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Rheology of Attractive Emulsions

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We show how attractive interactions dramatically influence emulsion rheology. Unlike the repulsive case, attractive emulsions below random close packing, ϕ_{RCP} , can form soft gel-like elastic solids. However, above ϕ_{RCP} , attractive and repulsive emulsions have similar elasticities. Such compressed attractive emulsions undergo an additional shear-driven relaxation process during yielding. Our results suggest that attractive emulsions begin to yield at weak points through the breakage of bonds, and, above ϕ_{RCP} , also undergo droplet configurational rearrangements.

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I. INTRODUCTION

Emulsions are suspensions of droplets of one immiscible fluid in another. They are widely used in technological applications requiring the transport and flow of the dispersed fluid; these include oil recovery, food products, pharmacology, coatings, and cosmetics. The droplets are typically stabilized by a surfactant adsorbed on their interfaces; this ensures that there is a short-range repulsive interaction between them, which prevents their coalescence. Such a repulsive emulsion becomes a disordered elastic solid as it is compressed: this behavior can be characterized by the complex shear modulus, $G^*(\omega) = G'(\omega) + iG''(\omega)$, where G' is the storage modulus, G'' is the loss modulus, and ω is the angular frequency. For droplet volume fractions, ϕ , approaching random close packing of spheres, $\phi_{RCP} \approx 0.64$, from below, a repulsive emulsion exhibits a weak elasticity that arises from thermal fluctuations [1]. By contrast, if ϕ is increased above ϕ_{RCP} , the droplets are forced to deform; as a result, the elasticity is determined by the Laplace pressure scale of the droplets, σ/a , where σ is the interfacial tension between the dispersed and continuous phases and a is the average droplet size [1]. Even though it is an elastic solid, such an emulsion can nevertheless be made to flow quite easily: the imposition of sufficiently large shear causes it to yield. This behavior can be elucidated using oscillatory measurements of G' and G'' performed at constant ω and varying maximum strain amplitude γ . The viscoelastic moduli of a repulsive emulsion above ϕ_{RCP} become strain-dependent for sufficiently large γ as the emulsion yields. For increasing γ , the nonlinear G'' exhibits a single, well-defined peak at a strain γ_r^* before falling as $\gamma^{-\nu_r''}$; G' concomitantly decreases as $\gamma^{-\nu_r'}$ with $\nu_r' \approx \nu_r''/2$ [1, 4, 5]. The pronounced peak in G'' is a characteristic feature of soft glassy materials; it is a direct consequence of a structural

relaxation process and thus provides an effective way to characterize yielding [5]. This approach is particularly useful for repulsive emulsions above ϕ_{RCP} , for which the peak in G'' reflects the irreversible rearrangements of the densely-packed droplets [4, 6].

Another widely-encountered class of emulsions is characterized by droplets with additional attractive interactions between them. In stark contrast to the repulsive case, such an attractive emulsion can form an elastic solid even for ϕ well below ϕ_{RCP} [7]; the bonds between droplets result in a connected network of aggregates that can support a shear stress [7, 8, 10, 11]. As a result, an attractive emulsion must exhibit different flow and yielding behavior [12]. However, despite its broad industrial applications, exactly how this behavior occurs is unknown. Thus, measurements of the characteristic γ -dependent yielding of attractive emulsions are essential to elucidate how emulsion rheology depends on interdroplet interactions.

In this Article, we explore the rheology of attractive emulsions using oscillatory measurements over a range of ϕ . For increasing γ , $G''(\gamma)$ of attractive emulsions below ϕ_{RCP} exhibits a single peak at a strain $\gamma_1^* \ll \gamma_r^*$ that increases with ϕ . By contrast, $G''(\gamma)$ of attractive emulsions above ϕ_{RCP} exhibits two peaks at γ_1^* and $\gamma_2^* \approx \gamma_r^*$, unlike the repulsive case; these reflect two distinct structural relaxation processes. The time scales of both of these processes vary with shear rate as $\dot{\gamma}^{-\nu}$ with $\nu \approx 0.8 - 1$. Our results provide insight into the elasticity and yielding of attractive emulsions and highlight the sensitivity of emulsion rheology to attractive interactions.

II. EXPERIMENTAL DETAILS

We use emulsions comprised of silicone oil droplets dispersed in formamide, a solvent with negligible evaporation; the droplets are sterically stabilized by Pluronic P105, a non-ionic amphiphilic copolymer [13]. The mechanical measurements are performed at $T = 23^\circ\text{C}$ on strain- or stress-controlled rheometers (TA ARES G2 or Anton Paar Physica MCR 501, respectively) using

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a parallel-plate geometry. The sample environment is controlled using a solvent trap. The plates are roughened to eliminate wall-slip, and we verify that measurements are independent of the gap size; furthermore, the results are similar to those obtained using a cone-and-plate geometry, indicating that they are not significantly influenced by the non-uniform strain field characteristic of a parallel-plate geometry. We pre-shear the samples prior to each measurement by imposing a 50s^{-1} constant shear-rate flow for 30s, followed by oscillatory shear of γ decreasing from 300% to 0.01% over a period of 230s. We do not observe sample creaming over the measurement duration.

