

Origin of the Slow Linear Viscoelastic Response of Aqueous Foams

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We have studied the slow linear viscoelastic response of wet aqueous foams by macroscopic creep compliance measurements, combined to a diffusing-wave spectroscopy investigation of the local dynamics. The data strongly suggest that this rheological response arises from two distinct relaxation mechanisms: The first is due to the coarsening induced bubble rearrangements and governs the steady-state creep; the second results from the interplay between surface tension and surface viscosity of the gas-liquid interfaces and gives rise to a transient relaxation.

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Aqueous foams are complex fluids consisting of concentrated dispersions of gas bubbles in a soapy liquid. Subjected to small stresses, they behave as viscoelastic solids whereas, beyond a yield stress, non-Newtonian viscous flow sets in [1]. Some features of their rheological behavior, such as weakly frequency dependent viscoelastic dissipation down to very low frequencies or jamming phenomena, are common to a large class of soft materials, including concentrated emulsions, gels, and pastes [2]. These similarities have prompted several authors to propose generic theoretical models of the rheology of “soft glassy materials.” In this framework, the viscoelastic dissipation at low frequencies is interpreted as a consequence of mesoscopic structural rearrangements [3,4]. In aqueous foams, gas diffusion between adjacent bubbles drives a coarsening process, leading to a local buildup of strain released by intermittent structural rearrangements [5,6]. A 2D quasistatic numerical simulation has shown that such coarsening induced rearrangements can indeed relax an applied macroscopic strain [1]. Recent experiments also strongly suggest that the slow viscoelastic response of foams is related to coarsening [7]. Moreover, the 2D rheology of the gas-liquid interfaces has been predicted to have a major influence on the low frequency dissipation in foams [8,9], and bulk viscous effects in the liquid films have also been considered [10]. Let us note that both foam rheology and coarsening are coupled to drainage [11]. To clarify the respective contributions of these various proposed mechanisms to the measured low frequency viscoelasticity in foams, we have coupled rheological macroscopic experiments to *in situ* multiple light scattering investigations of the local bubble dynamics [5,6], using samples of the same gas volume fraction but widely differing coarsening rates.

The samples consisted of either Gillette shaving cream [12] or foams generated by injecting a gas and a polymer-surfactant-based aqueous solution into a column filled with glass beads, as described elsewhere [13]. The foaming formulation contained sodium α -olefin sulfonate (AOK, Witco Chemicals), polyethylene-oxide ($M_w =$

$2 \times 10^6 \text{ g mol}^{-1}$, Aldrich), and dodecanol (Aldrich) (concentrations: 1.5% g/g, 0.4% g/g, and 0.2% g/g, respectively). The injected gas was either pure nitrogen or nitrogen containing perfluorohexane vapor, which slows down the coarsening process [14]. In the following, we will call these two kinds of samples N_2 foam and $\text{N}_2/\text{C}_6\text{F}_{14}$ foam, respectively. The physicochemical properties of the Gillette foaming solution (surface tension $\gamma = 29.5 \text{ mN/m}$, viscosity reported by Gopal *et al.* [15] $\eta_w = 1.9 \text{ cP}$) and the AOK solution (surface tension $\gamma = 22.6 \text{ mN/m}$, viscosity $\eta_w = 1.9 \text{ cP}$) are similar. The measured gas volume fraction of all the foam samples is equal to $(93.0 \pm 0.5)\%$. The temporal evolution of the foam structure was monitored by diffuse-transmission spectroscopy [16] and videomicroscopy: For each kind of foam, the average bubble diameter d was found to grow with the time t_a elapsed since foam production (foam age) following a parabolic law. Over the range of studied ages, the $\text{N}_2/\text{C}_6\text{F}_{14}$ foam has the slowest evolution, while the Gillette foam exhibits a bubble growth rate intermediate between that of N_2 and $\text{N}_2/\text{C}_6\text{F}_{14}$ foams. All experiments are performed at foam ages and over durations, for which drainage as well as bubble coalescence are negligible.

