Aqueous foams are tightly packed collections of gas bubbles separated by a continuous liquid phase [1, 2]. Like elastic solids, bulk foams resist shear, completely unlike the gases and liquids from which they are comprised. The origin of this striking behavior is that the bubbles are jammed, unable to flow around one another and explore configuration space under thermal energy. Thus bubbles distort, rather than rearrange, when subjected to small shear deformations. The resulting extra internal gas-liquid surface area costs energy in proportion to the surface tension, and this provides a restoring force. The shear modulus is roughly surface tension divided by bubble radius, depending precisely on the volume fraction, \( \varepsilon \), of the continuous liquid phase [3, 4, 5]. As a foam is made wetter, the bubbles become progressively rounder, and the shear modulus decreases. The elasticity completely vanishes at the point where the bubbles are close-packed spheres. This is one example of unjamming [6].

In this paper we explore other ways to unjam the bubbles in a foam. Each could correspond to a different trajectory in a global jamming phase diagram [7]. For example, one could imagine raising the temperature so that the bubbles are jammed, unable to flow around one another and explore configuration space under thermal energy. Under flow, shear-induced rearrangements compete with coarsening-induced rearrangements. The macroscopic consequences are captured by a novel rheological method in which a step-strain is superposed on an otherwise steady flow.

Our samples are a commercial aqueous foam, consisting of nearly-spherical polydisperse gas bubbles, 92\% by volume, that are tightly packed in an aqueous solution of stearic acid and triethanolamine (Gillette Company, Boston MA). Samples are surrounded by a water bath held at 25.0\(^\circ\)C and are measured after the foam has aged for approximately 100 minutes. By this time, the average bubble size is approximately 60 microns and is growing reproducibly via coarsening [8]; stresses due to the loading process have also relaxed. Test durations are sufficiently short that gravitational liquid drainage and bubble coalescence are negligible.

Our measurements are performed with a Paar Physica UDS 200 rheometer, controlling the rotational speed and angular displacement of a solid cylinder whose axis is vertical and concentric with a fixed surrounding cup. The sample cell has an inner radius of 20.0 mm, and a 4.1 mm gap; these dimensions ensure that the foam can be treated as a bulk material with uniform stress. To minimize end-flow effects, the 98 mm long inner cylinder is much shorter than the depth of the surrounding cup yet much longer than the gap width. Wall slip is precluded by coating both the cylinder and cup with a fine-grade sandpaper. Samples are loaded through a 5 mm hole at the bottom of the cup, after lowering the cylinder to the test position. DWS measurements indicate the absence of shear-banding and other secondary flows [11]. To re-confirm, we compared with a similarly coated cone-and-plate cell, with a 10 cm radius and 10\(^\circ\) cone angle. Identical rheology results were obtained for both cell configurations, implying that the imposed shear deformation is uniform. Diffuse light transmission indicates that bubbles do not burst, and voids do not form, even under high shear [9].

**Effect of coarsening on mechanical response.** To quantify linear response, we measure both the complex shear
to within instrumental limits. An empirical fit to the step strain up to the time beyond which stress is zero agrees very good, demonstrating conclusively that the range corresponding to the time range of the fit. The transform \([15, 16]\). The time range for our modulus, \(G^*(\omega) = G'(\omega) + iG''(\omega)\) \([12, 10]\), and the stress relaxation modulus, \(G(t)\) \([12, 10]\). Our data are displayed in Fig. 1. Note that \(G'(\omega) > G''(\omega)\), meaning that the response is primarily elastic rather than dissipative. The frequency range for our \(G^*(\omega)\) data spans almost six decades, from \(2\pi\) divided by sample age (an absolute minimum below which measurement is not possible) up to a maximum set by limitations of the rheometer. Note that different amplitude strains give the same result, demonstrating absence of wall-slip and other geometry-dependent artifacts and hinting at linearity of response. A more stringent test of linearity is comparison with \(G(t)\), which should be related to \(G^*(\omega)\) by Fourier transform \([12, 10]\). The time range for our \(G(t)\) data spans over five decades, from the time needed to achieve the step strain up to the time beyond which stress is zero to within instrumental limits. An empirical fit to the \(G(t)\) data is shown in Fig. (b) by a solid curve; this fit is transformed and plotted in Fig. (a) over a frequency range corresponding to the time range of the fit. The agreement is very good, demonstrating conclusively that the sample is linear. This is further supported by an empirical fit to \(G^*(\omega)\) data at high-\(\omega\) and the comparison of its transform with \(G(t)\) data at short-\(t\).

