Optical techniques to probe internal dynamics of soft materials

Klebert Feitosa
Assistant professor of Physics and Astronomy
James Madison University
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
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
Soft Materials

Foams

Gels

Vesicles

Grains

Cells

Pastes

Emulsions

Colloids

Liquid crystals
Soft Materials

- Foams
- Pastes
- Liquid crystals
- Emulsions
- Colloids
- Cells
- Grains
- Vesicles
- Gels
- Cells
- Pastes
- Liquid crystals
- Emulsions
- Colloids
- Cells
- Grains
- Vesicles
- Gels
- Foams

Images of various soft materials are shown, including a sandcastle, a toothbrush with toothpaste, and a jar of mayonnaise.
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

Storage modulus: (elasticity) weak frequency dependence

Loss modulus: (viscosity) anomalous behavior

Frequency dependence of storage modulus → broad distribution of relaxation rates

[Gopal & Durian, PRL (2003)]
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 **internal structure** of the foam and its dynamics is essential to answer these questions.
What keeps foams stable?

- Pure water → bubbles attract and coalesce easily
- Effect of surfactants
  - Disjointing pressure
  - Reduce surface tension
Structure and Meta-stability

**Structure:** random packing of bubbles

**Dynamics:** evolution driven by
- Liquid drainage (through Plateau borders)
- Gas diffusion (through films)
- Film rupture
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 $\rightarrow$ **optically clear** and **neutrally buoyant** emulsion

Foam-like structure & dynamics

**Dispersed phase:** Bromohexane + isoctane (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
- Tracking of droplet displacements in time

3D reconstruction

Droplet gliding and rearrangement
Tracking rearrangements

- 3D Localization of droplets using image analysis
- Tracking of droplet displacements in real time

3D reconstruction

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 provide opportunity to connect microscopic interactions with bulk properties of aqueous foam.
Acknowledgments

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Source of elasticity

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

\[ G' \sim \frac{\gamma}{d} \]

- Beyond a threshold, bubbles rearrange and the foam flows

[Princen, JCIS (1983)]
Liquid drains through plateau borders

Force balance:
- Viscosity (liquid viscosity, $\eta$)
- Capillarity (bubble radius, $R$)
- Gravity (bubble volume, $R$; liquid fraction, $\epsilon$)

$u \equiv \text{flow speed}$

$u \sim \frac{R^2 \epsilon^{1/2}}{\eta}$  

[Koehler, et al., PRE (1998)]
Gas diffusion makes bubbles grow

- Laplace pressure: \[ \Delta p \sim \frac{\gamma}{r} \] (Surface tension)
- Lower pressure (Bubble radius)
- Soluble gas

- Foam coarsening, scaling behavior,

\[ \frac{\partial R}{\partial t} \sim \frac{1}{R} \]

\[ R \sim t^{1/2} \]

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”
Step 2

Tracking Plateau Borders
Deciding What is a Plateau Border
New Plateau Borders
A recognizable network

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

$\begin{align*}
t_1 &= 0 \text{ min} \\
t_2 &= 5.6 \text{ min}
\end{align*}$

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 avalanche-like 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 ($\bar{d} \propto t^{1/2}$)

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

[Manoharan & Crocker, unpublished (2006)]