Immediately after its production, the foam was injected into the measuring cell of a rheometer. We have used two different instruments: The first (CVOR-150, Bohlin) is equipped with a cylindrical Couette cell. The second is a sliding plate rheometer where the sample is confined between two parallel transparent glass plates, allowing *in situ* light scattering studies. In both instruments, the surfaces in contact with the foam are rough to prevent wall slip, and the air in contact with the samples is saturated with humidity to avoid evaporation. All the experiments were carried out at a temperature of $21 \pm 1^\circ\text{C}$.

To probe accurately the long time end of the viscoelastic relaxation spectrum, the creep compliance $J(t) = \varepsilon(t)/\sigma_o$ was studied as a function of time t . $\varepsilon(t)$ is the strain response, and σ_o is a constant shear stress applied to the sample during a time interval $\Delta t = 100 \text{ s}$. Before

and after this time interval, no stress is applied. Δt is sufficiently short for bubble growth induced changes of quasistatic elasticity to remain negligible. The measured $J(t)$ is independent of the gap width in the sliding plate geometry and in the cylindrical Couette cell, indicating that wall slip is negligible in our experiments.

To measure the rate of bubble rearrangements *in situ* during the creep experiment, we have performed diffusing-wave spectroscopy (DWS) experiments in the sliding plate rheometer. For the N_2 foam, where the bubbles are rapidly rearranging, single-speckle DWS [5] was used, whereas for the N_2/C_6F_{14} foam and Gillette foam we used multispeckle DWS, which is best suited to investigate very slow dynamics [6]. The sample is illuminated through one of the plates by an extended laser beam and the temporal fluctuations of the backscattered speckle intensity $I(t)$ are measured with either a photomultiplier and a digital correlator (single-speckle DWS) or a charge-coupled device camera and an image analysis software (multispeckle DWS), as described elsewhere [6]. To characterize the temporal intensity fluctuations, the autocorrelation function $g_2(\tau) = [\langle I(t)I(t+\tau) \rangle - \langle I \rangle^2] / [\langle I^2 \rangle - \langle I \rangle^2]$ is calculated. The brackets denote an average over realizations of the structural disorder in the sample. The results are analyzed using the well-established formalism of DWS [17,18] which relates $g_2(\tau)$ to a characteristic time τ_0 of the dynamics of the light scatterers, the photon transport mean-free path ℓ^* , and a parameter z_e describing the optical boundary conditions. For foams of 93% gas volume fraction, $z_e \cong 1.0$ [16], and for our samples we have measured $\ell^* \cong 3.8d$, in agreement with [16]. The sample thickness L is chosen to ensure that $L/\ell^* > 10$. In aqueous foams, τ_0 represents the mean time interval between bubble rearrangements at a given place in the sample [5]. If these rearrangements occur randomly throughout the sample, at a rate R per units of volume and time, one obtains $\tau_0^{-1} \approx Rv_o\ell^{*3}$, where $v_o\ell^{*3}$ is the volume in which a typical rearrangement perturbs the foam structure so strongly that the phase of diffusive light paths going through this region is randomized. For each studied type of foam, we have determined v_o by comparing R , obtained by counting rearrangements visible at the surface, to τ_0^{-1} measured by DWS [5] and the measured value of ℓ^* . We find $v_o = 43 \pm 15$ for N_2 foam, $v_o = 11 \pm 2$ for N_2/C_6F_{14} foam, and $v_o = 13.5 \pm 1.2$ for Gillette foam.

