Experimental Studies of Bubble Dynamics in a Slowly Driven Monolayer Foam

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We report a study of the topological rearrangements in a Langmuir-monolayer foam subjected to a constant rate of strain. Measurements of the size distribution for the rearrangements are compared with three simulations that find a power-law distribution for a gas area fraction $\phi = 1$, a power law for $\phi = 0.84$, and an exponential cutoff in the size distribution. No evidence for power-law scaling is found in the experiments for $0.85 \leq \phi \leq 0.95$. These comparisons suggest that the nature of the dissipative mechanisms is an important factor in the determination of the size distribution. [S0031-9007(97)02815-9]

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Random cellular structures are ubiquitous in nature. They occur in such diverse systems as shaving cream, dense emulsions, magnetic domains, grain boundaries in thin metals, and monolayers of amphiphilic molecules at the air-water interface, i.e. Langmuir monolayers. These structures are dominated by geometry and are essentially independent of microscopic properties [1]. Two relatively simple systems that have been extensively studied are aqueous foams [1] and Langmuir-monolayer foams [2–4]. Aqueous foams consist of gas bubbles separated by fluid walls. Foams in Langmuir monolayers are one-component systems composed of bubbles of a gaseous phase separated by thin walls of a liquid phase. They are inherently two-dimensional because the molecules are confined to the air-water interface. The structure and evolution of monolayer foams have been found to be closely similar to those for quasi-two-dimensional aqueous foams trapped between closely spaced plates [3,4].

One of the most remarkable, and technologically relevant, features of foams is their range of mechanical properties. For sufficiently small stresses, foams behave like a solid and are capable of supporting static shear stresses. This solidlike behavior can be understood in terms of the linear response of individual bubbles, which results from the competition between surface tension and shape distortion. When the stress or applied strain is sufficiently large, the foam flows like a fluid. This liquidlike behavior is inherently nonlinear, involving topological rearrangements of the bubbles from one metastable state to another. The connection between the topological rearrangements of individual bubbles and the macroscopic flow properties of foams is not well understood.

Various models of two-dimensional foams [5–11] have been studied by computer simulation with the goal of elucidating the dynamics of sheared foams. In this paper, the experimental results will be discussed in the context of three different models proposed by Kawasaki and co-workers [5–7], Durian [8,9], and Weaire and co-workers [10,11]. (Henceforth, we will refer to the work in Refs. [6] and [7] as Kawasaki's simulation and the work in Refs. [10] and [11] as Weaire's simulation.) We chose these three simulations because they correctly predict the qualitative behavior of the macroscopic flow [6–11]. However, the quantitative predictions of the simulations for the size distribution and frequency of nonlinear bubble rearrangements above the yield strain differ. (For small values of the rate of strain, the yield strain is the value of the strain below which the foam responds elastically and above which the foam flows.)

Foams may be characterized by the area fraction of gas, ϕ. For $\phi < 0.84$, the foam "melts" into a froth that is composed exclusively of circular gas bubbles. Foams near this transition are said to be "wet." The dry-foam limit, $\phi = 1$, is an idealized foam with no liquid content and infinitely thin walls. In Kawasaki's simulation [7], a power-law distribution for the event size is found at $\phi = 1$ that is proposed to be an example of self-organized criticality [12]. In contrast, Weaire's simulation [11] suggests power-law behavior in the wet limit, and Durian's simulation [9] suggests an exponential cutoff of the large events.

Because they are inherently two dimensional, Langmuir-monolayer foams provide a useful test of these models. We report here the measured statistics of the topological rearrangements for a range of ϕ and the strain rate. Our results are most consistent with the behavior reported by Durian [9], and comparisons with the models suggest that the source of dissipation in a foam is an important factor in determining the behavior of the topological rearrangements.

Langmuir monolayers exhibit a first-order transition between a low-density gaseous (G) phase and a denser liquid-expanded (LE) phase [13]. Equilibrium properties of G-LE monolayer foams have been studied for a series of long-chain alkanoic acids and esters [2–4]. We observed foams of ethyl heptadecanoate and of myristic acid by fluorescence microscopy and recorded the images on video tape for analysis; 1% NBD-hexadecylamine was added as a fluorescent probe. Monolayer foams have also been observed by Brewster-angle microscopy [14], which does not require the use of a probe, so their existence cannot be associated with the probe impurity.

