Yielding and Rearrangements in Disordered Emulsions

P. Hébraud, F. Lequeux, and J. P. Munch

Laboratoire de Dynamique des Fluides Complexes, 3 rue de l'Université, 67070 Strasbourg, France

D. J. Pine

Departments of Chemical Engineering and Materials, University of California, Santa Barbara, California 93106

We use diffusing-wave spectroscopy to measure the motion of droplets in concentrated emulsions subjected to a periodic shear strain. The strain gives rise to periodic echoes in the correlation function which decay with increasing strain amplitude. For a given strain amplitude, the decay of the echoes implies that a finite fraction of the emulsion droplets never rearranges under periodic strain while the remaining fraction of droplets repeatedly rearranges. Yielding occurs when about $4-5\%$ of the droplets rearrange. [S0031-9007(97)03423-6]

There are a number of soft materials that yield when subjected to a moderate shear stress. To a first approximation, the response of the material is elastic below some yield stress and plastic above. Some of these materials have a crystalline structure, and the yielding originates in the motion of dislocations [1–3]. But many other materials, such as concentrated emulsions and colloidal suspensions, foams, and clays, have an amorphous structure and also exhibit a yield stress [4]. The origin of the yield stress in these glassy materials is not well understood.

The structure of glassy materials typically evolves extremely slowly at rest because the particles explore restricted domains of space under the action of thermal fluctuations [5]. Flow dramatically changes the structure, forcing the particles to follow trajectories very different from the ones they explore under thermal fluctuations. This leads to very strong nonlinearities in the mechanical properties, including yielding and cracking. However, the particle trajectories associated with yielding in these disordered systems have never been properly determined.

In this Letter, we use diffusing-wave spectroscopy [6] (DWS) to probe the irreversible motion of droplets which accompanies yielding of concentrated emulsions subjected to an oscillating shear flow. In the absence of shear, DWS provides accurate information about the Brownian motion of particles which multiply scatter light. In concentrated glassy emulsions, however, Brownian motion is suppressed because of the crowding of droplets, and very little droplet motion is observed. The application of shear flow causes emulsion droplets to move, however, and this motion can be detected using DWS [7]. For oscillating shear flow, one expects the motion of the emulsion droplets to be elastic and largely reversible for sufficiently small amplitude strains. For strains large enough to cause the emulsion to yield, however, one expects there to be irreversible droplet movements. The key is to distinguish the irreversible droplet movements from the large background of reversible motion in an oscillating shear flow. We accomplish this by detecting

"echoes" in correlation functions measured using DWS. Our method is described below.

In DWS, one measures the temporal decay of the intensity autocorrelation function of the multiply scattered light [6]. The correlation function is sensitive to very small relative motions of the scatters and completely decays when the scattering particles move a small fraction of the wavelength of light. Thus, in an oscillatory shear flow, the correlation function decays very rapidly upon the application of a straining motion. If the straining motion is reversed, however, the correlation function will fully recover to its initial value and an "echo" will be detected, provided each scatterer returns precisely to its initial position after one period. In fact, for a perfectly elastic system, a train of echoes would be observed at integral multiples of the period. By contrast, if each application of the strain causes some random fraction of the particles to rearrange and undergo irreversible motion, then the height of each subsequent echo will be diminished. The technique is reminiscent of NMR spin echo measurements where one probes how spins return to their initial orientation under the action of a symmetric magnetic field pulse sequence. Here, we detect the positions of the scatterers, and not the spins, and the macroscopic strain plays the role of the magnetic field.

In these experiments, we study yielding in simple concentrated emulsions consisting of hexadecane droplets in water, stabilized by sodium dodecyl sulfate at a concentration of 20 mM. These systems have been studied intensively both by rheometry and by DWS for samples at rest and are known to exhibit a yield stress [4]. We prepared emulsions with a mean droplet radius of $a = 0.9\ \mu$m and a polydispersity of about 10%, as measured by dynamic light scattering from a dilute suspension. Samples with volume fractions of oil ranging from $\phi_{oil} = 0.67$ to 0.92 were obtained by centrifugation.

