Controlling and Predicting Droplet Size of Nanoemulsions: Theoretical Predictions with Experimental Validation

S1. Details of rheology and interfacial tension measurement

Shear viscosity measurements were performed using a cone and plate rheometer for all the oil phases used for preparation of O/W nanoemulsions. The diameter and angle of the cone used in rheological experiments were 60mm and 2^0 respectively. The shear rate ($\dot{\gamma}$) was varied from 1 s^{-1} to 500 s^{-1}. The results from the cone and plate experiments have been plotted in Figure 1. As the figure shows, all the oil phases show Newtonian behavior as viscosity is independent of shear rate. Also, we could get almost two orders of magnitude variation in viscosity which helped in validating our theory for the large Oh regime.
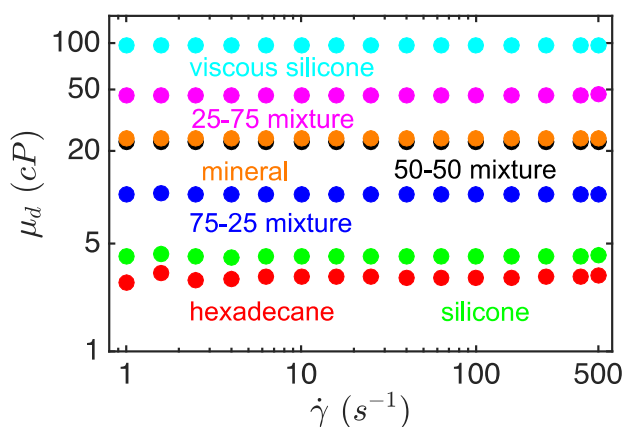

Figure 1. Data for viscosity of different oils as a function of shear rate.

Interfacial tension measurements were performed using inverted pendant drop experiments. An inverted drop of oil was created in aqueous solution with 175mM SDS. The interfacial tension was measured using the drop shape analyzer software provided by Rame-Hart instruments co. The experiments were repeated multiple times to gain confidence on the values of the interfacial tension. The uncertainty in measurements was observed to be around 20%. The interfacial tension snapshots for different oil systems have been reported below.
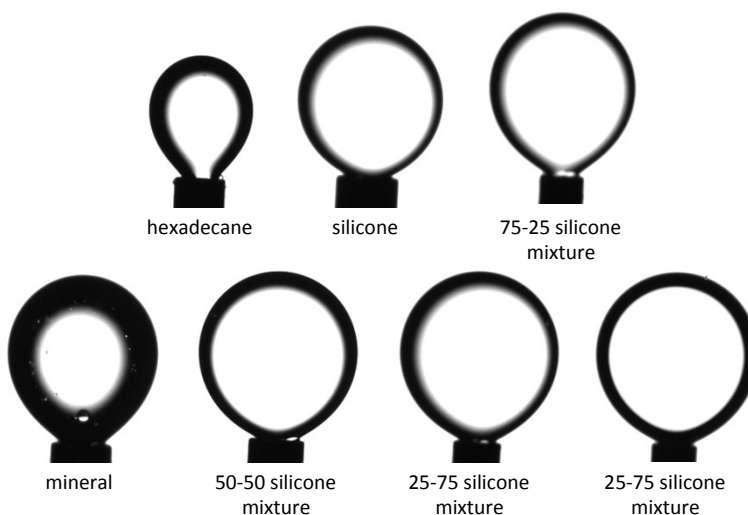

Figure 2. Snapshots of an inverted oil droplet suspended in aqueous solution with 175mM SDS for interfacial tension experiments.

