Diffusing-wave spectroscopy of a flowing foam

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(Received 15 November 1993)

Diffusing-wave spectroscopy has been applied to a model foam (shaving cream) subjected to shear stress. The observed data are consistent with the hypothesis [D.J. Durian *et al.*, Phys. Rev. A **44**, R7902 (1991)] that the dynamic process reflected in the light scattering involves local rearrangement events in the foam. The rate of such events is increased in flowing foam subject to shear stress. In this situation a second, slower process appears in the dynamic light scattering data, the origin of which remains conjectural.

PACS number(s): 83.70.Hq, 68.90.+g, 83.50.−v

I. INTRODUCTION

Foams are concentrated dispersions of gas bubbles in liquids, the bubbles being separated by relatively thin liquid lamellae [1,2]. Apart from their myriad practical applications they are of fundamental scientific interest as exemplars of disordered cellular materials. The direct study of the structure and dynamics of foam, except in the two-dimensional case, has until recently been precluded by the strong scattering of light which is apparent in the white color of foams. However, it has recently been shown that this very feature can be exploited to study the evolution of the typical bubble size as foam coarsens, and to probe fundamental dynamic processes in foam [3,4]. This application of so-called diffusing-wave spectroscopy (DWS) has thus opened a new chapter in foam studies.

In *highly* multiply scattering materials light can be regarded as diffusing through the medium [5]; the usual interference between light following several paths through the material gives rise to speckle, fluctuations in the interference terms causing the speckle to flicker, leading to spectral broadening of the scattered light. The phase change of $\approx \pi$ necessary to cause a change from constructive to destructive interference is here accumulated over many events distributed over the *entire* path of light through the medium, rather than in a single event as in conventional dynamic light scattering [6]. Thus, in DWS the scattered light carries information on the system dynamics, and can be sensitive to movements very much smaller than the wavelength of light. Further, the diffusive propagation of light enables spatially or temporally rare events to be observed by DWS; it is this aspect which has been exploited in studies of foam.

Among the unique properties of foam, underlying many applications, is its rheology [7]: foam acts as an elastic solid at low shear stress yet flows as a liquid at high shear stress. The fundamental processes underlying this behavior are not well understood. In the DWS studies mentioned above [3,4], restricted to static foam, it was concluded that a fundamental process involved in the temporal evolution of foam was an elementary rearrangement event: a local neighborhood some ten bubbles across spontaneously reordered as coarsening caused some critical value of the local stress to be exceeded due to changed packing conditions. Such processes should play a significant microscopic role in the macroscopic response of foam to applied stress. Indeed, while theoretical studies of foam rheology have largely been confined to the two-dimensional case [7], a "hopping" or rearrangement mechanism has been identified as an idealized micromechanical mechanism to explain the observed macroscopic yield behavior and flow [8]. Such *local* rearrangements would permit unbounded, permanent macroscale deformations while the cellular distortions remain finite.

The association of the DWS dynamics with such rearrangements remains somewhat hypothetical, and such dynamics have not been studied in foam subject to a shear stress. We have, therefore, applied DWS to foam subject to a flow involving applied stress. In such flows the stress should induce more rapid occurrence of the elementary rearrangement events in the foam, significantly modifying the DWS signal.

II. EXPERIMENTAL

The experimental material was Gillette shaving foam [9], a complex mixture comprising an aqueous solution of triethanolamine stearate, with smaller quantities of sodium lauryl sulfate and polyethylene glycol-(23) lauryl ether, together with hydrocarbon gas as a propellant. This material produces stable and reproducible foam samples, comprising some $92 \pm 1\,\%$ bubbles by volume [3].

In preliminary experiments on foam samples in square cells of varying thicknesses we confirmed the essential features of the previous results [3,4]. The measured correlation functions were indeed approximately exponential in time (τ) for forward scatter, and roughly exponential in $\sqrt{\tau}$ for backscatter. The measured values of the

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first cumulant Γ_1 in forward scatter and the characteristic time τ_0 in backscatter were in reasonable accord with published data [3,4]. The DWS results, and other quantities (such as mean bubble diameter, determined by image analysis of micrographs of foam in contact with a glass wall) exhibited power-law scaling with time after an initial latency period of about ten minutes, as shown by Durian *et al.* [4]. This gives us confidence in the functioning of our DWS setup.