At the temperature and concentrations used here, P105 forms freely-dispersed globular micelles in formamide with radius $a_m = 6.5\text{nm}$, aggregation number $\nu_m = 31$ and critical micelle concentration $c^* = 20.2\text{mM}$ [14]. These micelles induce attractive depletion interactions between emulsion droplets [3], whose magnitude at interdroplet contact U we calculate using the Vrij model [15]: $U/k_B T = 4\pi a a_m^2 N_A (c - c^*)/\nu_m$, where a is the average droplet radius, c is the P105 concentration, k_B is Boltzmann's constant, T is temperature, and N_A is Avogadro's number. These interactions preserve a lubricating layer of formamide between the droplets, and hence are pairwise centrosymmetric and do not resist bending. Because ions do not appreciably self-dissociate in formamide, and because we use a non-ionic surfactant, we do not expect electrostatics to play a significant role [27].

To investigate the influence of attraction on the rheology of emulsions, we prepare repulsive emulsions with $U = 0$ ($c = 7\text{mM} < c^*$) and attractive emulsions with $U = 7 - 9k_B T$ ($c = 26.8 - 28.7\text{mM}$) over a range of ϕ using high-shear rate homogenization or sonication with a probe tip. We densify the emulsions using centrifugation and verify that they are stable against coalescence or Ostwald ripening [25]. We measure $\sigma = 6 - 9\text{mN/m}$ using a du Noüy ring. The oil volume fraction ϕ is determined by measuring the masses of all components making up a sample. The droplets have $a = 100, 106$, or 128nm and relatively low polydispersity $\sim 30 - 35\%$ as measured using dynamic light scattering. We also account for the thickness t of the surfactant layer adsorbed at the droplet surfaces to obtain the effective volume fraction $\phi_{eff} \approx \phi(1 + t/(a - t))^3$. We estimate $t \approx 3.1\text{nm}$ based on neutron scattering data [13, 14] and further verify this by fitting viscosity measurements of dilute repulsive samples to simulation data appropriate for emulsions [4, 16]. This estimate for t is likely to be unchanged even at the highest ϕ studied: the pressure required to compress the surfactant layer $\sim k_B T/s^3$, where πs^2 is the interfacial area per polymer molecule, is approximately two orders of magnitude larger than the maximum osmotic pressure exerted on the droplets $\sim 0.1\sigma/a$ [1, 26].

To test the generality of our results, we also study silicone oil-in-water emulsions stabilized by an ionic surfactant, SDS. All of the data presented in this paper are for

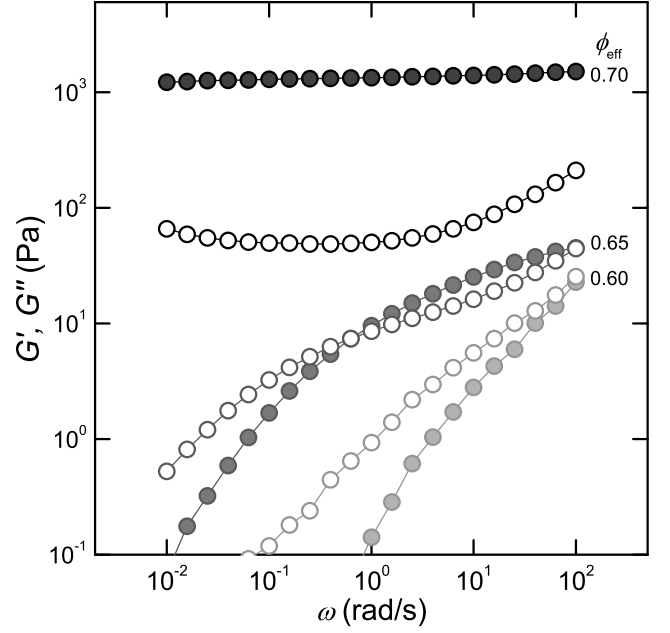


FIG. 1: **Repulsive emulsions become fluid-like below random close packing.** Linear storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, of repulsive emulsions with $U = 0$, $a = 128\text{nm}$, and $\phi_{eff} \approx 0.70, 0.65$, and 0.60 (progressively lighter colors).

