Supporting Information

Coalescence of water drops at an oil-water interface loaded with microparticles and surfactants

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The Supporting Information contains models to obtain suitable estimators for the drainage time of the film. Two asymptotic cases are analyzed: the film with immobilized surfaces and with fully mobile interphases.

Film with immobile interphases

For thin enough films, a low Reynolds flow develops and the quasi-stationary lubrication theory describes the drainage of the liquid on the film. Since the film has a spherical shape of radius R, we use the coordinate system (θ, ψ, y) in Figure S1. It is a spherical coordinate system located at the center of the spherical cup but the radial coordinate is replaced by the distance to the drop surface y. Axis z is extended along the axis of symmetry of the drop. For thin films, R is almost constant since the equilibrium forces on the drop determine it and the film weight is negligible (Princen 1962).

We assume an axisymmetric film whose geometry is defined by the thickness at each polar angle $h(\theta)$. Besides, we consider that this thickness is much smaller than the radius $h << R$. The phase inside the film and the one in the drop are called the continuous and dispersed phases, respectively. We assume that the interphase between the continuous and the dispersed is plane at infinity and it is located at $z = 0$ (Figure S1).

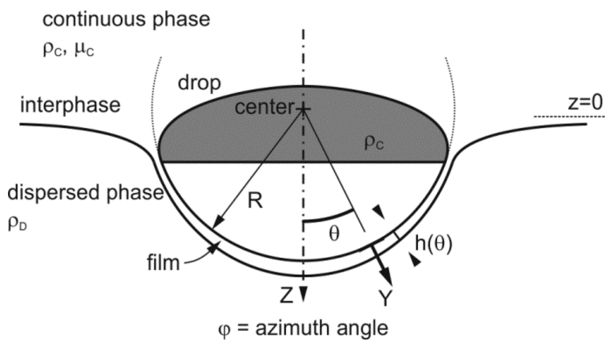

Fig. S1: Coordinate system

Since the film surfaces are immobile, the fluid in the bottom bulk of liquid is still and the pressure is hydrostatic. Using the Young-Laplace equation, the piezometric pressure inside the film p^*_f is:

$$p^* = p - \rho g z = p_0 + \sigma\frac{2}{R} + \Delta\rho g z_C + \Delta\rho g R\cos\theta \qquad (S1)$$

In the previous equation, p is the pressure inside the film, p_0 the pressure on the interphase at infinity ($z = 0$), σ the surface tension, $\Delta\rho = \rho_D - \rho_C$ the difference of densities between the dispersed and the continuous phases, respectively. z_C is the coordinate of the spherical cap center.

Assuming a quasi-unidirectional flow parallel to the film surfaces, the piezometric pressure is almost constant in the radial direction and $p^* = p^*(\theta)$. The momentum equation in the θ direction is:

$$0 = -\frac{p^*{,_\theta}}{R} + \mu u_{\theta,yy} = \Delta\rho g \sin\theta + \mu u_{\theta,yy} \tag{S2}$$

$\varsigma,_\theta$ denotes the partial derivative of the generic variable ς with respect θ and u_θ is the polar velocity of the continuous phase in the film. In this section, we assume that the gradients of surface tension are strong enough to absorb the tangential viscous stress at the film boundary and the interphase is immobile in the polar direction. The velocity profile is obtained by integrating equation (S2) with the boundary conditions $u_\theta(y = 0) = u_\theta(y = h) = 0$. The integration of this velocity profile gives the flow per unit length in the polar direction q_θ:

$$u_\theta = \frac{1}{2}\frac{\Delta\rho g \sin\theta}{\mu} y(h-y) \Rightarrow q_\theta = \int_0^h u_\theta dy = \frac{1}{12}\frac{\Delta\rho g \sin\theta}{\mu} h^3 \tag{S3}$$

The so-called Reynolds equation is the continuity equation integrated along the y direction. The corresponding result in the current problem is:

$$h,_t R^2 \sin\theta + (q_\theta R \sin\theta),_\theta = 0 \Rightarrow h,_t \sin\theta + \alpha(\sin^2\theta h^3),_\theta = 0 \text{ with } \alpha = \frac{1}{12}\frac{\Delta\rho g}{\mu R} \tag{S4}$$

Equation (S4) requires the initial geometry of the film $h_0(\theta) = h(t = 0, \theta)$. The analytical solution seems to be unaffordable. However, the approximation for small polar angles greatly simplifies this equation. Thus, it is reduced to the next expression.

$$h,_t + \alpha(2h^3 + 3\theta h^2 h,_\theta) = 0 \tag{S5}$$

Using the initial condition, the following equation gives the solution $h(\theta, t)$ in a parametric form.

$$\begin{cases} \dfrac{1}{h^2} = 4\alpha t + \dfrac{1}{h_0{}^2(\theta_0)} \\ \dfrac{\theta}{\theta_0} = \left(\dfrac{h_0(\theta_0)}{h}\right)^{3/2} \end{cases} \tag{S6}$$

The parameter θ_0 is the polar angle of the initial condition. This solution "spreads" the film thickness from the central zone (small θ) towards the periphery (large θ) while the propagated thickness h_0 decreases to a new value, h. Since the initial thickness of the film decreases with the polar angle, (S6) implies that the film thickness is a decreasing function of θ at any time. However, the uniformity of the film thickness increases as time goes by.

