Bubble Dynamics Relaxation in Aqueous Foam Probed by Multispeckle Diffusing-Wave Spectroscopy

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We study the bubble rearrangement dynamics in aqueous foam during the passage from liquidlike to solidlike behavior which follows a transient shear deformation that perturbs the bubble packing. The local dynamics is probed using multispeckle diffusing-wave spectroscopy. We show that following the perturbation the average time between rearrangements relaxes exponentially, with time elapsed since the end of the perturbation. The observed scaling of the characteristic relaxation time with perturbation amplitude and foam age is explained by a schematic coarse-grained model based on the scaling state hypothesis.

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Aqueous foams exhibit strikingly different mechanical behaviors depending on the applied strain. If it is smaller than a yield strain, neighboring bubbles remain in contact, and foam behaves as a viscoelastic solid, whereas, for larger applied strains, neighboring bubbles are torn apart and foam flows like a viscous liquid. From a phenomenological point of view, the rheological behavior of foam resembles that of concentrated emulsions, pastes, clay slurries, and other soft disordered metastable materials. To explain the macroscopic rheological response of these "soft glassy materials," several generic models in which local structural rearrangements play a central role have recently been proposed [1,2]. However, these models do not explicitly take into account the internal dynamics in foams due to the coarsening of its structure that progresses with the time elapsed since foam production ("foam age"). The importance of this feature for the nonlinear rheology of stable foams has been shown by a recent study of the passage from liquidlike to solidlike behavior induced by the application of a transient oscillating shear strain. After such a mechanical perturbation, the shear modulus slowly relaxes with a characteristic time which increases with foam age following a power law [3]. In this Letter, we study how the rate of local structural rearrangements in foam evolves with time following such a mechanical perturbation using diffusing-wave spectroscopy (DWS). Since conventional DWS experiments intrinsically require analyzing the intensity fluctuations of a few (ideally one) speckles of diffuse light emerging from the sample over a time much longer than the typical time between rearrangements, a new experimental approach is needed to resolve the relevant dynamical processes in time. We therefore use a variant of DWS which consists in analyzing simultaneously the light intensity fluctuations of a large number of speckles. This multispeckle DWS allows probing transient internal dynamics of foams and other turbid media with a temporal resolution enhanced by several orders of magnitude compared to single-speckle DWS [4]. We show that, immediately after the cessation of a sinusoidal shear strain, the average time between bubble rearrangements is increased and undergoes an exponential relaxation whose characteristic relaxation time scales with strain amplitude and foam age. This scaling is predicted by a new simple model that takes into account the coarsening-induced statistically self-similar growth of the foam structure.

In all the experiments, shaving cream ("Gillette regular" [5]) is used as a sample. It has a gas volume fraction of $(92.5 \pm 0.3)\%$, and it is stabilized with respect to drainage and coalescence [6]. The foam samples are injected immediately after their production between the transparent glass plates of a plane Couette rheometer. To prevent the evaporation of the water contained in the sample, the air in contact with the foam is saturated with humidity. All the experiments are carried out at a temperature of $21 \pm 0.5\,^{\circ}\mathrm{C}$. The rheometer is used to apply oscillating shear strains of controlled amplitude and duration to the sample. The frequency is equal to 10 Hz for all the experiments presented here. The surfaces in contact with the foam sample are rough and hydrophobic to prevent wall slip. The experiments are carried out for gaps between the plates L of either 2.0, 3.1, or 5.1 mm. Since neither the complex shear modulus measured *in situ* nor the bubble rearrangement rate depend on the plate separation, we conclude that wall slip and fracture phenomena are negligible in our experiment. To probe the bubble dynamics, the sample is illuminated through one of the plates by the expanded beam of a laser (Verdi, Coherent Inc., wavelength 532 nm). The backscattered speckle pattern of polarization perpendicular to that of the incident light is recorded using a charge-coupled device (CCD) camera with a 12-bit dynamic range. A beam splitter deviates part of the light coming towards the camera to a pinhole that selects a few speckles. Their intensity fluctuations are analyzed using a photomultiplier and a digital correlator (Flex99LQ, Correlator.com). During these optical measurements, no shear strain is applied to the sample. The data are analyzed using the well-established formalism of DWS [7–9]. This technique has previously been used to study the dynamics