We built a shear cell consisting of two parallel glass plates with a variable gap. For most of our measurements, the gap was 2.0 mm. Oscillatory straining motion was realized by moving the upper plate, mounted on a

precision translation stage, with a piezoelectric device. The motion of the piezoelectric device could be amplified by a lever which enabled the device to achieve amplitudes from 1 μm to 1 mm at a frequency of approximately 58 Hz. The glass plates were roughened by sandblasting to prevent slippage between the emulsion and the plates. We confirmed that the emulsions did not slip by visual observation and by checking that we obtained identical results independent of thickness. The roughening did not affect the light-scattering measurements, since the sample was already highly multiply scattering.

For the DWS measurements, we used an Ar-ion laser and collected multiply scattered light in both the backscattering and transmission geometries [6]. A key feature of our technique was the use of a Brookhaven Instruments BI-9000 correlator which allows one to specify the distribution of delay channels with great flexibility. For this experiment, this meant we could concentrate a high density of linearly spaced delay channels in the few narrow regions of delay times that we were interested in, specifically, at those delay times where the echoes would appear (at integral multiples of the oscillation period).

Figure 1(a) shows a typical correlation function obtained for a sinusoidal strain of constant amplitude. The correlation function decays and then exhibits very narrow echoes centered around multiples of the strain period. In Fig. 1(b), we show the shapes of the initial decays and echoes for three different strain amplitudes. The initial decay is caused by the affine motion of the particles, and the decay time scales with the mean inverse shear rate. Similarly, the widths of the echoes also scale with the mean inverse shear rate.

The height of the echoes is determined by the fraction of the sample which undergoes reversible motion. If all the scatterers were to exhibit a perfectly reversible periodic motion under the periodic strain, the correlation function would return to its initial value after each multiple of the oscillation period. To verify that this is indeed the case, we performed measurements on latex particles included in a polymer gel. In this case, the echoes recovered the amplitude of the initial decay for all strain amplitudes. By contrast, with emulsions, the height of the echoes decreases as the amplitude of the strain is increased. Thus, the strain induces irreversible rearrangements of the emulsion droplets.

The most surprising feature of the correlation functions we measure is that, after the decay of the first echo, *the amplitudes of the echoes remain constant* from the first to the sixteenth echo. This is observed for both backscattering and transmission measurements. This observation has strong implications. First, it means that there is a finite fraction of particles inside the sample which follows reversible trajectories over many periods. Second, it means that there is another finite fraction of the sample which follows irreversible chaotic trajectories. Third, it means that these two fractions of particles are disjoint sets. That is, the particles that rearrange between the
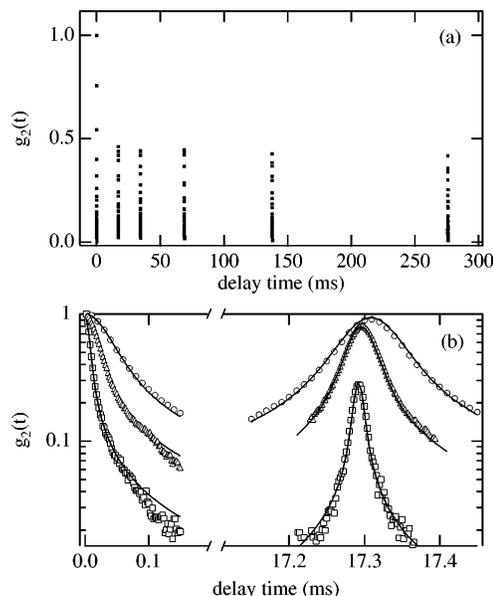
FIG. 1. Normalized intensity correlation functions obtained from an 85% oil-in-water emulsion subjected to oscillatory shear strain. (a) Correlation function displayed using an axis with a linear delay time spacing. To obtain the maximum delay, the correlator channels were set to measure only the initial decay and the first, second, fourth, eighth, and sixteenth echoes. Other echoes were omitted in order to devote a sufficient number of channels to each echo so that the echo heights could be accurately determined. Limitations in the correlator design prohibit accumulating echoes at delay times greater than 32 000 times the fundamental sample time. The strain amplitude is $\gamma_0 = 0.05$. (b) Expanded view of the echoes for different strain amplitudes: $\gamma_0 = 0.01$, top (circles); $\gamma_0 = 0.02$, middle (triangles); $\gamma_0 = 0.06$, bottom (squares). The solid lines through the data are computed from Eq. (3) for the different strain amplitudes without any adjustable parameters except for the echo heights.

