Emulsification in Viscoelastic Media

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We have created stable monodisperse emulsions by shearing and rupturing crude polydisperse emulsions of larger droplets into smaller droplets having a unique size. To eliminate inhomogeneous fracture flow which can lead to nonuniform rupturing and broad polydispersity, we use a shearing geometry with a narrow gap. We can control the final droplet size by altering the shearing conditions and the emulsion's viscoelasticity which depends on its composition. We argue that the high degree of monodispersity, indicated by Bragg scattering from colloidal crystals of droplets, may result from a capillary instability that includes the role of the emulsion's viscoelasticity. [S0031-9007(96)01203-3]

Emulsification is the process of dispersing one immiscible fluid in another by rupturing large droplets into smaller ones using a shear flow. The shear flow must be sufficiently large to overcome the interfacial tension σ between the fluids to deform and break the droplets. The ruptured droplets can be prevented from recombining by coalescence through the use of surfactants which provide a strong short-ranged interfacial repulsion [1]. This barrier against coalescence permits the emulsion to persist long after the shear has been stopped and gives rise to many important products such as foods, cosmetics, and paints [2]. Many commercial recipes are used to make emulsions; these vary in composition, in the way the two fluids are introduced into the shear, and the nature of the shear itself. However, all lead to polydisperse emulsions containing a broad distribution of droplet radii, although the average droplet radius can sometimes be adjusted empirically [3].

Despite the widespread use of emulsification, the fundamental understanding is essentially limited to the rupturing of a single droplet of viscosity, η_i, suspended in a fluid having viscosity η_e at low Reynold's numbers [4]. For droplet deformation to occur, the viscous stress of the external phase, $\eta_e \dot{\gamma}$, must overcome the characteristic Laplace pressure σ/a, where a is the droplet's radius, neglecting the role of η_i [5]. For rupturing to occur, the capillary number, Ca $= \eta_e \dot{\gamma} a/\sigma$, defined as the ratio of the shear stress to the Laplace pressure, must exceed a critical value of order unity; this implies the droplet has been elongated by the viscous shear before rupturing. Such elongated droplets can resemble liquid cylinders that are susceptible to a capillary instability in which the surface tension drives the rupturing of the cylinder into spheres having less total surface area [6]. Depending on the conditions, a droplet may be ruptured into two droplets of almost equal volume [7], or it may be stretched into a "liquid thread" that breaks into a chain of many droplets [8,9]. A complete theoretical description of the droplet deformation and bursting between these two regimes is complicated and depends on the capillary number, the viscosity ratio $\lambda = \eta_i/\eta_e$, and the type and history of the shear flow [4].

By contrast to the rupturing of isolated droplets in a viscous fluid, emulsification involves the rupturing of many droplets in a medium which may both partially store and partially dissipate shear energy, and, thus, may be effectively viscoelastic. This viscoelasticity may arise from the continuous phase itself, which can be a complex fluid (e.g., a surfactant or polymeric solution), or it may arise from the packing and deformation of the droplets found in compressed emulsions [10,11]. In this Letter, we show that emulsification using a highly controlled shear in viscoelastic media can lead to droplet rupturing down to a unique size. This monodispersity is a direct consequence of the rupturing, and does not result from droplet recombination. Moreover, because the droplets have one unique size, we are able to study how the droplet radius depends on the viscoelasticity and the shear.