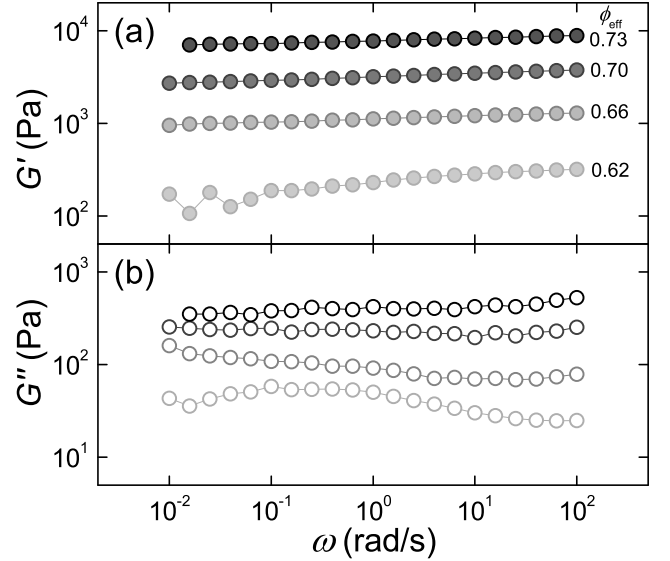


FIG. 2: **Attractive emulsions are elastic both above and below random close packing.** Linear storage and loss moduli, (a) $G'(\omega)$ and (b) $G''(\omega)$, of attractive emulsions with $U \approx 9k_B T$, $a = 100\text{nm}$, and $\phi_{eff} \approx 0.73, 0.70, 0.66$, and 0.62 (progressively lighter colors). For clarity, G' and G'' data are multiplied by a factor of 0.5, 0.2, or 0.07 for $\phi_{eff} = 0.70, 0.66$, or 0.62 , respectively.

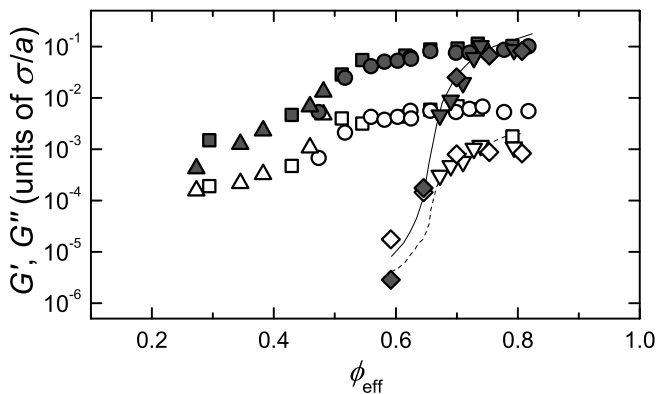


FIG. 3: **Elasticities of attractive and repulsive emulsions differ below random close packing but are similar above it.** Linear storage and loss moduli, G'_p (solid points) and G'' (open points), measured at $\omega = 1$ rad/s, normalized by the Laplace pressure σ/a , for both attractive and repulsive emulsions of varying ϕ_{eff} . Attractive emulsions have $a = 128\text{nm}$, $U \approx 9k_B T$ (circles), $a = 106\text{nm}$, $U \approx 7k_B T$ (upward triangles), and $a = 100\text{nm}$, $U \approx 9k_B T$ (squares); repulsive emulsions have $a = 128\text{nm}$ (diamonds) and $a = 106\text{nm}$ (downward triangles). The interfacial tension $\sigma = 6 - 9\text{mN/m}$ for the range of surfactant concentrations used. Previous measurements of G'_p (solid line) and G'' (dashed line) for monodisperse repulsive emulsions [1], horizontally shifted to account for polydispersity, agree with our data. We find $\phi_{RCP} \approx 0.68 - 0.72$, characteristic of ϕ_{RCP} for spheres of comparable polydispersity [17].

the oil-in-formamide emulsions stabilized by P105, with the exception of Figs. 7 and 8, which present data for the oil-in-water emulsions stabilized by SDS. These are well-defined and stable model systems characterized by very weak ($< 1k_B T$) or strong ($> 1k_B T$) attractive interdroplet interactions using an SDS concentration only slightly greater than or significantly greater than the critical micelle concentration ($c^* \approx 8\text{mM}$), respectively [1–3]. We prepare the emulsions using depletion fractionation; the droplets have $a = 250\text{nm}$ and have low polydispersity $\sim 10\%$. To investigate the influence of attraction on the rheology of emulsions, we study repulsive emulsions with $U < 1k_B T$ ($c = 10\text{mM}$) and attractive emulsions with $U \approx 21k_B T$ ($c = 200\text{mM}$). The effective volume fraction ϕ_{eff} is defined to incorporate the effects of the thin liquid film between adjacent droplets due to their electrostatic repulsion. We study the emulsions using oscillatory rheology on a strain-controlled rheometer using a roughened cone-and-plate geometry with a vapor trap. Further details and the rheology data for the SDS-stabilized repulsive emulsions are presented in [1, 2].

