Scaling behavior in shaving cream

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The coarsening of a three-dimensional foam is studied with multiple light-scattering techniques. Scaling behavior is observed with the average bubble diameter growing in time as t^z where $z = 0.45 \pm 0.05$. Changes in the packing conditions during coarsening give rise to a dynamical process that also exhibits temporal scaling. Neighboring bubbles undergo sudden structural rearrangement events at a rate per unit volume that decays as t^{-y} where $y = 2.0 \pm 0.2$.

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Foams are cellular materials that consist of a random dispersion of gas bubbles in a small volume fraction of liquid. They find wide application because of their low density and ability to trap solids, liquids, and vapors [1, 2]. Foams also have unique rheological properties. For example, they respond elastically like a solid at low shear stress, but flow like a fluid at high shear stress [3]. Foams, however, are intrinsically unstable and tend to coarsen over time. In applications where the production of foam is desirable, one seeks to suppress this instability since it can limit a foam's useful lifetime. By contrast, the instability of foam can be important in minimizing its undesirable production in many industrial processes. More fundamentally, the coarsening of foam is an important example of a large class of nonequilibrium processes for which the dynamics is poorly understood [4]. Thus, one of the most important aspects of all foams is their stability and temporal evolution.

In general, foams can evolve by a variety of means. The liquid in between bubbles can drain in response to gravity, or adjacent bubbles can coalesce if the liquid film becomes too thin and ruptures. Most importantly, foams can coarsen by the diffusion of gas from smaller bubbles to larger bubbles. This process is driven by pressure differences between bubbles of different sizes and serves to decrease the total interfacial surface area with time. Since all foams are comprised of a random distribution of bubble sizes, coarsening by diffusion of gas cannot be eliminated and will always occur. This coarsening is similar to grain growth and is a very general phenomenon widely encountered and extensively studied in the kinetics of phase separation [4]. Typically, the growth process is described in terms of a "statistically self-similar" size distribution, where the shape of the asymptotic distribution is independent of time when scaled by a single time-dependent length that grows as a power law [5]. For a foam, this length would reflect the mean bubble size. Such scaling behavior has been examined for the case of two-dimensional foams, whose structure can be directly visualized [6–9]. By contrast, scaling behavior has never been observed for three-dimensional foams because direct visualization of the internal structure is precluded by the strong multiple scattering of light which give foams their characteristic white appearance.

In this paper, we show that the coarsening of three-dimensional foams exhibits scaling behavior in excellent accord with theoretical predictions. We find that the average bubble size increases in time as t^{-z}, where $z = 0.45 \pm 0.05$. In addition, as the foam coarsens, we observe random rearrangements of localized regions of bubbles that occur on very short time scales. The rate of these rearrangement events also exhibits a scaling behavior in time: t^{-y}, where $y = 2.0 \pm 0.2$. This scaling behavior necessarily implies that the bubble-size distribution is statistically self-similar. Our measurements employ both static and dynamic light-scattering techniques and exploit the strong multiple-scattering characteristic of foams by approximating the transport of light as a diffusive process [10]. Thus, the average bubble size can be determined directly from the total transmitted light through the foam, while the rate of rearrangement events can be determined from the temporal fluctuations of the scattered intensity. This provides a probe of the structure and dynamics of the foam which allows us to noninvasively follow its time evolution.

We study coarsening in a commercial brand of shaving cream, Gillette Foamy Regular, which provides reproducible and convenient samples [11]. The key ingredients (water, stearic acid, triethanolamine, and hydrocarbon gases) produce a foam with $92 \pm 1\%$ bubbles by volume. A photograph of the surface of Foamy shaving cream against glass, as seen through an optical microscope, is shown in Fig. 1. It reveals a random distribution of nearly spherical bubbles in close proximity. While the size distribution appears to be broad in comparison with the average, there are no extraordinarily large bubbles nor is there a preponderance of very small bubbles. We never observe the coalescence of neighboring bubbles via film rupture, and gravitational drainage of the liquid is not significant during the course of our experiments. Thus, the coarsening of the foam results solely from gas diffusion between bubbles.