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of quiescent as well as sheared foams [6,10–14]: The temporal fluctuations of the speckle intensity $I(t)$ are analyzed by calculating the correlation function $g_2(\Delta t) = [\langle I(t)I(t+\Delta t)\rangle - \langle I\rangle^2]/(\langle I^2\rangle - \langle I\rangle^2)$. The brackets denote an average over realizations of the structural disorder in the sample. In foams, the coarsening-induced bubble rearrangements change the realizations of the disorder in the bubble packing so that a temporal average corresponds to the disorder average. The following expression relates $g_2(\Delta t)$ obtained in a DWS backscattering experiment to a characteristic time τ of the scatterer dynamics [7–9]:

$$g_2(\Delta t) = \left\{\frac{L + 2z_e\ell^*}{L - \ell^* + z_e\ell^*}\,\frac{sh[\sqrt{6\Delta t/\tau}\,(L/\ell^* - 1)] + z_e\sqrt{6\Delta t/\tau}\,ch[\sqrt{6\Delta t/\tau}\,(L/\ell^* - 1)]}{(1 + 6z_e^2\Delta t/\tau)sh[\sqrt{6\Delta t/\tau}\,L/\ell^*] + 2z_e\sqrt{6\Delta t/\tau}\,ch[\sqrt{6\Delta t/\tau}\,L/\ell^*]}\right\}^2. \qquad (1)$$

ℓ^* is the photon transport mean-free path, and the parameter z_e depends on the optical boundary conditions at the sample surfaces [15]. Durian *et al.* further showed that, for foam, τ corresponds to the mean time interval between bubble rearrangements at a given place in the sample [10]. Since the rapid evolution of τ in solidifying foam cannot be resolved using single-speckle DWS, we record speckle images taken by the CCD camera, allowing us to average $g_2(\Delta t)$ over about 10^4 different speckles simultaneously. The strength of long range angular correlations between speckles decreases with the inverse of the Thouless number [16], which is larger than 10^6 for our experiments. Therefore, different speckles are statistically independent to an excellent approximation, and we expect that averages of $g_2(\Delta t)$ over simultaneously measured speckles and over realizations of the sample disorder are equivalent as has been shown in previous dynamic light scattering experiments [17–19]. To verify this hypothesis experimentally, we have measured $g_2(\Delta t)$ for the same quiescent foam sample using the two averaging schemes. In both cases, the data were analyzed using expression (1) with $z_e = 1$ [15] and measured values of ℓ^* that are in agreement with previously published data [10]. Results are shown in Fig. 1, where the evolution of τ is represented as a function of foam age. Clearly, the data obtained by both averaging schemes are in good agreement and also correspond to results previously obtained for similar foam samples using single-speckle DWS [6]. Let us note that our multispeckle DWS data, obtained using an integration time of a few seconds, are much less scattered than those obtained by single-speckle DWS with an acquisition time of more than 5 min. Having tested the speed and accuracy of multispeckle DWS, we have used this technique to study the solidification of aqueous foam.

To perturb or to "melt" the bubble packing, the foam sample is subjected during one minute to a sinusoidal shear strain of amplitude γ, chosen in the range 4% to 98%. The age t_p, at which such a perturbation is applied, is varied between 10 and 80 min. Figure 2 shows that, just after the perturbation, $g_2(\Delta t)$ decreases much more slowly than before. Then, $g_2(\Delta t)$ progressively recovers its initial form. This is in qualitative agreement with previous single-speckle DWS data obtained by Gopal and Durian

