Simplified Model for Droplet Growth in Shear Flow

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A numerical model was previously developed for the evolution of the size distribution for dilute dispersions of slightly deformable drops in linear flows at low Reynolds numbers, based on population dynamics equations for polydisperse drop sizes and coalescence kernels calculated from a combination of lubrication theory and local boundary-integral theory for close approach and film drainage between two drops (Rother and Davis, 2001). To make the method more useful, we develop here a simplified analytical model for droplet growth for the specific case of viscous shear flow, which is of particular interest in the processing of immiscible polymer blends. Attention is restricted to modest drop-to-medium viscosity ratios and mobile drop interfaces without surfactants. The analytical model is in good agreement with our previous numerical work, as well as with the recent experiments of Burkhart et al. (2001).

Model Development

We consider drop growth due to collisions and coalescence in a dilute, sheared emulsion of nearly spherical drops. From Swift and Friedlander (1964), based on the assumption that the drops can be approximated as monodisperse, the rate of increase in the characteristic drop diameter is

$$\frac{dD(t)}{dt} = \frac{4}{\pi}(2-2^{2/3})\phi_0 \gamma D(t) E_0 \tag{1}$$

where ϕ_0 is the volume fraction of the drop phase, γ is the shear rate, and E_0 is the collision efficiency or, equivalently, the coalescence probability. The collision efficiency is generally less than unity and accounts for the effects of hydrodynamic interactions and interfacial deformation, which inhibit coalescence, and molecular attractions, which promote coalescence. Example numerical results from the trajectory analysis of Rother and Davis (2001) are shown in Figure 1 for a model system based on the physical properties of ethyl salicylate (ES) drops in a matrix of diethylene glycol (DEG) with shear rate $\gamma = 1\ s^{-1}$, external-medium viscosity $\mu_c = 0.35$ g/cm-s, drop-to-medium viscosity ratio $\hat{\mu} = 0.1$, interfacial tension $\sigma = 1.9$ dyn/cm, and composite Hamaker constant $A_H = 5 \times 10^{-14}$ erg (Rother and Davis, 2001). The collision efficiency is essentially unaffected by deformation and equal to E_{sph} for sufficiently small drops that remain spherical, and then it decreases rapidly as the drop diameter increases beyond a critical value D_{cr} due to film flattening, dimpling, and slow drainage before attractive molecular forces lead to film rupture and drop coalescence.

Recently, Vinckier et al. (1998) used Eq. 1 in a simplified model of the coalescence process for simple shear flow, based on the scaling arguments of Chesters (1991), plane-parallel films, and constant interaction forces, leading to a coalescence probability which decays exponentially with the ratio of the predicted film-drainage and drop-interaction times during a collision

$$E_0 = \exp\left(-[mD(t)]^{5/2}\gamma^{3/2}\right), \quad m = 0.358\left(\frac{\hat{\mu}}{h_c}\right)^{2/5}\left(\frac{\mu_c}{\sigma}\right)^{3/5} \tag{2}$$

where the critical-rupture thickness h_c is assumed constant and used as a fitting parameter to experimental data, although scaling arguments predict that h_c increases weakly with drop size for film rupture due to attractive van der Waals

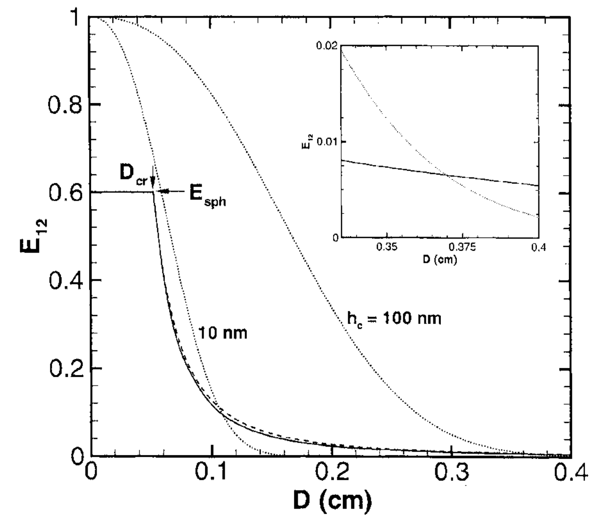

Figure 1. Collision efficiencies for an ES/DEG system as determined by Eq. 2 from Vinckier et al. (1998) with $h_c = 10$ and 100 nm (dotted lines), new model of Eq. 3 (dashed line), and numerical simulations from Rother and Davis (2001) (solid line).