The Couette apparatus for studying monolayers under shear consists of two concentric cylinders with their axes aligned vertically. The monolayer is formed on the surface of water, which fills the channel between the cylinders. The channel is 0.5 cm wide and 1.7 cm deep. The cylinders are made of gold-plated brass that was coated with a self-assembled monolayer of octadecylthiol. The thiol layer ensures a contact angle of 90° between the water and the cylinder walls, and provides a flat interface. We were able to examine rates of strain between about 0.011 and 0.003 s^{-1} by an appropriate choice of motor speeds and gears. The field of view of the microscope is roughly circular with a diameter of 0.03 cm. Details of the apparatus will be reported elsewhere [15].

Foams were prepared by depositing a solution of the amphiphile and probe in chloroform on the water surface with a microsyringe. The amount of material was adjusted so that the layer was in the G-LE coexistence range with a value of $\phi \approx 0.3$. This produced a roughly uniform distribution of small gas bubbles. A relatively uniform foam with gas area fractions in the range 0.8 to 0.95 was then produced by aspirating a small amount of material from the surface.

In this geometry, both the water subphase and the monolayer are sheared. The flow profile of the pure LE phase was measured and agrees with the usual Couette solution for flow between concentric cylinders. In the experiments with the foams, two Teflon barriers were inserted into the channel in order to isolate a roughly 4.5 cm long region in which the foams were made. Without the barriers, surface flows throughout the channel during deposition produced very heterogeneous monolayers. In the presence of the barriers, the flow in the LE phase was altered by a counterflow along the stationary wall. An example of the measured flow profile across a section of the trough is shown in Fig. 1 for a rotation rate of the outer cylinder of 28 μm/s.

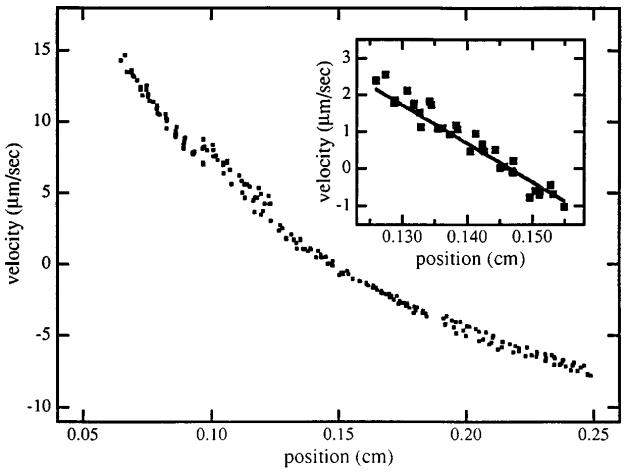

FIG. 1. Velocity profile for the liquid-expanded phase of the monolayer. The position is taken as the radial distance from the outer cylinder. The inset shows the velocity profile across the field of view used in this experiment, and the solid line is a linear fit to the profile.

The foam was observed in the region where the velocity goes through zero so that a fixed set of bubbles could be observed.

In the absence of shear, the coarsening of the foam induces two main topological processes [1]: An exchange of neighbors, which is known as a T1 process [shown schematically in Fig. 2(a)], and the disappearance of three-sided bubbles, which is called a T2 process [Fig. 2(b)]. Occasionally, the breakage of a bubble wall results in the coalescence of two bubbles. The rate of T1 and T2 processes in an unsheared foam decreases as a power law in time [1]. Therefore, the system was equilibrated for 30 min to ensure that the rate of T1 and T2 events due to the static evolution was sufficiently slow that shear-induced events dominated during the period of observation. With shear, only T1 events were observed.