III. RESULTS AND DISCUSSION

The elastic behavior of emulsions is characterized by a ω -independent regime of $G'(\omega)$; two examples, a repulsive

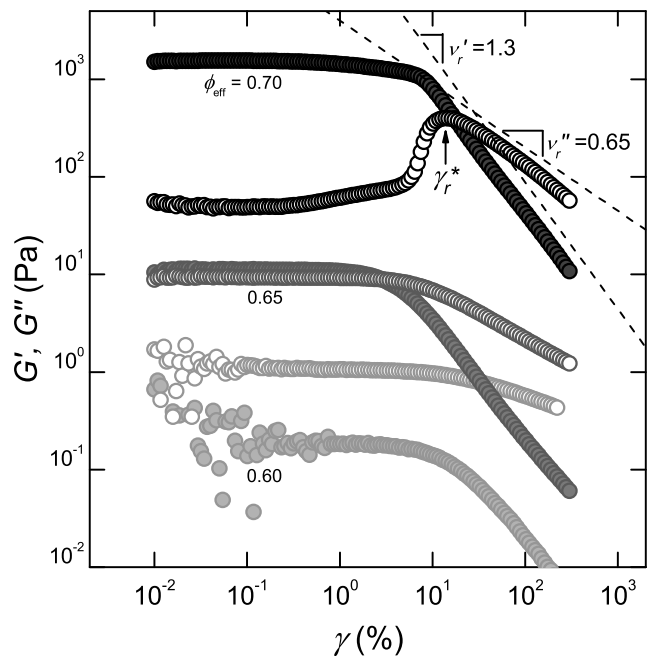


FIG. 4: **Repulsive emulsions above random close packing exhibit one peak in $G''(\gamma)$ at γ_r^* while those below random close packing do not exhibit a peak in $G''(\gamma)$.** Viscoelastic moduli $G'(\gamma)$ and $G''(\gamma)$ measured at $\omega = 1$ rad/s of repulsive emulsions with $U = 0$, $a = 128\text{nm}$, and $\phi_{eff} \approx 0.70, 0.65$, and 0.60 (progressively lighter colors).

emulsion with $\phi_{eff} = 0.70$ and an attractive emulsion with $\phi_{eff} = 0.73$, are shown in the top curves of Figs. 1 and 2, respectively. Repulsive emulsions are solid-like when packed above ϕ_{RCP} but become fluid-like as ϕ_{eff} is decreased below ϕ_{RCP} [Fig. 1] [1]. By contrast, attractive emulsions are solid-like over a wider range of ϕ_{eff} [Fig. 2]. To summarize this behavior, we plot the plateau modulus G'_p , measured at $\omega = 1$ rad/s, as a function of ϕ_{eff} . Above ϕ_{RCP} , G'_p has the same magnitude for both attractive and repulsive emulsions as shown in Fig. 3. This indicates that the elasticity in both cases is dominated by the repulsive forces deforming the droplets. However, G'' is an order of magnitude larger for attractive emulsions, as compared to the repulsive case [Fig. 3]. For repulsive emulsions, G'_p drops precipitously as ϕ_{eff} is decreased below ϕ_{RCP} , indicating that the droplets are no longer compressed [1]; by contrast, the elasticity of attractive emulsions persists far below ϕ_{RCP} , as shown by the upper symbols in Fig. 3.

To elucidate the microscopic mechanisms for emulsion flow, we investigate the yielding of emulsions with different ϕ_{eff} by measuring the γ -dependence of G' and G'' at $\omega = 1$ rad/s. Repulsive emulsions above ϕ_{RCP} begin to yield at $\gamma_r^* \sim 10\%$ and G'' exhibits a single, well-defined peak at this strain, as indicated by the arrow in Fig. 4 [1, 4, 5]. Attractive emulsions above ϕ_{RCP} begin to yield at much smaller strain. Unexpectedly, G'' exhibits two well-defined peaks, a first at $\gamma_1^* \sim 1\% \ll \gamma_r^*$ and a sec-

