

THE MELTING OF AQUEOUS FOAMS

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ABSTRACT

Diffusing-wave spectroscopy measurements show that ordinarily solid aqueous foams flow by a series of stick-slip avalanche-like rearrangements of neighboring bubbles from one tight packing configuration to another. Contrary to a recent prediction, the distribution of avalanche sizes do not obey a power-law distribution characteristic of self-organized criticality. This can be understood from a simple model of foam mechanics based on bubble-bubble interactions.

INTRODUCTION

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 μm 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.

The Long-Range Goal: is to exploit rheological and multiple-light scattering techniques, and ultimately microgravity conditions, in order to quantify and elucidate the unusual elastic character of foams in terms of their underlying microscopic structure and dynamics. Special interest is in determining how this elastic character vanishes, i.e. how the foam melts into a simple viscous liquid, as a function of both increasing liquid content and shear strain rate.

General Approach: The unusual elastic character of foams will be quantified macroscopically by measurement of the shear stress as a function of static shear strain, shear strain rate, and time following a step strain; such data will be analyzed in terms of a yield stress, a static shear modulus, and dynamical time scales. Microscopic information about bubble packing and rearrangement dynamics, from which these macroscopic non-Newtonian properties presumably arise, will be obtained non-invasively by novel multiple-light scattering diagnostics such as diffusing-wave spectroscopy (DWS). Quantitative trends with materials parameters, such as 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.

Need For Microgravity: Aqueous foams are intrinsically nonequilibrium systems; with time, the gas and liquid components inexorably separate by some combination of coarsening (gas diffusion from smaller 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. 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.

Significance: The utility and fascination of foams are derived 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. The planned research 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, colloidal 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 better stability.

In this paper: we focus on recent results regarding the melting of foams, not as a function of liquid content, but rather as a function of shear rate. Foam is confined between parallel glass plates which have been roughened to impose a no-slip condition as one plate is slid relative to the other. To study the dynamics of bubble rearrangements induced by the applied shear, we employ DWS and thus measure fluctuations in the transmitted intensity of light from a coherent laser. This yields a normalized electric field autocorrelation function, $g_1(\tau)$, which is subsequently analyzed using the formalism of diffusing-wave spectroscopy (DWS). We begin with a discussion of technical advances in the DWS technique followed by application to our specific foam system under shear. Lastly the experimental results are understood using a new model of foam mechanics.

ADVANCES IN DIFFUSING-WAVE SPECTROSCOPY (DWS)

To extract useful information from DWS measurements requires that the propagation of light through the multiple-scattering sample be accurately modeled. Traditionally, this is done using a diffusion approximation wherein the number density of photons is assumed to have no direction dependence and to obey the diffusion equation [3]. This approach neglects the ballistic nature of photon transport between successive scattering events, and requires that additional assumptions be made about the treatment of the source terms and boundary conditions. The traditional formalism thus fails near the source and boundary, for strong absorption, and for samples that are not optically thick. Even within the range of validity, the accuracy can still be unacceptably poor if the source terms and boundary conditions are not properly treated. Furthermore, there is no means within diffusion theory to incorporate the effects of scattering anisotropy. By use of computer simulation and experiment, we have shown how best to implement the source terms [4] and boundary conditions [5, 6] within diffusion theory, and have quantified the accuracy of the resulting predictions [7]. In particular, we have shown how to average the penetration depth over an appropriate distribution and that the extrapolation length can be deduced from the angular dependence of diffusely transmitted light.

We have also proposed a two-stream theory of DWS that makes no diffusion approximations but can be solved analytically [8]. It provides a natural means of incorporating the effects of boundary reflections and, for the first time, ballistic propagation and scattering anisotropy. Predictions are compared with simulation in Figure 2, showing that these effects are of considerable magnitude in typical experimental situations and that they now can be accurately accounted for. These developments help transform DWS into a quantitative tool on the same level of accuracy as traditional single-scattering techniques, and will thus be crucial to the ultimate success of our approach.

DWS APPLIED TO A FLOWING FOAM

The nature and rate of bubble-switching rearrangements in a coarsening foam can be measured using DWS [9]. Here, experimental electric field correlation functions are shown in the inset of Figure 3 before, during, and after imposed shear strain [10]. Also shown are excellent fits using the formalism of DWS and the assumption that events have a characteristic size and occur at random with a characteristic rate. This gives a nearly-exponential form for the decay with a time scale set by the optical thickness and the rearrangement rate. The main plot shows the ratio of this rate to that in a quiescent sample as a function of applied strain rate. At low strain rates, the ratio is one, implying that coarsening induced events dominate the dynamics. At high strain rates, the ratio is well-described by the form $1 + A(V/L)\tau_{oq}$, where V/L is the strain rate, plate speed divided by separation, τ_{oq} is the time

between rearrangements in the quiescent sample, and A is an adjustable parameter. This implies that rearrangements are induced by shear at a rate given by the shear strain rate. From the value of A , we deduce that the events consist of a small core of bubble, approximately four across, undergoing sudden topology change. Macroscopic deformation and flow of foams are thus accomplished by a series of these sudden stick-slip, locally avalanche-like, events of neighboring bubbles from one configuration to another.