The foams can be characterized by their gas area fraction. To compute ϕ, the gray-scale images of the foam were thresholded to produce a binary image, and ϕ was taken as the fraction of black pixels. We report measurements for two area fractions, $\phi = 0.92 \pm 0.04$ and $\phi = 0.85 \pm 0.07$. (The error reflects the range of reasonable choices for a threshold value for the images.) Another estimate of the dryness of the foams can be obtained from the average number of sides of a bubble, p, which Weaire [11] plots as a function of ϕ. For the drier foam, $p = 5.7 \pm 0.2$, and $p = 5.2 \pm 0.2$ for the wetter one. These values of p correspond to foams in Weaire's simulations with $\phi = 0.96$ and $\phi = 0.92$, respectively.

Another characteristic of the foams is μ, the second moment of the bubble side distribution. For both area fractions, $\mu = 1.7 \pm 0.6$. This is consistent with previous measurements of μ for monolayer foams [3]. In Weaire's simulation, μ decreases significantly with increasing strain [10], but we find that it is independent of the total applied strain.

In both Kawasaki's and Durian's simulations, topological rearrangements are found to be avalanchelike when $\dot{\gamma}$

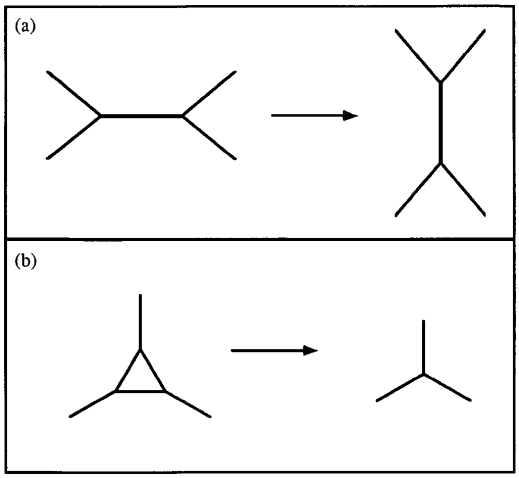

FIG. 2. (a) Schematic representation of a T1 process. (b) Schematic representation of a T2 process. In both figures, the lines represent bubble walls.

is slow compared to τ_d, the characteristic relaxation time for the bubbles [6–9]. For our experiment, τ_d can be estimated by stretching an isolated bubble in an extremely wet foam and measuring its relaxation. Both the ethyl heptadecanoate and myristic acid foams have a relaxation time on the order of 1 s; therefore, our studies cover dimensionless rates of strain from 3×10^{-3} to 1×10^{-2}.

We find that for small values of strain, the monolayer foams respond elastically. Figures 3(a) and 3(b) show images of the foam before shear and during the initial elastic response. The individual bubbles stretch and rotate in response to the applied strain by an amount that is related to the size of the bubble. When the rotation of the outer cylinder is stopped, the foam relaxes back to its original state within a few minutes. All three simulations predict that the elastic energy of the foam increases monotonically until the yield strain is reached. Above the yield strain, sudden drops in the energy are used as a measure of the event size, or size of the rearrangements [7,9,11]. In the monolayer, bubble area is conserved, so the total length of the walls should provide a measure of the elastic energy. The length of the walls in the foam does increase slightly with applied strain, but the signal-to-noise ratio is too small to determine either a precise value of the yield strain, or to measure event sizes based on energy drops. Our measurements were limited by the number of bubbles, ambiguities in defining the wall length for wet regions of the foam, and the large polydispersity in bubble size. Other attempts to define an energy suffered from similar limitations.

In addition to changes in energy, T1 events [6,11] and actual bubble motions were monitored in the simulations. In our experiments, T1 events only occurred for values of the strain $\gtrsim 1$. Because a T1 event represents a relatively large release of energy, this provides an upper bound on the yield strain. The largest yield strains in the simulations were also of order one, so this result cannot distinguish between the various models.

