

# MICROGRAVITY FOAM STRUCTURE AND RHEOLOGY

Douglas J. Durian and Anthony D. Gopal  
UCLA Department of Physics  
405 Hilgard Avenue  
Los Angeles, CA 90024-1547

## ABSTRACT

Our long-range objective is to establish the fundamental interrelationships between the microscopic structure and dynamics of foams and their macroscopic stability and rheology. Foam structure and dynamics are to be measured directly and noninvasively through the use and development of novel multiple light scattering techniques such as diffusing-wave spectroscopy (DWS). Foam rheology is to be measured in a custom rheometer which allows simultaneous optical access for multiple light scattering. Microgravity conditions will ultimately be required to eliminate the increasingly rapid gravitational drainage of liquid from in between gas bubbles as the liquid:gas volume fraction is increased toward the rigidity-loss transition.

## INTRODUCTION: FOAM STRUCTURE AND PROPERTIES

Foams are nonequilibrium dispersions of discrete gas bubbles in a smaller, continuous, volume of liquid which contains surface-active macromolecules [1-2]. They are familiar in everyday life from cleaning, food, and cosmetic products, and are important in a truly wide variety of industrial and research settings, whether fabricated for specific applications or inhibited and destroyed where undesirable. A hierarchy of structure and self-organization at progressively smaller length scales, as shown schematically in Figure 1, is ultimately responsible for the unique properties which make foams such fascinating and useful materials. The largest structural length scale, above which the foam appears homogeneous, is set by the average bubble size and can typically vary from 1 cm to 10  $\mu\text{m}$  depending on method of preparation and foam age. At the very smallest structural length scale, surface-active molecules are preferentially adsorbed at the gas/liquid interfaces and give rise to several physical-chemical effects which deter the coalescence of neighboring bubbles and thereby lend stability to the foam. An important intermediate length scale is the thickness of the liquid film separating neighboring gas bubbles; its value depends on details of the interfacial forces, and hence on the molecular composition of the liquid, but is typically on the order of 100 nm as is familiar from the colorful interference patterns in isolated soap films.

In addition to this cascade of structural length scales, a key compositional parameter is the volume fraction occupied by the liquid phase. For relatively wet foams, such as depicted in Figure 1, the gas bubbles are very nearly spherical and the foam microstructure is most readily described as the random close packing of a polydisperse collection of spheres. For relatively dry foams, by contrast, the bubbles are very nearly polyhedral and the foam microstructure is more readily described as a continuous random network of thin liquid films. The influence of liquid volume fraction on bubble shape is depicted schematically in Figure 2. The amount of liquid which separates the "wet" and "dry" regimes depends not only on the bubble size distribution, but also on the competition between surface tension, which favors spherical bubbles, and repulsive interfacial forces, which favor polyhedral bubbles. The influence of this competition on bubble shape is also depicted schematically in Figure 2.

## Stability

Aqueous foams are intrinsically nonequilibrium materials. With time, the liquid and gas portions separate by some combination of three basic mechanisms: gravitational drainage of liquid from in between gas bubbles, direct coalescence of neighboring bubbles via film rupture, and diffusion of gas from smaller to larger bubbles, which is known as coarsening. In practice, film rupture can be made negligible by suitable choice of liquid composition; however, it is not possible to eliminate the other two mechanisms. Coarsening always occurs because the bubble size distribution is naturally polydisperse. Gravitational drainage also cannot be prevented, on earth, because the mass densities of the liquid and gas portions are always significantly different and cannot be matched.

## Rheology

Aqueous foams which are relatively stable can be considered as a form of matter which is unusual in sharing the hallmark features of both solids, liquids, and vapors [3]. Even though foams consist mainly of gas and a small amount of liquid, they can support shear elastically, like a solid, through the distortion of tightly packed bubbles away from area-minimizing shapes. If applied stresses are sufficiently great, the bubbles can hop around each other allowing the foam to flow and deform indefinitely like a liquid. And, in addition, foams are as readily compressible as gasses. The combination of elastic/solid-like and viscous/liquid-like behavior in foams is further surprising in that it is unlike the linear viscoelasticity exhibited by many complex fluids: Foam behavior is liquid-like at high shear strain rates and solid-like at low shear strain rates, while the rheology of polymers and colloids is the reverse.

