

Anomalous Viscous Loss in Emulsions

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We propose a model for concentrated emulsions based on the speculation that a macroscopic shear strain does not produce an affine deformation in the randomly close-packed droplet structure. The model yields an anomalous contribution to the complex dynamic shear modulus that varies as the square root of frequency. We test this prediction using a novel light scattering technique to measure the dynamic shear modulus, and directly observe the predicted behavior over six decades of frequency and a wide range of volume fractions.

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An emulsion is a dispersion of liquid droplets suspended in a second, immiscible liquid that contains a surfactant to stabilize the interfaces. Because they are deformable, droplets can be packed to very high volume fractions while still retaining integrity. These concentrated emulsions are remarkable because they are highly elastic, even though they are made up entirely of liquids [1,2]. They also possess viscous properties; this makes them viscoelastic. Such materials are often characterized by their complex dynamic shear modulus, $G^*(\omega) = G'(\omega) + iG''(\omega)$, where $G'(\omega)$ is the elastic or storage modulus and $G''(\omega)$ is the viscous or loss modulus. These moduli reflect the in-phase and out-of-phase responses to a small oscillatory shear at frequency ω . For concentrated emulsions, $G'(\omega)$ is large compared to $G''(\omega)$ at low frequencies, reflecting their elastic nature. However, $G'(\omega)$ is anomalously low compared to any reasonable expectation based on the droplet deformations [2]. By contrast, $G''(\omega)$ is anomalously large compared to any reasonable expectation based on the fluid viscosities [3]. While most work to date has focused on the storage modulus [1,2,4–7], the behavior of the loss modulus is equally important and interesting, and many dissipative mechanisms have recently been considered [3].

Here we suggest an alternate mechanism that may describe the origin of the puzzling behavior of the loss modulus. We speculate that a macroscopically applied shear strain does not produce an affine deformation because the droplets are randomly packed. Instead, some regions slip instead of deforming. This increases the viscous dissipation and decreases the elasticity. In this Letter, we focus on those regions that slip, and present a simple model to account for the anomalous behavior of the loss modulus. We show that, if the directions of the local planes of easy slip are randomly oriented, there is a contribution that varies as $\omega^{1/2}$. This contribution can dominate the usual viscous contribution proportional to ω (which controls the very high frequency behavior) as well as the constant elastic contribution

(which controls the very low frequency behavior). We test this prediction by exploiting a new light scattering technique [8] that enables us to measure the moduli of concentrated emulsions over the required extended frequency range. We directly observe the predicted $\omega^{1/2}$ contribution over several decades of frequency for a wide range of volume fractions.

The central assumption of our model is that slip can occur in a local region, but only parallel to a certain plane. One physical realization of this weak plane is two well-aligned layers of droplets that can slip relative to each other. However, more complex realizations are also possible because the droplets can shift their positions. The essential requirement is that there is no linear restoring force, and therefore no local static shear modulus, for strains of the entire region where the displacement gradient is normal to the local weak plane. Because the droplet packing is disordered, the orientations of these weak planes vary randomly throughout the sample. Thus the material has randomly anisotropic shear moduli. This randomness leads to a broad range of stress relaxation rates, which yields the predicted power-law behavior of the macroscopic dynamic shear modulus.

To calculate the dynamic shear modulus, we construct the elastic free energy of a local region with a weak plane. We assume that the system is incompressible. We define a local Cartesian coordinate system $\{abc\}$ and take the local weak plane to be normal to the c axis. We assume that the region is isotropic in the a - b plane and has $c \rightarrow -c$ reflection symmetry; however, this degree of symmetry is not crucial. The elastic free energy of a region centered at \vec{r} can then be written as [9]

$$F = \frac{1}{2} \lambda_1(\vec{r}) u_{cc}^2 + \lambda_2(\vec{r}) [(u_{aa} - u_{bb})^2 + 4u_{ab}^2] - \lambda_3(\vec{r}) u_{aa} u_{bb} + \lambda_4(\vec{r}) (u_{ac}^2 + u_{bc}^2), \quad (1)$$

where u_{ij} is the symmetric strain tensor [9]. The first term represents the energy cost of uniaxial compressions