initial decay and the first echo are the only particles that ever undergo rearrangements over the time scale of our measurements. If this were not so, and *different particles* underwent irreversible motions during the time between the first and subsequent echoes, then the subsequent echo heights would be lower than the first echoes. This is not what we observe. Thus, we conclude that some droplets always exhibit chaotic motion, while the others always exhibit purely periodic motion during oscillating shear flow of a fixed amplitude. Such a state might be realized, for example, if there were domains of chaotic droplets acting as boundary grains in polycrystals.

In Fig. 2(a), we show the measured echo height as a function of strain amplitude. These data were obtained using the backscattering geometry [6] for a sample thickness of 3.0 mm. For a given oil concentration, the echo height decreases monotonically with increasing strain amplitude. Thus, an increasing fraction of the oil droplets undergoes irreversible rearrangements as the strain amplitude is increased.

At some critical value of the strain, we expect that the emulsion yields. Thus, it is instructive to compare
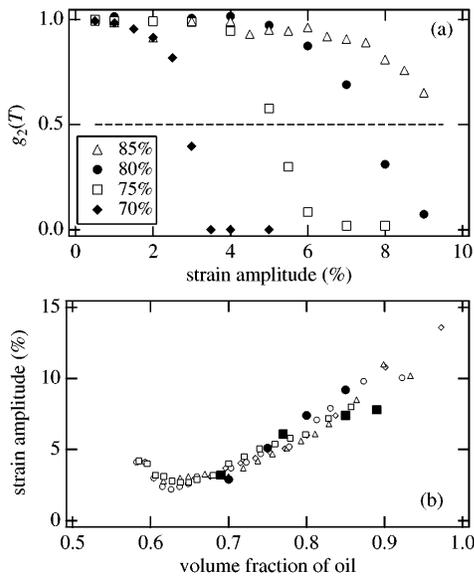
FIG. 2. (a) Echo height (normalized to $g_2(T)$ with no shear) obtained from backscattering measurements as a function of strain amplitude for samples with four different volume fractions of oil. The dashed line at $g_2(T) = 0.5$ is used to estimate the critical strains displayed in the lower plot. (b) Comparison of the critical strain obtained from the decay of echo heights (solid symbols) with the yield strains obtained by rheological measurements in Ref. [4] (smaller open symbols). The solid symbols are obtained from estimates of where the decay of the echo heights falls to 0.5. The solid circles are obtained from the data displayed above in (a); the solid squares in (b) are from data not displayed in (a) (for clarity).

mechanical measurements of the yield strain to the decrease in echo height with increasing strain amplitude. For this purpose, we plot in Fig. 2(b) the mechanical yield strain measured by Mason *et al.* [4] from the crossover between the linear elastic response and nonlinear behavior in oscillatory strain measurements. In the same figure, we also plot the strains at which the correlation functions displayed in Fig. 2(a) have decayed to half their initial value. From the data in Fig. 2(b), we see that the decrease in echo height with increasing strain scales approximately with the yield strain. While the criterion we use to estimate the yield strain is somewhat arbitrary, it lends support to our expectation that these measurements probe particle rearrangements that are associated with the yielding of the emulsion.

A more detailed analysis of our data allows us to gain insight and to determine quantitatively the volume fraction of the chaotic domains. To this end, we write down the general expression for the electric field correlation function for multiply scattered light [6]:

$$g_1(t) = \int_0^\infty P(s) e^{-x(t)s/l^*} ds, \qquad (1)$$

where l^* is the transport mean free path of the scattered light, $P(s)$ gives the optical path length distribution through the sample, and $x(t)$ is a function that depends on the motion of the scatterers. The integration of

