ and require $\Sigma(\Delta E/\text{time})=0$:

$$u = u_o \left(1 - \sqrt{\frac{\varepsilon_c}{\varepsilon}} \frac{\xi}{\varepsilon} \frac{\partial \varepsilon}{\partial z} \right) \times \begin{cases} \varepsilon & \text{shear in PB's}^* \\ \varepsilon^{1/2} & \text{shear in vertices}^* \end{cases}$$

 $\left\{ u_o \approx \rho g R^2 / \eta \text{ (characteristic flow speed)}, \quad \xi \approx \gamma / \rho g R \text{ (capillary rise length)}, \quad \varepsilon_c \approx 0.36 \right\}$



Drainage Equation: PDE for
$$\varepsilon(z,t)$$

• continuity equation for liquid conservation:

$$0 = \frac{\partial \varepsilon}{\partial t} + \frac{\partial (u\varepsilon)}{\partial z} + \frac{u\varepsilon}{A} \frac{\mathrm{d}A}{\mathrm{d}z}$$

 $\varepsilon(z,t) =$ liquid volume fraction u(z,t) = liquid flow speed (previous slide) A(z) = cross - sectional area of container

• boundary conditions:

$$\varepsilon|_{boundary} = \varepsilon_c$$
 (flow at bottom), or $\frac{\varepsilon}{\partial \varepsilon / \partial z}\Big|_{boundary} = \xi \sqrt{\frac{\varepsilon_c}{\varepsilon}}$ (no flow at top or bottom)



Equilibrium capillary profile

• u=0 everywhere: gravity balanced by capillarity

 $\varepsilon(z) = \varepsilon_c / [1 - (H - z)/2\xi]^2$, H = column height





Forced-drainage

- pour liquid onto foam column at constant rate Q
 - wetness front propagates at constant speed & shape (solitary wave)





Convection & size segregation

• but don't pour too hard!



 $Q >> Q_m$ convection & size segregation





Free-drainage in straight column

- no analytic solution is known!
 - initially, becomes dry/wet at top/bottom; ε=constant in interior
 - leakage begins when $\varepsilon \rightarrow \varepsilon_c$ at bottom
 - eventually, rolls over to equilibrium capillary profile





Free-drainage in Eiffel Tower

• exponentially-flaring shape: $A(z) \sim Exp[z/z_o]$



simple analytic solution (ignoring boundary conditions)



vol. of drained liquid: $\frac{V(t)}{V_t} = 1 - \frac{1}{(1 + t/t_o)^{1/m}}$





Eiffel Tower - data

- uniform drying (no ε-gradients, until late times)
- but much faster than predicted
 - capillarity in BC's slows down leakage
 - must be due to effects of coarsening...





Drainage-coarsening connection

• vicious cycle:

– etc. •

- dry foams coarsen faster...
- large bubbles drain faster...

- to model this effect:
 - combine with RdR/dt=1/Sqrt[ϵ]
 - add one more ingredient...





- Previous treatments assume spatial homogeneity, which isn't the case for freely draining foams
 - gradient causes net gas transport



• curvature contributes to bubble growth



• The full <u>coarsening equation</u> must thus be of the form $\partial R/\partial t = D[X + (R^2/\alpha)\partial^2 X/\partial z^2]:$

$$\frac{\partial R}{\partial t} = D \left[\frac{1}{\sqrt{\varepsilon R}} + \frac{R^2}{\alpha} \frac{\partial^2}{\partial z^2} \left(\frac{1}{\sqrt{\varepsilon R}} \right) \right]$$



Compare with data

• simultaneously capture straight and flaring columns:





Next time...

- Foam rheology
 - linear response (small-amplitude deformation)
 - bubble rearrangements and large-deformation flow