Let us now consider the frequency and time dependence of the moduli in Fig. 1. The fit for \(\omega > 5 \text{ rad/s}\) is to the form \(G^*(\omega) = G_o(1 + \sqrt{i\omega/\omega_n})\) with free parameters \(G_o = 2300 \text{ dyne/cm}^2\) and \(\omega_n = 156 \text{ rad/s}\). The former represents the static shear modulus, roughly surface tension divided by bubble size \([3, 1, 8]\). The latter represents the effect of nonaffine deformation of the bubbles under shear due to local packing configurations that are strong or weak with respect to the shear direction \([17]\). This fit, including the parameters, is consistent with the \(G^*(\omega)\) data in Ref. \([18]\), where the frequency range \((0.3 - 20 \text{ rad/s})\) was too small to fully demonstrate the functional form. According to the theory of \([17]\), the characteristic frequency is \(\omega_n \propto G_o/\eta_\infty\), where the very-high frequency response is \(G^*(\omega) = i\eta_\infty\omega\). The numerical prefactor was not predicted; experimentally, it was found to depend on \(\varepsilon\) and was not of order 1. To compare, the value is \(\omega_n \approx 600 \text{ rad/s}\) for a \(\varepsilon = 0.38\) emulsion of 0.5 \(\mu\)m oil droplets in water \([17, 19]\) (NB: by our definition, \(\omega_n\) may be easily read off a plot by locating where \(G'(2\omega_n) = 2G_o\) and \(G''(2\omega_n) = G_o\)).

The fit to \(G_o(1 + \sqrt{i\omega/\omega_n})\) fails for \(\omega < 5 \text{ rad/s}\); the corresponding transform fails for \(t > 20 \text{ s}\). At longer times, the \(G(t)\) data decay slowly below \(G_o\), almost logarithmically, over a few decades before relaxing more rapidly at around 1000 s. The transform of this final decay corresponds to the peak in \(G''(\omega)\) at \(10^{-3} \text{ rad/s}\). At lower frequencies, \(G^*(\omega)\) is unmeasurable; but since the integral of \(G(t)\) over all time is finite, the very-low frequency behavior is formally \(G''(\omega) \propto \omega\) as required by causality \([20]\). Thus the full frequency-dependence of \(G^*(\omega)\) for our foam is truly known and well-behaved. This resolves a long-standing puzzle \([20]\) raised by earlier measurements \([18, 19, 21]\) where \(G^*(\omega)\) was roughly constant down to the lowest measured frequencies.

All that remains is to understand the origin of the low-\(\omega\) / long-\(t\) behavior. We contend that evolution of the foam structure by coarsening is responsible. One clue is that the onset of deviation from the high-\(\omega\) fits corresponds to the time \(\tau_{eq} = 20 \text{ s}\) given by DWS for the time between coarsening-induced rearrangements at each site. Another clue is that the final decay of \(G(t)\) and, equivalently, the peak in \(G''(\omega)\) correspond to the sample age. Since coarsening gives power-law growth, it takes of order the sample age for the structure to completely change. It is interesting that coarsening-induced rearrangements relax microscopic coarsening-induced stress inhomogeneities far more quickly than the relaxation of macroscopically-imposed stress. Rather, the cumulative effect of many rearrangements and a change in bubble size is needed to relax global stress. The net result is a rheology that obeys linear response. This is remarkable given that the microscopic relaxation mechanism isn’t thermal motion, but rather evolution. In effect, coarsening unjams the foam, so that at low frequencies the rheology is \(G'(\omega) \ll G''(\omega) = \eta\omega\) like an ordinary equilibrium liquid.
induced rearrangements.

The salient features of the stress relaxation are shown in Fig. 3 vs strain rate. The first plot is of elastic storage, $G(0, \dot{\gamma})$, the value when the superimposed step-strain is achieved (below about 0.1s). This decreases very slowly, and is nearly constant, for strain rates less than about 0.05/s; for higher strain rates it abruptly vanishes. The second plot is of stress relaxation times. One such measure is $t_e$, when stress falls to $1/e$ of the initial value. Another measure is $t_p$, where $H(t, \dot{\gamma})$ reaches a global maximum. At zero and very low strain rates, these times are different since there are two competing relaxation mechanisms (evolution and shear). For strain rates higher than about $3 \times 10^{-4}$/s, the stress relaxation is essentially exponential and the two relaxation times are hence indis-tinguishable. In this regime, shear completely dominates the relaxation. It is puzzling that the relaxation time decreases with increasing strain rate as $\dot{\gamma}^{-1/2}$, since on dimensional grounds one would have expected $\dot{\gamma}^{-1}$.