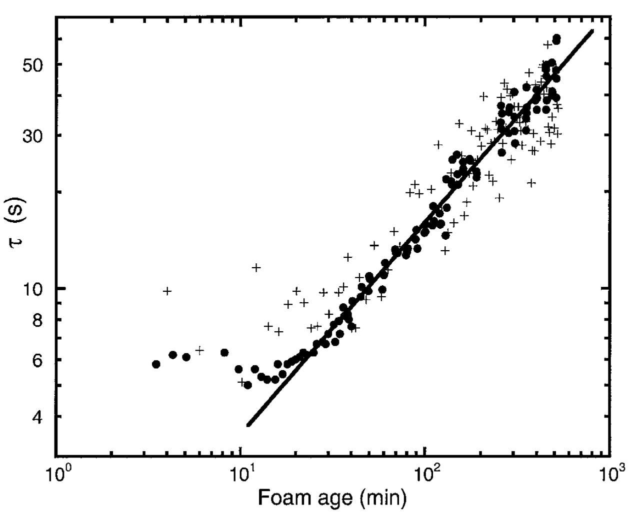

FIG. 1. Average time interval between bubble rearrangement τ in a coarsening foam, simultaneously measured *in situ* by multispeckle DWS (solid circles) and single-speckle DWS (crosses). The sample thickness is equal to 5.1 mm. The continuous line represents a power law fit to the multispeckle data: $\tau \propto t^{0.66\pm0.02}$ for foam ages t superior to 20 min.

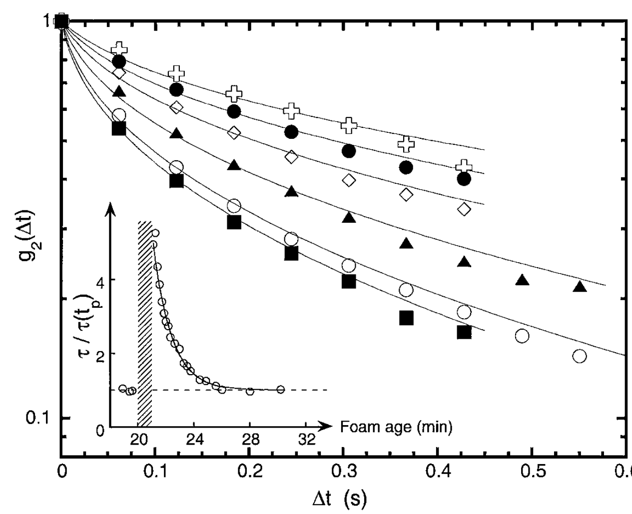

FIG. 2. Light intensity autocorrelation functions $g_2(\Delta t)$ versus time delay Δt, before and after a sinusoidal shear strain of amplitude 0.52, applied at a foam age of 20 min. The sample thickness is 3.1 mm. $g_2(\Delta t)$ is measured 24.0 s before the beginning of the strain (squares), and 13.2 s (crosses), 31.8 s (solid circles), 69.0 s (diamonds), 135.6 s (triangles), and 267.6 s (open circles) after the end of the strain. The continuous lines correspond to fits by expression (1). The inset shows the evolution with foam age of the normalized average time interval between bubble rearrangements explained in the text, fitted by an exponential law.

on similar samples subjected to a transient steady shear at a foam age of 100 min [12]. Moreover, our data are well fitted by expression (1) with τ as the only free parameter. The inset of Fig. 2 shows the temporal evolution of τ following the perturbation, normalized by its value just before the perturbation $\tau(t_p)$. Within a few minutes, τ decreases back to its value corresponding to a quiescent foam. As can be seen in Fig. 3, *the relaxation of* τ *is exponential* and can be fitted to a law of the form $\tau(t')/\tau(t_p) - 1 \propto \exp(-t'/T_R)$, where t' denotes the time elapsed since the end of the perturbation and T_R the relaxation time. Such a relationship is observed in the entire investigated range of γ. The evolution of T_R with strain amplitude and foam age is shown in Fig. 4.