S2. Prediction of power density for homogenizer and ultrasonicator

Power density input is the power input per unit mass. Hence, prediction of power density for homogenizer ε_h is straightforward since power input is $\Delta P \times Q$, where ΔP is the pressure drop across the homogenizer and Q is the flowrate in the homogenizer. The total mass of liquid inside the homogenizer is $\rho_c V_{homogenizer}$, where ρ_c is the density of the continuous phase and $V_{homogenizer}$ is the volume of the homogenizer. Hence, one can write the power density for the homogenizer as:

$$\varepsilon_h = \frac{\Delta P \times Q}{\rho_c V_{homogenizer}}$$

For Avestin-C3 homogenizer, we know that $\Delta P \sim 1000$ bar and $Q = 3L/hr$. Also, $\rho_c = 1000\ kg/m^3$. $V_{homogenizer}$ is difficult to predict since homogenization is a dynamic process and involves continuous movement of the homogenizing valve. Also, since gap height is function of ΔP, some portion of homogenizer volume might also change with ΔP. For the sake of simplicity, we assumed the volume of homogenizer is not a function of time and ΔP. With this assumption, we can estimate $V_{homogenizer}$ volume as diameter of the valve is on the order of $1\ mm$ (measured) and the height between the homogenizer walls is also $1\ mm$ (fair assumption since the gap height is on the order $1-10\ \mu m$ and sudden expansion takes place after that). This predicts a $V_{homogenizer} \sim 10^{-9}\ m^3$. Since we have assumed $V_{homogenizer}$ is constant, $\varepsilon_h \propto \Delta P$.

For predicting the power density on the ultrasonicator ε_s, since the ultrasonicator gives us the power consumed by ultrasonicator as a function of set amplitude, we can calculate the corresponding pressure amplitude (P_A). Now, we can use the correlations mentioned below to estimate bubble collapse time (τ_b) (taken from: Mason, Timothy J., and John P. Lorimer. "Applied sonochemistry." *The uses of power ultrasound in chemistry and processing* (2002): 1-48)

$$\tau_b \sim \frac{R_b}{\sqrt{\dfrac{P_A + P_{atm}}{\rho_c}}}$$

$$R_b \sim \frac{1}{\omega}(P_A - P_{atm})(\frac{1 + 0.67\left(\dfrac{P_A}{P_{atm}} - 1\right)^{\frac{1}{3}}}{\sqrt{\rho_c P_A}})$$

where, R_b is the cavitation bubble radius and ω is the frequency of ultrasonication. Once we obtained these values, we can write ε_s as:

$$\varepsilon_s \sim \frac{P_A + P_{atm}}{\tau_b \rho_c}$$

As one can observe, ε_s is not a monotonic function of P_A (or amplitude). In our system, we observed that the above correlations predict that ε_s is not a sensitive function of amplitude. Also, we find that $\tau_b \sim 1\ \mu s$, $P_A \sim 1\ atm$. Based on the correlations mentioned above, both ε_h and ε_s come to be on the order of $10^8 \frac{W}{kg}$.

S3. Universal collapse of $We_{crit,d}$ with Oh for homogenizer and ultrasonicator

As mentioned in the article, proposed scaling relation, $We_{crit,d} = C_4\ Oh^{0.4}$ showed excellent agreement with the droplet size data from both homogenizer and ultrasonicator. However, the values of C_4 were

similar for both preparation methods suggesting a universal collapse. Hence, we have re-plotted the data from homogenizer and ultrasonicator. The plot below shows the merit of approaching the problem of droplet size prediction in the dimensionless form.
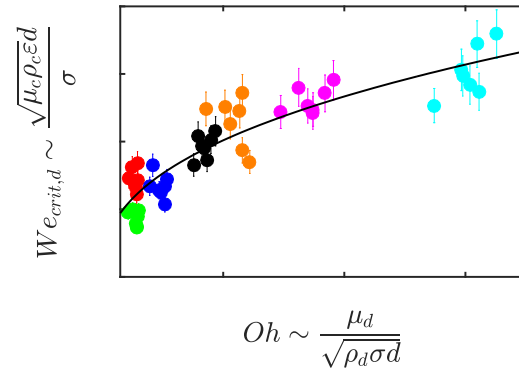