The essence of our discovery is embodied in the following experiment. We make a crude emulsion with a fixed composition by gently shear mixing oil into an aqueous surfactant solution, drop by drop, until the final desired volume fraction ϕ is obtained. The resulting polydisperse premixed emulsion of large droplets is shown in Fig. 1(a). This emulsion consists of silicone oil droplets ($\eta_i = 350$ cP) at $\phi = 0.7$ dispersed in an 60:40 mass ratio water-surfactant mixture; the surfactant we use is nonionic Tergitol NP7 (nonyl phenol ethoxy 7). We have verified that this surfactant-water mixture is a concentrated micellar phase (L_1). We place the crude emulsion between two glass slides separated by Teflon spacers which fix the gap at 10 μm and oscillate one slide relative to the other back and forth over a distance of about 1 cm in a period of about 1 s, thereby producing a spatially uniform simple shear. A single oscillation suffices to transform the polydisperse premixed emulsion of large droplets shown in Fig. 1(a) into the monodisperse emulsion of smaller droplets of radius $a \approx 2$ μm shown in Fig. 1(b). In Fig. 1(b)-inset, we show the small angle laser light scattering pattern from the same sample; the presence of a ring with six Bragg spots reveals that the monodispersity is good enough to allow some degree of long range order created by shear induced
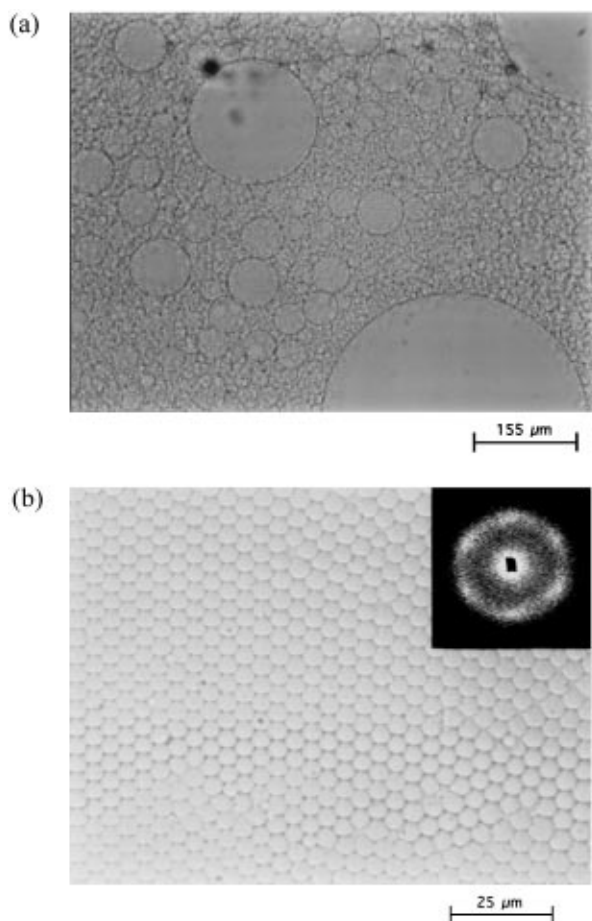
(a)

155 μm

(b)

25 μm

FIG. 1. Microscope images of the transformation of a crude polydisperse premixed emulsion (a) into a monodisperse emulsion of smaller droplets (b) through shear rupturing. The corresponding small angle light scattering pattern for the monodisperse emulsion (inset) is a diffuse ring with six bright spots.

ordering of the droplets. If we increase the amplitude or reduce the period, the droplet diameter can be decreased in a nearly continuous way down to about $a \approx 0.1$ μm.

To determine the origin of this phenomenon with precision, we investigate the roles of the peak oscillatory shear amplitude γ and frequency ω on the final droplet radius. We use a controlled-strain mechanical rheometer equipped with a parallel plate geometry having a radius $R = 2.5$ cm. The premixed emulsion is placed on the circular base plate and the upper plate is lowered until the gap spacing between the two plates reaches $d = 200$ μm; this gap spacing ensures a homogeneous shear deformation of the emulsion along the direction normal to the plate surface. The shear amplitude increases linearly with the radius r from the center of the plate and the angular displacement θ of the motor: $\gamma(r, \theta) = r\theta/d$. After shearing with a fixed peak angular amplitude, we measure the droplet radius by gently separating the two plates, placing a slide in contact with the exposed emulsion, and microscopically viewing the slide. Since the droplet volume fraction is near close packing, it is simple to determine the droplet radius