Figure 4 shows the number of T1 events as a function of applied strain, N, for three different runs. In each case, the strain is in bins of 0.03, and only strains well above the yield strain are considered. Figure 4(a) is for an ethyl heptadecanoate foam with $\phi = 0.92$ and $\dot{\gamma}\tau_d = 0.003$, and Fig. 4(b) is for a myristic acid foam with $\phi = 0.92$ and $\dot{\gamma}\tau_d = 0.011$. For comparison with the simulations, we computed the average number of T1 events per bubble per strain, $\overline{N}$. For $\dot{\gamma}\tau_d = 0.005$, $\overline{N} = 0.13 \pm 0.02$, and for $\dot{\gamma}\tau_d = 0.011$, $\overline{N} = 0.15 \pm 0.03$. This is consistent with the Kawasaki simulation [6] in which $\overline{N}$ is found to be independent of $\dot{\gamma}$. (Because of the similar relaxation times for the ester and the acid, the dynamics of the foams were essentially independent of the material used. The acid foams were slightly more elastic.) The measured value of $\overline{N}$ is more consistent with the prediction of Durian's simulation [9], $\overline{N} = 0.15$, than with the result of Kawasaki's simulation [6], $\overline{N} = 0.5$. Weaire does not compute this quantity.

The most significant discrepancy between our results and the simulations of Kawasaki and Weaire is the distribution of the size of the events. We observe no evidence for large-scale events involving either vortexlike motion as in Ref. [7] or large numbers of neighbor switching as in Ref. [11]. For $\phi = 0.92$, the largest events involved at most three simultaneous T1 events. There are slight motions of the surrounding bubbles as the foam adjusts after these events, but nothing like the large-scale, vortexlike motions observed by Kawasaki [7]. Durian only computes statistics for the energy released in an event, not for T1 events *per se*. However, he tracked the bubble motions and found that the largest energy releases corresponded to rearrangements that involved only a few T1 events [9]. This is consistent with our results. Further simulations are being carried out to compute the statistics for the T1 events that occur in simulations of Durian's model.

Even though no system-wide avalanches were observed for either area fraction, the number of simultaneous T1

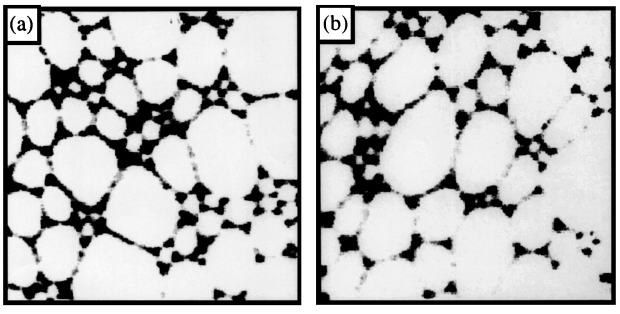

FIG. 3. (a) Image of a foam that is not being strained. (b) Image of a foam during an applied strain. Both images are of a 0.022 cm square region. The outer cylinder, i.e., the moving cylinder, is located to the left of the images. For clarity, negative images are shown.

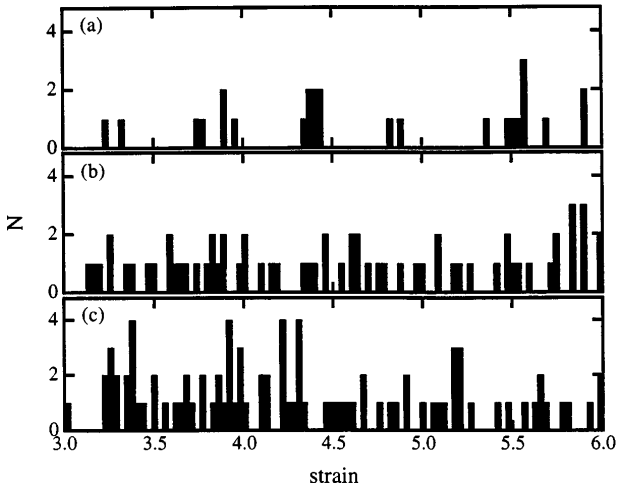

FIG. 4. Three examples of the number of T1 events as a function of applied strain: (a) ethyl heptadecanoate foam with 55 bubbles, $\phi = 0.92$, and $\dot{\gamma} = 0.003$; (b) myristic acid foam with 150 bubbles, $\phi = 0.92$, and $\dot{\gamma} = 0.011$; (c) ethyl heptadecanoate foam with 140 bubbles, $\phi = 0.85$, and $\dot{\gamma} = 0.011$.