Figure 1 shows the temporal evolution of a typical compliance for each kind of foam. All of the samples respond elastically to the initial step stress by an instantaneous compliance J_o , which is followed, after a few seconds, by a steady-state flow, characterized by a viscosity η_o . After the stress is removed, the elastic deformation is recovered within 10% in a few seconds, and the irreversible part of the deformation remains. For each type of foam at a given age, this compliance response is independent of the amount of applied stress σ_o in the investigated range far below the yield stress, indicating

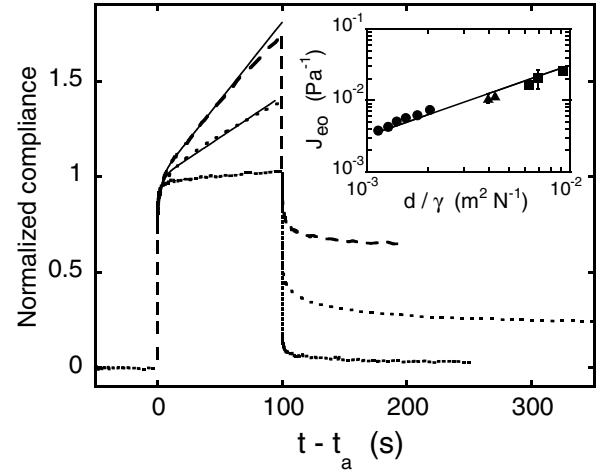


FIG. 1. Typical shear creep and recovery compliances as a function of time. The stress σ_o is applied at a foam age t_a , during 100 s. The compliances are normalized by the steady state compliance J_{eo} defined in the text. The different line styles correspond to the three kinds of foam: long-dashed line, N_2 foam ($t_a = 12$ min, $\sigma_o = 0.5$ Pa); short-dashed line, Gillette foam ($t_a = 60$ min, $\sigma_o = 3.0$ Pa); and dotted line, N_2/C_6F_{14} foam ($t_a = 40$ min, $\sigma_o = 0.8$ Pa). For each data set, the thin line corresponds to a fit to Eq. (1). The inset shows J_{eo} as a function of the average bubble diameter d divided by the surface tension γ for the three kinds of foam, together with a linear fit. The symbols correspond to N_2 foam (■), Gillette foam (●), and N_2/C_6F_{14} foam (▲). The error bars are within the point size unless they are drawn.

linear viscoelastic behavior. Remarkably, the data are in all cases well fitted by an expression of the form

$$J(t) = J_o + \frac{t - t_a}{\eta_o} + J_1 \left[1 - \exp\left(-\frac{t - t_a}{J_1 \eta_1}\right) \right], \quad (1)$$

where the parameters J_o , J_1 , η_o , and η_1 depend on the physicochemical characteristics of the foam. Equation (1) shows that the low frequency or long time *linear* viscoelastic behavior involves only two relaxation times, which is in contrast to the predictions of a “soft glassy rheology” model [3]. The inset of Fig. 1 shows that the steady-state compliance, $J_{eo} = J_o + J_1$, which describes the elastic deformation during steady flow, increases linearly with the inverse of Laplace pressure d/γ , in agreement with the Princen law predicting the static shear modulus of aqueous foams [19–21]. As can be seen in Fig. 2(a), the viscosity η_o evolves with foam age only very weakly for a given foam, but it strongly differs from one kind of foam to the other. This variety of macroscopic rheological responses is correlated with differences among the average time intervals between structural rearrangements τ_0 . Using DWS, we find the following: For N_2 foam, $\tau_0 = (1.3 \pm 0.2)$ s at $t_a = 8$ min, a value that increases slightly to (1.5 ± 0.2) s for the largest age $t_a = 30$ min. For N_2/C_6F_{14} foam, $\tau_0 = (94 \pm 21)$ s for $t_a \leq 130$ min. For Gillette foam, τ_0 increases from (9.4 ± 2.0) s to (22.4 ± 4.5) s as t_a varies from 30 to 120 min. These values are