Eq. (1) has been performed for both backscattering and transmission geometries [6]. For shear strain, $x(t) = [k_0 l^* \gamma(t)]^2/15$, where k_0 is the wave vector of the light and $\gamma(t)$ the time-dependent macroscopic strain [7]. For *oscillatory* shear strain, where $\gamma(t) = \gamma_0 \sin(\omega t)$, the strain is not stationary, and we must integrate the intensity correlation function over all the initial values of the strain. Thus, we substitute

$$x(t, t_0) = \frac{1}{15} [k_0 l^* |\gamma(t + t_0) - \gamma(t_0)|]^2 \qquad (2)$$

into Eq. (1) and integrate t_0 over one oscillation period to obtain the intensity autocorrelation function:

$$g_2(t) = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} |g_1[x(t, t_0)]| \, dt_0. \qquad (3)$$

Performing this integration numerically, we obtain the shapes of the decay of the correlation function and of the echoes. We have determined l^* (typically 100 μm) by measuring the transmitted intensity [6]. We have also determined l^* independently from our DWS measurements, as discussed below, and obtain consistent results.

For the transmission geometry, we find that the initial decay of $g_2(t)$ is completely insensitive to l^*, and depends only on the strain amplitude γ_0, as expected for shear flow [7]. This allows us to compare the expression for $g_2(t)$ calculated from Eq. (3) to the initial decay of our data without any adjustable parameters. The agreement between the data and Eq. (3) is excellent, as shown in Fig. 1(b). The excellent fit confirms our earlier assertion that there is no slip between the glass slides and the emulsions. It also confirms that on the time scale of the decay of $g_2(t)$, the flow is approximately affine. In backscattering, the initial decay of the correlation function depends on the value of l^* as well as γ_0. In this case, we obtain excellent fits to all the data when we use the single, strain-rate-independent value of l^* determined from the measurements of the transmitted intensity.

We can describe the full shape of the correlation functions, including the decrease in echo height, by taking into account three contributions: the oscillatory shear strain discussed above, the spontaneous decay in the absence of shear strain, and shear-induced rearrangements. The spontaneous decay in the absence of shear strain arises from thermal motion of the emulsion droplets and is significant only for $\phi_{\mathrm{oil}} \lesssim 0.7$ for our systems. In this case, the contribution to $x(t)$ is $k_0^2 \langle r^2(t) \rangle/3$ [6] where $\langle r^2(t) \rangle$ is mean square displacement of a droplet arising from Brownian motion and can be determined from the correlation function in the absence of shear. The contribution to the decay of the correlation function from shear-induced rearrangements leads to an absorption-like term. In this case, the probability for an optical path to scatter from a region that has suffered a shear-induced rearrangement is $\exp[-n\Phi(t)]$, where $\Phi(t)$ is the volume fraction of the sample that has rearranged after a time t and n the number of times the photon scatters in traversing the sample.

Since $n = s/l^*$, we see from Eq. (1) that rearrangements contribute to $x(t)$ by the addition of $\Phi(t)$. This result is exactly equivalent to the result derived previously by Durian *et al.* [8] in order to describe spontaneous rearrangements in foams driven by coarsening. The difference is that in this case, the rearrangements are driven by shear strain rather than occurring spontaneously. Thus, including all three contributions, the full expression for $x(t)$ is

$$x(t) = \frac{1}{3} k_0^2 \langle r^2(t) \rangle + \frac{1}{15} [k_0 l^* |\gamma(t + t_0) - \gamma(t_0)|]^2 + \Phi(t) .$$

Substituting this expression into Eq. (3), and using the fact that $\Phi(t)$ is constant over the width of an echo, we obtain excellent fits to both the initial decay and to all the echoes, as shown in Fig. 1(b). For $\phi_{oil} < 0.7$, we must take Brownian motion into account by including the effective diffusion coefficient D determined from equilibrium measurements. The only adjustable parameter, then, is $\Phi(t)$, which is varied to obtain a good fit to the echo height. The fact that the echo heights do not change after the first echo means that $\Phi(t)$ does not change after one strain period, confirming our earlier argument that the droplets that rearrange between the initial decay and the first echo are the only droplets that undergo rearrangements over the time scale of our measurements.