## SCIENCE OBJECTIVES

In spite of their commercial importance, and long-standing basic scientific interest, there is little fundamental understanding of the detailed interrelationships between foam microstructure and dynamics and the key features of their macroscopic stability and rheology [2-3]. Our long-range goal is to elucidate such interrelationships through critical use of new multiple light scattering techniques and microgravity conditions. Basic questions we intend to answer quantitatively include: How does liquid composition and content affect the rates of the three evolution mechanisms, and how does the foam microstructure then evolve with time? What are the dynamical time scales associated with the structural length scales, and how do they influence foam rheology? More specifically, what is the rate and duration of the so-called T1 neighbor-switching topology changes depicted in Figure 3? How does the striking shear elasticity of foams vanish with increasing liquid content? How, and to what extent, does foam stability and rheology scale with surface tension and average bubble size?

## RELEVANCE TO APPLICATIONS

Applications involving foams fall into two categories: those where a foam is designed and produced to perform a particular task exploiting its unusual materials properties, and those where a foam is to be destroyed or the inadvertent foaming of a multi-component liquid is to be prevented. In addition to familiar cleaning, food, and cosmetic applications, important examples of the first type also include firefighting, physical and chemical separation processes, froth flotation, isolation and cleanup of toxic spills, application of dyes to textiles, and enhancing oil recovery. Examples of the undesirable generation of foams abound in the paper, paint, textile, leather, adhesive, and polymer industries as well as in waste water treatment and in polluted natural waters. In all cases, control of foam stability is crucial, but is only imperfectly achieved through trial and error; the fundamental understanding which we seek may lead to improved means of preserving, destroying, and inhibiting foams as needed. For applications involving special purpose foams, control of material properties is also currently achieved through trial and error; the fundamental understanding of foam rheology we seek may provide rational guidance for improved foam materials. In addition, the experimental techniques developed in our work should prove useful for monitoring foams and foam processing, and can be applied to a wide variety of other multiple light scattering materials such as colloids, emulsions, and biological tissues.

## RESEARCH APPROACH

The lack of fundamental quantitative understanding of foam stability and rheology is due in part to the inherent complexity of the phenomena and is exacerbated by experimental difficulties which follow from the unavoidably large density and refractive index mismatches of the liquid and gas components of foam. The difficulty caused by the density mismatch is that the gravitational drainage of liquid from in between gas bubbles is rapid and cannot be prevented on earth. The difficulty caused by the refractive index mismatch is that incident light strongly scatters from the bubble interfaces; this unavoidably restricts optical imaging of foam structure to surface behavior, thereby making bulk properties inaccessible. As described below, we have formulated an experimental approach which can overcome both difficulties and should yield rapid progress in elucidating the origin of foam stability and rheology in terms of their underlying structure and dynamics.

## Multiple Light Scattering

My experimental approach centers on the use and development of quantitative probes of structure and dynamics which actually take advantage of the generic multiple light scattering character of foams, namely static transmission (ST) and diffusing-wave spectroscopy (DWS) [4]. With ST, the fraction of incident light which is transmitted is measured and analyzed within a diffusion theory for the value of the transport mean free path of light. This general technique gives information about the density and spatial arrangement of scattering sites, which, for a foam, are the bubble interfaces. I have previously shown how such measurements give information on the average bubble size [5], but I also expect that information on the bubble shapes and average separation may also be extracted (such efforts are in progress, but will not be further discussed in this report). With DWS, intensity fluctuations in a speckle pattern are measured and analyzed within a diffusion theory for the average motion, or dynamics, of the scattering sites. I have previously shown how such measurements give information on the rate of T1 rearrangements, as shown in Fig. 3, in a coarsening foam [5].

An important feature of ST and DWS is that they are noninvasive measurements and can therefore be used to study stability issues directly in terms of the time evolution of structural parameters [6]. Furthermore, they can be performed simultaneously with stress-strain measurements in a custom-designed glass-walled rheometers; this will permit unprecedented and direct study of the interplay between structure, dynamics, and rheology.