BUBBLE-MODEL SIMULATIONS

Sudden rearrangement of bubbles during flow has been predicted in several models of foam rheology. In the classic Princen-Prud'homme model of the foam as a periodic hexagonal network, the happen simultaneously throughout the entire system [11, 12]. However, all foams are naturally disordered and this significantly changes the nature of actual events, as shown in the models of Weaire and Kawasaki and their co-workers [13, 14]. Weaire's model is based on a caricature of individual soap films separating adjacent bubbles. It thus allows for liquid content to be varied over a small range, but is strictly quasi-static and difficult to implement in higher than two dimensions. Kawasaki's model is based on a caricature of the vertices where three films meet and the dissipation that occurs when the films move, but is strictly limited to two dimensional foams with zero liquid content. Both models predict that avalanche-like rearrangement events can be triggered by small strain increments, and that the distribution of these events is sufficiently broad to be considered as a deterministic example of self-organized criticality. Our experiments seem to rule this out, however, and so here we present an alternative microscopic model of foam rheology.

Rather than focus on interfaces, films, or vertices, we focus instead on entire bubbles and their interactions [15]. If two bubbles in a sea of liquid are pushed together, then their shapes will distort away from spherical and the increase in surface area will give rise to a repulsive central force. And any relative motion of the two interacting bubbles will be retarded by a viscous drag in approximate proportion to their velocity difference. We seek the simplest possible model that includes these two crucial ingredients. Our new model is thus constructed by summing pair-wise interactions between neighboring gas bubbles as approximated in terms of their center positions $\{\bar{r}_i\}$, velocities $\{\bar{v}_i\}$, and radii $\{R_i\}$. No degrees of freedom are introduced for details of the bubble shapes. The equation of motion for bubble i can then be written as

$$\bar{v}_i = \langle \bar{v}_j \rangle + \frac{F_o}{b} \sum_j \left[\frac{1}{|\bar{r}_i - \bar{r}_j|} - \frac{1}{R_i + R_j} \right] (\bar{r}_i - \bar{r}_j) + \frac{\bar{F}_i^a}{b}, \quad (1)$$

where F_o is set by surface tension, b is set by viscous drag, where the sum includes only neighboring bubbles j that satisfy $|\bar{r}_i - \bar{r}_j| < R_i + R_j$, and where \bar{F}_i^a is an externally applied force for edge bubbles. The first term represents viscous dissipation due to relative motion, and the second represents a repulsive spring force due to shape distortion. By contrast with all other models, ours is trivial to implement for foams of arbitrary dimensionality and liquid content. It is also complementary in being a closer approximation to reality in the limit of wet foams, whereas previous models are closer in the limit of dry foams.

Like previous models, ours predicts sudden avalanche-like rearrangements to be triggered by small strain increments during slow, steady shear. Unlike previous models, however, we do not find a broad distribution of event sizes characteristic of self-organized criticality. Figure 4 shows the bubble configuration before and after the very largest rearrangement event seen, as measured in terms of energy release. Just as in our DWS experiments, the event does not span the system but instead involves only a small core of bubbles undergoing topology change. We speculate that a combination of finite liquid content, which allows bubbles to rearrange more readily, and viscous dissipation, which slows down the bubble motion and hence hinders event propagation, are responsible for setting an upper limit on the event size and thus preventing self-organized criticality.

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. 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.

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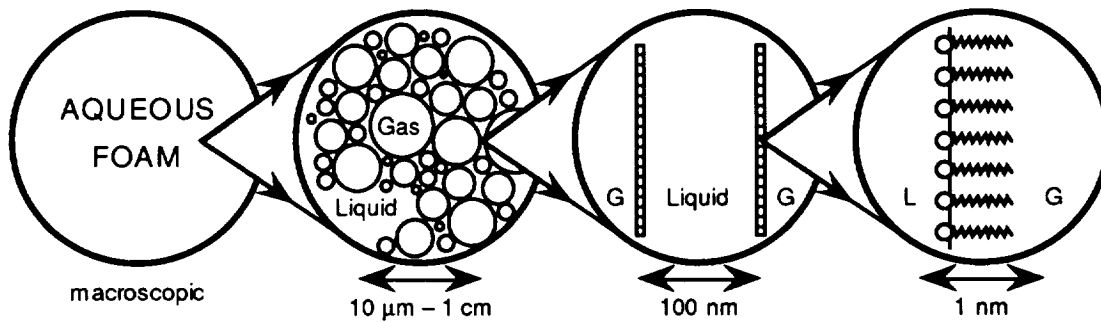


Fig. 1 – Hierarchy of structure and self-organization in an aqueous foam. Large gas bubbles are separated by thin liquid films which are stabilized against rupture by physical-chemical effects arising from the presence of adsorbed surfactants.