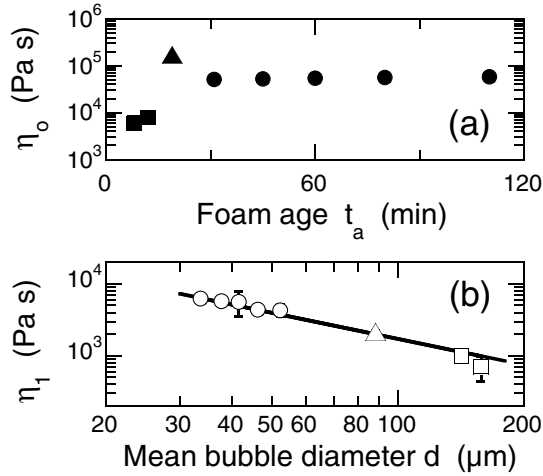


FIG. 2. Steady shear creep viscosity η_o versus foam age (a) and viscosity η_1 versus mean bubble diameter (b). η_o and η_1 are obtained by fitting Eq. (1) to the creep data. The symbols correspond to N_2 foam (■, □), Gillette foam (●, ○), and N_2/C_6F_{14} foam (▲, △). In (b), the straight line is a fitted power law with an exponent $-(1.2 \pm 0.1)$. In (a) and (b), the error bars are within the point size unless they are drawn.

independent of σ_o in the investigated range, and they are the same as those measured in quiescent samples. In contrast to η_o , the viscosity η_1 exhibits a well-defined dependence on the average bubble diameter, following a power law [cf. Fig. 2(b)].

We now focus on the physical processes at the origin of the slow linear viscoelastic behavior, described by Eq. (1). Our light scattering data show that the applied stress does not enhance the rate of bubble rearrangements. Therefore, we exclude rearrangements induced by macroscopic strain as a dominant mechanism. We propose the following schematic model to explain the observed steady-state creep: Upon a coarsening induced rearrangement, the bubble packing locally settles into a new configuration of minimal energy, so that the elastic strain induced by the applied macroscopic stress is at least partly converted into an irreversible strain. The local elastic stress existing prior to the rearrangement is thus relaxed. Using standard self-consistent mechanical homogenization techniques [22], we estimate the average increment of macroscopic compliance ΔJ that accompanies rearrangements in a sample volume fraction denoted ν : Up to a dimensionless prefactor of the order of 1, one obtains $\Delta J/J_{eo} \cong \nu$, provided $\nu \ll 1$. The fraction rearranged over a time interval Δt can be written as $\nu = Rv_m \ell^{*3} \Delta t$, where $v_m \ell^{*3}$ is the effective volume of the region where the local stress is relaxed and which we expect to be on the average of the order of a few bubble volumes. Thus, the time derivative of the creep compliance in the steady state is given by $\dot{J} \cong Rv_m \ell^{*3} J_{eo}$ and we predict the relation $\eta_o J_{eo} = 1/(Rv_m \ell^{*3})$. This scaling is in full agreement with the data shown in Fig. 3 for Gillette and N_2/C_6F_{14} foams. Moreover, we infer $v_m \cong 0.7$ corresponding to rearrangement events of a volume

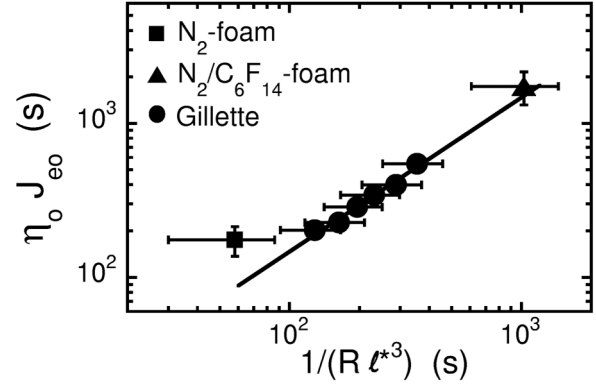


FIG. 3. Characteristic time of the steady-state creep, $\eta_o J_{eo}$, versus the average time interval between bubble rearrangements in a volume ℓ^{*3} , $1/(R \ell^{*3})$, measured by DWS. The line is a linear fit to the data of Gillette and N_2/C_6F_{14} foams: $\eta_o J_{eo} = (1.47 \pm 0.03)/(R \ell^{*3})$.