To discuss these results, we recall that, in the framework of the generic models describing the rheology of soft glassy materials, foam is considered as a metastable collection of "mesoscopic" regions whose size is intermediate between the scale of the bubbles and the macroscopic scale [1,2]. When the local strain γ_l inside a region exceeds the local yield strain, the bubbles inside this region rearrange and γ_l is reset to zero. The local and macroscopic strain rates are supposed to be equal as long as there are no rearrangements. On this basis, several constitutive equations describing the evolution for the probability $P(\gamma_l)$ of finding a region with a strain γ_l have been proposed. The predictions strongly depend on the extent to which rearrangements induce changes of local strain in other regions. The experimental evidence for foams suggests that this effect must be weak: The function that fits the DWS data in Fig. 2 was derived assuming that rearrangements are statistically independent [10]. Moreover, Durian *et al.* have shown that the average size of a region modified upon a rearrangement is only of the order of ten bubbles in diameter [10,12].

To explain our data, we propose a minimal model taking into account the features mentioned in the previous paragraph as well as the evolution of local strains induced by the coarsening process: Because of Laplace pressure differences, gas diffuses from smaller to larger neighboring bubbles leading to a buildup of strains that are released by intermittent rearrangements. For our samples, a scaling state is reached at a foam age of about 20 min [6] so that the mean bubble radius $\langle R \rangle$ as well as any characteristic length of the foam structure increase with foam age t following a parabolic law: $\langle R \rangle^2 - \langle R \rangle_0^2 \propto t - t_0$, where $\langle R \rangle_0$ is the mean radius at age t_0 [6,20–22].

In our minimal description, we suppose that the local yield strain γ_c is identical for all regions and that, for a quiescent coarsening foam, $P(\gamma_l)$ is uniformly distributed between $-\gamma_c$ and γ_c. Under these assumptions, when a transient macroscopic oscillating shear strain is applied, every region in which the absolute value of the local strain exceeds γ_c will rearrange. Therefore, just after such a perturbation, the probability density $P(\gamma_l)$ will be suppressed for $|\gamma_l| > \gamma_c - \gamma$. Then, due to gas exchange between bubbles, local strains will progressively evolve, but it is only after a recovery time necessary for $|\gamma_l|$ to reach γ_c in some regions that rearrangements will again occur and the initial distribution $P(\gamma_l)$ will progressively be recovered. This is in qualitative agreement with our experimental results provided that the relaxation time T_R is identified with the recovery time.

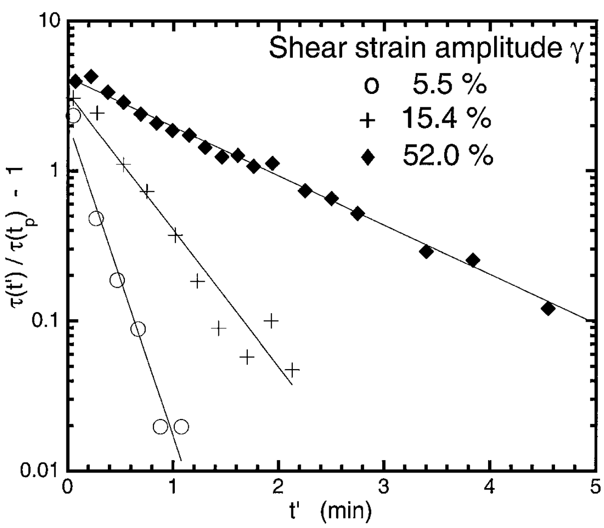

FIG. 3. Bubble dynamics relaxations for different strain amplitudes as labeled, applied at an age $t_p = 20$ min. The sample thickness is equal to 3.1 mm. t' is the time elapsed since the end of the perturbation. The straight lines correspond to fitted exponential laws.