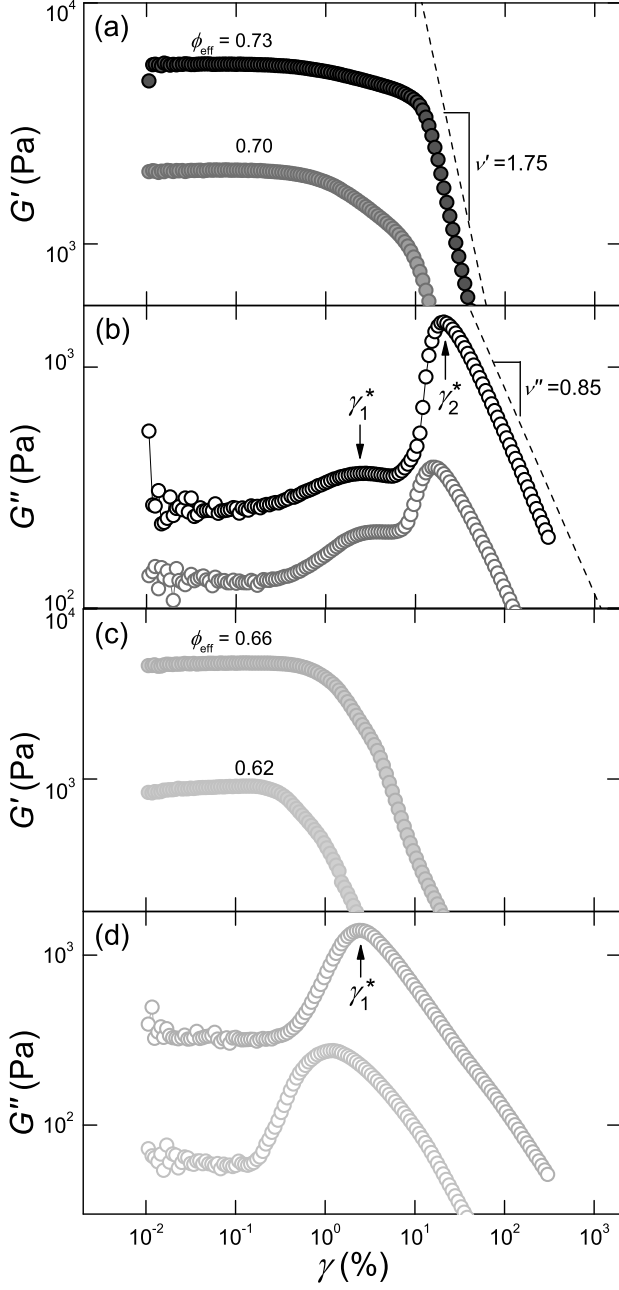


FIG. 5: **Attractive emulsions above random close packing exhibit two peaks in $G''(\gamma)$ at γ_1^* and γ_2^* while those below random close packing exhibit one peak at γ_1^* .** Viscoelastic moduli $G'(\gamma)$ and $G''(\gamma)$ measured at $\omega = 1$ rad/s of attractive emulsions with $U \approx 9k_B T$ and $a = 100\text{nm}$ (a-b) above ϕ_{RCP} ($\phi_{eff} \approx 0.73$ and 0.70 , progressively lighter colors) and (c-d) below ϕ_{RCP} ($\phi_{eff} \approx 0.66$ and 0.62 , progressively lighter colors). For clarity, G' and G'' data are multiplied by a factor of $0.7, 0.3, 0.8$, or 0.2 for each ϕ_{eff} going from top to bottom. Straight lines indicate $G', G'' \sim \gamma^{-\nu'}, -\nu''$ for large γ .

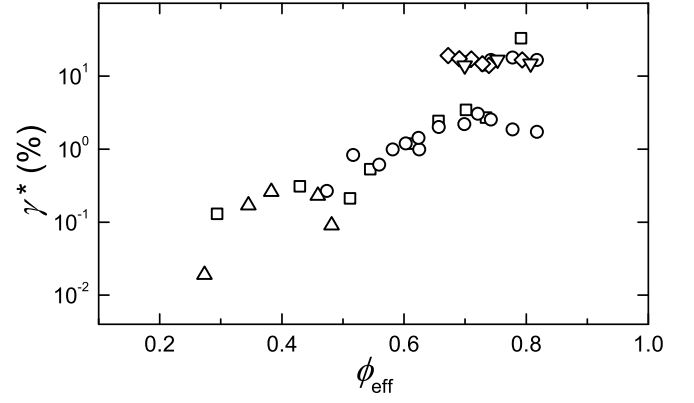


FIG. 6: **Position of peaks in $G''(\gamma)$ for varying ϕ_{eff} .** Lower symbols represent γ_1^* , upper symbols represent either γ_2^* or γ_r^* . Attractive emulsions have $a = 128\text{nm}$, $U \approx 9k_B T$ (circles), $a = 106\text{nm}$, $U \approx 7k_B T$ (upward triangles), and $a = 100\text{nm}$, $U \approx 9k_B T$ (squares); repulsive emulsions have $a = 128\text{nm}$ (diamonds) and $a = 106\text{nm}$ (downward triangles).

ond at $\gamma_2^* \approx \gamma_r^*$, before falling as $\gamma^{-\nu''}$, as indicated by the arrows in Fig. 5(b). Correspondingly, G' decreases weakly for $\gamma > 0.5\%$ before falling as $\gamma^{-\nu'}$ for $\gamma > 10\%$, with $\nu'' \approx \nu'/2$ [Fig. 5(a)]. By contrast, G'' of attractive emulsions below ϕ_{RCP} only exhibits a single peak at γ_1^* , as shown in Fig. 5(d), and G' decreases smoothly for $\gamma > 0.01 - 1\%$ [Fig. 5(c)].

