Supporting Information

Diffusing wave microrheology of highly scattering concentrated monodisperse emulsions

H.S. Kim, N. Şenbil, C. Zhang, F. Scheffold, and T.G. Mason

Emulsion preparation, handling, and characterization. We prepare 500 mL of a crude microscale premix emulsion having oil droplet volume fraction $\phi = 0.20$ in 2.5 mM aqueous SDS solution using a mixer (Fisher Scientific, PowerGen 1000 S1, speed 3). After allowing any residual foam to disappear, we process this premix emulsion using a high flow rate microfluidic homogenizer (Microfluidics, M-110P; 75 $\mu$m diameter Y-chamber) at a liquid pressure of about 70 MPa. We process the resulting emulsion through this homogenizer 4 additional times before collecting and diluting the resulting emulsion in 500 mL of 60 mM aqueous SDS solution after the final pass. We repeat the above procedure until we obtained a large volume of polydisperse emulsion ($\sim 20$ L). We prepare a master sample of concentrated monodisperse emulsions by performing size-fractionations on obtained large batch of polydisperse emulsions. We use size-fractionation steps developed by Bibette et al. (39) to decrease the polydispersity and form relatively monodisperse emulsions. We concentrate the resulting uniform emulsions to a higher droplet volume fraction via centrifugation (Beckman L8-55 ultracentrifuge, SW-28 swinging bucket, 10k rpm, 1.25 hr). When these uniform droplets are randomly concentrated to high droplet volume fractions, PDMS emulsions form a dense plug of cream, which is a soft viscoelastic solid (40–42), at the top of a rigid polycarbonate sample with 10 mM SDS solution using an analytical balance $\pm 0.729$ mg. We have characterized the droplet volume fraction of this master sample ($\phi = 0.562$, top to bottom, on left), for a fractionated oil-in-water emulsion having average radius $a = 459$ nm, stabilized using 10 mM SDS, at a fixed peak shear strain of $\gamma = 0.01$. Measured plateau values of the mechanical shear storage modulus $G_p$, (open squares at 1 rad/s) are almost equal to $|G^*|$, over the frequency range explored.

Mechanical shear rheometry. Before making measurements on emulsions, we ensured that our rheometer was calibrated by using a polymeric viscoelastic standard in an oscillatory frequency sweep; both the magnitude and frequency associated with the crossover matched reported values for the standard to within $\pm 10\%$. At each $\phi$, the loaded emulsion was subjected to a pre-shear at a strain rate $\dot{\gamma} = 100$ s$^{-1}$ for a duration of 60 s. After this pre-shear, the emulsion was allowed to relax for 300 s prior to starting the oscillatory rheological tests. At a shear strain $\gamma = 0.01$, a frequency sweep was performed from an angular frequency $\omega = 10$ rad/s down to 0.01 rad/s. A strain sweep at $\omega = 1$ rad/s from $\gamma = 0.002$ up to 2 was also performed, and we verified that the strain of 0.01 selected for the frequency sweep was below the yield strain, ensuring that reported $|G^*|$ and $G_p$ values correspond to the linear regime. In the reported frequency sweeps, at lower $\phi$, the reliable range of is limited by the rheometer’s torque transducer at low $\omega$ and by the inertia of the cone at high $\omega$, so reported frequency sweeps at the lowest do not cover as wide a range in as at higher. The temperature $T$ during all measurements using mechanical rheometry was regulated by a circulating water bath to $T = 20 \pm 1^\circ$C. The magnitudes of the linear complex shear modulus $|G^*|$ for the set of 10 mM SDS-stabilized PDMS O/W monodisperse emulsions, which all have an average droplet radius of $a = 459$ nm, are characterized by mechanical rheometry at room temperature $T = 20^\circ$C. The frequency dependent behavior of $|G^*|$ for $0.562 < \phi < 0.729$ is shown in Fig. S1. Over the range of $\phi$ measured, the emulsions are dominantly elastic and exhibit a nearly frequency-independent dominant
elastic storage modulus $G_{\text{p,mех}}$, which spans about three orders of magnitude. At the lowest $\phi$ for which torques are above the lower limit of the rheometer’s transducer, we find that the rise in both $|G'|$ and $G_{\text{p,mех}}$ is very rapid as $\phi$ is increased only slightly, consistent with prior linear rheological measurements on similar monodisperse emulsions that have different average $a$ (41).