by counting the number of droplets over a given distance. By marking where the center of the two plates is on the slide's surface, $a(\gamma)$ can be found by simply translating the slide relative to this point and viewing microscopically. We have used one hundred cycles to ensure complete rupturing for the smallest strains; the final radii do not change for a greater number of cycles. Figure 2 shows the amplitude dependence of the droplet radius for three fixed frequencies, $\omega = 1$, 10, and 100 rad/s; the solid symbols represent the unique radius of a monodisperse emulsion, while the open symbols represent the average radius of a polydisperse emulsion. For small deformations below a threshold $\gamma_c \approx 6$, as shown by the vertical dashed line on the plot, the resulting emulsion is not monodisperse, regardless of ω. At deformations immediately above γ_c, it is possible to obtain monodisperse emulsions for fast oscillations $\omega \geq 10$ rad/s. By contrast, for $\omega \ll 1$ rad/s, we cannot obtain monodisperse emulsions even at the largest accessible γ. For a fixed frequency, the radius decreases and becomes nearly independent of the strain amplitude at large γ. For a fixed strain amplitude, the radius becomes smaller for larger frequencies. These results support the idea that the maximum shear rate, $\dot{\gamma} = \omega\gamma$, sets the radius, provided γ exceeds the critical value for rupturing.

To test this idea, we explore how the final droplet radius of the emulsion depends on its viscoelasticity and $\dot{\gamma}$ for steady shearing conditions. We have measured the effective viscosity of the premixed emulsion as a function of shear rate, as shown by the points in the inset of Fig. 3. The emulsion is shear thinning, exhibiting a smaller effective viscosity at higher shear rates following an empirical power law behavior of $\eta_{\text{eff}} \sim 210\dot{\gamma}^{-1/2}$ P, shown by the solid line in the inset, up to a maximum shear rate of $\dot{\gamma} = 10^2$ s^{-1}, limited by the maximum torque of the rheometer's transducer. This effective viscosity is more than 10 times larger than the viscosity of the continuous phase alone, reflecting the influence of ϕ. We apply larger shear rates to induce
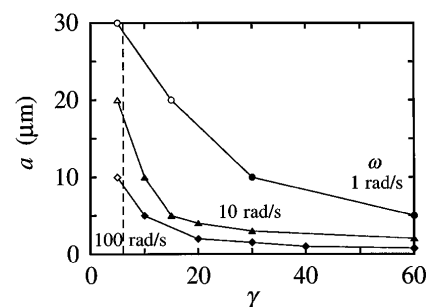

FIG. 2. The dependence of the droplet radius, a, on the strain amplitude γ for the fixed frequencies of $\omega = 1$ rad/s (circles), 10 rad/s (triangles), 100 rad/s (diamonds). The open symbols represent average radii of polydisperse emulsions, while the solid symbols represent unique monodisperse radii. To the left of the vertical dashed line, the emulsion is polydisperse.

droplet rupturing and measure the radius as a function of $\dot{\gamma}$, as shown by the points in Fig. 3. Above $\dot{\gamma} \approx 10^2$ s^{-1}, the radius drops sharply and saturates at higher $\dot{\gamma}$.

This saturation suggests that the emulsion's effective viscosity is involved in setting the average droplet size [3] and that its shear-thinning nature may enhance the monodispersity. To estimate the final droplet radius, we compare the Laplace pressure of the ruptured droplets with the effective viscous stress, $\eta_{\text{eff}}\dot{\gamma}$, yielding the scaling law

$$a = C\sigma/\eta_{\text{eff}}\dot{\gamma}, \qquad (1)$$

where C is a geometrical constant of order unity. The interfacial tension, $\sigma = 2$ dyn/cm, has been measured using a pendant drop technique. To compare the scaling form with our data, we extrapolate the measured viscous stress to higher $\dot{\gamma}$ where droplet rupturing occurs; this assumes that the reduction of the droplet size does not significantly increase η_{eff}. We obtain excellent agreement between the measured and predicted droplets sizes by adjusting $C = 0.45$, supporting the assumption that the emulsion can be treated as an effective medium with a macroscopic shear-thinning viscosity that governs the rupturing.

Since the effective viscosity can be strongly modified by the volume fraction, we have measured $a(\phi)$ using the same continuous phase composition and fixing $\dot{\gamma} = 10^3$ s^{-1}, as shown in Fig. 4. Near and above random close packing (RCP) of monodisperse spheres, $\phi_{\text{RCP}} \approx 0.63$, the droplet radius decreases, qualitatively consistent with the increase of the effective viscoelasticity due to droplet deformation [10,11]. Below ϕ_{RCP}, η_{eff} is set primarily by the continuous phase itself, resulting in the ϕ-independent radius.