and must always be positive. The second and third terms represent costs of deformations within the a - b plane. Since the a - b plane is the weak plane, there is no energy cost for a shear gradient in the c direction, and the coefficient $\lambda_4(\vec{r})$ must vanish. To calculate the macroscopic mechanical response, we must average over the orientational variation in space of the $\{abc\}$ coordinate system with respect to the Cartesian coordinates in the lab frame, $\{xyz\}$. This is analogous to the problem of randomly oriented smectics, for which the free energy is given by Eq. (1) with $\lambda_2(\vec{r}) = \lambda_3(\vec{r}) = \lambda_4(\vec{r}) = 0$, and with \hat{c} varying randomly in space [10,11]. Model (1) with $\lambda_4(\vec{r}) = 0$ has also been used to describe anisotropic glasses [12] and “decoupled” lamellar phases of tethered membranes [13]. Note that it is ill behaved when $\lambda_4(\vec{r}) = 0$; in the lamellar case, there are higher order gradient terms in the elastic free energy, namely, bending elastic terms, that stabilize the free energy. In the case of emulsions, however, it is unclear whether the appropriate stabilizing term is of the form of a bending energy. Fortunately, the bending modulus does not affect the dynamic shear modulus at frequencies above a low frequency cutoff, ω_{\min} [10]. We may therefore neglect the bending modulus for frequencies above ω_{\min} , which is found experimentally to be about 10 Hz for emulsions.

To obtain the macroscopic dynamic shear modulus, we must average the stress-stress correlation function $S(\vec{r}, t) = \langle \sigma_{xy}(\vec{r}, t) \sigma_{xy}(0, 0) \rangle$ over all \vec{r} . Thus $G^*(\omega)$ depends on the spatial Fourier transform of the stress-stress correlation function at zero wave vector,

$$\tilde{S}(k = 0, t) \equiv \langle \tilde{\sigma}_{xy}(k = 0, t) \tilde{\sigma}_{xy}(k = 0, 0) \rangle. \quad (2)$$

Here, tildes refer to spatial Fourier transforms, and $\sigma_{xy}(\vec{r}, t)$ is the xy component of the stress at position \vec{r} and time t . The brackets correspond to both thermal and disorder averages [10]. We use the fluctuation-dissipation theorem to obtain the dynamic shear modulus,

$$G^*(\omega) = i\omega\eta(\omega) = \frac{i\omega}{k_B T} \int_0^\infty dt e^{-i\omega t} \tilde{S}(k = 0, t). \quad (2)$$

The stress is the derivative of the free energy with respect to the strain, calculated in the laboratory coordinates $\{xyz\}$:

$$\begin{aligned} \sigma_{xy}(\vec{r}, t) = & a_x(\vec{r})a_y(\vec{r}) \frac{\delta F}{\delta u_{aa}(\vec{r}, t)} + b_x(\vec{r})b_y(\vec{r}) \frac{\delta F}{\delta u_{bb}(\vec{r}, t)} \\ & + c_x(\vec{r})c_y(\vec{r}) \frac{\delta F}{\delta u_{cc}(\vec{r}, t)} \\ & + \frac{1}{2} [a_x(\vec{r})b_y(\vec{r}) + a_y(\vec{r})b_x(\vec{r})] \frac{\delta F}{\delta u_{ab}(\vec{r}, t)}, \end{aligned} \quad (4)$$

where $a_i(\vec{r})$, $b_i(\vec{r})$, and $c_i(\vec{r})$ are the components of the local Cartesian coordinates $\{abc\}$. Using Eq. (4) in Eq. (2), we can express the stress-stress correlation function $S(\vec{r}, t)$ in terms of a sum over products of disorder averages of the form $\langle a_x(\vec{r})a_y(\vec{r})a_x(0)a_y(0) \rangle$ and strain-strain correla-

tion functions of the form $\langle u_{aa}(\vec{r}, t)u_{aa}(0, 0) \rangle$ [10]. The essential approximation in this step is the breaking of averages over the coordinate axes $\{abc\}$ and strain variables u_{ij} . The strain-strain correlation functions are difficult to compute because \hat{a} , \hat{b} , and \hat{c} also vary with r . We avoid this difficulty by assuming that the dominant contribution comes from regions over which the coordinate system $\{abc\}$ is highly correlated [10]. Therefore the response of a given correlated region to shear is calculated as if the region were infinite in extent, and individual regions are assumed to be uncorrelated from each other. This approximation is clarified by an alternate approach which considers the zero-temperature response of the system to an externally applied strain [11]. The desired quantity $\tilde{S}(k = 0, t)$ can therefore be expressed as a sum of integrals over wave vector \vec{q} of products of disorder averages of the form $\langle \tilde{a}_x(\vec{q})\tilde{a}_y(\vec{q})\tilde{a}_x(-\vec{q})\tilde{a}_y(-\vec{q}) \rangle$ and strain-strain correlation functions of the form $\langle \tilde{u}_{aa}(\vec{q}, t)\tilde{u}_{aa}(-\vec{q}, 0) \rangle$ [10]. To evaluate the disorder averages, we assume that the coordinate axes $\{abc\}$ are correlated only over a characteristic distance ξ , the size of the local region of slip:

$$\langle \tilde{a}_x(\vec{q})\tilde{a}_y(\vec{q})\tilde{a}_x(-\vec{q})\tilde{a}_y(-\vec{q}) \rangle = f(q^2\xi^2). \quad (5)$$

Since the local axes are uncorrelated with each other, correlation functions of the form $\langle \tilde{a}_x(\vec{q})\tilde{a}_y(\vec{q})\tilde{b}_x(-\vec{q})\tilde{b}_y(-\vec{q}) \rangle$ vanish. Finally, the strain is a derivative of the displacement, so the strain-strain correlation functions can be written in terms of displacement correlation functions: $\langle \tilde{u}_{aa}(\vec{q}, t)\tilde{u}_{aa}(-\vec{q}, 0) \rangle = q_a^2 \langle \tilde{u}_a(\vec{q}, t)\tilde{u}_a(-\vec{q}, 0) \rangle$, where $q_a = \vec{q} \cdot \hat{a}$. The displacement correlations are calculated from the Langevin equation for $\tilde{u}(\vec{q}, t)$, which includes contributions from both elastic and viscous forces [10]. The Langevin equation yields overdamped modes for frequencies low compared to $\omega_0 = \eta/\rho(2\pi/\xi)^2 \approx 10^6$ Hz, where $\rho \approx 1$ g/cm³ is the mass density, $\eta \approx 1$ cp is the film viscosity, and $\xi \approx 3$ μ m, several droplet diameters, is the estimated size of a local slip region. There are only two modes due to incompressibility. Thus

$$\begin{aligned} \tilde{S}(k = 0, t) = & \int d\varphi d \cos(\theta) \\ & \times [f_1(\theta, \varphi) e^{-\Gamma_1(\theta, \varphi)t} + f_2(\theta, \varphi) e^{-\Gamma_2(\theta, \varphi)t}], \end{aligned} \quad (6)$$

where $\Gamma_i(\theta, \varphi)$ are the relaxation rates for the two modes with wave vector q oriented at Eulerian angles θ and φ relative to the local coordinates $\{abc\}$. The functions $f_i(\theta, \varphi)$ depend on integrals over the magnitude $q = |\vec{q}|$ of $f(q^2\xi^2)$ defined in Eq. (5). Since the low frequency behavior of $G^*(\omega)$ is controlled by the long time behavior of $\tilde{S}(k = 0, t)$, we need only consider the long time limit of Eq. (6). By low frequencies, we mean $\omega \ll \omega_c \equiv \sigma/\eta a$, where the high frequency cutoff $\omega_c \approx 10^7$ Hz is a characteristic relaxation frequency, given by the ratio of an elastic constant to the viscosity. For an emulsion, the elastic constants are of order σ/a , where σ is the surface tension and a is the droplet radius. Because there is a

weak plane, one of the relaxation rates, Γ_1 , vanishes for $\theta = \pi/2$, while the other always remains of order ω_c . Therefore values of θ near $\pi/2$ dominate the integral in Eq. (6) at long times, and we may neglect the second term in the integrand. Physically, the regions with weak planes nearly parallel to the direction $\hat{q} = \vec{q}/q$ of the shear gradient exhibit the most solidlike response and therefore have the slowest stress relaxation rates Γ_1 . We find that Γ_1 depends on the projection $\hat{q}_c = \hat{q} \cdot \hat{c} \equiv \cos\theta \approx \pi/2 - \theta$. By symmetry, Γ_1 cannot depend on the sign of \hat{q}_c . Thus we find that at long times the integral is of the form $\tilde{S}(k=0, t) \sim \int dx e^{-x^2 t}$, where $x = \pi/2 - \theta$. This Gaussian integral yields $\tilde{S}(k=0, t) \sim t^{-1/2}$, and hence our main result $G^*(\omega) \sim (i\omega/\omega_c)^{1/2}$.