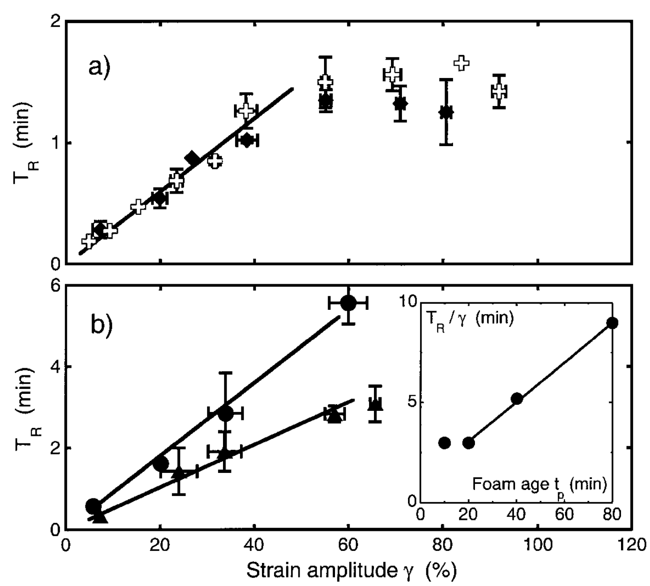

FIG. 4. The characteristic time T_R explained in the text is plotted as a function of strain amplitude γ, for foam ages t_p, respectively, equal to 10 min (diamonds) and 20 min (crosses) in (a), and to 40 min (triangles) and 80 min (closed circles) in (b). The straight lines represent linear fits. The inset of (b) represents the dependence of the corresponding slopes on foam age. The straight line is a linear fit for $t_p \geq 20$ min.

To predict the scaling of T_R with the foam age t_p at which the perturbation is applied, we estimate the evolution of strains in a given neighborhood induced by coarsening during a time interval δt. Let us consider a spherical bubble whose radius R changes by $\dot{R}\delta t$ and which is placed in an effective continuous homogeneous linear elastic medium constituted by its neighbors. The components of the induced strain field will vary with R, δt, and the distance from the bubble center r as $R^2\dot{R}\delta t/r^3$. The superposition of such strain fields generated by the neighboring bubbles will determine the evolution of the local strain at any given place in the foam. The statistical self-similarity hypothesis implies that the distribution of the distances r scales with foam age as does the bubble size distribution [21]. A dimensional argument on this basis predicts that the root mean square of the spatial fluctuations of local strain, accumulated over a time interval δt, should scale as $\delta t/\langle R\rangle^2$. Since, after a perturbation of amplitude γ, the suppression of rearrangements will last until the local strain has increased by γ in some of the regions, we expect that the relaxation time T_R, which is the time necessary for local strain to vary by γ due to the coarsening, scales as $T_R \propto \langle R\rangle^2\gamma$. The linear dependence of T_R on strain amplitude γ shown in Figs. 4(a) and 4(b) is in good agreement with this prediction. If γ is chosen larger than γ_c, our model predicts that T_R should be independent of γ, in qualitative agreement with the data shown in Fig. 4(a). Furthermore, for a given amplitude γ, T_R should increase linearly with t_p since $\langle R\rangle^2 - \langle R\rangle_0^2 \propto t - t_0$ in the scaling state, that is, for $t_p \geq 20$ min. This is indeed what is observed in the inset of Fig. 4(b). This linear dependency of T_R on t_p is consistent with the general prediction according to which, in the scaling state, the time required for any characteristic length to change by a fixed fraction of its value should vary linearly with foam age [6].

To make our analysis more quantitative, the schematic assumptions concerning the drop of γ_1 upon a rearrangement and the value of γ_c would have to be refined. This may allow to relate quantitatively the foam age dependencies of τ and T_R. In this context, as well as to confirm our argument based on continuum mechanics, an extension of numerical *ab initio* simulations of sheared foam that include coarsening and disorder would be of great interest [23,24].

By using multispeckle DWS, we have shown that, following a transient shear, the bubble dynamics in stable aqueous foam is strongly slowed down. It returns to the dynamics of a quiescent foam through a nonlinear relaxation process which depends on shear amplitude and foam age. By taking into account the coarsening in a simple model derived from previously proposed coarse-grained descriptions, we predict the observed scaling. Thus, the results reported in this Letter provide insight into the interplay between the internal dynamics and the macroscopic deformation of foam, and they will help to establish a quantitative model of nonlinear foam rheology.

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