The scaling argument which we considered in Eq. (1) neglects the role of the internal droplet viscosity, which may also affect the droplet radius. In Fig. 4-inset, we present $a(\eta_i)$ for fixed $\phi = 0.7$, $\dot{\gamma} = 10^3$ s^{-1}, and continuous phase composition. We use silicone oils in all cases. We speculate that the increase in droplet radius at higher η_i may occur when the internal phase viscos-

ity becomes greater than the emulsion's effective viscosity at the strain rate used for rupturing. To make this comparison, we assume that η_{eff} is independent of the internal viscosity. We determine the effective viscosity by extrapolating $\eta_{\text{eff}}(\dot{\gamma})$ shown for $\eta_i = 350$ cP in Fig. 3 to $\dot{\gamma} = 10^3$ s^{-1}, where we find $\eta_{\text{eff}} \approx 500$ cP. For $\eta_i > \eta_{\text{eff}}$ at this strain rate, we find an increase in the droplet radius by a factor of 4 over two decades in η_i. For one decade below $\eta_i = \eta_{\text{eff}}$ at his strain rate, we find the droplet size is constant. These results are consistent with $a(\eta_i)$ for isolated droplets ruptured in a purely viscous fluid [12].

One might imagine a scenario in which a monodisperse droplet size could be obtained by a kinetic equilibrium between droplet growth and rupturing under shear. The growth may be due to coalescence reminiscent of nucleation in a binary liquid mixture under shear [13]. By shearing a premixed emulsion composed of two different viscosity oil drops, we have obtained a binary alloy of droplets having two discrete radii. If coalescence had been present, then only one droplet size would have been found, corresponding to the average viscosity if the two oils had been mixed together before making the premixed emulsion. However, we find two discrete droplet sizes, supporting the absence of coalescence and the conclusion that the monodispersity can be obtained by droplet rupturing alone.

For an emulsion possessing a yield stress, τ_y, and an effective viscosity that is perfectly shear thinning with $\eta_{\text{eff}} = \tau_y/\dot{\gamma}$, the scaling form in Eq. (1) predicts a single droplet size independent of the shear rate, $a \sim \sigma/\tau_y$. Thus, it may be possible to produce monodisperse emulsions even in conditions of relatively inhomogeneous shear where $\dot{\gamma}$ varies spatially in the mixer. We have observed this limit by using a continuous phase (a hexagonal phase of sodium dodecyl sulfate at 40% by mass in water) possessing a strong yield stress, $\tau_y \approx 5 \times 10^5$ dyn/cm^2 and interfacial tension $\sigma \approx 10$ dyn/cm. The premixed emulsion at low ϕ contains oil droplets which very eas-
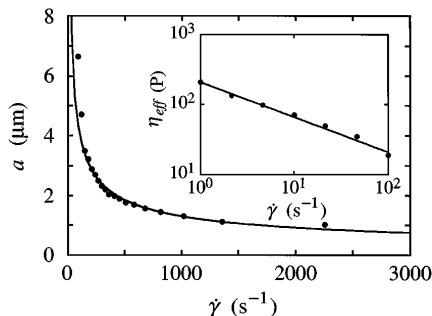

FIG. 3. The dependence of the droplet radius, a, on the steady shear rate $\dot{\gamma}$ (points). The solid line is a fit using the scaling form, Eq. (1), using the measured $\dot{\gamma}$ dependence of the effective viscosity η_{eff}, shown by the points in the inset. The solid line in the inset is an empirical power law, $\eta_{\text{eff}} \sim 210\dot{\gamma}^{-1/2}$ P, which is extrapolated to higher $\dot{\gamma}$ for use in the scaling form.
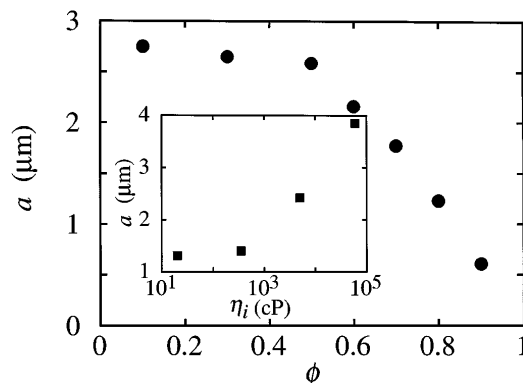