## The Need for Prolonged Microgravity Conditions

While ground-based multiple light scattering and rheology measurements can be performed, they are restricted to foams for which the rate of drainage, while never zero, is negligibly small; in practice this limits attention to relatively dry foams with small average bubble sizes. This is especially unfortunate because a key parameter affecting the behavior of foams is their liquid-to-gas volume fraction: for dry foams, the bubble shapes are nearly polyhedral and their tight packing gives rise to shear elasticity; for wetter foams, the bubbles become increasingly spherical and the shear rigidity ultimately vanishes when the bubbles are no longer closely packed. The rate of coarsening and gravitational drainage also depend on the liquid content: wetter foams coarsen more slowly and drain more rapidly. Near the rigidity loss transition, drainage becomes so rapid that the 'foam' is a seething froth of bubbles which quickly ceases to exist; this is unavoidable since liquid and gas cannot be density matched. On earth, it is not possible to experimentally study the dependence of foam structure, rheology, and stability on liquid content without interference from gravity. Microgravity conditions are critically needed in order to systematically measure a sequence of foams with increasing liquid content, especially for wet foams and near the rigidity loss transition.

## RECENT SCIENCE RESULTS

In the current funding period we have made important progress both in terms of the development of multiple light scattering techniques and their application to a model foam system. As for the former, analysis of multiple light scattering data crucially assumes that photon propagation can be described by a diffusion approximation with source and boundary terms set by a phenomenological penetration depth and extrapolation length, respectively. While the accuracy of this approach can in principle be no greater than about 1%, far greater errors are introduced in practice due to inappropriate treatment of source and boundary terms. I have determined how to average over the penetration depth [7], and how to experimentally deduce the extrapolation length [8]. My objective, which is now nearly achieved, is to put ST and DWS theories on firmer theoretical ground and advance the reproducibility and accuracy of their application down from the 10% level to the 1% level. This is crucial if ST and DWS are to be truly quantitative probes of foam structure and dynamics. In addition, I have introduced a new optical configuration for DWS experiments which provides for significantly better photon-counting statistics and is less susceptible to systematic errors from imperfect laser beam conditioning.

To move towards our goal of simultaneous light scattering and rheology measurements, graduate student Anthony Gopal and I have recently completed a series of experiments on the response of foam dynamics to shear deformations in a sample cell consisting of two parallel glass plates, one of which can be translated at uniform velocity in order to shear the foam. The normalized electric field autocorrelation function is found to decay nearly exponentially with time. The value of the cumulant is set by the ratio of sample cell thickness to the transport mean free path of light and the rate  $\tau_o^{-1}$  of rearrangement events:  $\Gamma \equiv (L/\ell^*)^2 \tau_o^{-1}$ . Figure 4 shows how the rate

of rearrangement varies with the applied shear strain rate,  $\dot{\gamma}$ . If  $\dot{\gamma}$  is small compared to the rate  $\tau_{00}^{-1}$  of rearrangements in the quiescent foam, then the measured rate is unchanged. If it is larger, however, the rearrangement event rate increases and appears to be equal to the shear strain rate. At still higher strain rates, the shape of the correlation function begins to change and it appears that the foam is beginning to melt; in this regime, the duration of rearrangement events may be the significant time scale [9].

Following the cessation of an imposed shear strain, we have also measured intensity fluctuations and find that the rate of rearrangements decreases if the total shear strain suffered is greater than about 5%, as shown in Figure 5. For strains greater than on the order of one, we find that the rate of rearrangement decreases by a factor of roughly two and remains depressed until the foam coarsens significantly. This implies that there are important correlations between neighboring bubbles which result from the coarsening process and that this self-organized structure is naturally marginally stable.

## RESEARCH PLANS

In brief, our plans for ground-based research on the connection between foam dynamics and rheology are as follows. We first intend to construct an all-glass Couette cell in which a foam sample can be sheared at higher rates and for longer periods of time. We should then be able to reproduce and extend our recent work, and also begin to explore other foam systems. At the same time we would like to commence stress-strain measurements using a commercial rheometer in order to gain the necessary experience to convert our Couette cell into an instrument for simultaneous light scattering and rheology measurements. Such an instrument would allow us to explore both rheology and stability issues on the widest range of foams possible on earth, and would also serve as a prototype for the ultimate flight experiments in which the volume fraction of liquid is to be varied through the rigidity loss transition.

## CONCLUSIONS

Foams are familiar and important materials which remain of basic scientific interest due to lack of microscopic understanding of their fascinating and unusual properties. We have formulated, and are now implementing, a comprehensive research program which will overcome traditional experimental difficulties and serve to elucidate the fundamental interrelationships between foam composition, structure, dynamics, stability, and rheology. Rapid progress is now being made in the ground-based component of our approach in which new multiple light scattering techniques are developed and used to noninvasively probe foam structure and dynamics. The second key component to our approach will be the use of microgravity conditions in order to examine sequences of foams with fixed composition and topology but increasing liquid content. The need for microgravity is clear and compelling: It is crucial to vary the liquid content towards the rigidity loss transition, however this cannot be done on earth due to the intrinsic density mismatch of the liquid and vapor portions of foam and the rapidly increasing rate of drainage on earth as the transition is approached.