The film thickness during the last stages of drainage is much smaller than the initial size ($h << h_0$), leading to the next estimator of the film thickness at the periphery and for $t \to \infty$.

$$h \simeq \left(3\frac{\mu R}{\Delta\rho g t}\right)^{1/2} \text{ valid for } t \gg 3\frac{\mu R}{\Delta\rho g h_0{}^2} \tag{S7}$$

with R being the radius of the spherical film. Princen (1963) calculated the shape of a drop placed on the interface by means of numerical methods, obtaining R in function of the radius of the free drop $r = (3V / 4\pi)^{1/3}$. The whole range of numerical results in Princen (1963) fit well to the proposed correlation (S8).

$$\frac{R}{r} = 0.68823\exp\left[-(cr^2)^{0.58893}\right] + 1.3575 \text{ with } c = \frac{\Delta\rho g}{\sigma} \tag{S8}$$

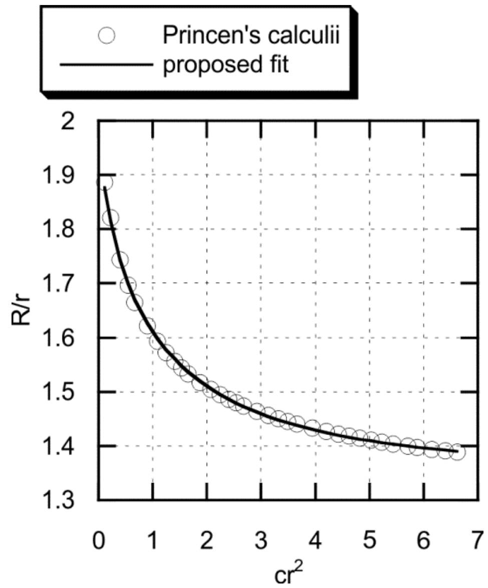

Fig. S2: Radius of the spherical cap *R* vs. the size of the free drop *r*. Comparison of the Princen's data and the proposed correlation.

Figure S2 compares Princen's data with (S8). The ratio R / r varies from a value close to 2 in very small drops to about 1.3 for very large sizes.

The non-dimensional sizes of the drops in our study, cr^2, lie in the interval (0.10, 1.2), inside the region where (S8) is valid.

Film with fully mobile surfaces

Assuming an ideal flow at the dispersed phase (drop and the bulk of liquid below) and no Marangoni effects, the tangential stress on the film surfaces is considered to be negligible. Thus, the profile of the polar velocity u_θ inside the film should be constant, depending just on the polar angle. In addition, the film is completely drained in a finite time when ideal flow is considered, in contrast to the results of the viscous theory.

In this section, the spherical coordinate (θ, ψ, r) is more convenient. Here, $r = R + y$, i.e. the radial coordinate with origin at the center of the spherical film (Figure S1). The flow equations in this spherical coordinate system are:

$$\text{Continuity: } \frac{1}{r^2}\left(r^2 u_r\right)_{,r} + \frac{1}{r\sin\theta}\left(u_\theta \sin\theta\right)_{,\theta} = 0 \qquad \text{(S9)}$$

$$\theta \text{ momentum eq.: } \rho\left(u_{\theta,t} + u_r u_{\theta,r} + \frac{u_\theta}{r} u_{\theta,\theta} - \frac{u_\theta u_r}{r}\right) = -\frac{p^*{}_{,\theta}}{r} \qquad \text{(S10)}$$

$$\text{r momentum eq.: } \rho\left(u_{r,t} + u_r u_{r,r} + \frac{u_\theta}{r} u_{r,\theta} - \frac{{u_\theta}^2}{r}\right) = -p^*{}_{,r} \qquad \text{(S11)}$$

Estimations of the order of magnitude lead to ignore the smallest terms. The equations are simplified as follows:

$$\theta \text{ momentum eq.: } \rho\left(u_{\theta,t} + \frac{u_\theta}{R} u_{\theta,\theta}\right) = -\frac{p^*{}_{,\theta}}{R} \qquad \text{(S12)}$$

$$\text{r momentum eq.: } \Delta_r p^* \sim \rho {U_\theta}^2 \frac{h}{R} \ll \rho {U_\theta}^2 \sim \Delta_\theta p^* \Rightarrow p^*(\theta,r) \simeq p^*(\theta) \qquad \text{(S13)}$$

Integrating the continuity equation (S9) along the r coordinate along with the kinematic condition $h_{,t} = u_r(r = R + h) - u_r(r = R)$ and assuming $R + h \approx R$, we recover eq. (S4) with the polar flow per unit length and the polar gradient pressure given by the next equations:

$$q_\theta = \int_R^{R+h} u_\theta dr \simeq u_\theta h \text{ and } p^*{}_{,\theta} = -\Delta\rho g R \sin\theta \qquad \text{(S14)}$$

The proper initial conditions are:

$$h(\theta,t=0)=h_0(\theta) \text{ and } u_\theta(\theta,t=0)=u_0(\theta) \tag{S15}$$

The solution must satisfy equations (S12), (S4) with the expressions of q_θ and $p^*{}_{,\theta}$ in eq. (S14) as well as the initial conditions (S15). Again, the problem is too complex to get a general analytical solution.

Next calculations aim at calculating the order of the drainage time. From the integrated continuity equation (S4) we obtain:

$$T \sim \frac{h}{h_{,t}} \sim \frac{R}{U_\theta} \tag{S16}$$

T and U_θ are the characteristic drainage time and polar velocity, respectively. The following approximation is obtained using the polar momentum equation:

$$\rho {U_\theta}^2 \sim \Delta_\theta p^* \sim \frac{w_{app}}{\theta^2 R^2} \sim \Delta\rho g R \tag{S17}$$

with w_{app} denoting the apparent weight of the drop $\Delta\rho g 4\pi R^3/3$. Substituting eq. (S17) in (S16), we obtain the final estimator:

$$T \sim \left(\frac{\rho\ R}{\Delta\rho g}\right)^{1/2} \tag{S18}$$