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Towards a constitutive relation for emulsions exhibiting a yield stress

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Constitutive relations are needed to predict the behavior of complex fluids in nonviscometric flows. This is an area that is largely unexplored for yield stress materials because of the difficulty describing the elastoviscoplastic behavior for arbitrary flows. Here, we measure the shear and extensional rheology of a simple tunable yield stress system: emulsions with different oil volume fractions that allow one to vary the flow properties over a large range. We propose universal concentration scaling laws that produce master curves for the shear and extensional rheology with a minimal number of known emulsion parameters. The extensional viscosity is obtained experimentally using a theory for inelastic shear-thinning materials, demonstrating that elastic stresses are unimportant in the pinching dynamics, and the elastic normal stress differences contribute minimally to the von Mises yield surface. Hence, this shows that material elasticity is unimportant, and an explicit constitutive equation of, for example, Criminale-Ericksen-Filby type, with a Herschel-Bulkley viscosity and a modulus equal to the Laplace pressure is adequate to describe the behavior of such concentrated soft-sphere systems in general steady and low Deborah number unsteady Eulerian and Lagrangian flows.

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Many materials encountered around us are neither simple inelastic liquids nor perfectly elastic solids. Generically, the modeling of the flow behavior of non-Newtonian fluids or solids concentrates on finding a constitutive relation that relates the stress to the deformation and deformation rate. In order to compute the deformation and associated physical properties in arbitrary geometries for such materials, a properly invariant constitutive equation relating the stress to the strain or strain rate is essential. Yield stress fluids, or elastoviscoplastic fluids, are ubiquitous [1], and the development of proper constitutive formulations remains an active area of research. Below the yield stress these materials respond as elastic or viscoelastic solids, while above the yield stress they behave as viscoelastic-plastic fluids [2–5].

We are concerned here with simple yield stress fluids, which are nonthixotropic, i.e., the physical properties remain constant in time. Emulsions, which have long been recognized as prototypical viscoelastic liquids, are the benchmark systems to study the rheological response of simple yield stress materials made up of repulsive soft spheres. In this work we study a model nonthixotropic...
emulsion of oil droplets in an aqueous continuous phase exhibiting a yield stress and establish an invariant constitutive equation that requires only measurements in simple shear [2,6–8]. It is currently well accepted that the shear stress $\sigma_y$ in simple shear of concentrated emulsions and similar yield-stress materials is well described by the phenomenological Herschel-Bulkley equation [3]:

$$\sigma_y(\dot{\gamma}) = \sigma_y + k\dot{\gamma}^n.$$  \hspace{1cm} (1)

Here $\sigma_y$ is the emulsion yield stress, $\dot{\gamma}$ the shear rate, $k$ the flow consistency index, and $n$ the power-law exponent describing the shear-thinning behavior (where $n$ is typically of order 0.5).

The Herschel-Bulkley equation is a good empiricism that is widely applicable, but any equation that fits the shear data (e.g., Caggioni et al. [9]) can be substituted in place of Herschel-Bulkley in the invariant constitutive formulation that is developed here. Emulsions exhibit nonzero normal stress differences in shear, so the Herschel-Bulkley description is incomplete and cannot predict the stress distribution in nonviscometric flows. Invariant constitutive equations that have been developed for yield stress materials (e.g., [10–14]) are generally adaptations of models developed for viscoelastic polymeric liquids, in which memory is an important element. The concentrated emulsions are weakly elastic and do not require such a description.

We show here that the emulsions can be described by a “short memory” explicit equation, such as the Criminale-Ericksen-Filby model [15], which requires three material functions; for the emulsions these functions are the shear viscosity function, a constant modulus that is uniquely determined by the Laplace pressure, and the ratio of the second to first normal stress differences. The material memory scale, which is required to calculate the Deborah number (the ratio of the characteristic time scale of the material to the process time scale) is equal to the shear viscosity divided by the modulus and always leads to small Deborah numbers for the flows studied here. One consequence of the small Deborah number is that the extensional viscosity is close to three times the shear viscosity (a Trouton ratio of three) and can be measured using a methodology derived for inelastic shear-thinning liquids.