To test this prediction, we must measure the dynamic shear modulus over a wide frequency range, extending to frequencies higher than those accessible to traditional mechanical rheometers. We use a recently developed light scattering technique [8] that relies on the fluctuation-dissipation theorem, much in the spirit of our calculation. We measure the motion of a particle due to thermal fluctuations, as parametrized by the mean square displacement, $\langle \Delta r^2(t) \rangle$. In a viscoelastic material, this motion reflects both viscous loss and energy storage in the medium. The modulus is obtained by generalizing the Stokes-Einstein relation to finite frequencies,

$$\overline{G}(s) = s\overline{\eta}(s) = \frac{k_B T}{\pi a s \langle \Delta \overline{r}^2(s) \rangle}. \quad (7)$$

Here, it is most convenient to work with the Laplace frequency, s , with bars representing Laplace-transformed quantities. The modulus $\overline{G}(s)$ is related to $G^*(\omega)$ through the analytic continuation $s = i\omega$ [8]. This relation provides physical intuition about the meaning of $\overline{G}(s)$: Nearly frequency-independent behavior reflects a large elastic contribution since $G'(\omega)$ dominates; linear behavior in s reflects a large viscous contribution since $G''(\omega)$ dominates. An intermediate frequency dependence reflects contributions to both components.

We use monodisperse emulsions [14] so that the droplets themselves can be used as the probes [8]. Our emulsion is comprised of $1 \mu\text{m}$ diameter silicone oil droplets in water, stabilized by sodium dodecylsulphate at a concentration of 10mM . The emulsion is concentrated by centrifugation, and the volume fraction is determined by weighing, before and after evaporating, the continuous water phase. We measure $\langle \Delta r^2(t) \rangle$ with diffusing-wave spectroscopy (DWS) in the transmission geometry [15,16]. The interpretation assumes that the scattered intensity can be determined from the product of a form factor and structure factor. Independent scattering measurements [17] of monodisperse emulsions, whose continuous phase has been adjusted by adding glycerol to index-match the oil phase, show that this factorization is valid even at the high volume fractions studied here.

To determine the modulus of the emulsion, we numerically calculate the Laplace transform of $\langle \Delta r^2(t) \rangle$ from our

DWS measurements, and use Eq. (7). Typical results are shown by the open symbols in Fig. 1(a) for an emulsion with $\phi = 0.67$. The data extend over seven decades to very high frequencies, illustrating the utility of this technique. They also exhibit the expected behavior; at low frequencies, they are nearly independent of s , reflecting the dominant elastic behavior of a compressed emulsion; at high frequencies, they approach a linear dependence on s , reflecting the dominant viscous behavior of a system comprised solely of fluids. To determine the frequency dependence in the intermediate regime, we subtract from the data a constant, reflecting the low frequency elasticity, and a term proportional to s , reflecting the high frequency viscous loss. The sum of these terms, adjusted to match the asymptotic limits of the data, is shown by the dashed line in Fig. 1(a). The resulting difference, $\Delta\overline{G}(s)$, is shown as the solid symbols in Fig. 1(a). Its frequency dependence is $s^{1/2}$, as shown by the solid line through the data. This reflects a contribution to the modulus beyond the purely elastic and purely viscous components. Similar $s^{1/2}$ contributions are observed for higher volume fractions [see Fig. 1(b)]. The $s^{1/2}$ contribution results in an $(i\omega)^{1/2}$ contribution to $G^*(\omega)$, providing direct experimental support for our proposed model.

To quantify the dependence of the $s^{1/2}$ contribution on volume fraction, we fit the data by

$$\overline{G}(s) = G_p + A(\phi)s^{1/2} + \eta_\infty s, \quad (8)$$

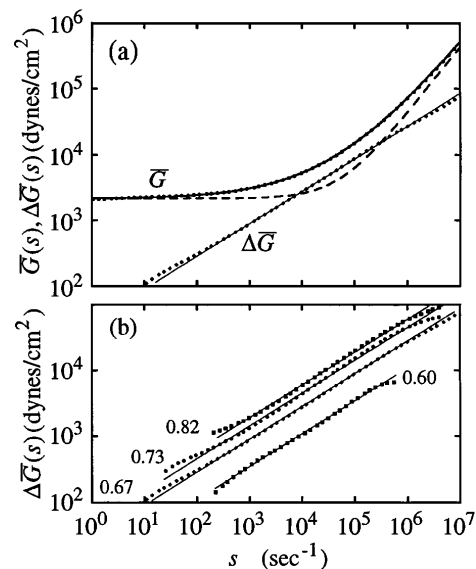


FIG. 1. (a) The upper set of symbols shows the light scattering measurements of the dynamic shear modulus $\overline{G}(s)$ as a function of the Laplace frequency s for an emulsion with $a = 0.5 \mu\text{m}$ and $\phi \approx 0.67$. The dashed line represents the asymptotic contributions of an elastic component at low frequencies and a viscous component at high frequencies. The difference, $\Delta\overline{G}(s)$, shown by the lower set of solid points, represents the additional contribution to the modulus, and exhibits an $s^{1/2}$ frequency dependence, as shown by the solid line. (b) The $s^{1/2}$ contribution, $\Delta\overline{G}(s)$, for the same emulsion at several volume fractions.