For the light-scattering experiments, foam is sealed into rectangular glass cells of thickness $L = 0.3, 0.4, 0.7$, or 1.0 cm. One side of the cell is illuminated with a plane wave of laser light with wavelength $\lambda = 488.0$ nm. We measure T, the fraction of light transmitted through the sample, and $g_1(\tau)$, the normalized electric-field correlation function for both the transmitted and backscattered light. The $g_1(\tau)$ are obtained from the temporal
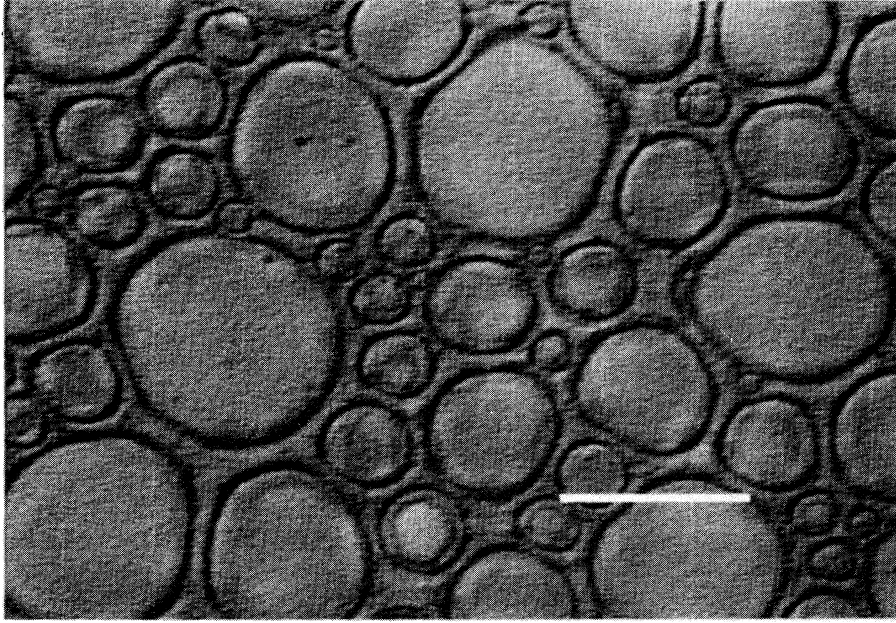
FIG. 1. Photograph of fresh Gillette Foamy Regular against a smooth glass surface. The size marker is approximately 30 μm.

fluctuations in the scattered intensity and are analyzed within the framework of diffusing-wave spectroscopy [10]. For backscattered light, $g_{1,B}(\tau)$ is nearly exponential in $\sqrt{\tau}$ with a time constant τ_0 defined by $g_{1,B}(\tau) \approx \exp(-2\sqrt{6\tau/\tau_0})$. For transmitted light, $g_1(\tau)$ is nearly exponential in τ with a first cumulant Γ_1 defined by the small-τ behavior, $-\ln[g_{1,T}(\tau)] \sim \Gamma_1\tau$.

Data from a typical set of these multiple light-scattering experiments are shown in Fig. 2. The transmission T through a thickness $L = 0.7$ cm of foam is shown in Fig. 2(a). As with all quantities shown in Fig. 2, T exhibits power-law behavior after the first 10 to 20 min. In Fig. 2(b), we show the time evolution of τ_0 obtained from dynamic backscattering measurements. The wide scatter in the data is expected since the time over
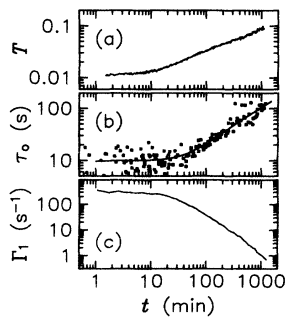

FIG. 2. Typical multiple light-scattering data vs foam age: (a) the average static transmission T through a sample of thickness $L = 0.7$ cm, (b) τ_0 from dynamic backscattering from a sample of thickness $L = 1.0$ cm, and (c) Γ_1 from dynamic transmission with $L = 0.4$ cm. All three data sets exhibit nearly power-law behavior after about 20 min.

which intensity correlations were averaged was not very large compared to τ_0. The solid curve in Fig. 2(b) represents a running average of the data and shows that τ_0 also exhibits power law behavior. In Fig. 2(c), we show the time evolution of Γ_1 obtained from dynamic transmission measurements through a thickness $L = 0.4$ cm. Again, the asymptotic behavior is reasonably well-described by a power-law. The power-law dependence of all these quantities is a convincing illustration of scaling behavior in the coarsening foam.

