Elasticity of Compressed Emulsions

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The elastic shear modulus of monodisperse emulsions is shown to exhibit a universal dependence on droplet volume fraction ϕ when scaled by the Laplace pressure of the droplets, increasing as $\phi(\phi - \phi_c)$, where $\phi_c \approx 0.635$, the value of random close packing of solid spheres. Surprisingly the osmotic pressure required to compress the emulsions to increase ϕ is nearly the same as the shear modulus over a large range of volume fraction, while the bulk osmotic modulus differs significantly. Models based on the structural disorder of the emulsions are discussed to account for these data.

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Emulsions are droplets of one fluid dispersed in a second immiscible fluid and are stabilized by a surfactant. One of their most important and useful attributes is their rheology; despite being comprised solely of fluids, emulsions can nevertheless be elastic solids. This elasticity is achieved precisely because the droplets are fluid. When an osmotic pressure Π is exerted on the droplets, their volume fraction ϕ is increased and their shape is distorted, storing energy in their interfaces [1]. The elasticity can result from the energy stored by additional deformation of the shape induced by an applied strain. The energy scale that controls this deformation is the internal or Laplace pressure of the droplets σ/r, where σ is the interfacial tension and r is the radius of the undeformed droplet.

The key to the origin of the elastic modulus of an emulsion is its dependence on ϕ and hence on osmotic pressure. However, this intrinsic relationship is not well understood. For $\phi \approx 1$, an emulsion should resemble a dry foam, where the elasticity results entirely from the stretching of the interfaces [2]. An extension to lower ϕ for a two-dimensional lattice of deformable cylinders suggested that the shear modulus should exhibit only a weak volume fraction dependence as ϕ decreases, until it falls precipitously to zero when the droplets no longer touch and thus are not deformed [3]. More exact, three-dimensional calculations for ordered lattices arrive at a similar conclusion [4,5]. However, results from an extensive series of experiments were in sharp disagreement with these predictions; the measured shear modulus was found to very as $G' \sim \phi^{1/3}(\phi - \phi_c)\sigma/r$, where $\phi_c \approx 0.71$ [6]. This emulsion was comprised of polydisperse droplets, complicating a precise comparison to the theoretical prediction and suggesting the discrepancy results from polydispersity.

In this Letter, we present measurements of the ϕ dependence of the elastic modulus of emulsions comprised of monodisperse droplets. Thus the Laplace pressure is the same for each droplet, enabling a precise comparison with theoretical expectations. We show that the shear modulus exhibits a universal ϕ dependence when scaled by

σ/r, which can be described by $\phi(\phi - \phi_c)$; however, here $\phi_c \approx 0.635$, the volume fraction of randomly close packed spheres. More surprisingly, we show that the osmotic pressure is nearly the same as the shear modulus over a large range of ϕ. By contrast, the longitudinal counterpart of the shear modulus, or the bulk osmotic modulus, has a markedly different ϕ dependence. We also measure the frequency dependence of both the storage, or elastic modulus G', and the loss, or viscous modulus G''. Their behavior is reminiscent of a glass, consistent with the observed structure of the emulsion droplets. This suggests that the origin of the ϕ dependence of the elasticity is the structural disorder of the droplets.

The emulsions were comprised of silicon oil droplets in water, stabilized by $0.01M$ sodium dodecylsulphate (SDS), and purified using a crystallization fractionation technique [7]. The polydispersity was about 10% of the radius, while the interfacial tension was $\sigma = 9.8$ dyn/cm. The volume fraction was set by centrifugation and was measured by weight before and after evaporation of the water. The droplet structure remained disordered at all values of ϕ. The linear viscoelastic shear moduli were measured by applying an oscillatory strain and measuring the resultant stress. A cone and plate geometry was used for higher ϕ while a double wall Couette geometry was used for lower volume fractions. The walls of both containers were roughened to a scale comparable to the droplet size, completely eliminating any slip at the boundaries [8].

Typical results for both G' and G'' as functions of the maximum applied oscillatory strain γ are shown in Fig. 1 for several volume fractions of an emulsion with $r \approx 0.53$ μm. The elastic modulus increases by nearly four decades as ϕ increases; moreover, it is always larger than the loss modulus at sufficiently small strains. By contrast, at larger strains, the apparent G'' initially rises and then decreases but is always larger than the apparent G'. This presumably reflects the increased loss due to large scale structural rearrangements or flow of the

droplets as the strain increases above the yield value. All our measurements are made at sufficiently small strains so that both G' and G'' are in the γ independent regime.