We use emulsions made of castor oil in water stabilized by sodium dodecyl sulfate (SDS) as a model system [7,16,17]. A batch of emulsion at a volume fraction $\phi = 0.80$ is prepared by dispersing oil in a 2 wt.% SDS solution with a high-speed emulsifier (Silverson); this results in an emulsion of mean drop radius $\langle R \rangle = 1.6$ $\mu$m and 10% polydispersity as determined from a log-normal distribution fit, see the inset of Fig. 1(a). This emulsion is diluted with the same SDS solution to obtain emulsions with lower $\phi$. The rheological measurements are performed with an Anton Paar MCR 302 rheometer. A 50 mm-diameter cone-and-plate geometry is used with a 1° cone (truncation gap size of 0.101 $\mu$m) and roughened surfaces to avoid wall slip. The experiments are performed at a temperature of 22 $^\circ$C set by a Peltier system. A humidity chamber around the geometry suppresses evaporation during the measurement time. Steady shear measurements are performed using shear rate sweeps from $10^{-3}$ to $10^3$ s$^{-1}$ on samples presheared at a shear rate of 100 s$^{-1}$ for 30 s, and then followed by a rest period of 30 s to create a controlled initial state. The flow curves are fitted to Eq. (1) to determine $\sigma_y$, $n$ and $k$ as functions of volume fraction $\phi$. For the (athermal) model system considered here, the dependence of the yield stress on volume fraction is well characterized as a power law in the distance to the random close packing maximum volume fraction $\phi_j \sim 0.64$:

$$\sigma_y(\phi) = \sigma_0(\phi - \phi_j)^\Delta,$$  \hspace{1cm} (2)

with the Laplace pressure $\sigma_0 = \Sigma_{o/w}/\langle R \rangle$, where $\Sigma_{o/w}$ is the interfacial tension of the two phases and $\Delta$ a constant characterizing the nature of the jamming transition [16]. We also expect a concentration-dependent shift factor with dimensions of time for the shear rate,

$$\tau_0(\phi) = \frac{\eta_0}{\sigma_0(\phi - \phi_j)^\Gamma},$$ \hspace{1cm} (3)

with $\eta_0 = 1$ mPa s the viscosity of the continuous phase and $\Gamma$ a constant [16]. It has been shown that using $\Delta$ and $\Gamma$, with $\Delta/\Gamma \approx 0.5$, leads to a universal rescaling of all concentration-dependent
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FIG. 1. Universal constitutive laws for shear stress and first normal stress differences in concentrated emulsions. (a) A cone-plate geometry is used to investigate the shear stress and normal stress difference ($N_1$) of an oil in water emulsion. The close up shows a typical confocal microscopy picture of the investigated system and the droplet size distribution. (b) Shear stress as a function of shear rate for different volume fractions $\phi$ between 0.72 and 0.80. Continuous lines are Herschel-Bulkley fits of the experimental data [Eq. (1)]. (c) Collapse of shear flow curves onto a master curve when plotted according to Eqs. (2) and (3). The black line corresponds to a Herschel-Bulkley fit with $\Delta/\Gamma = 0.55$. (d) First normal stress difference as a function of shear rate for the same set of emulsions (same color code). Continuous lines are values predicted by Eq. (4). (e) Collapse of the normal stress difference curves when plotted according to Eq. (6). Solid line is the fit using the Herschel-Bulkley parameters.