To understand these results, we examine the ϕ_{eff} -dependence of γ_1^* . Below ϕ_{RCP} , γ_1^* decreases with decreasing ϕ_{eff} , as shown by the lower symbols in Fig. 6 [18]; interestingly, this is similar to behavior predicted for particulate colloidal gels connected by “weak links” [9]. The elasticity of these emulsions results from the attractive interdroplet bonds; these induce the formation of a stress-bearing connected network comprised of compact droplet aggregates [8, 10, 11]. We expect the elasticity to be dominated by the weakest bonds in the network, and hence yielding begins when these are broken. In this picture, a macroscopic deformation ΔL deforms such a bond by $\Delta L/(L/\zeta)$, where L is the system size and ζ is the characteristic distance between the weakest bonds. The force on such a bond is thus $k_a \Delta L/(L/\zeta) = k_a \zeta \gamma$, where k_a is the characteristic bond stiffness. Assuming that the bond breaks at a fixed critical force $F^* = k_a \zeta \gamma_1^*$, the critical strain amplitude $\gamma_1^* \propto \zeta^{-1}$. Our measurements of γ_1^* thus imply that ζ increases with decreasing ϕ_{eff} , suggesting that yielding begins at fewer, sparser weak points as ϕ_{eff} is decreased. This may reflect the changing connectivity of the emulsion: the characteristic size ξ of the droplet aggregates comprising the emulsion also increases with decreasing ϕ_{eff} [8, 11, 19]. If the bonds between droplet aggregates are the weakest in the emulsion [20, 21], we would expect $\zeta \approx \xi$ to increase with decreasing ϕ_{eff} , consistent with our results.

For increasing γ , attractive emulsions both below and above ϕ_{RCP} begin to yield and exhibit a peak in G''

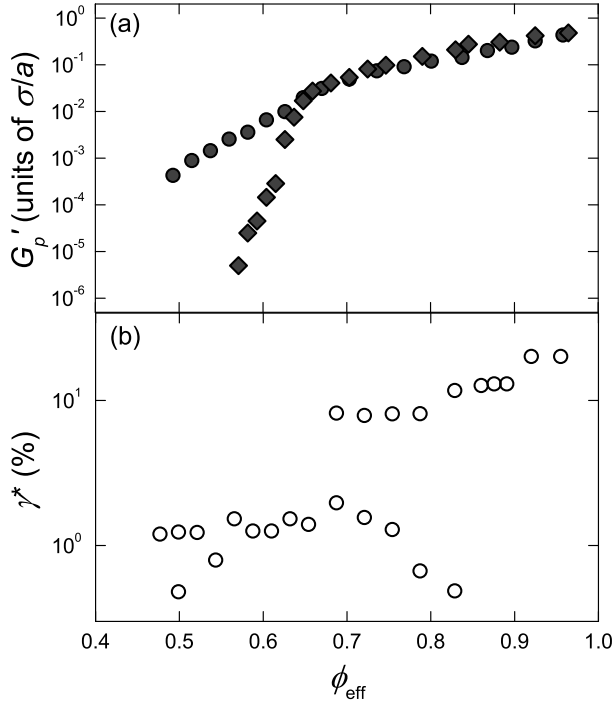


FIG. 7: **Volume fraction-dependent behavior is similar for oil-in-water emulsions stabilized by SDS.** (a) Linear plateau storage modulus, G'_p [2], normalized by the Laplace pressure σ/a and (b) position of peaks in $G''(\gamma)$, for varying ϕ_{eff} . Emulsions have $a = 250\text{nm}$; attractive emulsions have $U \approx 21k_B T$ (circles) while repulsive emulsions have $U < 1k_B T$ (diamonds). The interfacial tension $\sigma = 9.8\text{mN/m}$ for the range of surfactant concentrations used. Upper symbols in (b) represent γ_2^* while lower symbols represent γ_1^* .

at $\gamma \sim \gamma_1^*$; in contrast, those above ϕ_{RCP} exhibit an additional peak in G'' at $\gamma \sim \gamma_2^*$ [Fig. 5]. This observation implies the existence of an additional process by which the structure of these emulsions must relax before they can flow. This is likely due to the compression of the droplets: above ϕ_{RCP} , attractive emulsions require larger strain to fully yield through the irreversible rearrangements of densely-packed droplets, just as in the repulsive case [4, 6]. This hypothesis is supported by our observation that $\gamma_2^* \approx \gamma_r^*$. The height of the first yielding peak in $G''(\gamma)$ decreases as ϕ_{eff} increases above ϕ_{RCP} , as shown in Fig. 5(b), reflecting the increasing relative importance of these repulsive interactions as the droplets are increasingly compressed [22].

To test the generality of these results, we perform similar measurements on an oil-in-water emulsion stabilized by a different surfactant. The droplets are electrostatically stabilized by SDS, an ionic surfactant that also forms freely-dispersed globular micelles, and have low polydispersity ($\sim 10\%$) [1, 2]. Similar to the case of P105-stabilized emulsions, G'_p measured for the SDS-stabilized emulsions has the same magnitude for both attractive and repulsive emulsions packed above $\phi_{RCP} \approx 0.64$ [Fig.