The frequency dependence of the moduli is shown in Fig. 2 for several ϕ. In all cases, there is a plateau in $G'(\omega)$; at high ϕ, this extends over the full four decades of frequency measured, while for the lowest ϕ, the plateau is no longer strictly independent of ω but can still be uniquely identified by the inflection point G'_p. By contrast, for all ϕ, $G''(\omega)$ exhibits a shallow minimum G''_m, the frequency of which increases with ϕ. This minimum must result from an increase in $G''(\omega)$ at both higher and lower frequencies. The low frequency rise in G'' implies the existence of relaxation processes resulting from very slow structural rearrangements of the droplets [9]. The high frequency rise in G'' reflects the ultimate domination of the viscous relaxation of the fluid phase at very high frequencies, well above those measured. We use G'_p to characterize the static elasticity at frequencies above the extremely slow rearrangements of the glassy structure, and G''_m to characterize the associated loss modulus.

We measure the ϕ dependence of both G'_p and G''_m for samples with different radii and normalize the results by the energy density of the undeformed droplets σ/r. We also account for the consequences of the thin water film of thickness h between the droplet interfaces [10] due to the screened Coulomb repulsion between them. This repulsive force is often called a disjoining pressure [11]. The thickness of this film must very with volume fraction, as the droplets are squeezed together and become increasingly deformed, forcing the repulsive films closer together. For low ϕ, we find $h \approx 175$ Å, consistent with force-distance measurements for these emulsions where the screening length is ~ 50 Å [12]; at the highest ϕ, we estimate $h \approx 50$ Å by comparison to measurements of the film thickness at similar osmotic pressures [13]. We interpolate linearly between these two values for $\phi \geq 0.64$ to obtain an effective volume fraction $\phi_{eff} \approx \phi(1 + 3h/2r)$. This includes the film with the volume of the droplets and focuses

FIG. 2. The frequency dependence of the storage G' (solid points) and loss G'' (open points) moduli of a monodisperse emulsion with $r \approx 0.53$ μm for $\phi_{eff} = 0.80$ (diamonds), 0.63 (triangles), and 0.60 (circles). The results for the two larger ϕ_{eff} were obtained with $\gamma = 0.005$, while those for the lowest were obtained with $\gamma = 0.015$.

on the consequences of the droplet packing, independent of the effects of the repulsive interaction. The scaled data for G'_p all fall onto a single curve, as shown by the solid points in Fig. 3; the data for G''_m also fall onto a single curve, as shown by the open points in Fig. 3. The scaled G'_p rise by nearly four decades as ϕ_{eff} increases from 0.60 to 0.65. Moreover, over all ϕ_{eff} shown, G'_p dominates over G''_m; this becomes increasingly pronounced at high ϕ_{eff}. The scaling with σ/r confirms that the elasticity results from the storage of energy at the droplet interfaces. Moreover, the scaling indicates that the elasticity of these compressed, monodisperse emulsions is universal, dependent only on the packing geometry of the droplets.

Like the elasticity, the osmotic pressure also reflects energy storage in the interfaces as they are deformed with increasing ϕ. To compare the osmotic pressure with the shear modulus, we measured its ϕ dependence using an emulsion with $r \approx 0.48$ μm. At high ϕ, Π was set by dialysis using calibrated polymer mixtures [14], while at lower ϕ, it was set by gentle centrifugation. The value of ϕ_{eff} corresponding to each Π was determined and the data, normalized by σ/r, are plotted as the large open circles in Fig. 3. Remarkably, to within experimental uncertainty, Π is nearly the same as G'_p, until it diverges at high ϕ_{eff}.

To understand these results, we consider the behavior in different regimes of volume fraction. Near $\phi_{eff} \approx 1$, the behavior of the emulsion should be analogous to a dry foam assuming the imposed shear stretches the films as the droplets deform, rather than further squeezing the droplets together. A random, dry foam, is predicted to have $G' \approx 0.55\sigma/r$ [2]. Our results suggest that G' approaches $0.6\sigma/r$, in excellent agreement with this prediction. The osmotic pressure is affected by the repulsive interactions and should diverge as the droplets are increasingly deformed, as observed in our data.
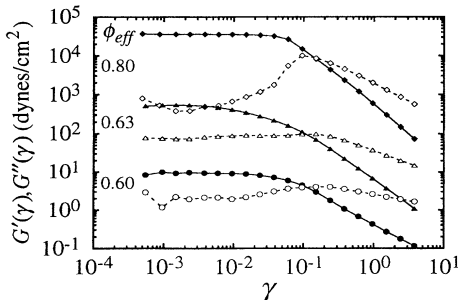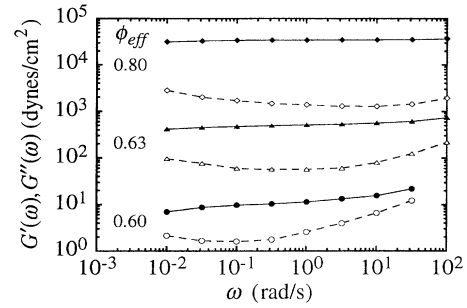

