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Dynamics and coarsening in three-dimensional foams

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Abstract. We show that diffusing-wave spectroscopy can be used as a non-invasive probe of the bulk properties of three-dimensional foams. A new picture accounting for the origin of the temporal fluctuations of multiply scattered light is developed and corroborated with direct observations through a microscope. Our interpretation and measurements yield the growth law for the coarsening of foam bubbles and new insight into their dynamics.

The kinetics of phase separation and coarsening are phenomena of long standing interest [1]. Soap froths are common and fascinating examples, thought to be useful models of grain growth [2]. Recent experiments have focused on two-dimensional systems, where the structure and coarsening are readily observable [3–6]. By contrast, because of the problem of visualizing an opaque system, no analogous experiments have been performed on three-dimensional foams. Nevertheless, such foams are of great scientific interest and have many industrial and commercial applications [7]. In this paper, we present a novel interpretation of the origin of temporal fluctuations of multiply scattered light in foams and obtain new information about the structure, dynamics, and time evolution of three-dimensional foams.

For convenient and highly reproducible foam samples, we used a commercially available brand of shaving cream. Gillette Foamy Regular [8] consists mainly of an aqueous solution of mixed ionic surfactants (stearic acid and triethanolamine) which is supersaturated with hydrocarbon gases (isobutane, propane, and butane). When these contents are released, the gases come out of solution, surfactants adsorb to bubble interfaces, and a foam is produced. By weighing known volumes of foam, we find that the first 10–50 g of Foamy expelled from a new can have a constant density of $(7.77 \pm 0.08) \times 10^{-2}$ g cm^{-3}, corresponding roughly to 0.92 volume fraction of bubbles. Foam samples were always taken from this range.

To estimate the behaviour of Foamy, we first viewed a portion from below with an optical microscope. The foam consisted of a collection of nearly-spherical bubbles of about 20 μm average initial diameter. While the polydispersity was considerable, no very large bubbles were observed. This permitted the average size of surface bubbles to be followed by eye to within about 15% as shown by the full circles in figure 1. As the foam aged, the coarsening process was directly observed: small bubbles shrank and disappeared while large bubbles grew larger. In addition, a different type of

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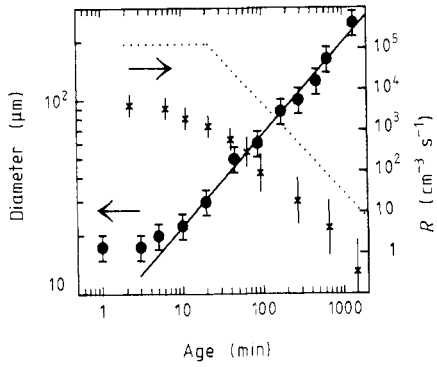

Figure 1. Time evolution of Gillette Foamy Regular: average bubble diameter (●) and frequency of rearrangement events per unit volume (×), both estimated from inspection of surface bubbles. The dotted curve represents $1/\tau_0(l^*)^3$.

dynamics in the foam was observed: sudden local rearrangement events in which 3–10 bubbles moved a significant fraction of their diameter. The frequency of such events per volume, estimated from the observed frequency per area and bubble size, decreased with foam age as shown by the crosses in figure 1. Bubbles never seemed to coalesce through film rupture. Over a period of 24 h there was negligible gravitational drainage of the liquid between bubbles.

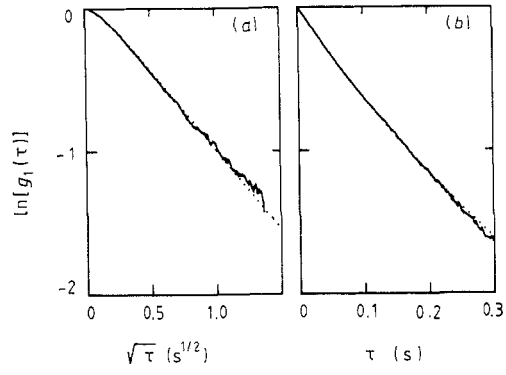

Figure 2. Multiple scattering field correlation functions for (*a*) backscattering from a 1.0 cm sample of Foamy and (*b*) transmission through a 0.3 cm sample of Foamy, both at age 100 min. The dotted curves are fits to (1) and (2) for τ_0 and Γ_1, respectively.

It is common experience that shaving cream is white and, therefore, multiply scatters light. Our experiment takes advantage of this property and is similar to multiple scattering studies of colloidal suspensions [9, 10]. A laser beam of wavelength $\lambda = 488.0$ nm was expanded such that the central portion fell onto the foam. The sample cells consisted of rectangular glass tubing, of inner dimensions 1 cm × 3 cm and 0.3 cm × 0.9 cm, with valves at each end. After introducing foam into the cell at time zero, the valves were closed. A few speckle spots from either backscattered or transmitted light were observed with a photomultiplier tube, whose output was analyzed with a digital correlator. Typical field correlation functions, $g_1(\tau)$, obtained by

collecting data for 10 min when the foam had aged 100 min, are shown in figure 2. In the backscattering geometry we measured three series of correlation functions by collecting data for 10%, 20% and 30% of the total foam age for ages from 0.5 to 1200 min. No dependence on data collection time or polarization of the backscattered light was found. In the transmission geometry we made similar measurements, collecting data for one tenth of the foam age. Once again, there appears to be no dependence on data collection time. We conclude that the time scale for coarsening of the foam is well separated from that of the internal dynamics responsible for the decay of the correlation function. This makes multiple light scattering measurements feasible.

