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Foam Optics and Mechanics

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FOAM OPTICS AND MECHANICS

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ABSTRACT

The Foam Optics and Mechanics (FOAM) project will exploit the microgravity environment to more accurately measure the rheological and optical characteristics of wet aqueous foams. Using both rheology and laser light scattering diagnostics, the goal is to quantify the unusual elastic character of foams in terms of their underlying microscopic structure and dynamics. Of particular interest is determining how the elastic character vanishes, i.e., how the foam "melts" into a simple viscous liquid, as a function of both increasing liquid content and increasing shear strain rate. The unusual elastic character of foams will be quantified macroscopically by measurement of the shear stress as a function of shear strain rate and of time following a step strain. Such data will be analyzed in terms of a yield stress, shear moduli, and dynamical time scales. Microscopic information about bubble packing and rearrangement dynamics, from which the macroscopic non-Newtonian properties ultimately arise, will be obtained non-invasively by multiple-light scattering: diffuse transmission spectroscopy (DTS) and diffusing wave spectroscopy (DWS). Quantitative trends with materials parameters, most importantly average bubble size and liquid content, will be sought in order to elucidate the fundamental connection between the microscopic structure and dynamics and the macroscopic rheology.

INTRODUCTION

Aqueous foams are intrinsically non-equilibrium systems; with time, the gas and liquid components inexorably separate by some combination of coarsening (gas diffusion from smaller bubbles to larger bubbles), film rupture, and the gravitational drainage of liquid from in between gas bubbles. While coarsening is often slow and film rupture can be eliminated, gravitational drainage cannot be prevented on Earth since it is not possible to density match gas and liquid; furthermore, the rate of drainage increases rapidly with liquid content. This fundamentally precludes the possibility of ground-based study of foams near the melting transition. Prolonged microgravity conditions are therefore required in order to eliminate drainage for experimental study of the intrinsic structure, dynamics, and rheology of foams with liquid content varying up to, and beyond, the melting transition.

The utility and fascination of foams derive largely from the surprising fact that they have a solid-like elastic character, in spite of being mostly gas with a few percent volume fraction of liquid, but can nevertheless flow under shear. The physical origin of such unusual rheology in terms of microscopic structure and dynamics is poorly understood and remains a subject of basic scientific interest to physicists, chemists, and chemical engineers. The proposed flight experiment promises important new insight into these issues, and could also have significant consequences for our understanding of flow in other dense randomly-packed systems such as emulsions, colloids, suspensions, slurries, bubbly liquids, and granular materials. Furthermore, all foam applications are empirically based and the proposed research may generate valuable fundamental guidance for the development of materials with more desirable rheology and stability characteristics.

FOAM PROPERTIES

Aqueous foam is a nonequilibrium collection of polydisperse gas bubbles packed in a smaller amount of water containing surfactants, or other surface-active macromolecules.[1-3] These preferentially adsorb at the gas-liquid interfaces and give rise to repulsive forces that prevent bubble coalescence. The typical bubble size can range from 10 μm to 1cm, and their minimum surface separation distance, i.e., the soap film thickness, can range from 10 Å to 1 μm. The volume fraction of liquid can be as small as 0.01%, such that the bubbles are nearly polyhedral, or as large as about 8% on Earth, such that the bubbles appear slightly spherical. If made wetter, however, the liquid will rapidly drain under the influence of gravity; thus, the close-packing limit of about 35% liquid, where the bubbles are perfectly spherical, cannot be reached on Earth. The following photos show the actual bubble-scale structure in two very different foams. One is a single-surfactant foam (SDS in water), where the bubble size is 3 mm and where drainage and the influence of liquid content on bubble shape are evident. The other is a commercial shaving foam (Gillette™ Foamy Regular), where the bubble size is 30 μm. Note that in spite of differences in chemistry and size scale, the foams are very similar where the liquid contents are equal. As we shall see, liquid content is the single most important parameter to vary—but this cannot be done to the extent needed in the presence of Earth's gravity.