**Entropic-Electrostatic-Interfacial Emulsion Model.** We use the entropic-electrostatic-interfacial (EEI) model to calculate the predicted $G'_p$ for our emulsions as described in reference (30). For our specific fractionated emulsion system and measurement conditions, we use the following parameter values: average radius $a = 459$ nm and temperature $T = 293$ K. Other parameters that we use in the EEI model have been obtained for SDS-stabilized PDMS oil-in-water emulsions having the same bulk SDS concentration of 10 mM: surface tension $\sigma = 9.8$ mN/m, effective surface potential $\psi_0 = 270$ mV; Debye screening length $\lambda_D = 3.4$ nm, disordered hard sphere jamming point $\phi_c = 0.646$, and dimensionless prefactor parameters $\alpha = 0.85$ and $\xi = 0.15$. We identified the range of $\phi$ at which the contributions to $G'_p$ are dominated by the entropic, electrostatic, and interfacial contributions to the free energy per droplet, and labeled these regimes entropic, electrostatic jamming, and interfacial jamming regimes, respectively (see Fig. 1).

**Diffusing Wave Spectroscopy.** From the measured normalized intensity autocorrelation function $g_1(t)$, we extract the normalized field correlation function $g_2(t)$ using the Siegent relation $g_2(t) = 1 + \beta g_1(t)$, where $\beta = 0.95$ is the instrument-specific coherence factor that can be obtained experimentally (5) by extrapolation to $t \to 0$. We then determine dimensionless $x(t)$, describing the ensemble- and time-average droplet translational dynamics, in the transmission slab geometry using (31):

$$g_1(t) = \frac{(\frac{x}{t} + \frac{1}{2}) \sqrt{x(t)}}{(1 + \frac{x}{t} \sinh (\frac{\sqrt{\gamma_M} \sqrt{x(t)}}{x} \cosh (\frac{\sqrt{\gamma_M} \sqrt{x(t)}}{x})],$$

where $k = 2\pi a / \lambda_{\text{DWS}}$ is the wavenumber in the solvent and $x(t) = k^2 \langle \Delta r^2(t) \rangle$. To obtain the true self-motion probe MSD we multiply the apparent MSD, $\langle \Delta r'^2(t) \rangle$, with the average structure factor: $\langle \Delta r'^2(t) \rangle = \langle S(q) \rangle (\Delta r^2(t))$. We determine the average structure factor using the CSA: $\langle S(q) \rangle = \ell_{\text{DSA}} / \ell^*$, based on the experimental values of $\ell^*$ shown in Fig. 3 (b). The validity of this relation has been demonstrated for micron sized Mie scatterers, polystyrene spheres with $n \approx 1.6$ in water, up to concentrations of $\phi \approx 0.5$ (35). We emphasize however, that in the Rayleigh-Gans-Debye limit, $\frac{2\pi}{\lambda_D} a |1 - \frac{\pi a}{\lambda_D}| \ll 1$, CSA is not restricted to $\phi < 0.5$. It is strictly valid as long as the scatterers retain their spherical shape, and it is independent of any prior knowledge about $S(q)$. In our case $\frac{2\pi}{\lambda_D} a |1 - \frac{\pi a}{\lambda_D}| = 0.3$ and we thus expect the CSA to hold quantitatively up to concentrations $\phi \approx 0.75$, beyond which droplets start to deform. Based on the EEI model, we calculate that the average surface area per droplet has changed by only $\approx 2\%$ at the largest $\phi = 0.729$ we probe, so the droplets remain nearly spherical for all $\phi$ in our study. In the backscattering geometry, we independently determine the $\gamma_{\text{DWS}}$ factor for cross-polarized detection and also the photon loss parameter $c$ using 910 nm diameter polystyrene spheres, which have $c' \sim 200$ $\mu$m similar to the emulsion samples, by matching backscattering $g_1(t)$ with transmission $g_1(t)$ using:

$$g_1(t) \propto \exp \left(-\frac{\gamma_{\text{DWS}} \sqrt{x(t) + c}}{1 + \frac{2}{\sqrt{x(t) + c}}} \right).$$

The photon loss parameter $c$ accounts for light leakage out of the cuvette’s side walls or via transmission (5). Using these independently determined values, $c = 0.07$ and $\gamma_{\text{DWS}} = 1.95$, the MSDs for droplets in the backscattering geometry are then calculated. We find that MSD’s obtained from transmission and backscattering experiments for the same emulsions overlap. The transmission experiment probes longer light paths and thus are more accurate for smaller displacements (i.e. short times, high concentrations), whereas backscattering experiments perform better at larger displacements, extending the range of long-time plateau displacements that can be probed by DWS.