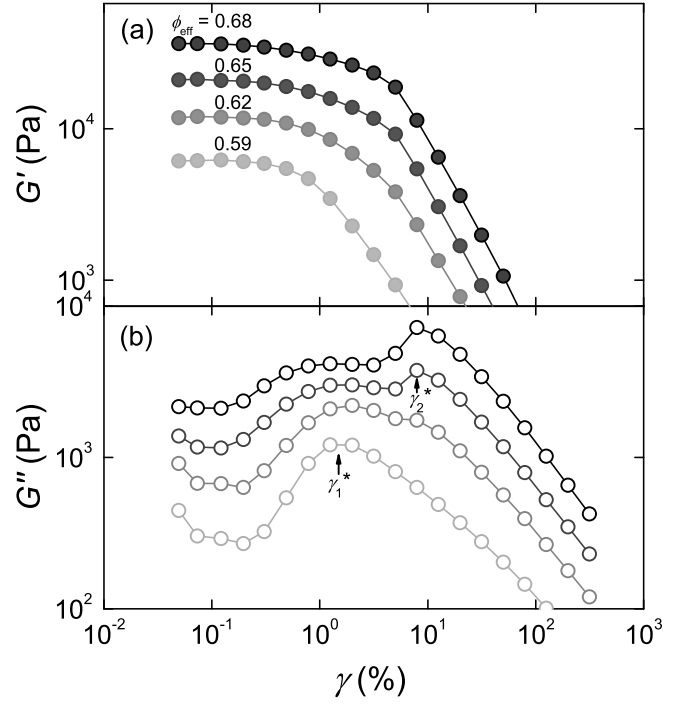


FIG. 8: **Strain-dependent behavior is similar for oil-in-water emulsions stabilized by SDS.** Viscoelastic moduli (a) $G'(\gamma)$ and (b) $G''(\gamma)$ of attractive emulsions stabilized by SDS with $U \approx 21k_B T$ and $a = 250\text{nm}$ for $\phi_{eff} \approx 0.68, 0.65, 0.62$, and 0.59 (progressively lighter colors). Emulsions above ϕ_{RCP} (top two curves) show peaks in G'' at γ_1^* and γ_2^* while those below ϕ_{RCP} (lower two curves) show a single peak at γ_1^* . For clarity, G' and G'' data are multiplied by a factor of $0.7, 0.6$, or 0.5 for $\phi_{eff} = 0.65, 0.62$, or 0.59 , respectively.

7(a)]; this indicates that the elasticity is dominated by the repulsive forces deforming the droplets. For the repulsive emulsions, G'_p drops precipitously as ϕ_{eff} is decreased below ϕ_{RCP} ; by contrast, the elasticity of the attractive emulsions persists far below ϕ_{RCP} [Fig. 7(a)]. Moreover, $G''(\gamma)$ of SDS-stabilized attractive emulsions above ϕ_{RCP} exhibits two peaks at strains $\gamma_1^* \sim 1\% \ll \gamma_r^*$ and $\gamma_2^* \approx \gamma_r^*$, as indicated in Fig. 8(b). Correspondingly, G' decreases weakly for $\gamma > 0.5\%$ before falling more quickly for $\gamma > 10\%$ [Fig. 8(a)]. By contrast, $G''(\gamma)$ of the attractive emulsions below ϕ_{RCP} exhibits a single peak at a strain γ_1^* , and G' decreases smoothly for $\gamma > 1\%$ [Fig. 8]. These data are similar to those obtained for P105-stabilized emulsions; this confirms that our results are more general.

The frequency-dependent mechanical response of emulsions directly reflects the time scales of their structural relaxation. For repulsive emulsions above ϕ_{RCP} , $G''(\omega)$ exhibits a shallow minimum at $\omega \sim 0.1 - 10 \text{ rad/s}$ resulting from the combination of viscous loss at high ω and the configurational rearrangements of the individual droplets at low ω [Fig. 1] [1, 5]. In contrast, for attractive emulsions, $G''(\omega)$ exhibits a minimum at $\omega_{min} \geq 10$