In Fig. 3, we plot the volume fraction Φ of the emulsion which rearranges versus strain amplitude γ_0. Data obtained in transmission and backscattering are plotted for oil volume fractions from 0.67 to 0.92. As expected, the softer emulsions, i.e., those with the smallest ϕ_{oil}, exhibit the most rearrangements with increasing strain amplitude. A more surprising feature of the data is that the volume fraction Φ that undergoes irreversible rearrangements seems to increase *linearly* with γ_0 for small γ_0 rather than quadratically. A quadratic dependence might be expected from the simple argument that the number of rearrangements should not depend on the sign of γ_0. It may be that a Φ does depend quadratically on γ_0, but only at strain amplitudes too small for us to resolve (i.e., $\gamma_0 \lesssim 0.01$). Alternatively, $\Phi(\gamma_0)$ may be nonanalytic at small γ_0. We also notice that for $\gamma_0 \lesssim 0.05$, the data obtained from backscattering measurements are higher than the data obtained from transmission measurements. Visual observations under a microscope rule out slippage at the wall. Thus, these data suggest that a greater fraction of the sample may be undergoing irreversible rearrangements *near* the wall than in the bulk.

By comparing the yield strain as a function of γ_0 by measured Mason *et al.* [4] to our determination of Φ shown in Fig. 3, we estimate that yielding occurs when
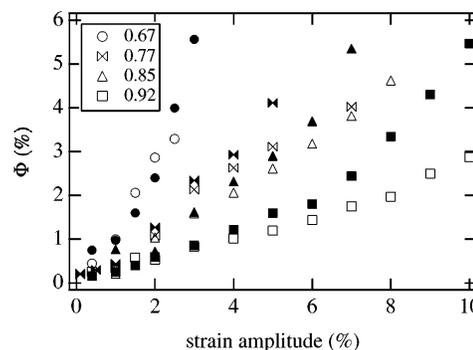
FIG. 3. Volume fraction Φ of emulsion which undergoes irreversible rearrangements as a function of strain amplitude for samples containing different volume fractions of oil droplets. The shear strain causes droplets to rearrange more readily as the volume fraction of droplets decreases. The open symbols were obtained from transmission data; the closed symbols were obtained from backscattering data.

$\Phi \sim 4\%$, i.e., when approximately 4% of the emulsion droplets have undergone irreversible rearrangements.

We note that rearrangements are observed down to $\gamma_0 \sim 0.01$, the smallest strain amplitudes for which we could measure an appreciable decrease in the echo heights in $g_2(t)$. Since there is no measurable decay of $g_2(t)$ in our experiments for $\phi_{oil} \gtrsim 0.7$, this means that the number of rearrangements caused by shearing is greater than those resulting from thermal fluctuations when $\gamma_0 \gtrsim 0.01$. This is consistent with a simple estimate of the critical strain γ_c, which equates the mechanical energy for such a strain to the thermal energy, i.e., $G\gamma_c^2 a^3 \simeq k_B T$, where G is the elastic shear modulus and a is the radius of a droplet. Realistic values of G [9] give $\gamma_c \sim 10^{-3}$–10^{-4}.

We thank Dave Weitz for supplying the yield strain data reported by Mason *et al.* in Ref. [4].

[1] D. A. Weitz, W. D. Dozier, and P. M. Chaikin, J. Phys. Colloq. (France) **46**, 257 (1985).

[2] L. B. Chen *et al.,* Phys. Rev. Lett. **69**, 688 (1992).

[3] L. B. Chen, B. J. Ackerson, and C. F. Zukoski, J. Rheol. **38**, 193 (1994).

[4] T. G. Mason, J. Bibette, and D. A. Weitz, J. Colloid Interface Sci. **179**, 439 (1996).

[5] W. van Megen and P. N. Pusey, Phys. Rev. A **43**, 5429 (1991).

[6] D. A. Weitz and D. J. Pine, in *Dynamic Light Scattering: The Method and Some Applications* (Oxford University Press, Oxford, 1993), pp. 652–720.

[7] X.-l. Wu *et al.,* J. Opt. Soc. B **7**, 15 (1990).

[8] D. J. Durian, D. A. Weitz, and D. J. Pine, Science **252**, 686 (1991).

[9] T. G. Mason, J. Bibette, and D. A. Weitz, Phys. Rev. Lett. **75**, 2051 (1995).