**DWS Collective Effects: Distinct Part of the Hydrodynamic Function.** When considering collective scattering effects, we have neglected an additional possible $q$-dependent term due to hydrodynamic interactions, known as the distinct part of the hydrodynamic function $H^d(q)$ (31, 34, 44). The contribution of $H^d(q)$ is secondary to $(S(q))$, and over the range of densities previously studied, it exhibits relatively weak $q$-dependent oscillations $\pm 20\%$, which largely cancel out when taking the average over all scattering vectors. For $q \gg q_{\text{max}}$, it vanishes completely. Moreover, hydrodynamic effects would not be expected to influence the measured long-time plateau MSD of a solid emulsion.

**Micro rheological Plateau Storage Modulus and Creep Compliance.** The generalized Stokes-Einstein relation (GSER) for the frequency-dependent viscoelastic shear modulus using a 3D MSD, assuming stick boundary conditions, and ignoring inertia is given by (6):

$$\tilde{G}(s) = \frac{k_B T}{\pi a s (\Delta r^2(s))},$$

where $s$ is the Laplace frequency, $a$ is the radius of a probe sphere, $k_B$ is Boltzmann’s constant, and $T$ is the temperature. We re-write this, solving for the MSD in the Laplace domain in terms of the $s$-dependent shear modulus $\tilde{G}$:

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

We assume that a suitable model for the viscoelastic modulus of dense emulsions includes constant and linear terms appropriate for a harmonically bound Brownian particle as well as a term proportional to $s^{1/2}$ (8, 38):

$$\tilde{G}(s) = G'_p [1 + (s \tau)^{1/2}] + \eta_\infty s.$$  

Here, while retaining all terms in Mason et al.’s prior work, we have introduced a time scale $\tau$, associated with the $s^{1/2}$ power-law term, that was not in this prior work. Moreover, we reason that the magnitude of this $s^{1/2}$ term is most appropriately set by $G'$, since either electrostatic or interfacial contributions to the quasi-equilibrium free energy can dominate $G'$ over the range of $\phi$ that we explore in our study. We substitute this model into the equation for the Laplace-domain MSD and re-express the resulting expression using the denominator in the integrator that can be readily separated:

$$\langle \Delta r^2(s) \rangle = \frac{k_B T}{\pi a \eta_\infty} \frac{1}{s(s^{1/2} + y)(s^{1/2} + z)},$$
where we have defined \( y \) and \( z \) such that
\[
y + z = G_p' \Delta^3/\eta_\infty \quad \text{(S7)}
\]
and
\[
yz = G_p'/\eta_\infty. \quad \text{(S8)}
\]
Here, the value of \( G_p' \) is related to the long-time plateau value of the MSD through the GSER in that limit:
\[
G_p' = k_B T \left( \frac{\pi a}{\eta_\infty} \right). \quad \text{(S9)}
\]
The prefactor in this equation for plateau values differs from the prefactor proposed in earlier work (see eq. (16) of reference (8)), and the above equation for plateau values is completely self-consistent with the broader framework of the GSER. The complete time-domain MSD is given by the inverse Laplace transform operation, \( L^{-1} \), acting on the frequency domain MSD:
\[
\langle \Delta r^2(t) \rangle = L^{-1} \left\{ \langle \Delta \tilde{r}^2(s) \rangle \right\}. \quad \text{(S10)}
\]

Using Mathematica functions `Apart` and `InverseLaplaceTransform`, we obtain the time-domain MSD involving the complementary error function, erfc:
\[
\langle \Delta r^2(t) \rangle = \frac{k_B T}{\pi a \eta_\infty} \frac{(y - z) + z e^{yz^2} \text{erfc}(y \sqrt{t}) - ye^{z^2} \text{erfc}(z \sqrt{t})}{y^2 z - y z^2}. \quad \text{(S11)}
\]