events was greater in the wetter foams. Also, $\overline{N} = 0.2$ in the wet foams, which is roughly double the value in the drier foams [see Fig. 4(c)]. This increase in event size for wetter foams suggests that the lack of system-wide events may simply reflect the range of ϕ that we were able to study. All of the foams examined were consistent with $\phi > 0.9$, and the power-law tails predicted by Weaire's simulation [11] occur when $\phi < 0.9$. The increase of events in the wetter foam suggest that the power-law tails might be seen if this limit is pushed.

Similarly, the discrepancies with the simulation of Kawasaki may result from the restriction of the model to the dry-foam limit. This limit assumes perfectly straight walls connecting the vertices and only polygonal bubbles. Even the driest monolayer foams studied here contained some circular bubbles, and it is not unreasonable to expect that all of the bubbles have to be polygonal for the dynamics to reproduce the $\phi = 1$ limit. In fact, because of the singular nature of the $\phi = 1$ limit, it may not actually be possible to experimentally test results based on the vertex model.

In contrast to the simulations of Weaire and Kawasaki, Durian's model corresponds to foams with gas area fractions of 0.9 to 0.95, which are consistent with the values of ϕ in our experiments. It is therefore not surprising that our results are most consistent with the predictions of his model. However, the comparisons with Durian's model emphasize the possible importance of different sources of dissipation for determining the nature of the nonlinear rearrangements and provide a context within which the different effects can be tested.

Weaire's simulation is an equilibrium calculation involving quasistatic steps in the strain that do not involve any dissipation. Kawasaki's simulation includes the dissipation due to the flow of the liquid out of the plateau borders. In our experiments, however, the coupling between the monolayer and the subphase provides an additional source of dissipation [16]. This additional dissipation could provide a natural cutoff to the size of the nonlinear rearrangements.

In Durian's model, dissipation is accounted for by a term in the equation for the bubble velocity given by the average velocity of a bubble's neighbors, $\langle v_j \rangle$. Within the context of the model, there are two alternate ways to evaluate this term. The calculations in Ref. [9] used the mean-field approximation, $\langle v_j \rangle = \dot{\gamma} y_i \hat{x}$, where y_i is the position of the bubble being considered, and $\hat{x}$ is the unit vector in the imposed flow direction. This form for $\langle v_j \rangle$ is precisely what one expects when an individual bubble is coupled to a background viscous fluid undergoing shear. On the other hand, if one evaluates the equation of motion for the neighboring bubbles and directly computes $\langle v_j \rangle$, this corresponds to a system for which the dissipation is predominately in the flow of liquid in the bubble walls. Simulations are currently being carried out with this version of the model [17].

In our geometry, because the subphase is also driven by the outer cylinder, the coupling between the subphase and monolayer corresponds to the mean-field case. The coupling can be characterized by $L = \mu R/\mu_s$, where μ is the viscosity of the subphase, μ_s is the surface viscosity of the monolayer, and R is a characteristic length scale of the flow [16,18]. When $L \gg 1$ the dissipation occurs primarily in the subphase and when $L \ll 1$, the monolayer dissipation dominates and the flow is two dimensional. The viscosity of the LE phase has been estimated [16,18] to be 10^{-5}–10^{-6} g s^{-1}. If we take R to be a few μm, the width of a foam cell wall, and $\mu = 0.01$ g cm^{-1} s^{-1}, L is of order unity. Thus in LE-G foams the dissipation is divided between subphase and monolayer. By using materials with a higher μ_s and foams of LE bubbles with walls of a more viscous fluid phase, we will be able to study the case where the viscous dissipation in the monolayer is dominant. Comparison of these experiments with the simulations where $\langle v_j \rangle$ is computed directly should be very useful in elucidating the effects of various sources of dissipation on the nature of the nonlinear rearrangements.

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