To obtain exponents quantifying the time evolution of physical foam properties, further analysis of the data must be performed. We exploit the diffusive nature of the photon propagation inside the foam [12]. Physically, incident photons travel on average one transport mean free path ℓ^* before they lose memory of their initial direction and commence a random walk of step size ℓ^*. The length ℓ^* is determined by the foam structure and directly reflects the average bubble size d. For our samples, $\ell^* = (3.5 \pm 0.5)d$ [12]. In the limit of $L \gg \ell^*$ and no absorption, $T \propto \ell^*/L$. Thus, T provides a quantitative measure of the average bubble size in the foam and allows us to noninvasively follow its time evolution. A second corroborating estimate of d can be obtained from the dynamic light-scattering data. Physically, the temporal intensity fluctuations arise from rearrangement events and τ_0 characterizes the average time between events at a given location inside the foam [12]. In transmission, these rearrangement events are reflected in the first cumulant of $g_{1,T}(\tau)$, which is given by $\Gamma_1 \approx (L/\ell^*)^2/\tau_0$ [10, 12]. Since τ_0 is known from the backscattering data, we can obtain an independent measure of ℓ^* from Γ_1, and hence, determine the time evolution of d. In the analysis of both the static and dynamic transmission data, we average over cells of different thickness L and include small

corrections for both finite L/ℓ^* and absorption [10].

In Fig. 3 we plot the two independent measurements of d, based on static (——) and dynamic (o) light-scattering measurements. Both sets of data exhibit the same behavior. At early times, the average bubble size is approximately a constant. After about 20 mins, scaling behavior is observed, with the average bubble size d growing as a power law, t^z, where $z = 0.45 \pm 0.05$. In contrast with recent work on two-dimensional foams [6–8], this is a measurement of the scaling behavior and the growth exponent for the coarsening of a three-dimensional foam. These results also imply that the bubble-size distribution is statistically self-similar, which is consistent with visual observations of the surface of the foam at different ages.

These results can be compared to theoretical predictions for two limiting cases. For a wet foam of well-separated spherical bubbles, the concentration of gas diffusing in the liquid surrounding each bubble is spherically symmetric and the coarsening is analogous to Ostwald ripening as considered by Lifshitz and Slyozov, with $z = \frac{1}{3}$ [13]. By contrast, for a relatively dry foam of bubbles in close proximity, there is a linear concentration profile of diffusing gas in each wall between neighboring bubbles. In this case, a different growth exponent is predicted, $z = \frac{1}{2}$ [14]. Within experimental uncertainty, our result is consistent with $z = \frac{1}{2}$, but falls somewhat below this value. This may arise because our foam lies between the two limiting cases of dilute spherical bubbles and space filling polyhedral bubbles. Thus, the concentration field of gas diffusing between bubbles is neither radial nor one dimensional. In this intermediate regime, the growth of d may be only approximately power law, although any deviation from power-law behavior may be difficult to observe experimentally.

Additional evidence for scaling behavior in our foam is obtained from the time evolution of the internal foam dynamics as probed by the temporal intensity fluctuations. These fluctuations are caused by localized rearrangement events in which several neighboring bubbles move by a large fraction of their diameter. The duration of these events is short compared to the interval between successive events at the same location and this latter time, in turn, is short compared to the time for d to significantly increase by coarsening. The rearrangement events occur, presumably, because of changes in the packing conditions. As the coarsening proceeds, bubbles deform and
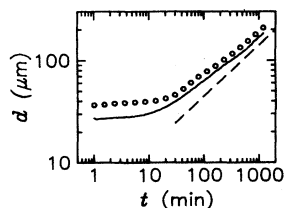
local stresses build until a threshold is reached and bubbles suddenly move.

The rate R per unit volume of these events is obtained from dynamic light scattering using a model of diffusing-wave spectroscopy for foams, which correctly predicts the full functional form of the observed $g_1(\tau)$ in both transmission and backscattering [12]. We find that the average time between rearrangement events at a given location is $\tau_0 \approx 1/(Rr^3)$, where r is the average event size. Since the foam is characterized by a single length scale, r must be proportional to the average bubble size. For our foam, $r \approx 10d$ [12]. Thus, $R \propto 1/(\tau_0 \ell^{*3})$. Using the first cumulant of the dynamic light-scattering data in transmission and the value of ℓ^* obtained from static transmission, the rate of rearrangement events is given by $R \propto \Gamma_1/(L^2\ell^*)$. The temporal evolution of R is shown in a logarithmic plot in Fig. 4. Scaling behavior is again observed. After approximately 20 mins, the rate decreases as a power law in time: $R \sim t^{-y}$ with $y = 2.0 \pm 0.2$.