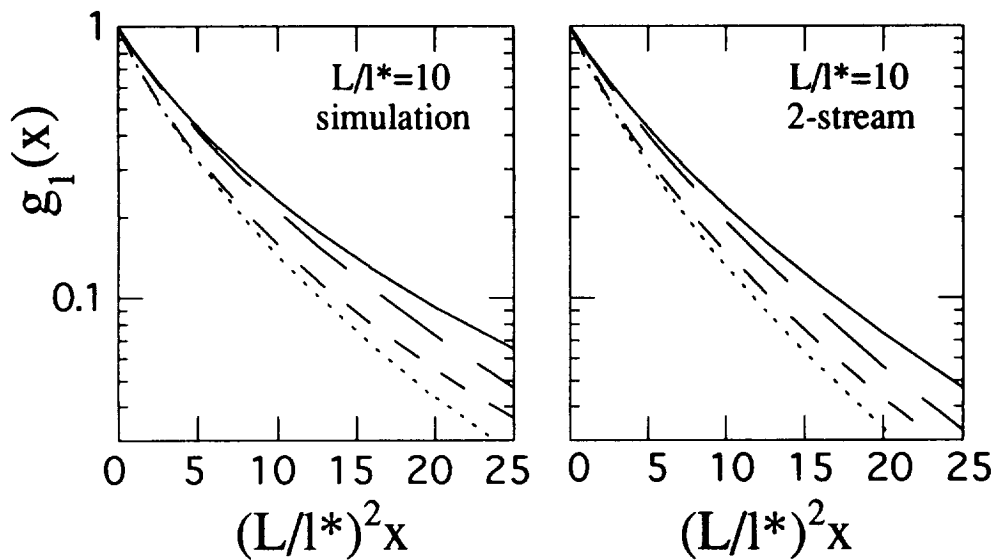


Fig. 2 – DWS correlation function as a function of the dynamical variable $x = k^2 \langle \Delta r^2(\tau) \rangle$ for a transmission through a slab of thickness ten transport mean free paths. The boundary reflectivity and scattering anisotropy are signified by curve type: solid for $R = 0$ and $l^*/l_s = 1$; long dash for $R = 0$ and $l^*/l_s = 10$; short dash for $R = 1/2$ and $l^*/l_s = 1$; dotted for $R = 1/2$ and $l^*/l_s = 10$.

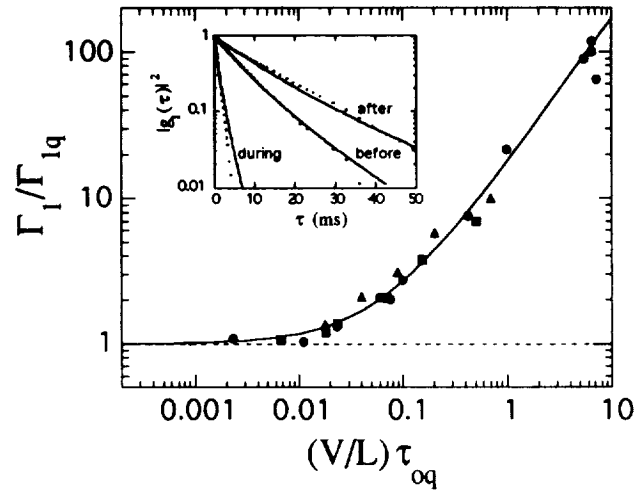


Fig. 3 – Inset: Typical DWS correlation functions for foam before, during, and after application of shear along with fits for the rate of rearrangements. Main: the ratio of rearrangement rate in sheared to quiescent samples as a function of plate speed, separation, and time between events in quiescent sample. Triangles, circles, and squares are for samples of thickness 6, 8, and 10 mm. The solid curve is a fit to $1 + A(V/L)\tau_{oq}$, from which we deduce that rearrangement events involve topology changes with in small core region only 4 bubbles across.

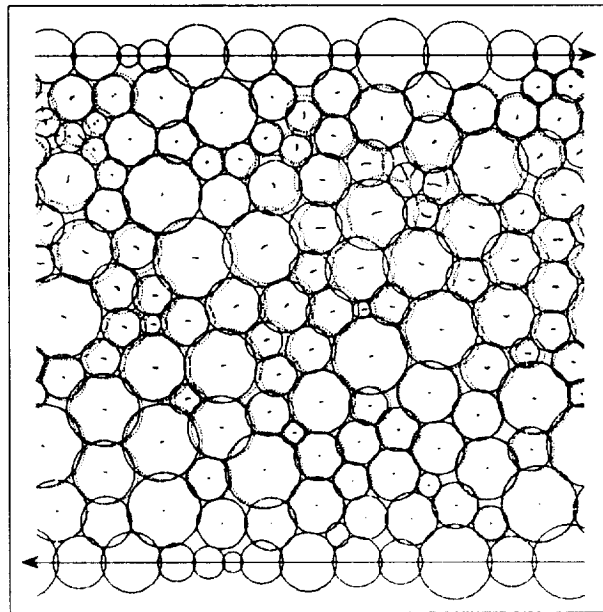


Fig. 4 – Bubble configurations before (light) and after (heavy) a simulated rearrangement; the dotted curves show the bubble center positions during motion. This particular event produced the largest observed energy release, but only involves topology change to a small core of bubbles, consistent with experiment.