FIG. 4. The ϕ dependence of the droplet radius, a, for $\dot{\gamma} = 10^3$ s^{-1}, keeping the continuous phase composition fixed. Inset: The dependence of the droplet radius, a, on the internal phase oil viscosity η_i, fixing the continuous phase composition, $\dot{\gamma} = 10^3$ s^{-1}, and $\phi = 0.7$.

ily form highly elongated liquid threads under shear. These threads ultimately break into hundreds of tiny monodisperse droplets when the thread's radius becomes sufficiently small so that the Laplace pressure roughly exceeds the yield stress, inducing a capillarylike instability that has a characteristic wavelength of approximately σ/τ_y. Our microscopic observations of chains of adjacent droplets with $a \approx \sigma/\tau_y \approx 0.2$ μm after shearing confirm that this one-to-many droplet rupturing mechanism may likewise yield monodisperse emulsions.

To avoid fracturing [11], which can lead to nonuniform rupturing and increased polydispersity, the gap must be kept very thin. To estimate the maximum gap thickness which ensures homogeneous flow, we compare it to the thickness of the fracture plane l for an ideal yield stress (plastic) material sheared between two plates which move at a relative velocity v. The ideal plastic resists flow elastically until the applied stress exceeds τ_y, and it flows with a simple viscosity η_p, within the fracture plane. Outside the fracture plane, the strain rate is zero, while inside the fracture plane, it is really $\dot{\gamma} = v/l$, much larger than the apparent applied strain rate. At either edge of the fracture plane, the viscous stress $\eta_p \dot{\gamma}$ of the flowing material must balance the limiting elastic stress of the unyielded material τ_y. Solving for l, we find $l = \eta_p v/\tau_y$. For concentrated emulsions, we assume $\tau_y \approx \sigma/a$, and we take η_p to be the continuous phase viscosity $\eta_p \approx \eta_c$. This ignores the ϕ dependence of η_p for $l \gg a$ and underestimates η_p. Substituting, we find $l \sim \eta_c v/(\sigma/a)$; it is proportional to viscosity and inversely proportional to the Laplace pressure. For a concentrated emulsion with little surfactant, $a = 1$ μm, $\sigma = 10$ dyn/cm, $v = 10$ cm/s, and $\eta_c \approx 10^{-2}$ P, so the fracture plane is $l \approx 10^{-6}$ cm, much smaller than the droplets themselves. This implies that a thin lubricating film of water can separate one plane of packed droplets as it slips by another plane. This prediction supports our observations of rupturing to polydisperse emulsions at low NP7 concentrations even when the emulsion is highly concentrated and has a yield stress. However, for a concentrated surfactant solution having $\eta_c \approx 10^2$ P, the thickness increases to $l \approx 10^{-2}$ cm, much larger than the droplet size. This distance is sufficiently large that we can make the gap less than l, thereby forcing a homogeneous flow so that all droplets can be ruptured at the same $\dot{\gamma}$. This condition is exactly that under which we have observed monodispersity.

The monodispersity can degrade for several reasons. For $\phi > 0.95$, we have observed a sparse population of isolated large droplets in a sea of smaller monodisperse droplets after shearing, indicating that the shear may induce film rupturing and coalescence between highly deformed droplets. Greater polydispersity is also found when the premixed emulsion contains droplets smaller than the desired size before the controlled shear is applied; these small droplets contaminate the final emulsion.

We have demonstrated that monodisperse emulsions may be made solely through shear-induced fragmentation. The $\dot{\gamma}$ dependence of a can be predicted using the measured η_{eff}, according to Eq. (1). We speculate that the monodispersity can result from the suppression of the capillary instability until the droplet is sufficiently elongated so that its Laplace pressure overcomes the material's elasticity, thereby allowing the material to flow and the rupturing to occur.

The direct production of monodisperse emulsions through droplet rupturing in viscoelastic media represents a new and well-controlled way of making colloidal fluid dispersions. It's applicability to a broad range of fluids makes it a good candidate for commercial emulsion production [14].

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