## REFERENCES

- [1] A. J. Wilson, Ed., *Foams: Physics, Chemistry, and Structure* (Springer-Verlag, New York, 1989).
- [2] D. J. Durian and D. A. Weitz, in *Kirk-Othmer Encyclopedia of Chemical Technology* J. I. Kroschwitz, Ed. (Wiley, New York, 1994).
- [3] A. M. Kraynik, *J. Fluid Mech.* **20**, 325 (1988).
- [4] D. J. Pine, D. A. Weitz, J. X. Zhu and E. Herbolzheimer, *J. Phys. (Paris)* **51**, 2101 (1990).
- [5] D. J. Durian, D. A. Weitz and D. J. Pine, *Science* **252**, 686 (1991).
- [6] D. J. Durian, D. A. Weitz and D. J. Pine, *Phys. Rev. A* **44**, R7902 (1991).
- [7] D. J. Durian, "Penetration depth for diffusing-wave spectroscopy", preprint (1994).
- [8] D. J. Durian, "Influence of boundary reflection and refraction on diffusive photon transport", to appear in *Phys. Rev. E* (August 1994).
- [9] S.S. Park and D.J. Durian, *Phys. Rev. Lett.* **72**, 3347 (1994).

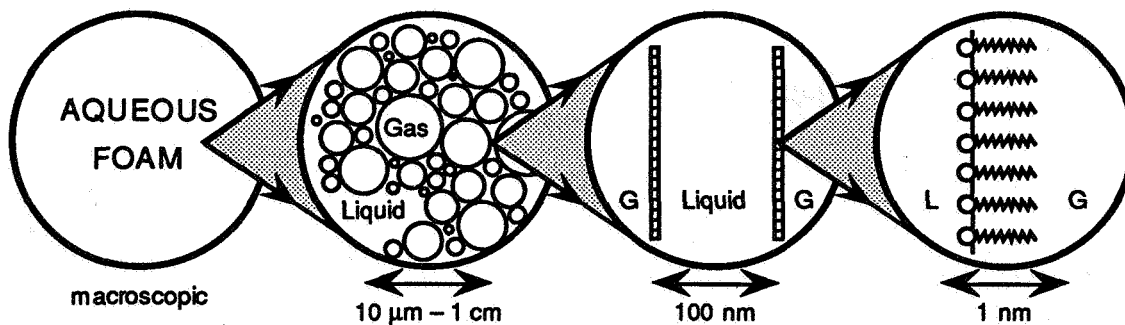


Fig. 1 – Hierarchy of structure and self-organization in an aqueous foam. Large gas bubbles are separated by thin liquid films which are stabilized against rupture by physical-chemical effects arising from the presence of adsorbed surfactants.

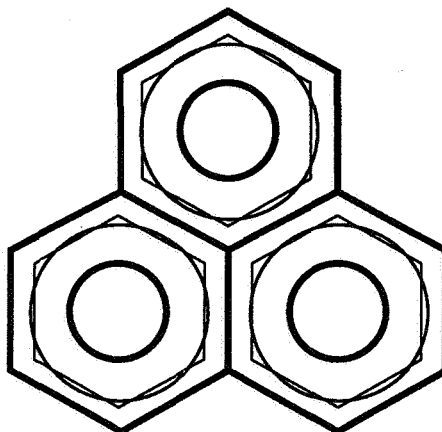


Fig. 2 – Influence of liquid content and physical-chemical effects on the shape of gas bubbles in a foam. In wet foams the bubbles are well-separated and nearly spherical, while in dry foams the bubbles are polyhedral; this is indicated by the heavy lines. For foams with fixed, nonzero, liquid content, however, the bubble shape can also vary in response to the competition between surface tension and repulsive interfacial forces; this is depicted by the light lines.