Aqueous foams are continually-evolving systems far from equilibrium. With time, the gas and liquid portions inexorably separate by some combination of three basic mechanisms. First, if the quality or concentration of surfactants is too low, then adjacent bubbles can coalesce by rupture of the intervening soap film. This film-rupture mechanism can be eliminated easily by suitable choice surfactant and concentration. Second, the Laplace pressure difference between bubbles of different sizes causes gas to diffuse through the intervening soap film from the small to the larger bubble; thus, large bubbles grow and small bubbles shrink. This coarsening mechanism cannot be eliminated, but can be slowed by decreasing the surface tension of the interfaces and the solubility and diffusivity of the gas. Third, the unavoidably large density mismatch between gas and surfactant solution causes the bubbles to rise and the liquid to sink; as this proceeds, the soap films can become so thin as to rupture by thermal fluctuations. Gravitational drainage cannot be eliminated on Earth; however, it can be slowed by decreasing the bubble size and by increasing

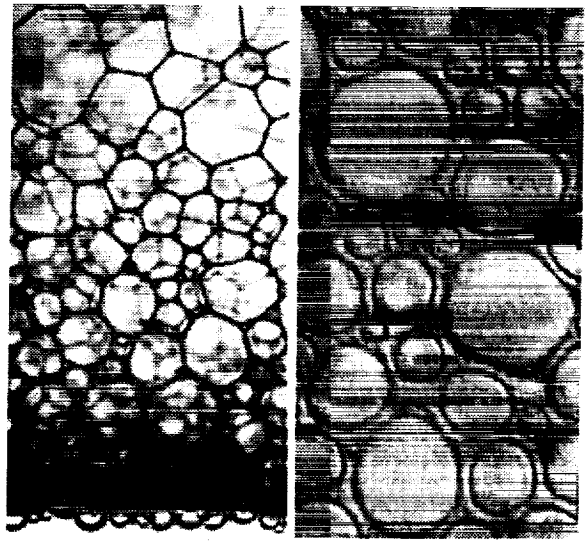

Figure 1. Bubble scale structure

the liquid viscosity and the gas content. Of these mechanisms, only coarsening represents a behavior intrinsic to all foams, since it cannot be eliminated even in principle. By contrast, rupture and drainage serve to complicate and mask intrinsic behavior and to prevent wide variation of key structural parameters such as liquid content.

As a form of matter, foam is neither solid, liquid, nor vapor—yet it possesses the hallmark mechanical features of all three forms of matter. Under small applied shear forces, it can respond elastically, like a solid. Under large applied shear forces, it can flow and deform arbitrarily without breaking, like a liquid. Under pressure or temperature perturbations, it can proportionally change its volume, like a gas. This unusual rheological behavior in combination with low density and high interfacial area is the basis for our common fascination with everyday foams and for their utility in a wide variety of applications.

FOAM APPLICATIONS

Liquid-based foams are familiar from everyday life in the form of detergents, foods, and cosmetics of all sorts. They also find use in a wide array of unique applications like firefighting, isolating toxic materials, and spreading/delivering chemicals. They are also used in physical and chemical separations, most notably in the froth-flotation method of refining ores. In the petrochemical industry they are used in a variety of ways to enhance oil recovery. And liquid-based foams are also of course the precursors to all synthetic cellular solids, whether polymer or metal. Foams also tend to

arise in unwanted circumstances whenever multi-component liquids are processed. This is the bane of pulp and paper, paint and coating, textile, leather, adhesives, and other industries. This effect is also familiar from the ugly yellow/brown foams telltale of polluted natural waters.

Whether a special-purpose material or a unwanted byproduct, in all cases it is crucial to control both the mechanical and stability properties of foams. Unfortunately, our current fundamental understanding is so limited that these tasks are still accomplished by trial-and-error on a case-by-case basis.

DIAGNOSTICS

In this section we describe and illustrate the major diagnostics. The schematic geometry for the proposed experiment is shown in Figure 2.

Video Microscopy

The most straightforward diagnostic of foam structure is to estimate the bubble size distribution, $\rho(d)$, from still-frames of bubbles at the surface where a bulk foam is pressed against an optically clear wall. This is also important for verifying that the sample is homogeneous, without any empty pockets filled with gas. From real-time video recordings, the sudden bubble-scale rearrangements can be directly observed near the surface and analyzed in terms of the key time scale, τ_d, the event duration.

Diffuse Transmission Spectroscopy

In this diffusing-light spectroscopy, the probability T_d for incident photons to be diffusely transmitted is estimated from measuring the time-averaged transmitted intensity, $\langle I \rangle$, and normalizing by the intensity I_o of the incident light: $T_d=\langle I \rangle / I_o$. From ancillary knowledge/measurement of the extrapolation length ratio z_e and slab thickness L, the transport-mean free path l^* of the photons is then extracted using the diffusion-theory prediction $T_d=(1+z_e)/(L/l^*+2z_e)$. This provides a second measure of the foam structure since l^* is approximately equal to the bubble diameter divided by the square-root of the liquid fraction,[4] as shown in Figure 3.