The theory of diffusing-wave spectroscopy (DWS) is highly successful in quantitatively predicting the correlation functions for light multiply scattered by suspensions of colloidal particles [9, 10]. A key assumption is that photons execute a random walk in the sample and can be described by a diffusion equation. The predicted correlation functions for Brownian particles measured in backscattering and transmission are, respectively

$$g_{1,B}(\tau) \approx \exp\left[\sqrt{a} - \sqrt{a + 6\gamma^2\tau/\tau_0}\right] \tag{1}$$

$$g_{1,T}(\tau) \approx \sqrt{6\Gamma_1\tau}/\sinh(\sqrt{6\Gamma_1\tau}) \qquad \Gamma_1 = (L/l^*)^2(1/\tau_0). \tag{2}$$

Here $\tau_0 = 1/Dk_0^2$ is the time it takes a particle to diffuse the wavelength of light, L is the sample thickness, l^* is the transport mean free path of light in the sample (assumed to be much less than L), and $\gamma \approx 2$ except for very small particles. The term a conveniently describes initial curvature in $g_{1,B}(\tau)$; for an absorption length ℓ_a, it is given by $a = 3\gamma^2 l^*/\ell_a$. If L is not much greater than l^*, or if there is significant absorption, then the form of $g_{1,T}(\tau)$ is more complex and the first cumulant, Γ_1, only approximately equals $(L/l^*)^2/\tau_0$.

We find that the experimental correlation functions for Foamy foam are of the form (1) and (2); typical data and fits are shown in figure 2. Thus, both backscattering and transmission correlation functions decay exactly as those for colloidal particles undergoing diffusive motion. The time evolution of τ_0, obtained from backscattering, is shown in figure 3. We find $\tau_0 \approx 8$ s up to 20 min of age, after which it grows as a power law with exponent 0.68 ± 0.15. The transmission measurements of Γ_1 are combined with τ_0, using (1), to estimate $l^* \approx \sqrt{\Gamma_1^{-1}L^2/\tau_0}$; results are shown in figure 3. This gives $l^* \approx 100$ μm up to 20 min, after which it grows as a power law with exponent 0.47 ± 0.05.

These results can be interpreted in terms of foam structure and dynamics. A natural hypothesis is that l^* scales with the only length in the structure of the foam, i.e. the average (bulk, time-dependent) bubble diameter $d(t)$. Comparing figures 1 and 3, we find $l^* \approx Cd(t)$ where $C \approx 3.5$. Note that the growth exponent we observe is consistent with the predicted [11, 12] value of $\frac{1}{2}$. Furthermore, note that $C \approx 3.5$ is reasonable in that several scattering events should be required to randomize the photon direction.

The interpretation of τ_0 is especially interesting, because a mechanism for the origin of temporal fluctuations of the intensity of multiply scattered light based on the internal dynamics of the foam is required. Phenomena which we believe provide unsatisfactory explanations include ballistic interface motion, capillary waves, and diffusive motion of bubbles. We propose, instead, that local rearrangement events, characterized by a rate constant R, are responsible for the observed temporal fluctuations of

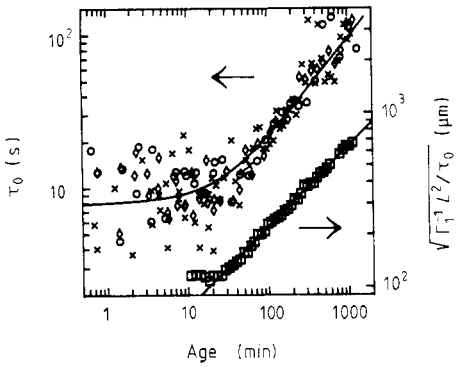

Figure 3. Time evolution of characteristic time and length scales; different symbols represent different collection times. The expression on the right axis combines Γ_1 and τ_0 to approximate l^*, the transport mean free path of light.

scattered light. Suppose that a light path of length s samples a volume of foam, sA, and that its phase is completely randomized if a local rearrangement event ocurrs along its length. The probability of this happening is proportional to the path volume and grows linearly with time. The theory of DWS then predicts correlation functions of the form (1) and (2) with $\tau_0 = 1/RAl^*$. We expect that the area A, like l^*, scales with the mean bubble size; therefore $A \propto (l^*)^2$. Our model thus predicts that R is of the order $1/\tau_0(l^*)^3$; these quantities are compared in figure 1 where we find, remarkably, that $40R \approx 1/\tau_0(l^*)^3$ for all ages. The factor of 40 may be related to the size of a typical rearrangement event. We believe that the frequency of rearrangement events per unit volume, R, is an important physical quantity which characterizes a phenomenon not previously recognized in the literature.

In conclusion, we have shown that the structure and internal dynamics of three-dimensional foams can be studied with diffusing-wave spectroscopy. These experiments provide a detailed measure of coarsening, through the time evolution of l^*, as well as new insight into the internal dynamics of the bubble structure, through the rate constant R. The dynamics of rearrangement events, and the relation of l^* to bubble size, require further experimental and theoretical investigation.

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