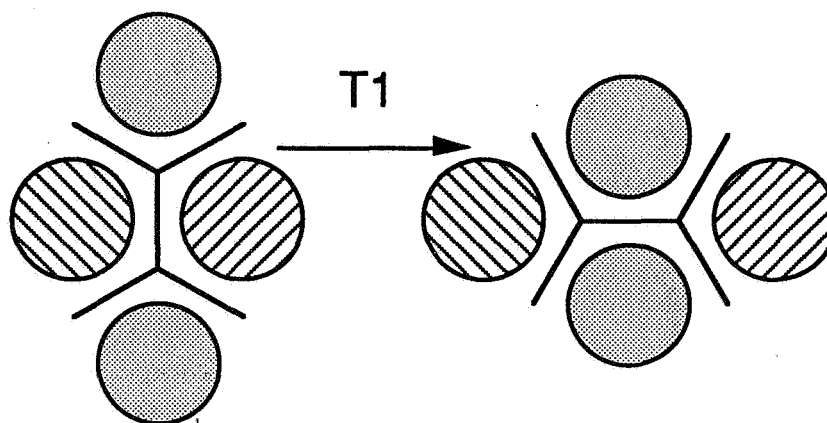


Fig. 3 – Schematic depiction of the T1 neighbor-swapping topology change; note that the number of bubbles and their relative sizes are unaffected by such rearrangements.

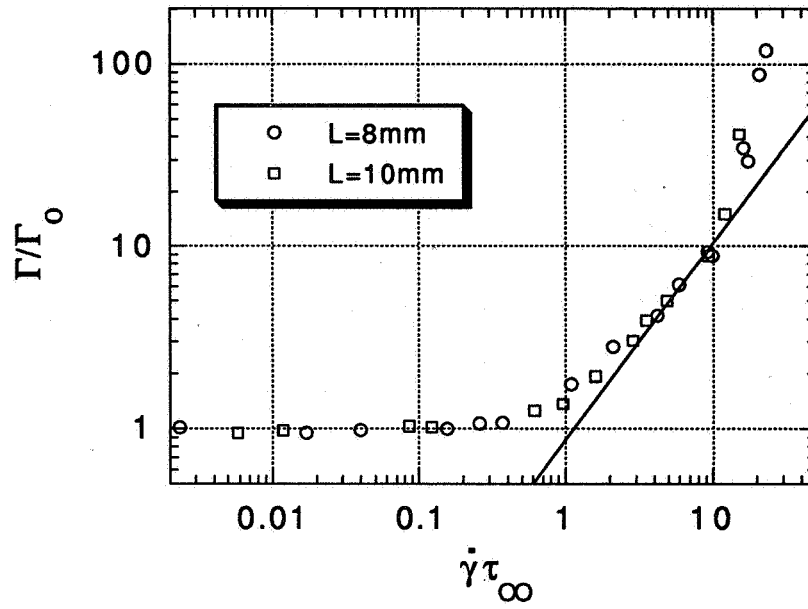


Fig. 4 – The rate of topological rearrangements vs the shear strain rate as measured by DWS.

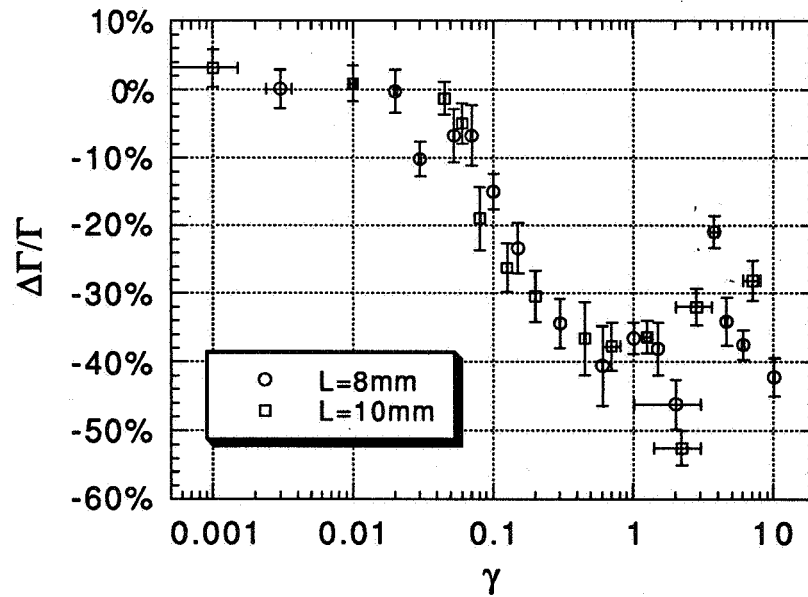


Fig. 5 – The change in rate of rearrangements following a step-strain as measured by DWS.