The inset is for $h_c = 100$ nm at large drop size.

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forces (Chesters, 1991). Equation 2 is plotted in Figure 1 with $h_c = 10$ nm, a typical order of magnitude for small drops with $D \approx 100$ μm (Vinckier et al., 1998; Yang et al., 2001), and also with a larger value of $h_c = 100$ nm. As seen in the figure, Eq. 2 gives the correct qualitative behavior for the collision efficiency, but it overpredicts the full numerical results for small drops and then falls below the numerical results for sufficiently large drops.

Using our recent numerical results for collision efficiencies (Rother and Davis, 2001), we instead fit E_0 to an expression of the form

$$E_0 = \begin{cases} E_{sph} & D \le D_{cr}; \\ E_{sph} \dfrac{(D_{cr} - D^*)^2}{(D - D^*)^2}, & D > D_{cr}, \end{cases} \tag{3}$$

and then Eq. 1 can be integrated analytically to find $D(t)$ explicitly for $D < D_{cr}$ and implicitly for $D > D_{cr}$

$$D(t) = D_0 \exp\left(\frac{4}{\pi} (2 - 2^{2/3}) E_{sph} \phi_0 \gamma (t - t_0) \right), \quad D \le D_{cr}, \tag{4a}$$

$$\frac{1}{2}\left(D^2(t) - D_{cr}^2 \right) - 2D^* \left(D(t) - D_{cr} \right) + (D^*)^2 \ln\left(D(t)/D_{cr} \right) = \frac{4}{\pi}(2 - 2^{2/3}) E_{sph} (D_{cr} - D^*)^2 \phi_0 \gamma (t - t_{cr}), \quad D > D_{cr}, \tag{4b}$$

where D_0 is the initial drop diameter, t_0 is the initial time, and t_{cr} is the time at which $D = D_{cr}$ from Eq. 4a. In Eq. 3, E_{sph} is a characteristic collision efficiency for spherical drops in the absence of van der Waals forces. The case of equal-sized drops is used to determine E_{sph}, which then depends only on the viscosity ratio of the system. For $0.1 \le \hat{\mu} \le 10$, the following equation approximates the numerical results of Rother and Davis (200l), with a maximum error of about 2.2%

$$E_{sph} = \left[0.7949 \hat{\mu} + 0.1061 \ln(\hat{\mu}) + 1.8284 \right]^{-1}. \tag{5}$$

The drop diameter D_{cr} at which the collision efficiency decreases rapidly from the value for spherical drops due to the film-drainage effects is determined from our thin-film code (Rother and Davis, 2001). As in our previous work for buoyancy (Rother et al., 1997), we can make a first approximation to the drop size at which small deformations become important by expanding the force balance near $\theta = \pi/2$ in the plane of shear, where θ is the angle between the line of centers and the flow direction of the applied shear. The result for equal-sized drops is

$$D_{cr} \approx 0.840 \left[\frac{(\hat{\mu} + 1.02 \ln \hat{\mu} + 14.9)}{\hat{\mu}^2} \left(\frac{\hat{\mu} + 1}{\hat{\mu} + 2/3} \right)^2 \frac{A_H \sigma^3}{(\gamma \mu_e)^4} \right]^{1/6} \tag{6}$$