FIG. 1. The γ dependence of the storage G' (solid points) and loss G'' (open points) moduli of a monodisperse emulsion with $r \approx 0.53$ μm for $\phi_{eff} \approx 0.80$ (diamonds), 0.63 (triangles), and 0.60 (circles), measured at $\omega = 1$ rad/sec.
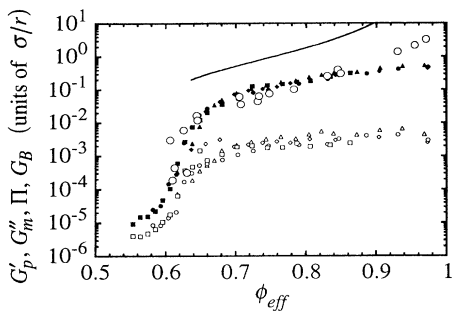
FIG. 3. The plateau value of the elastic modulus G'_p and the minimum of the loss modulus G''_m normalized by σ/r for emulsions with $r \approx 0.25$ (solid circles), 0.37 (triangles), 0.53 (squares), and 0.74 μm (diamonds), plotted as functions of $\phi_{\rm eff}$. Excellent scaling of the data is observed, demonstrating the universal nature of the elasticity. The large open circles are the measured values of the osmotic pressure, normalized by σ/r for an emulsion with $r \approx 0.48$ μm. The osmotic pressure is nearly the same as the elastic modulus, until it diverges at very high volume fractions. The solid line represents the bulk osmotic modulus.

Below $\phi_c \approx 0.635$, packing constraints do not force the droplets to deform, yet the emulsion still retains its elastic behavior, despite the fact that Π is orders of magnitude less than the Laplace pressure. Here entropic effects must play a significant role since the droplets are small enough that their Brownian motion is important. Thus the behavior might be understood by comparison to solid colloidal spheres. For $\phi \geq 0.55$, solid spheres also exhibit a plateau in $G'(\omega)$ and a minimum in $G''(\omega)$, with G'_p larger than G''_m; this results from the packing constraints of a colloidal glass [15]. Dynamic light scattering measurements from index matched emulsions confirm the presence of a colloidal glass transition at $\phi_{\rm eff} \approx 0.58$ [16]. Thus, by analogy, near ϕ_c the emulsion elasticity is entropic in origin and should scale as $k_B T/r^3$ rather than σ/r; however, our data are insufficient to ascertain this.

The most unusual behavior occurs above ϕ_c, where packing constraints force the droplets to deform. Here G'_p decreases approximately linearly with $\phi_{\rm eff} - \phi_c$; we show this in Fig. 4 where we replot the data above ϕ_c on a logarithmic plot. We emphasize, however, that this behavior does not persist to the lowest $\phi_{\rm eff}$ where G'_p continues to decrease. This linear dependence is reminiscent of that observed for polydisperse emulsions [6]; however, here ϕ_c corresponds to random close packing of monodisperse spheres. The data for Π also exhibit an approximately linear increase above ϕ_c, although with more scatter, until they diverge near $\phi_{\rm eff} \approx 0.8$. Therefore, the bulk osmotic modulus $G_B = \phi d\Pi/d\phi$ must increase sharply at ϕ_c and thus exhibits a dramatically different $\phi_{\rm eff}$ dependence than the shear modulus, as shown schematically by the solid line in Fig. 3.

To understand this behavior, we first consider the behavior of a single droplet confined in a box, whose dimensions are decreased by a small amount δx below $2r$, thereby deforming the droplet shape and forming flat facets of area a at the walls. For small deformations, the Laplace pressure is unchanged, so the force on the facet is $a\sigma/r$, and the osmotic pressure of the droplet is $\Pi \sim a\sigma/r^3$. Both a and the change in the volume are linearly related to δx; thus $\Pi \sim (\phi_{\rm eff} - \phi_c)\sigma/r$. The facet behaves as a harmonic spring; the force is proportional to δx and hence to $\phi_{\rm eff} - \phi_c$, while the spring constant is σ/r. More detailed calculations of the energy of weakly deformed droplets arrive at a similar prediction, except with an additional logarithmic dependence that leads to a slight modification very close to ϕ_c [4]. This central spring picture can be generalized to describe a bulk emulsion by assuming that the neighboring droplets form the box. Then the osmotic pressure squeezes opposing interfaces together to form flat facets, each of which behaves as a harmonic spring. However, these springs can never be attractive but are always compressed; moreover, they support only central forces. Because of packing disorder, the flat facets pushing on each droplet are random in their direction. However, since each droplet cannot move, the total force exerted on it must sum to zero; as a result, all facets do not necessarily have equal areas, and thus all springs are not equally compressed.