Figure 3. Plot of $We_{crit,d}$ vs Oh for both homogenizer and ultrasonicator. The plot shows the universal collapse of the droplet size data to the predicted theory.
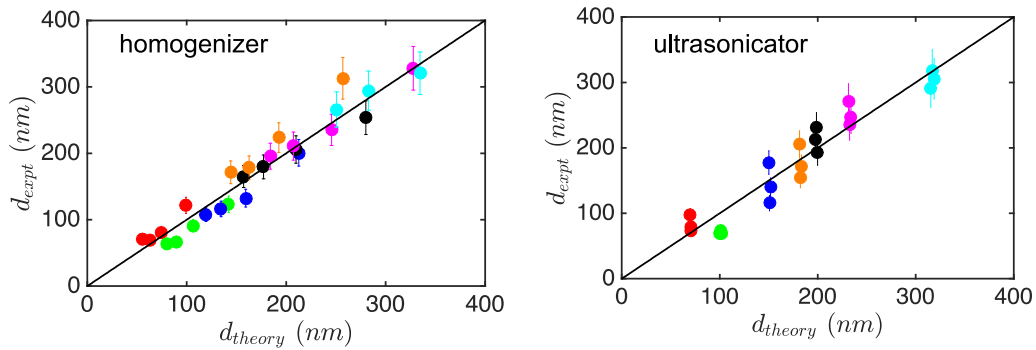
S4. Parity plots

Figure 4. Parity plot of $d_{experimental}$ vs d_{theory} calculated from $We_{crit,d}$ vs Oh. The observed trends show good agreement for data from both the homogenizer and ultrasonicator.

S4. Details of diameter and polydispersity calculation from raw DLS data

We performed the second-order cumulant analysis on the autocorrelation function in the following manner:

$$\ln g^1(\Gamma, q) = K_o - \Gamma\tau + \frac{\mu^2}{2}\tau^2$$

where,

$$\Gamma = q^2 D_m$$

$$q = 4\pi n\frac{sin\left(\frac{\theta}{2}\right)}{\lambda}$$

$$D_m = \frac{k_B T}{3\pi\mu_c d}$$

where q is the wavevector, D_m is the diffusion coefficient at infinite dilution, n is the refractive index of the continuous phase, λ is the wavelength of laser, k_B is the Boltzmann constant, T is the temperature, μ_c is the continupus phase viscosity, and d is the droplet size. The polydispersity was obtained by the expression μ_2/Γ^2. An example of cumulant fit on g^2 for silicone oil nanoemulsions prepared using homogenizer has been shown below.
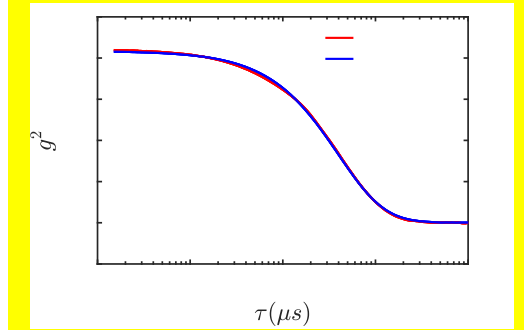

Figure 5. Second order cumulant analysis of raw DLS data for silicone oil nanoemulsions prepared using homogenizer.

S5. Estimation of continuous phase Reynolds number for ultrasonicator and homogenizer

In an ultrasonicator, if one assumes the scale of pressure amplitude, $P_A \sim 1\ atm$ (see S2), the velocity scale relevant to system at the length scale of cavitation bubble can be given by $u_c \sim \sqrt{\dfrac{P}{\rho_c}} \sim 10\ m/s$. Hence, the Reynolds number estimated on the cavitation bubble size (R_b) of around $100\ \mu m - 1\ mm$ (see S2) is,

$$Re \sim \frac{\rho_c u_c R_b}{\mu_c} \sim O(10^3 - 10^4)$$

Hence, the flow inside an ultrasonicator can be assumed to be turbulent.

Estimation of continuous phase Reynolds number for homogenizer is a non-trivial task because of the difficulty to evaluate the valve gap-height. Further, when the flow leaves the small gap, there is sudden flow expansion leading to a chaotic and turbulent flow (Floury, J., Bellettre, J., Legrand, J., & Desrumaux, A. (2004) *Chemical Engineering Science*, *59*(4), 843-853.). The above study shows that flow patterns inside the homogenizer become dynamic and turbulent when the fluid leaves the gap.