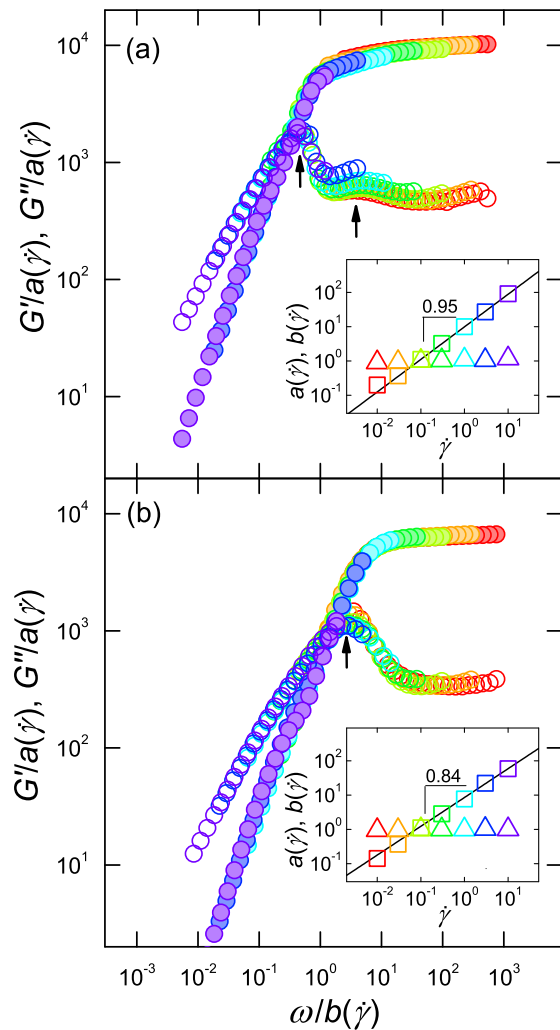


FIG. 9: (Color Online) **Yielding of attractive emulsions is a shear-driven process.** Constant $\dot{\gamma}$ frequency sweep measurements of viscoelastic moduli $G'(\omega)$ and $G''(\omega)$ for two samples with $a = 100\text{nm}$ and $U \approx 9k_B T$ above ϕ_{RCP} (a, $\phi_{eff} \approx 0.73$) and below ϕ_{RCP} (b, $\phi_{eff} \approx 0.66$), shifted onto a single master curve by normalizing by the shear-rate-dependent shift factors $a(\dot{\gamma})$ and $b(\dot{\gamma})$. Inset: corresponding amplitude and frequency shift factors $a(\dot{\gamma})$ (triangles) and $b(\dot{\gamma})$ (squares) versus $\dot{\gamma}$ (squares).

rad/s, as shown in Fig. 2. This further suggests that attractive interactions alter the structural relaxation of emulsions.

The structural relaxation process through which attractive emulsions yield occurs at frequencies much lower than is accessible in a linear rheological measurement, typical of soft glassy materials [5]. We circumvent this problem by performing ω -dependent measurements holding the strain rate amplitude $\dot{\gamma} = \gamma\omega$ constant for different values of $\dot{\gamma}$. A relaxation process of time scale τ gives rise to a peak in $G''(\omega)$ at a frequency proportional

to τ^{-1} [5]. We observe one peak in $G''(\omega)$ for attractive emulsions with $\phi_{eff} < \phi_{RCP}$; strikingly, we observe two peaks in $G''(\omega)$ for those with $\phi_{eff} > \phi_{RCP}$, as indicated in Fig. 9, in stark contrast to the repulsive case [5]. This provides further confirmation that attractive emulsions above ϕ_{RCP} undergo an additional relaxation process during yielding.

The data measured at different $\dot{\gamma}$ can be scaled onto a master curve by rescaling the moduli and frequency, as shown in Fig. 9. The frequency scaling factor $b(\dot{\gamma}) \sim \tau^{-1}$ [5]. We explore its dependence on $\dot{\gamma}$ to directly probe how the time scales of the structural relaxation processes of attractive emulsions depend on shear rate. We find $b(\dot{\gamma}) \sim \tau^{-1} \sim \dot{\gamma}^\nu$ with $\nu \approx 0.8 - 1$ for both relaxation processes in attractive emulsions having ϕ_{eff} both below and above ϕ_{RCP} ; two representative examples are shown in Fig. 9 (inset). This shear-driven behavior is similar to the yielding of colloidal gels [23] and to the yielding of repulsive emulsions above ϕ_{RCP} [5].

IV. CONCLUSION

Our data suggest a simple physical picture of emulsion flow. The rheology of emulsions with slippery bonds of magnitude $U < 1k_B T$ is similar to that of repulsive emulsions; in stark contrast, emulsions with $U > 7k_B T$ show a dramatically enhanced elasticity below ϕ_{RCP} . Moreover, their nonlinear rheology is markedly different from the repulsive case. These attractive emulsions begin to yield under sufficient shear through the breakage of interdroplet bonds at weak points in the emulsion [12]. Attractive emulsions above ϕ_{RCP} also undergo shear-induced configurational rearrangements of the densely-packed droplets, similar to the repulsive case, at larger strain. This is reminiscent of the two-step yielding of attractive colloidal glasses [24]. How this behavior changes with intermediate values of U remains to be explored.

Emulsions are often used to model many other diverse physical systems and are crucial in various technological processes. We find that their linear and nonlinear rheology depend sensitively on the interactions between the droplets. Our results may thus be a useful input to such models and could help guide processes designed to control emulsion elasticity and flow behavior.

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