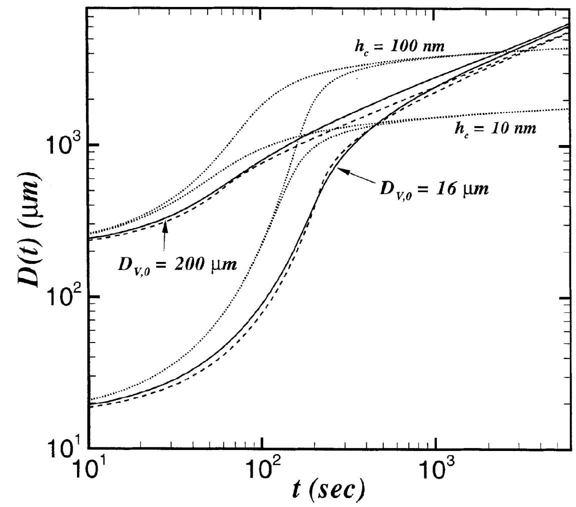

Figure 2. Two simplified models of droplet growth with full numerical simulations for an ES/DEG system in simple shear flow with $\phi_0 = 0.05$ and $\gamma = 1$ s^{-1}.

Solid lines are results from the numerical simulations of Rother and Davis (2001) for polydisperse systems, dotted lines from the monodisperse model of Eqs. 1 and 2 (Vinckier et al., 1998) with $h_c = 10$ and 100 nm, and dashed lines from the new monodisperse model of Eqs. 3 and 4.

We have compared Eq. 6 to full numerical calculations and verified that it is accurate within about 1.5% for $\hat{\mu}$ between 0.1 and 1. The maximum error increases to about 5% for $\hat{u} = 5$ and 7% for $\hat{\mu} = 10$, for a broad range of conditions. Equation 3 gives excellent agreement with the numerical results in Figure 1. For this system, $E_{sph} = 0.60$ from Eq. 5, D_{cr} 520 μm from Eq. 6, and $D^* = 123$ μm from fitting numerical data for the collision efficiency vs. drop diameter.

In Figure 2, simple-shear predictions are shown for the model system of Figure 1 for an initially narrow normal distribution with $D_{V,0} = 16$ μm and $\sigma_d = 0.78$ μm, and also for a broader distribution with $D_{V,0} = 200$ μm and $\sigma_d = 33$ μm. Here, $D_V = \sum_{i=1}^{n} n_i D_i^4 / \sum_{i=1}^{n} n_i D_i^3$, where n_i is the number of drops in the ith size category, n is the total number of bins, and σ_d is the standard deviation. The volume fraction and shear rate are $\phi_0 = 0.05$ and $\gamma = 1$ s^{-1}, respectively. Of particular note is that the monodisperse model of Vinckier et al. (1998) predicts a more rapid increase in the droplet growth followed by a more sudden leveling off than do the new monodisperse and previous polydisperse models. The major difference between the two monodisperse models is that the one presented by Vinckier et al. (1998) uses an exponential decrease in the collision efficiency from unity, while our results indicate an algebraic decline from $E_{sph} < 1$.

In Figure 3, comparison is made between the experimental data of Burkhart et al. (2001) and our monodisperse model. The system is polypropylene glycol (PPG) drops dispersed in polyethylene glycol (PEG) at 90°C, with physical parameters $\mu_e = 25$ g/cm·s, $\hat{\mu} = 0.2$, $A_H = 1 \times 10^{-12}$ erg, and $\sigma = 3.0$ dyn/cm. Two curves based on the new monodisperse model are shown at each shear rate: the dotted lines are from a best fit for D^* with the collision efficiency data for equal-sized

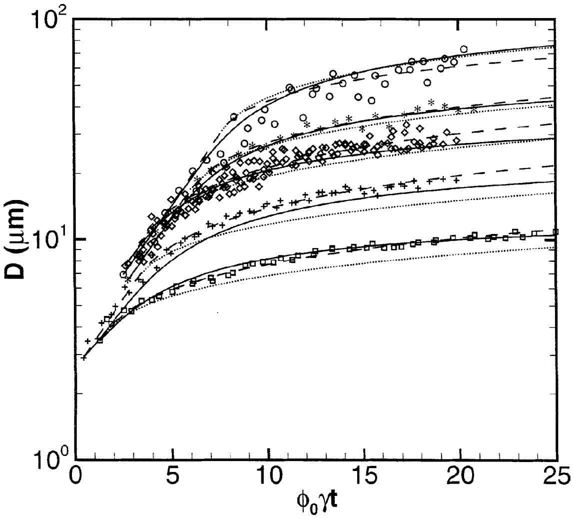

Figure 3. Simplified model of droplet growth with full numerical simulations (solid lines) and experiments (symbols) in Burkhart et al. (2001) for a PPG/PEG system in simple shear flow.