Figure 1(d) shows $N_1$ for different volume fractions. Normal force measurement of yield stress materials with commercial rheometers is notoriously difficult. Here we perform a shear rate sweep (from 50 to 3000 s$^{-1}$, remaining at each shear rate for 30 s to reach equilibrium) in order to minimize instrumental effects such as drift [18] and to obtain reproducible data [19]. After every shearing step of 30 s, a 15 second “rest” period is set, during which no shearing is applied. This allows a reset of the normal force in each step. An example of such a flow sweep test protocol can be found in Fig. 1 of the Supplemental Material [20], together with the corresponding normal and shear stress data obtained for $\phi = 0.8$. Combining the results shown in Figs. 1(b) and 1(d) also reveals that the first normal stress difference is a quadratic function of the shear stress [19],

$$N_1 = \alpha_1 \sigma_s^2,$$

with a proportionality coefficient $\alpha_1$ that is independent of the volume fraction of the emulsion (see Fig. 2 of the Supplemental Material [20]). We find $\alpha_1 = 8 \times 10^{-4}$ Pa$^{-1}$, which is equal to the inverse of the Laplace pressure $\sigma_0^{-1} = (R)/\Sigma_o/w = 8 \times 10^{-4}$ Pa$^{-1}$. The stress scale is therefore set by the droplet size and the interfacial tension of the two phases ($\Sigma_o/w = 2$ mN/m). Combining Eqs. (1)
FIG. 2. Universal constitutive laws for shear rheology and elongational rheology in concentrated emulsions. (a) Sequential photographs of liquid bridges between two plates moving apart, for volume fractions $\phi = 0.72$ and 0.80 (top to bottom), at times to breakup $t_c - t = 0.15, 0.05, 0.012,$ and 0.001 s (left to right). Scale bar is 150 μm. (b) Viscosity as a function of deformation rate for different values of $\phi$. Data points are obtained from elongational measurements. Continuous lines are Herschel-Bulkley predictions based on shear rheology measurements [Eq. (1)]. (c) Elongational flow curves collapse onto a master curve when plotted according to Eqs. (2) and (3) with $\Delta_1 = 2$ and $\Gamma_1 = 4$. The black line corresponds to a Herschel-Bulkley fit with $\Delta_1/\Gamma_1 = 0.55$.

and (4) yields

$$N_1(\dot{\gamma}) = \alpha_1(\sigma_y + \kappa \dot{\gamma}^n)^2$$
$$= \alpha_1(\sigma_y^2 + 2\sigma_y \kappa \dot{\gamma}^n + \kappa^2 \dot{\gamma}^{2n}).$$

In the limit of low shear rates, this reduces to

$$N_1(\dot{\gamma} \to 0) \equiv N_{1,0} = \alpha_1 \sigma_y^2$$
$$= \alpha_1 \sigma_0^2(\phi - \phi_j)^{2\Delta}$$
$$= \sigma_0(\phi - \phi_j)^{2\Delta}.$$

In Fig. 1(e), we plot the normalized first normal stress difference $N_1/N_{1,0}$ and show that all experimental curves collapse onto a master curve, where the Herschel-Bulkley parameters [Eq. (1)] are determined from the shear rheology measurements. This indicates that the normal stress values can be predicted from only the rescaled Herschel-Bulkley parameters and the Laplace pressure. In earlier work of Seth et al. [21], shear and normal stresses were also measured for emulsions but rescaled in a different manner, with the contact elastic modulus and the yield strain as parameters. In Fig. 3 of the Supplemental Material [20] we rescale the normal stress data from the work of Seth et al. [21] using only the parameters determined from the shear rheology measurements and show that for their data all experimental curves also fall onto our master curve. In addition, we find $\alpha_1 \approx 2.5 \times 10^{-4}$ Pa$^{-1}$ which equals the Laplace pressure $\sigma_0^{-1} = \langle R \rangle / \Sigma_{o/w} = 2.5 \times 10^{-4}$ Pa$^{-1}$, with the droplet size $\langle R \rangle = 1.25 \mu m$ and interfacial tension $\Sigma_{o/w} = 5$ mN/m [21]. Hence, we can anticipate that this relation between shear and normal stresses through the Laplace pressure is generally characteristic of concentrated emulsions.