The value of the exponent y that describes the time evolution of R is surprising. We might expect that the time τ_0 between rearrangements at a given location is set by the time required for some average bubble property F, such as the diameter or volume, to change by a fixed fraction of its value: $\frac{dF}{dt}\tau_0 \propto F$. If F has power-law time dependence, then $\tau_0 \sim t$. Since $r \sim d$ and $R \approx 1/(\tau_0 r^3)$, this would give $y = 2.35 \pm 0.09$, which is inconsistent with our observations. Furthermore, from the backscattering data shown in Fig. 2(b), the exponent for the power-law growth of τ_0 is 0.68 ± 0.15.

A prediction of the correct value of y must ultimately rely on a better understanding of the physical mechanisms that lead to the rearrangement events. It is perhaps significant that average distance moved by a bubble wall between consecutive rearrangement events is roughly independent of time:

$$\frac{d(d/2)}{dt}\tau_0 \sim t^{y-2z-1} \approx \text{const}, \qquad (1)$$

where the constant is approximately 50 nm. This motion is substantially less than one wavelength, ensuring that the coarsening process itself is not responsible for the fluctuations in the scattered light intensity. However, the magnitude of this length scale, its origin, and its relationship to the physical mechanisms responsible for the rearrangement events are all, as yet, unresolved.

Finally, we emphasize that the rearrangement events have both a well-defined average size, $r \approx 10d$, and an average time interval between events, τ_0. This is to be con-

FIG. 3. Average bubble diameter vs foam age as determined from static (——) and dynamic (o) multiple light-scattering measurements. The dashed line has slope $\frac{1}{2}$ and shows that the growth of d is nearly consistent with the scaling prediction for densely packed bubbles.
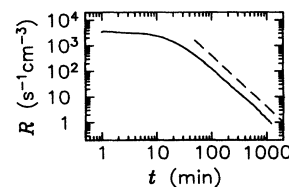
FIG. 4. Rate of rearrangement events vs foam age. The dashed line has slope -2 and shows that R exhibits scaling behavior.

trasted with examples of self-organized criticality, which are characterized by a broad distribution of event sizes all occurring at different rates [15]. If this were the case for the foam samples, the shape of the $g_1(\tau)$ would be qualitatively different from those observed.

The data presented in this paper provide clear evidence of scaling behavior in the coarsening of a three-dimensional foam. In addition, the discrete rearrangement events that occur during coarsening also exhibit temporal scaling. The light-scattering techniques used here are of sufficient generality that a wide variety of other foams and emulsions can also be investigated non-invasively. For example, the evolution of foam structure and dynamics resulting from film rupture or drainage can be examined. This will lead to increased understanding of the mechanisms controlling the rheology and stability of foams.

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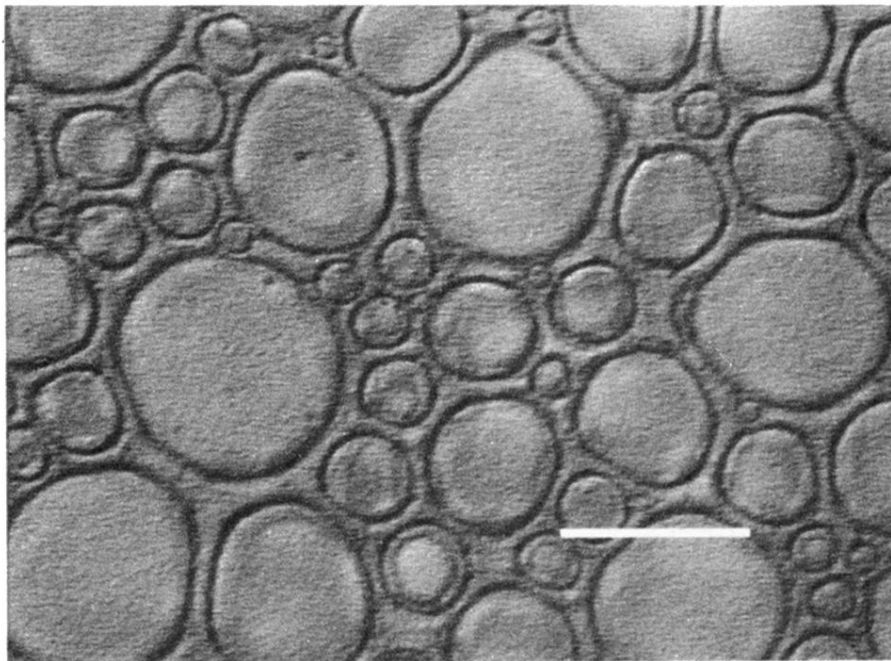[15] P. Bak, C. Tang, and K. Wiesenfeld, Phys. Rev. Lett. **59**, 381 (1987).

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