Now we may compare the macroscopic rheology with the nature of the microscopic bubble dynamics. Previously we used DWS to measure the strain rate dependence of two microscopic time scales: $\tau_o$, the time between localized discrete rearrangements, and $\tau_s$, the time for adjacent scattering sites to convect apart by one wavelength of light [13]. The observed DWS data are reproduced by the dashed curves in Fig. 3b). For very low strain rates, below about $3 \times 10^{-4}$/s, the rearrangements are discrete and the time between events, $\tau_o$, is not noticeably different from the quiescent value. The stress relaxation time is much much longer than $\tau_o$, not noticeably different from the quiescent value. The stress relaxation time is much much longer than $\tau_s$. The onset of this correlated shearing motion of bub-

Effect of shear on mechanical response. Next we in-

vestigate how the application of shear causes a simi-

lar loss of elasticity. For this we superimpose a small-

amplitude step-strain, $\Delta \gamma$, on top of otherwise steady 

shear at rate $\dot{\gamma}$. The resulting temporary increase in

stress defines the transient stress relaxation modulus,

$G(t, \dot{\gamma}) = [\sigma(t) - \sigma(0)]/\Delta \gamma$. A frequency-domain ver-

sion of this technique was developed for polymers [22].

Example data are shown in Fig. 2a). Note that as the 

strain rate increases, the elastic character of the foam 

melts away. There are two signs of this. First, the 

progressively smaller intercept, $G(0, \dot{\gamma})$, means less elastic 

energy storage. Second, the progressively shorter decay 

time means more liquid-like dissipation. At high enough 

strain rates, where there is no transient storage and only 

dissipation, the foam behaves like an equilibrium liquid. 

Similar behavior has now been observed in simulations of 

a model foam [23].

To further quantify the unjamming behavior appar-

ent in Fig. 2a), we first deduce the relaxation spectrum,

$H(t, \dot{\gamma}) \approx dG(t, \dot{\gamma})/d\ln t$ [15, 16]. Results are shown in 

Fig. 2b). For low and zero strain rates, there are two 

competing relaxation processes, reflected by a broad peak 

at very late times and long tail of short-time modes of 

nearly equal weight. The former reflects the coarsening 

process, and the latter the nonaffine bubble motion. As 

the shear rate increases, the coarsening peak gradually 

falls and another peak gradually rises over the nonaffine 

tail at short times. Presumably this is due to shear-

FIG. 2: (a) Stress relaxation moduli for foams sheared at 

various rates, as listed. This is given from the stress $\sigma(t)$ 

following the superposition of a step-strain $\Delta \gamma$ on steady shear: 

$G(t, \dot{\gamma}) = [\sigma(t) - \sigma(0)]/\Delta \gamma$. (b) The corresponding relaxation 

spectra, $H(t, \dot{\gamma}) \approx dG(t, \dot{\gamma})/d\ln t$.
FIG. 3: (a) Transient shear modulus, (b) transient shear relaxation times, and (c) viscosity, all as a function of shear rate. The vertical dotted lines denote the characteristic relaxation times, and (c) viscosity decreases across the whole strain range, though not quite as fast as \( \dot{\gamma}^{-1} \) (which would have indicated constant stress). There is at most a slight change in exponent at \( \dot{\gamma}_m \). Similar behavior is found in simulations [22]. Altogether this emphasizes the importance of the superposition method to measure \( G(t, \dot{\gamma}) \), since it provides a clear dramatic signature of the unjamming transition. With this tool, and by comparison with DWS data, we have succeeded in connecting the nature of microscopic bubble dynamics with the resulting macroscopic rheological behavior. We have thereby shown that the unjamming of foam can be accomplished both by time and by application of shear. The unjammed liquid-like state is very similar to what would be achieved by raising the temperature for a thermal system. An important next step would be to deduce an effective temperature, recently shown in simulation of a sheared model foam to have many of the attributes of a true statistical mechanical temperature [26].

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