When $\phi > \phi_c$, the droplets must be deformed, and the volume fraction dependences of both the osmotic pressure and the shear modulus depend on the behavior of the facets. As the osmotic pressure is increased and the droplets are further compressed, new facets must form. Thus one possible model for the behavior of the shear modulus is by analogy to a network of springs, which are cut randomly. Computer simulations, and effective medium theory, for an ordered network of harmonic springs suggest that the shear modulus decreases linearly in the number of springs, going to zero at the rigidity transition [17]. Stretched springs exhibit a similar behavior, although ϕ_c is modified [18].
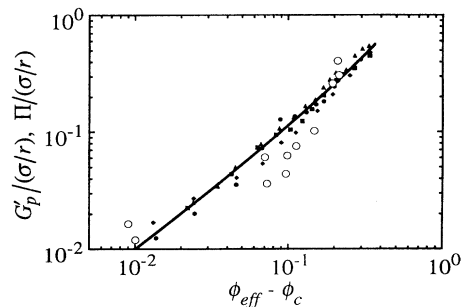

FIG. 4. The values of G'_p and Π normalized by σ/r and plotted logarithmically as a function of $\phi_{\rm eff} - \phi_c$. The solid line is the behavior predicted by the network spring model for $G'_p/(\sigma/r)$.

Assuming that the number of facets varies linearly with volume fraction, we might expect the shear modulus to decrease linearly as $\phi_{eff} - \phi_c$; the critical volume fraction is that of random close packing of the monodisperse spheres, where facets are first formed. This model is similar in spirit to a computer simulation of two-dimensional polydisperse disks, which exhibits a rigidity loss transition as ϕ is decreased [19]. Since the density of springs varies as ϕ_{eff}, we expect $G'_p \sim \phi_{eff}(\phi_{eff} - \phi_c)\sigma/r$; this does describe the data, as shown by the solid line in Fig. 4. However, this picture can only describe the behavior of the osmotic pressure if we assume that it is dominated by the facets that are first formed at ϕ_c. Each of these must be further compressed with increasing ϕ_{eff}; by contrast, any new facets are significantly less compressed when first formed and thus make a smaller contribution. In this case, $\Pi \sim \phi_{eff}(\phi_{eff} - \phi_c)\sigma/r$, until the approximation of constant droplet radium fails, whereupon the osmotic pressure diverges. This is also in accord with the data, as shown in Fig. 4.

While appealing, this picture probably does not adequately capture the physics as ϕ_{eff} approaches ϕ_c. The percolation effects inherent in this picture require a decreasing number of facets to cause the loss of elasticity. However, even at ϕ_c, each sphere has, on average, six nearest neighbors, restricting the total number of additional facets that can be formed with increasing ϕ_{eff} and thus the total change in the modulus that can be achieved. It is possible that the remnant polydispersity of the droplets leads to far fewer facets at ϕ_c, thereby broadening the transition and causing the linear decrease to persist. A much more likely possibility recognizes the effects of the disorder of the facets. Since the facets support only central forces, they cannot support a shear stress by themselves, but do so only because of their packing. However, because of their disorder, some facets may shift positions upon application of the shear. Indeed it is likely that some facets are always incipiently unstable and will rearrange with arbitrarily small strains. This rearrangement will cause an imbalance of the forces on the neighboring droplets, which in turn will cause them to move, thus causing a propagation of these rearrangements. As a result, the shear will cause the droplets to move, or slip, relative to each other, reducing the compression of the facets. After this rearrangement, the net forces on each interior droplet will again sum to zero, while the forces on the droplets at the surfaces will both oppose the osmotic pressure and provide the restoring force that leads to the shear modulus. Since this restoring force results from a rearrangement of the initial forces, whose magnitudes are themselves set by the osmotic pressure, it will itself be proportional to that same force and hence will scale with Π. Moreover, since the droplets are packed in, and cannot move macroscopic distances, it is reasonable to expect this force to scale with the applied strain. As a result, the strain in the emulsion will not be affine; instead the droplets will slip or rearrange instead

of deforming, reducing the shear modulus. We note that this picture is somewhat suggestive of the modulus predicted for random systems under an extensional pressure; the modulus has an important contribution which varies as the pressure [20].

If this spring-rearrangement picture is correct, a compressed emulsion would be a particularly unusual solid. It becomes a solid solely because of the compressional forces that result from the osmotic pressure; however, it supports a shear by shifting to a state of lower positional energy, thus requiring less deformation of the droplets. In this case, it is not clear whether the modulus is a truly causal quantity that obeys the Kramers-Kronig relations, even though the experimentally measured modulus is linear in strain [9]. The essential conclusion of this paper is the experimental observation of the scaling of the shear modulus and its similarity with the osmotic pressure. This behavior will serve as a critical test of the validity of any proposed theory.

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