We now turn to elongational deformations to get to a more complete rheological characterization of our emulsions. To study the elongational thinning of the emulsions we use a custom built filament stretching rheometer (see Fig. 4 of the Supplemental Material [20] for experimental details on the setup), similar to the one described in [17,22]: A 40 μL droplet is placed between two circular end plates of 5 mm diameter, initially spaced 3 mm apart, which are moved apart at a very slow and constant velocity of 20 μm/s, giving rise to a liquid bridge that eventually breaks (at time $t_c$) because of capillarity [17]. The evolution of the liquid bridge is recorded with a fast camera (Phantom V7)
allowing frame rates up to 10,000 frames per second. The camera is equipped with a microscope tube lens with an objective up to 12× magnification (Navitar) to record the drop profile with a spatial resolution of \( \sim 3 \mu m \) per pixel. The setup is placed in a closed chamber continuously flushed with humid air (80\% RH) to prevent evaporation during the measurements. Figure 2(a) shows a typical sequence of the breakup dynamics of the concentrated emulsions for two different volume fractions (top to bottom: 0.72 and 0.80). The corresponding minimum thread radius \( h_{min} \) as a function of the rescaled time can be found in Fig. 5(a) of the Supplemental Material [20]. This result allows us to extract the fluid viscosity from the thinning dynamics, using the following equation proposed by [23]:

\[
\eta_e/3 = \eta_s = 2^{n-1} n^n \phi_0(n) \Sigma_{emulsion/air} \left( \frac{dh_{min}}{dt} \right)^{-1},
\]

where \( \phi_0(n) \) is a constant tabulated in [23–25] and \( \Sigma_{emulsion/air} \) the interfacial tension of the emulsion with air. The prefactor \( 2^{n-1} n^n \phi_0(n) \) is determined from two-dimensional simulations for bridges of power-law fluids under creeping flow conditions [17,24]. For shear thinning inelastic fluids, analytical investigations utilizing a 1D approximation [23,25–27] suggest that the minimum neck radius \( h_{min} \) should scale as \( (t_c - t)^{\alpha} \), where \( t_c \) is the breakup time and \( n \) is the same exponent as the power law index measured from the shear rheology [Eq. (1)].

To test this, we use the shear-thinning exponent \( n = 0.5 \) obtained from the shear rheology measurements. Figure 2(b) shows the resulting shear viscosity \( \eta \) extracted from Eq. (7) as a function of the deformation rate \( \dot{\epsilon} = (2/h_{min})(dh_{min}/dt) \) obtained from the thinning dynamics (symbols). In this figure, we also include the fits of the data extracted from the shear rheology measurements of Fig. 1 (solid lines). We find good agreement between the shear rheology obtained from simple shear measurements and the elongational experiments when using Eq. (7) with \( n = 0.5 \) for an inelastic liquid.

The extensional data span only a limited range of deformation rates \( 0.1 \text{ s}^{-1} < \dot{\epsilon} < 100 \text{ s}^{-1} \), and a local power-law fit to the shear data over this deformation rate range would in fact give values ranging from just above \( n = 0 \) to \( n = 0.5 \) at each \( \dot{\epsilon} \). A value of \( n = 0.2 \) provides a better fit to the thinning dynamics at lower values of \( \dot{\epsilon} \), whereas \( n = 0.5 \) gives better agreement at higher shear rates [Fig. 2(b)], but the result is sufficiently robust using \( n = 0.5 \) over the entire range. The applied theory is rigorously valid for power law indices above 0.5 [24].

Our findings thus emphasize that a simple balance between capillary and viscous stresses allows one to retrieve the elongational rheology of an emulsion independently of its volume fraction: once the curves are rescaled, the same universal behavior as for the shear rheology is retrieved. It is important to note that the emulsions are viscoelastic liquids, but the fluid elasticity does not appear to play a major role in the extensional dynamics, which are analyzed here using a theory for inelastic liquids. This is likely because the Deborah number, the ratio of the relaxation time to the process time scale, is small (see the Supplemental Material [20]).