where η_∞ is the high frequency viscosity and $A(\phi)$ the magnitude of the $s^{1/2}$ term. As shown in Fig. 2, $A(\phi)$ increases by a factor of 4 to 5 as ϕ increases above 0.64, the close-packing density. This trend can be understood in terms of the ϕ dependence of the characteristic stress relaxation frequency $\omega_c = \sigma/\eta a$. Comparing Eq. (8) to our prediction following Eq. (6), we find $A(\phi) \sim 1/\sqrt{\omega_c}$, or $A(\phi) \sim \sqrt{\eta(\phi)a/\sigma}$, where $\eta(\phi)$ is an effective viscosity arising from dissipation in the liquid films. It should depend inversely on the film thickness [3], which decreases by a factor of 4 over this range of ϕ [2]. Thus our model predicts a factor of 2 increase in $A(\phi)$ over the measured range, in reasonable agreement with the experimental results. In addition, our model predicts a high frequency cutoff to the $s^{1/2}$ behavior of $\omega_c = \sigma/\eta a \approx 10^7$ Hz. This is in excellent agreement with the cutoff observed experimentally, as shown in Fig. 1 (the vertical scale in Fig. 1 is logarithmic). Thus the experimental results are in accord with the predicted power law, the high-frequency cutoff on the power-law behavior, and the volume-fraction dependence of the amplitude of the power law. This offers strong support for the model.

A similar $s^{1/2}$ term in $\overline{G}(s)$ is also observed for emulsions with $\phi < 0.64$, where packing constraints do not prevent the droplets from diffusing locally, as well as for colloidal suspensions below close packing [18]. In those cases, it is believed to result from the high-frequency contribution of Brownian motion [19]. We emphasize, however, that this physical mechanism cannot give rise to the $s^{1/2}$ term described here for concentrated emulsions with $\phi > 0.64$, as the droplets cannot freely diffuse, even locally.

The experimental observation of the predicted behavior of the dynamic modulus strongly supports our speculation that slip regions exist. Since such regions do not contribute to the elastic modulus in the low-frequency limit, the existence of these regions may also reduce the storage modulus $G'(\omega)$. Recent experiments [2] show that $G'(\omega)$ is much smaller than one would expect based on periodic packings of droplets, especially at volume fractions just above the onset of elastic behavior. Thus our picture may also provide the key to understanding the anomalous storage modulus of emulsions.

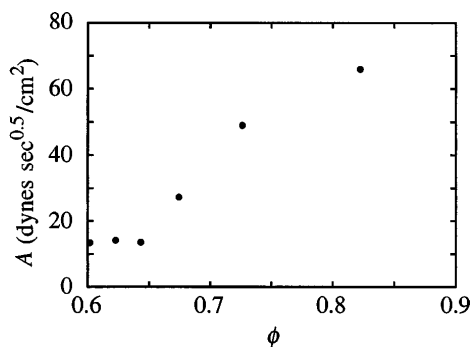


FIG. 2. The magnitude $A(\phi)$ of the $s^{1/2}$ contribution to the modulus, as a function of the volume fraction ϕ .

While our experiments focus on the high-frequency response, the dynamic modulus measured by our light scattering technique matches that measured by mechanical techniques at lower frequencies [2]. Since the light scattering measurements rely on thermal fluctuations, the measured moduli are definitely in the linear regime, even though motion along the weak planes can lead to changes in the droplet configurations. This is a direct consequence of disorder in the droplet packing. The success of the model in predicting an $\omega^{1/2}$ contribution to the dynamic shear modulus is especially remarkable since the loss modulus is sensitive to many different microscopic mechanisms of dissipation, including flow in the liquid films and flow in the surfactant films [3], which we have neglected. This suggests that our results may be applicable to other randomly close-packed materials, such as foams, dense colloidal suspensions, and non-Brownian particle suspensions.

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