The central part of our foam flow cell is shown diagrammatically in Fig. 1. The entire cell was 55 cm long, comprising two glass plates separated by 5 mm wide aluminum spacers shaped to form a parallel-sided, 5 cm high channel narrowing in the center as sketched. The cell was sealed by two polytetrafluoroethylene (PTFE) barriers, mechanically connected outside the cell so that they could be moved in parallel, forcing the cell contents along the cell and through the central constriction. In use, one barrier was removed, the cell was filled with foam, care being taken to exclude air, and the barrier was replaced to seal the foam into the cell. Barrier motion was induced with the pusher mechanism of an infusion pump, a speed of 1 mm/min being used in all the present experiments. Light scattering observations were made at three points on the center line of the flow cell (A, B and C in Fig. 1). Points A and C were chosen to be in regions of unstressed foam (C was at the midpoint of the constriction), point B being halfway along the tapered section.

A laser beam was normally incident on the foam cell and a few coherence areas of light forward scattered at 0° were selected for detection by a photomultiplier. From the measured intensity autocorrelation function of the scattered light the field correlation function $g_T^{(1)}(\tau)$ was extracted. Forward scattering was preferred to backscattering because of the large spread evident on the characteristic τ_0 in backscatter ([4] and our data), making it difficult to be sure of trends. Further, backscatter includes photon paths involving relatively few scattering events, so the diffusing-wave approximation may be better satisfied in forward scatter [10].

Due to the temporal evolution of the foam the system is not stationary. It is not possible to compare observations made at different times on different samples. We thus restrict ourselves to examining the behavior of foam at a single age, under a single set of flow conditions. There is a trade off between increased transmission of light through the cell as the bubble size increases with foam age, improving the statistics of $g_T^{(1)}(\tau)$, and a decrease in the first cumulant Γ_1 with foam age, leading to less effective averaging of the correlation function. As a compromise we aged the foam for 270 min before commencing DWS observations. Each data set thus derives from a separate sample of foam observed at a particular point in the flow at this age. All data were reproducible.

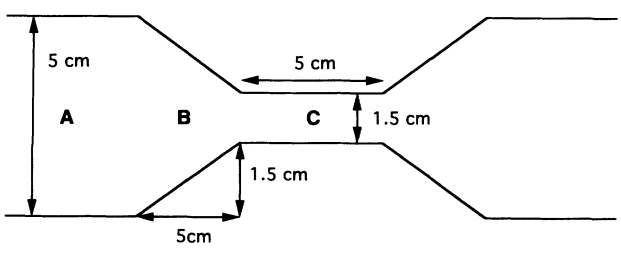

FIG. 1. A sketch (not to scale) of the central portion of the flow cell used. DWS observations were made at points indicated by A, B, and C. See the text for further description of the cell.

III. RESULTS

The time dependence of $g_T^{(1)}(\tau)$ is characterized by the first cumulant Γ_1, which relates to l^* and τ_0 via $\Gamma_1\tau_0 = (L/l^*)^2$, where l^* is the transport mean free path of light in the foam (associated with the average bubble size). τ_0 is interpreted as the average time between rearrangement events at a given location in the foam [3]. For foam samples of the same age, l^* should be the same [3,4], so that any variation of Γ_1 must reflect changes in τ_0^{-1}, the average rate of foam rearrangements at a given point in the foam.

Representative data are shown in Fig. 2: it is evident that different flow conditions do, indeed, affect the DWS dynamics. The observed $g_T^{(1)}(\tau)$ remain roughly exponential in τ, although at point B two very different time scales are apparent. The differences of the first cumulant Γ_1 between the three observation points are in general accord with the hypothesis that the time dependence of $g_T^{(1)}(\tau)$ is associated with elementary foam rearrangements [3]. It may be noted that over the time scales of

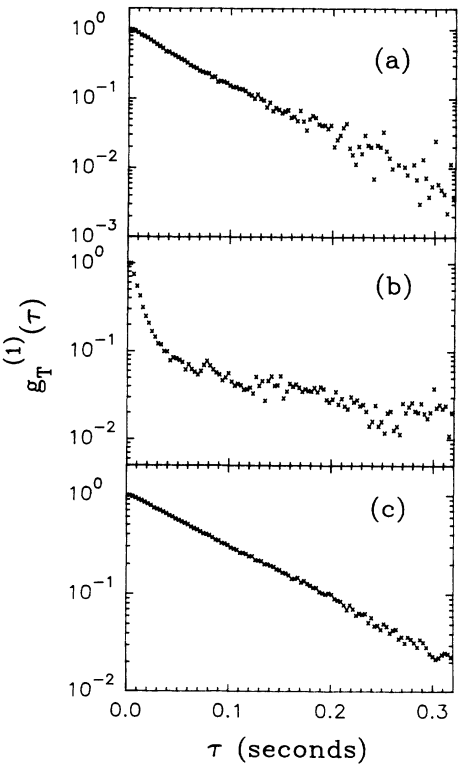

FIG. 2. Typical correlation functions observed at points A, B, and C in the flow cell. Note the different vertical scales. Data were collected for 1000 s in each case.

the data the bulk motion of the foam is rather small: a typical bubble takes about 12 s to pass a given point (at 270 min average bubble size ≈ 100 μm), whereas the measured correlation functions span $\tau \lesssim 0.3$ s.