While we measure finite elastic normal stresses in the shear experiments, which supports the notion that the emulsions are viscoelastic liquids in the flowing state, the elasticity appears to play little or no role in the extensional dynamics and is therefore unlikely to be important in other flows in which the process time significantly exceeds the relaxation time, which we estimate to be \( \approx 1 \times 10^{-4} \) Pa \(^{-1}\). We have data only for \( N_1 \) but \( N_2 \) is expected to have the same functionality and to be comparable in magnitude to \( N_1 \) [19]. Thus, near yielding we will obtain
$N_1^2, N_2^2/6\sigma_s^2 \ll 0.1$, implying that the normal stresses $(N_1, N_2)$ have a negligible contribution to the yield criterion [Eq. (8)] and that the yielding is close to that for an inelastic liquid.

Direct visualization of the liquid bridge during the elongational flow [Fig. 2(a)] also confirms the negligible effect of elastic forces. One should recover self-similar profiles in the breakup of emulsions for well controlled and sufficiently slow initial stretching rates [17]. This is confirmed in Fig. 6 of the Supplemental Material [20], where we plot the profiles just prior to pinch off for the different volume fractions. These results agree well with theory and simulations for the pinch off of inelastic power law fluids [23–25].

Finally, we show, in Fig. 2(c), that the reduced set of parameters used for rescaling the shear flow curves can be used to collapse the experimental elongational rheology curves onto a master curve. This curve is well predicted by the Herschel-Bulkley equation [Eq. (1)], already predetermined from the shear rheology measurements in Fig. 1(b). This affirms that one can predict the elongational rheology with the same parameters as for the shear flow deformation.

In conclusion, in this work we investigated the steady state strain rate dependence of the shear and elongational viscosities and the normal stresses of concentrated emulsions. The shear and elongational viscosities and the normal stresses are all the necessary ingredients for formulating a constitutive equation for steady-state and low Deborah number unsteady Eulerian and Lagrangian flows. The fact that the elongational stresses can be predicted using only shear data, as for an inelastic material, strongly suggests that the emulsion rheology in the flowing state does not require a memory-type equation like those incorporated in the constitutive models of Saramito [13] and de Souza Mendes and Thompson [14], but rather than an explicit small Deborah number equation like the Criminale-Ericksen-Filbey model (CEF) [15] should be sufficient, where the material time for use in computing the Deborah number equals the shear viscosity divided by the Laplace pressure:

$$\sigma = -p\mathbf{I} + \eta\mathbf{A}_1 - \frac{1}{2\sigma_0}\eta^2\beta\mathbf{A}_2 + \frac{1}{2\sigma_0}(1 + \beta)\eta^2\mathbf{A}_1^2. \tag{9}$$

The first and second Rivlin-Ericksen tensors are $\mathbf{A}_1 = \nabla v + \nabla v^T$ and $\mathbf{A}_2 = \frac{\partial \mathbf{A}_1}{\partial t} - (\nabla v)^T \cdot \mathbf{A}_1 - \mathbf{A}_1 \cdot (\nabla v)$. The CEF equation requires three functions of the deformation rate, all of which can be measured in a viscometric shear flow. For the emulsions studied here the rescaled Herschel-Bulkley equation and the Laplace pressure completely determine two of these functions, while the parameter $\beta = N_2/N_1$ is expected to be in the interval $-0.5 \leq \beta \leq -1$ [19]. The extensional viscosity of the CEF equation is three times the shear viscosity at the same deformation rate, plus a weak function of extension rate that is small for the normal stresses observed and estimated for the emulsions, which is why treating their rheology as approximately inelastic with a Herschel-Bulkley viscosity will be adequate for applications in which $De \ll 1$, i.e., when $\eta((\mathbf{A}_1 : \mathbf{A}_1)^{1/2}) \ll \Sigma \eta/w/\langle R \rangle$, where $\eta$ is the Herschel-Bulkley viscosity at the relevant value of the second invariant of the deformation-rate tensor.

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[20] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevFluids.8.123301 for more details on the experimental method and setup, the prefactor, the rescaling of the shear stress and normal stress difference data from Seth et al., the interpretation of the pinch off experiments and the spatial profiles of the fluid necks from the pinch off experiments. It includes the references [18,21,29].