In the microgravity experiments, the liquid fraction ε will be known, so the value of l^* will give the average bubble size in the bulk foam. Furthermore, the value of l^* is also a crucial ingredient needed for analysis of DWS data, discussed next.

Diffusing-Wave Spectroscopy

In this spectroscopy, temporal fluctuations in the diffusely transmitted light are characterized by real-time computation of the intensity autocorrelation function, $g_2(\tau)=\langle I(0)I(\tau)\rangle/\langle I\rangle^2$, using photon-counting and a digital correlator. This is similar to traditional dynamic light scattering, or photon-correlation spectroscopy, except that the detected photons have been multiply scattered, rather than singly by a selected scattering wavevector. The normalized field correlation function $g_1(\tau)=\langle E(0)E^*(\tau)\rangle/\langle EE^*\rangle$ is then extracted using the Siegert relation, $g_2(\tau)=1+\beta g_1(\tau)^2$; this, in turn, is analyzed in terms of the nature and time scales of the bubble motion using the theory of DWS. For example, discrete rearrangements and uniform shear give contributions to $g_1(\tau)$ that decay roughly exponentially in $(L/l^*)^2$ times τ/τ_o and $(\tau/\tau_s)^2$, respectively, where τ_o is set by the size and frequency of the discrete rearrangements, and

$$\tau_S^{-1} = \dot{\gamma}\ kl^*/\sqrt{30} \qquad (1)$$

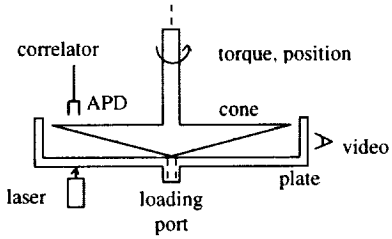

Figure 2. Schematic of the FOAM sample cell for simultaneous optical and rheological measurements.

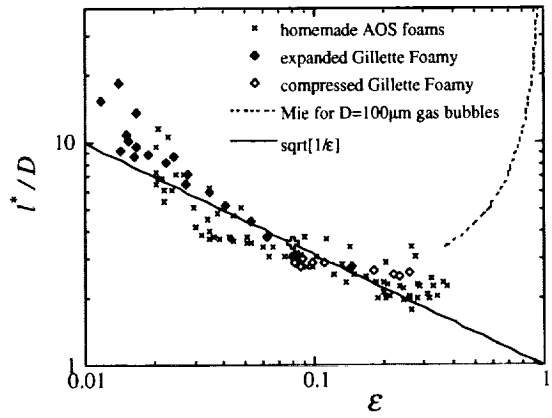

Figure 3. Photon mean free path l*, normalized by bubble diameter, as a function of liquid content.

is set by the strain rate of the homogeneous deformation. These features can be seen in the DWS data taken for a foam in our homemade Couette cell at a series of increasing strain rates, shown in Figure 4.

Note that digital correlators compute the average intensity as well as its temporal autocorrelation, and that therefore DWS measurements automatically yield DTS. The only extra requirement for doing DTS with a DWS set-up is to determine the normalization, which can be done by calibration or comparison with a known sample.

Stress Relaxation During Steady Shear

All rheological diagnostics reduce to measurements of torque and angular position of a rotating tool. Our geometry will be cone-plate. In this rheological diagnostic, the first task is to measure the average shear stress $\sigma(\dot\gamma)$ at the given angular rotation speed Ω or strain rate $\dot\gamma$. This gives the apparent viscosity of the foam, which is always shear-thinning but with a strange functional form,[5] as shown in Figure 5.

The next task is to superimpose a small amplitude step-strain $\Delta\gamma$ on top of the steady rotation and to measure the transient increase in stress $\sigma(t)$ and its relaxation back to the steady-state value $\sigma(\dot\gamma)$; in other words, to measure the generalized shear relaxation modulus $G(t, \dot\gamma)=[\sigma(t)-\sigma(\dot\gamma)]/\Delta\gamma$. This is to be checked for linearity by varying $\Delta\gamma$ and to be repeated for a range of rotation speeds, including zero where it reduces to the traditional shear relaxation modulus.