We fit our corrected DWS MSDs using this formula in Mathematica through the function `NonlinearModelFit`, yielding values for \( G_p' \), \( \tau \), and \( \eta_\infty \). The above equation for the time-dependent MSD directly translates into a prediction of linear viscoelastic response in terms of the shear creep compliance \( J(t) \), again assuming stick boundary conditions for the GSER (7):
\[
J(t) = \frac{\pi a \langle \Delta \tilde{r}^2(t) \rangle}{k_B T}, \quad \text{(S12)}
\]
which after substitution of the MSD yields:
\[
J(t) = \frac{(y - z) + z e^{yz^2} \text{erfc}(y \sqrt{t}) - ye^{z^2} \text{erfc}(z \sqrt{t})}{\eta_\infty (y^2 z - y z^2)}. \quad \text{(S13)}
\]
Considering the long-time limit, the plateau creep compliance \( J_\infty \) is proportional to the long-time plateau MSD:
\[
J_\infty = 1/G_p' = \frac{\pi a \langle \Delta \tilde{r}^2 \rangle}{k_B T}. \quad \text{(S14)}
\]

In the main text, microrheological DWS-GSER results given by the above equations have an additional subscript ‘GSER’ to distinguish them from mechanical results. Although our motivation for establishing these time-domain formulas is consistent with prior findings for emulsions (8, 38), we note that similar \( s^{1/2} \)-contributions to the linear viscoelastic shear modulus can arise from hydrodynamic interactions in dense suspensions of hard spheres (45), so the equations we have developed might also be applicable to these dense systems as well. These equations might also potentially apply to certain elastic polymer systems that are in a viscous solvent.

**DWS MSDs at very short sub-\( \mu \)s times.** Several different effects make the interpretation of DWS \( g_2(t) \) at very short times particularly challenging. Backscattering DWS creates a much shorter overall distribution of light paths, and this complicates analysis at very short times; so, our discussion here largely centers on transmission DWS. Besides the simple translational motion of the probes associated with an effective high frequency viscosity \( \eta_\infty \), the two most prominent influences on DWS \( g_2(t) - 1 \) are the effective inertia of the droplet-probes (3, 6) as well as their shape fluctuations (28). We have largely suppressed shape fluctuations by using a PDMS oil inside droplets that has a higher viscosity, over one order of magnitude, compared to the oil viscosity at which shape fluctuations of similarly sized oil droplets in water have been readily observed (28). However, the influence of the inertia of the droplet-probes in our study can still be seen for time scales shorter than the characteristic inertial time (3), and we find that DWS MSDs of droplets in our system have log-slopes greater somewhat larger than one for these very early times (i.e. extracted MSDs appear super-diffusive). Inertial effects are most evident at the few lowest values of \( \phi \) we have studied. Although we only fit DWS self-motion MSDs for times greater than the characteristic inertial time to obtain rheological parameters, the influence of probe inertia on the fit parameter \( \eta_\infty \) becomes evident at these lower values of \( \phi \). In Fig. S2, we report the values of the fit parameter \( \eta_\infty(\phi) \) for the emulsions in our study. The rise in \( \eta_\infty(\phi) \) for \( \phi > 0.60 \) could potentially be explained in the future by a model that considers the complex viscous flows in the continuous phase of a jammed and weakly deformed emulsion at high \( \phi \). Since the quasi-equilibrium EEI model does not include any hydrodynamic contributions, it can only be used to compare with experimental \( G_p' \). However, for \( \phi < 0.60 \) the fit parameter values for \( \eta_\infty \) in Fig. S2 cannot be taken literally as rheological values because of inertial effects. We find that the other two longer-time parameters \( G_p' \) and \( \tau \) do not strongly depend on deviations in \( \eta_\infty \) needed to make \( \eta_\infty(\phi) \) a monotonically increasing function, which would be expected rheologically. Exploring the very early time corrections for both inertia and shape fluctuations that would be required to extract translational DWS self-motion MSDs of droplet-probes over a wide range of emulsion compositions would be an interesting direction for future studies.