Electronic Supplementary Material (ESI) for Soft Matter

Supplementary Information

Calculation of the droplet packing fraction in a monodisperse 2D emulsion

Figure 4 in the manuscript displays the mean dispersed phase fraction $\langle\phi\rangle$ as a function of the reduced droplet column height H for a two-dimensional layer of the emulsion droplets. H is calculated as $H = r_{3D}\langle h\rangle\Delta\rho a/\sigma$, where r_{3D} is the radius of an undeformed droplet, $\langle h\rangle$ is the mean column height, $\Delta\rho$ is the density difference between the two phases, a is the radial acceleration, and σ is the liquid-liquid interfacial tension. $\langle\phi\rangle(H)$ can be obtained from the profile $\phi(H)$, which can be calculated from (1):

$$H(\phi) = \frac{1}{(\phi\phi_0)^{1/2}}\left[1 + \left(\frac{1-\phi_0}{1-\phi}\right)^{1/2}(2\phi - 1)\right] - 2 \quad (1)$$

The mean value $\langle\phi\rangle(H)$ is then calculated numerically from the curve $\phi(H)$:

$$\langle\phi\rangle(H) = \frac{1}{H}\int_0^H \phi(H')dH' \quad (2)$$

Calculation of drop-drop coalescence rates

The frequency of drop-drop coalescence events $dn_{c,dd}/dt$ in a uniform dense layer of emulsion droplets is given by (2):

$$\frac{dn_{c,dd}}{dt} = \frac{N_d}{2\tau_{dd}} \quad (3)$$

n_d is the number of droplets and τ_{dd} is the coalescence time. For non-deformable droplets (i.e. hard spheres), the coalescence time τ_{dd} for a droplet pair is given by (3):

$$\tau_{dd} = \frac{3\pi r_d^2\eta_c}{2F} ln\left(\frac{h_0}{h_c}\right) \quad (4)$$

In equation 4, F denotes the interaction force between the droplets. h_0 denotes the initial thickness of the continuous phase film, and h_c is the critical thickness for rupture of the film. For deformable droplets, the following equation is obtained (3):

$$\tau_{dd} = \frac{3\pi r_d^2\eta_c F}{16\sigma h_c^2} \quad (5)$$

In equation 5, σ denotes the liquid-liquid interfacial tension. Both equations assume that the interaction force F bringing the droplets together is constant, and that there is no barrier against coalescence, such as induced by the presence of surfactants. In that case, F is equal to the buoyancy force $F = N_c V_d \Delta\rho a$. N_c is the number of droplets in the emulsion column below the coalescing droplet, V_d is the volume of a droplet, $\Delta\rho$ the density difference between the continuous and dispersed phase, and a is the radial acceleration. Droplets at different heights in the emulsion column will thus be subjected to a different buoyancy force. In the simplest approximation, we shall use the average value of N_c which is $N_c/2$. The relation between N_c and the total number of droplets N_d is $N_c = 2\pi r_d^2 N_d/3wz$, where w and z are the width and depth of the sample chamber, respectively. Inserting this relation and the expressions for F and τ_{dd} for non-deformable droplets into equation 3 yields after integration:

$$n_c = \frac{\Delta\rho a V_d}{9wz\eta_c ln(h_0/h_c)} \int_0^t (N_d(t'))^2 dt' \tag{6}$$

For deformable droplets, we obtain:

$$n_c = \frac{3wzh_c^2 t}{\pi r_d^7 \Delta\rho a \eta_c} \tag{7}$$

References

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[3] A.K. Chesters. The modelling of coalescence processes in fluid-liquid dispersions: A review of current understanding. *Trans. IChemE*, 69A:259–270, 1991.