Optical techniques to probe internal dynamics of soft materials

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Outline

- Soft materials a new class of materials?
- Foam, the quintessential soft material
 - Major questions
 - Crash course on foam physics
- Optical techniques for foam research
 - Confocal microscopy
 - Optical Axial Tomography
- Summary



Soft Materials



A class of materials that share in common two unifying characteristics:

Complexity

- Soft Matter possess a variety of *internal structures* in a broad range of length scales
- Flexibility
 - Soft Matter display remarkable *fluid* and *mechanical* properties that emerges from its internal dynamics

Pierre-Gilles de Gennes, Nobel laureate 1991





Complexity: structure & microscopic processes



• Microscopic processes

• Gas diffusion, liquid flow, film rupture

Evolution and Meta-stability

Flexibility: foams: a solid or a fluid?

• Fluid: flow above an yield stress





• **Solid:** withstand small deformations

• **Aging:** memory loss caused by bubble rearrangements

Viscoelasticity: complex combination of elastic and viscous behavior



Frequency dependence of storage modulus \rightarrow broad distribution of <u>relaxation rates</u>



Important questions:

- Which are the **length and time scales** that dominate the viscoelastic behavior of foams?
- What is the role played by the **structure** in bubble rearrangements and flow?
- How can we explain the broad range of relaxation rates?

Access to the <u>internal structure</u> of the foam and its dynamics is essential to answer these questions

What keeps foams stable?

 Pure water → bubbles attract and coalesce easily



van de Walls force

Effect of surfactants

- Disjointing pressure
- Reduce surface tension





Film



Major challenge

 Foam is typically opaque → it is difficult to visualize its internal structure and dynamics

Can we overcome this obstacle?



Wet foam: confocal microscopy



Dry foam: optical axial tomography

Wet foam: confocal microscopy

 Mix 4 components + surfactant → optically clear and neutrally buoyant emulsion

Foam-like structure & dynamics





Dispersed phase: Bromohexane + isooctane (6.3%) **Continuous phase** Formamide + water (5%)

- Stabilized by non-ionic surfactant
- Fluorescent dye added to the continuous phase for visualization

Visualization: confocal microscope



Tracking rearrangements

 Localization of droplets using image analysis



3D reconstruction

 Tracking of droplet displacements in time



Droplet gliding and rearrangement

Tracking rearrangements

 3D Localization of droplets using image analysis



3D reconstruction

 Tracking of droplet displacements in real time



Droplet gliding and rearrangement

Dry foam: optical axial tomography

Foam

- de-ionized water (90.5%)
- glycerol (4.75%)
- detergent (4.75%)
- aged for 24 hrs



Photographs

- Nikon D70 camera
- 300mm lens
- uniform white background
- 360 pictures ($\Delta \theta = 0.5^{\circ}$)



How does axial tomography work?

- Take a photograph of the "shadow" of the specimen
- Dark shadow = light scattered or absorbed by specimen
- The sum of projections from all angles produces an image of the cross section of the specimen



http://genex.hgu.mrc.ac.uk/OPT_Microscopy/optwebsite/how_it_works/hiwtheory.htm

Tomographic reconstruction of foam cross section

Dry foam

Slice Reconstruction



3D reconstruction of the internal



Identifying individual bubbles

- Localization of vertices
- Geometrical calculation of faces using vector algebra





 Volume calculation by Monte Carlo methods





Summary

- We have implemented two powerful techniques for imaging internal structure and dynamics of foam
 - Confocal microscopy high liquid fraction
 - Optical axial tomography low liquid fraction
- These techniques provides opportunity to connect microscopic interactions with bulk properties of aqueous foam.

Acknowledgments





National Science Foundation WHERE DISCOVERIES BEGIN











Joice



Robbie

Source of elasticity

• Small deformations: energy is stored in the films; deformation increases area



[Princen, JCIS (1983)]

Beyond a threshold, bubbles rearrange and the foam flows



Liquid drains through plateau borders



Gas diffusion makes bubbles grow

(Surface tension)

(Bubble radius)

• Laplace pressure: $\Delta p \sim \frac{\gamma}{2}$

• Soluble gas



• Foam coarsening, scaling behavior,







$$\frac{\partial R}{\partial t} \sim \frac{1}{R} \quad \Longrightarrow \quad R \sim t^{1/2}$$

[Glazier and Weaire, J. Phys.: Condens. Matter (1992)]

How a confocal microscope works

- A laser beam is focused on the sample through a pinhole
- Light reflected from the sample crosses a beam splitter and hits the second conjugated pinhole
- Light coming from the focal plane goes through the second pinhole while any other is rejected.
- An image of the sample is constructed point by point in the detector (photomultiplier)



Vectorizing the emulsion

- Morphological distance operation
 - Generate a thresholded image
 - Assign Euclidian distance to nearest 'background' voxel



- Result
 - Landscape where dark voids (droplets) become cones
 - Peaks \rightarrow centers; Height \rightarrow effective radius
 - Process cones to obtain droplets coordinates and radii

*Similar to method described by Penfold, et.al., Langmuir 2005

Flying through the "foam"





Tracking Plateau Borders



Deciding What is a Plateau Border







New Plateau Borders





A recognizable network



Joseph Plateau

Plateau's rules for mechanical equilibrium (dry foam)

- Films have constant curvature and meet three at a time at 120°
- Borders intersect four at a time at 109.47°



Investigate rearrangements in 3D





Droplet marked in the micrograph

And painted blue in the next slide

Investigate rearrangements in 3D



Soft glass rheology model

- The elements of the system are trapped in potential wells of energy E
- They escape their traps
 via an activation process



In foams, disorder provides the energy barriers, and coarsening/rearrangements the activation process

Self-organized criticality

- The system arranges itself near a critical point
- Small disturbances produce avalanchelike collective rearrangements

In foam, coarsening could be the mechanism of self organization



A dynamic conspiracy

In foams coarsening and drainage occur simultaneously.

...bubble growth squeezes the Plateau borders, enhancing drainage which increase gas diffusion intensifying bubble growth...

Leads to an interdependent rate of coarsening and drainage!

Challenge:

Understand the mutual interplay of these dynamical processes to predict and control foam evolution

Coarsening is common to other systems

Coarsening emulsion

• Diffusion \rightarrow Scaling behavior ($\overline{d} \propto t^{1/2}$)



• Also domain growth in solid-liquid coexistence, binary alloys, proteins, etc