Plots of $\sigma(\dot\gamma)$ and $\eta=\sigma(\dot\gamma)/\dot\gamma$ vs. $\dot\gamma$, and of $G(t, \dot\gamma)$ vs. t and $\dot\gamma$, serve to characterize the shear rheology of the foam without further analysis. Of course, however, other quantities may be extracted in the context of models such as the shear modulus, yield stress, yield strain, plastic viscosity, spectrum of relaxation times, etc. Example data are shown in Figure 6, obtained with a Paar-Physica UDS-200 rheometer.[6]

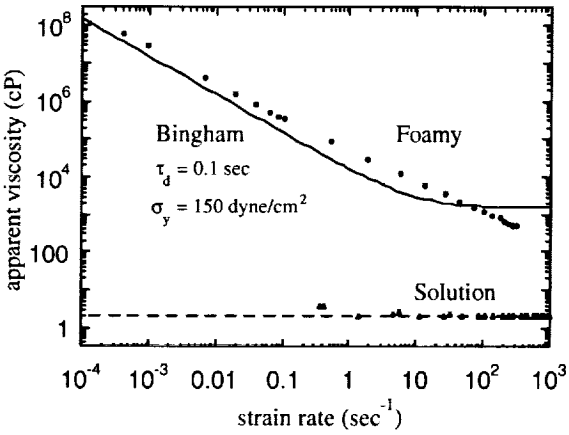

Figure 5. Shear-thinning of foam.

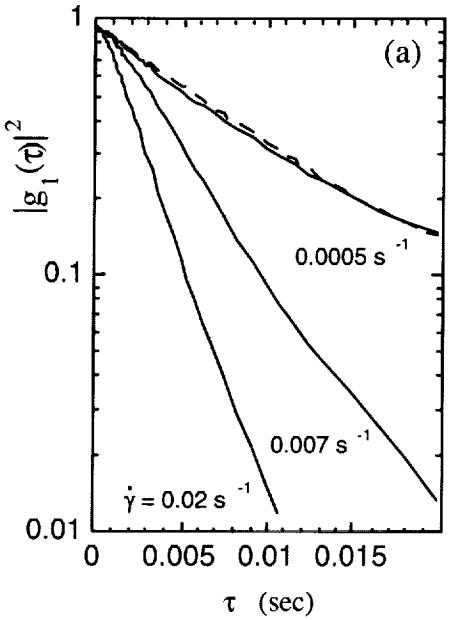

Figure 4. Microscopic dynamics of the foam is probed by DWS during steady shear.

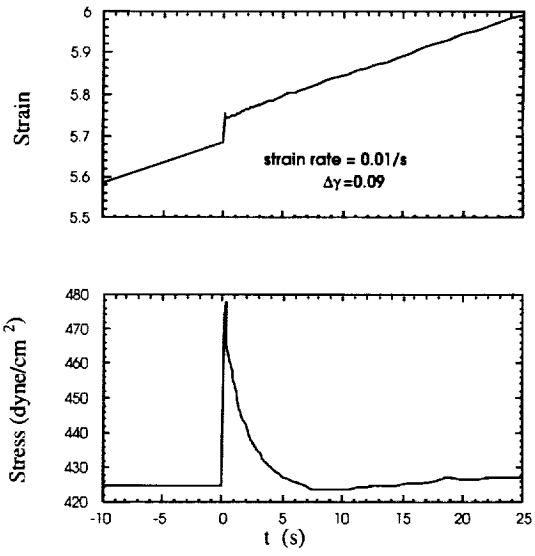

Figure 6. Stress relaxation in foam following a step-strain during steady shear.

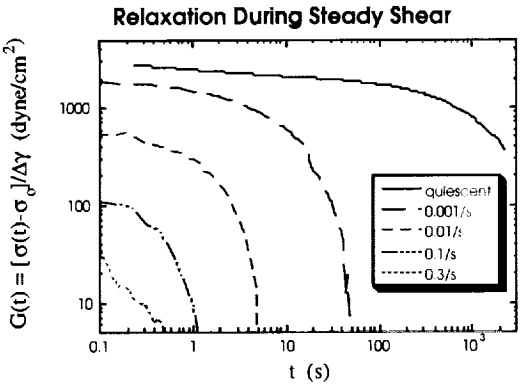

Figure 7. Stress relaxation for various shear rates.

From this data we extract both the viscosity and the shear-relaxation modulus. This gives stress vs. strain rate data shown earlier, and as well as the following picture of how the relaxation modulus decreases, and the foam becomes progressively more liquid-like, with increasing strain rate,[6] as shown in Figure 7.