The value of Γ_1 at point A, 25 ± 5 s^{-1}, accords well with data for static samples of foam (our own observations, and data from [4]). This suggests that the foam at point A is moving as a single entity and that the directed motion does not contribute to the time dependence of $g_T^{(1)}(\tau)$. Now DWS averages over all photon diffusion paths through the sample. Any boundary shearing layer near the glass walls must therefore be thin compared to the plug flow in the central region of the cell, as expected for slow flow in a smooth-walled vessel [7]. Visual observation of the flowing foam confirmed that it did slip on the glass walls, bubbles adjacent to the wall taking roughly the expected time to pass the observation point.

At point C the $g_T^{(1)}(\tau)$ is again nearly single exponential in nature, although Γ_1 is significantly lower than at A, at 8.1 ± 1.1 s^{-1}. The flow speed at point C must be roughly 3 times that at A. We assume that at the low flow speeds used any nonuniform flow due to the taper will have died away by point C, so that we will again have predominantly plug flow. We interpret the reduction in Γ_1 from A to C as arising from a reduced probability of rearrangements due to increased pressure and geometrical constraints in the foam in the constriction. Microscopic observation of the flowing foam suggested that the typical bubble size remained constant throughout the flow cell, so that the reduction in Γ_1 at C is not due to a more rapid aging of the stressed foam compared to the static case.

Turning now to point B, the major component of the decay of $g_T^{(1)}(\tau)$ is much faster than at points A or C. The second, slower component is much lower in amplitude. For the faster component $\Gamma_1 \approx 117 \pm 3$ s^{-1}, nearly five times that in a static foam (or at point A). We must conclude that, provided that the primary mechanism remains the same, rearrangement events occur much faster in foam subject to stress, exactly as naively predicted.

What process or processes could underlie the small slower component of $g_T^{(1)}(\tau)$ at point B, having $\Gamma_1 \approx 4 \pm 1$ s^{-1}? Prolonged microscopic observation of the flowing foam in the vicinity of point B revealed no obvious indications of the origin of this component of the dynamics. Stressing the foam would tend to promote bubble deformation, and perhaps foam coarsening due to enhanced diffusion of gas from small to large bubbles. However, the time constants of these processes differ considerably from that observed: bubble deformation (capillary waves) would be faster, while the time scale for foam coarsening at 270 min age is typically tens of minutes [4]. Bubble fusion might lead to a faster component of the coarsening process, but is not observed in our flowing foam, or in static samples [3]. Drainage of the liquid component of the foam is negligible over time scales of 270 min [11], and would be far too slow.

We recall that in DWS the temporal evolution of the scattered light may arise from an accumulation of tiny changes to individual scatterers or from spatially or temporally isolated events. While the latter mechanism appears to underlie the DWS signal for static foam (or the corresponding fast component at point B in the flow cell), the slow component might originate from visually imperceptible changes distributed throughout the foam. One possibility, which would also explain the slower relaxation at point C compared to A, is that it involves compression of the bubbles as the foam passes through the cell constriction. However, it is also possible that this component is associated with a different population of isolated rearrangement events from that previously observed. If, under stress, these were promoted to the same degree as the normal population, they would be essentially unobservable in static foam, as the high τ limit of $g_T^{(1)}(\tau)$ tends to be dominated by noise.

IV. CONCLUSIONS

The results presented here tend to confirm the interpretation placed upon the DWS data from static foam [3] that the underlying dynamics can be understood in terms of elementary cellular rearrangements. These are promoted in the presence of shear stress. While flow through a contraction, as in the present cell, is not viscometric [12], and is thus unsuited to study the fundamental basis of flow viscoelasticity, these results suggest that DWS should prove a most useful tool in studying the microscopic mechanisms responsible for the unique rheological behavior of foam.

However, the slow component observed in the correlation functions for the stressed foam is unexpected, and its origin remains speculative. Time scales in the flowing foam may depend upon bubble size differently than in static foam. Such open questions require more extensive experiments; for example, studies of the dependences of the time scales in the stressed foam upon flow velocity or on foam age should be illuminating.

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