$\approx (3.3d)^3$ each, which is of the expected order of magnitude. For N_2 foam, the discrepancy between the measured value of $\eta_o J_{eo}$ and that expected in the framework of our model might be related to residual drainage effects. This discussion extends the previous analysis of the link between coarsening and slow relaxation in foams by Gopal and Durian [7] by providing a quantitative interpretation of the creep mechanism, based on the dynamics at the mesoscopic scale measured *in situ*.

Having discussed the mechanism of steady-state creep, we now focus on the transient response, described in our phenomenological model Eq. (1) by the parameters J_1 and η_1 . For the three types of foam, we find experimentally $J_1 \propto d$, $\eta_1 \propto d^{-1.2}$, and a characteristic time scale $\tau_1 = J_1 \eta_1 \cong 3$ s. Thus, τ_1 weakly depends on the average bubble size which varies over almost a decade. Indeed, when only Gillette foam data are considered, τ_1 is strictly independent of d . Buzza *et al.* have predicted that the effective zero shear viscosity of foams should be dominated by the dilatational surface friction at the gas-liquid interfaces, and be of the order of the dilatational surface viscosity κ divided by a characteristic length [9]. This length is either set by the bubble diameter d or by the extent of a typical marginal regeneration region ρ . Our data fully agree with the first possibility. They agree with the second only if $\rho \propto d$. Among the possible linear viscoelastic mechanisms of dissipation [9], surface friction is indeed the only one compatible with the observed scaling of η_1 with bubble size. To understand the physical origin of the compliance J_1 , let us consider the structural evolution of the foam: At the instant where the step stress is applied, we expect viscous stresses to dominate over surface tension forces, leading to an initial strained structure that does not satisfy the Plateau rules [1]. The foam then relaxes towards the equilibrium structure of minimal interfacial energy, where the dominant stresses are due to surface tension. We associate the transient response with such a mode of deformation. To make this

interpretation more explicit, we consider a dry 2D hexagonal foam, taking into account surface viscosity. In this case, the tensile force acting on a film of length L is given by $2\gamma + (2\kappa/L)(\partial L/\partial t)$ [8]. This implies a relaxation time on the film level τ_1 proportional to κ/γ which is independent of the characteristic length scale L of the foam structure, and therefore of the bubble size, in full agreement with our data. Moreover, we have solved numerically the equations governing the linear viscoelastic relaxation after a step stress of such a 2D foam [8]. The calculated macroscopic strain relaxation is indeed governed by a characteristic time of order κ/γ . By identifying τ_1 to κ/γ , we estimate from our data that the surface viscosity of the AOK based and the Gillette foaming solutions should be, respectively, of the order of 0.05 and 0.15 kg s⁻¹, consistent with values of dilatational surface viscosity reported for solutions of dodecanol and sodium lauryl sulfate, a surfactant of chemical structure similar to that of the surfactants used in this study [23,24].

We have combined macroscopic rheometry and multiple light scattering to study the slow dynamics of a series of foam samples which differ by their rates of coarsening and mean bubble sizes. Two distinct mechanisms explaining the slow linear viscoelastic response in foams have thus been identified, each governed by a single characteristic time. The mechanism at the origin of steady-state creep is shown to be due to coarsening induced bubble rearrangements. Moreover, for the first time, the impact of interfacial rheology on macroscopic viscoelastic behavior is evidenced experimentally. We show that an interplay of surface viscous forces and surface tension leads to the observed transient creep. Our schematic models will help to construct a rheological constitutive equation for aqueous foams based on physically motivated bubble and microscale dynamics.

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