The melting transition as a function of increasing liquid content is expected to be rather different. According to simulation, the relaxation time actually increases while the static shear modulus goes to zero.

NEED FOR MICROGRAVITY

Since the rate of drainage in foams increases with liquid content,[7,8] the volume fraction of liquid accessible on Earth is restricted to a very narrow range, below about 10%, where the foam is still relatively dry with nearly polyhedral bubbles. Therefore the dramatic changes in foam structure, bubble dynamics, coarsening, and rheology that are expected on approach to the melting point at about 36% liquid cannot be studied by ground-based experiments.[9] Furthermore, the intrinsically large mass density difference between gas and liquid precludes broader variation of liquid content simply by clever choice of material, as in the density matching of colloids or binary-liquid mixtures.

One possibility to extend the range of accessible volume fractions on Earth is to establish a steady state where the liquid which drains out the bottom is replaced by a continuous rain of liquid from above. However, this is not satisfactory for several reasons: (a) The liquid preferentially travels down through Plateau borders such that the bubble shapes are different from what they would be in zero gravity but with the same average liquid content; this alters both coarsening and rheology. (b) We find that the downward flow of liquid can induce stratified convective rolls as well as size segregation of bubbles in polydisperse foams;[10] this alters both coarsening and rheology. (c) This "forced/steady-drainage" could be implemented in a Couette rheology geometry, but not in the cone-plate system.

Another possibility to extend the range of accessible volume fractions on Earth is to tumble the entire system or otherwise provide continuous mixing. However, this is not satisfactory for several reasons. (a) Same as reason (a) above. (b) Uniaxial spinning may merely replace vertical gravitational drainage with radial centrifugal drainage. Under more complex tumbling or stirring there is no guarantee that the volume fraction would be homogeneous throughout the system unless there is also rapid convection of bubbles; this would alter coarsening and rheology. (c) Even with rapid convection, our experience is that the system still becomes inhomogeneous, especially at high liquid content. Perhaps the single most important limitation is that: (d) Steady tumbling or stirring cannot be implemented simultaneously with rheological diagnostics. Nevertheless, it may offer some overlap with low-g DWS data for fairly dry foams, in the 5 to 20% liquid content range.

In short, progress can be made on Earth but only in carrying out the optical and mechanical diagnostics for relatively dry foams far from the melting point. However, even then, drainage is not absent and this (a) raises ambiguities as to its relevance and (b) prevents the long duration runs needed to obtain reproducible bubble-size distributions and to fully characterize coarsening.

The minimum time required for the structure of a freshly prepared foam to coarsen into a reproducible distribution of bubbles sizes ranges from tens of minutes to a few hours. After that, several hours to several days are needed to allow the coarsening process to proceed appreciably. Furthermore, the DWS and rheology diagnostics require tens of minutes at each point in the foam's lifetime. Thus, only DTS and video microscopy could be usefully performed in drop towers, aircraft, or sounding rockets; however, even then, the results would be ambiguous because the bubble size distribution would not be reproducible.

We thus make the following conclusions: (a) Microgravity conditions are the only viable alternative to eliminate drainage and hence to enable

study of the dramatic changes in foam structure, bubble dynamics, coarsening, and rheology that occur as the liquid content is increased toward the melting point. (b) Experiment durations of several hours to several days are needed in order to obtain reproducible self-similar bubble size distributions via the coarsening process, to observe appreciable self-similar coarsening of the foam, and in order to perform DWS and rheology diagnostics. (c) These requirements for prolonged microgravity conditions can be met only by accommodation in the International Space Station.

CONCLUSION

Aqueous foams are familiar and interesting materials with a wide variety of non-obvious uses and occurrences. However, fundamental understanding is still lacking of the interrelationships between bubble-scale structure and dynamics and the unusual macroscopic stability and rheology. We propose to make progress in establishing such knowledge via a coordinated application of newly developed diagnostics as a systematic function of key parameters. Namely, diffusing-light spectroscopies plus rheology and video microscopy vs. foam liquid content and age. This program has already been demonstrated for dry foams, where gravitational drainage is negligible. Prolonged microgravity conditions, however, are crucially needed to prevent drainage for wet foams and thus permit observation of dramatic changes in structure, dynamics, and rheology as the liquid content is increased toward the melting point.

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13. ABSTRACT ***(Maximum 200 words)***

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