From top to bottom, circles, asterisks, diamonds, crosses and squares are for shear rates of 2, 5, 10, 20 and 50 s^{-1}, respectively. Dashed lines are from Eqs. 3 and 4 using experimental data for $D(t)$ to determine D^*, and dotted lines are from Eqs. 3 and 4 using numerical collision efficiencies (Rother and Davis, 2001) to determine D^*.

drops, and the dashed lines are from a least-squares fit for D^* with the experimental data for $D(t)$. The collision efficiency for equal-sized spherical drops in this case is $E_{sph} = 0.55$. Table 1 gives the resulting values for D_{cr} and D^* for the simplified model. Up to the value of D_{cr}, as determined from Eq. 6, the two monodisperse results are identical. Good agreement for all times is obtained between the experiments and both monodisperse methods, except that the one based on a fit of the theoretical collision efficiencies slightly underpredicts the drop growth at higher shear rates. The small difference occurs because the collision efficiency for equal-sized drops (on which the monodisperse model is based) falls below that for smaller drop-size ratios at diameters greater than D_{cr} and so no longer dominates the drop growth (Rother and Davis, 2001).

Concluding Remarks

The new model for droplet growth due to collisions and coalescence in sheared emulsions is qualitatively similar to the oft-used model of Vinckier et al. (1998). Both models approximate drop dispersions as monodisperse and lead to simple analytical expressions for the drop growth rate. The primary difference is that the previous model is based on parallel-film scaling arguments and an exponential decay in the collision probability due to small deformations, whereas the present model fits an algebraic decay to recently reported numerical data for collision efficiencies which include hydrodynamic interactions of spherical drops prior to collision and then natural evolution of a nonparallel film shape during the collision. As a result, the new model predicts a slightly lower growth rate for short times (when the drops are sufficiently small that the effects of deformation are negligible) and a smaller decrease in the growth rate for long times (when the drops become sufficiently large that deformation and film drainage greatly retard coalescence). The new model has one adjustable parameter D^*, which may be fit to either full numerical data for the collision efficiencies or to experimental data for the rate of drop growth. The results in this article for a few physical systems give $D^*/D_{cr} \approx 0.25 - 0.50$; since the rate of change in the average drop diameter due to coalescence varies by a relatively small amount over this range (c.f. Figure 3), a value of $D^*/D_{cr} \approx 0.35$ near the middle of this range may suffice for a broad range of physical systems.

Finally, we note that the quantitative predictions of both the previous and new models are weakly sensitive to the assumed form of the disjoining pressure (defined as the local molecular attractive force per unit interfacial area) and the drop-to-medium viscosity ratio, and they are expected to depend more strongly on surfactant effects (especially the slowing of film drainage due to Marangoni stresses). Thus, careful experimental work on collisions and coalescence of two drops, such as that described by Hu et al. (2000), is needed to help refine the models.

Table 1. Critical Drop Diameter D_{cr} from Eq. 6 and Constant D^* in Eq. 3 for a PPG/PEG System Based on a Least-Square Fit

Shear Rate (s^{-1})	D_{cr} (μm)	D^* (μm)†	D^* (μm)‡
2	31.4	16.4	20.3
5	17.0	9.4	7.8
10	10.7	5.0	2.7
20	6.8	4.0	1.7
50	3.7	2.1	1.3

†With the numerical collision efficiences of Rother and Davis (2001).
‡With experimental data for $D(t)$ from Burkhart et al. (2001).

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Manuscript received Jan. 15, 2002.