Simulation of Mixing within Drops due to Surface Tension Variations

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We present the results of a numerical investigation of the mixing within drops caused by surface tension variations. With microfluidic applications in mind, we simulate drops surrounded by a fluid of equal density and viscosity. We investigate both stationary coalescing drops and steadily flowing drops, and study the influence of drop size ratio, viscous effects, and surface tension variations. We measure the mixing efficiency using the variance of the concentration distribution and find that surface tension variations may result in faster mixing than geometric effects.

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Drop coalescence is a complicated process that has been studied for decades [1–7]. Depending on the drop size, velocity, and composition, several outcomes are possible, most notably bouncing or coalescence, be it total, temporary or partial. The majority of earlier research has focused on the evolution of the drop interface, which is arguably the most important aspect of the coalescence, and undeniably the easiest to observe experimentally.

Another important aspect of drop coalescence is the fate of the internal fluids, and how well they become mixed [8]. While head on coalescence of identical drops results in perfectly separated halves in the final drop (by symmetry), variations in drop sizes and composition may cause significant mixing. Such mixing within drops is of particular importance in microfluidic networks in which droplets are used as microreactors where chemical or biological reactions may be observed using only tiny quantities of reagents [9]. The small size of these apparatus render mixing difficult, but several designs have been proposed to overcome this difficulty for flowing drops [10,11]. In the most basic setting, a drop flows in a straight horizontal tube, and the upper and lower halves do not mix. To generate mixing, the centerline separatrix is shifted and symmetry is broken by means external to the drop. However, a radically different mixing mechanism may be used if the reagents within the drops influence the surface tension of the interface.

Spatially varying surface tension provides an internal symmetry break for coalescing and flowing drops. The tangential flow generated by the surface tension mismatch, the Marangoni effect, can propel a drop and induce vigorous motion within it [12,13]. This effect, at the origin of Bénard-Marangoni convection, has been used to mix fluid layers [14,15], and perform manipulations within microfluidic devices [16]. Previous authors have investigated mixing within drops resulting from externally induced surface tension gradients [13,17,18]. Significantly, the time scale of Marangoni effects is very different than that of geometric mechanisms.

We study here drops where initially different composition, or temperature, are the only source of surface tension variation. This eliminates the requirement of spatially or temporally varying external agents. We investigate both coalescing and flowing drops and compare the time scales of classical mixing mechanism with those of surface tension variations generated mixing. We first describe how the physical system is simulated numerically.

We consider two miscible liquids, 1 and 2, surrounded by an outer fluid with which they are not miscible. We assume that all fluids have identical density, ρ, and viscosity, ν, but we allow liquids 1 and 2 to have different surface tensions with the outer fluid, σ_1 and σ_2, respectively. We introduce a concentration function, C_1, describing the proportion of liquid 1 relative to liquid 2, and let surface tension depend linearly on C_1. While this linear dependence is not necessarily realistic, our simulations were found to be rather insensitive to the specific dependence of surface tension on C_1.

Following earlier studies [19–21], we model the interface as a forcing term that we add to the momentum equation of the Navier-Stokes equations. The interface moves with the flow, and the concentration C_1 evolves under the combined influence of fluid advection and molecular diffusion. We nondimensionalize the governing equations using the drop radius, R, as a length scale and $\tau = (\rho R^3/\sigma_1)^{1/2}$ as a time scale. The governing dimensionless quantities are the Ohnesorge number, $\mathrm{Oh} = \nu\sqrt{\rho/\sigma_1 R}$, characterizing the ratio of viscous to inertial effects over a time scale τ, the surface tension difference $R_\sigma = (\sigma_1 - \sigma_2)/\sigma_1$, and the Schmidt number $\mathrm{Sc} = \nu/\kappa$, with κ the diffusivity of liquid 1 into liquid 2. Note that our simulations may also describe liquids of variable temperature, if C_1 stands for temperature and κ for thermal diffusivity. Our assumption of uniform density effectively nullifies the effects of gravity.

Numerical simulations of this system are performed in an axisymmetric cylindrical domain with the drop aligned on its axis. The core of the numerical simulations used here is identical to those described in [22], where extensive validation is presented. Diffusion of the field C_1 into the outer fluid is prevented by imposing a symmetry boundary condition across a rasterized approximation of the interface. No-slip and zero flux boundary conditions are imposed at the solid walls, which are positioned sufficiently far from the drops that they do not affect the coalescence process. To estimate the extent to which a drop is mixed, we use the variance of the concentration function C_1 within the drop.

We first simulate the coalescence of two stationary drops. Here, both fluids start from rest as two touching spheres. A typical velocity generated by the coalescence of a drop where inertial effects dominate viscous effects is $U_c \sim \sqrt{\sigma_1/\rho R}$ [4], which here is nondimensionalized to one. We compare this to the velocity generated by the mismatch of tangential forces when the two drops have different surface tensions. We study drops of identical sizes and observe the magnitude of the tangential velocity after one nondimensional time unit ($\sqrt{\rho R^3/\sigma_1}$). We recorded typical velocities along the interface for various Ohnesorge numbers and surface tension ratios (Fig. 1).

Over most of the regime investigated here, we find that the nondimensional tangential velocity is inversely proportional to Oh [Fig. 1(a)], while for Oh < 0.02 it appears to level off. The tangential velocity grows linearly with R_σ, for $R_\sigma < 0.4$, and grows more slowly for larger values. For $R_\sigma/\mathrm{Oh} < 20$, we thus find that the velocity is well approximated by $U_t = 0.05(\sigma_2 - \sigma_1)/\rho\nu$ and is comparable to, or less than, velocities generated by the coalescence itself, with $U_t \leq 1.5U_c$. Over this regime, Marangoni forces are therefore balanced by viscous forces as they cause a thin layer of fluid to be entrained along the interface. At higher velocities, we anticipate the tangential force $[(\sigma_1 - \sigma_2)/R]$ to be balanced by inertial effects (ρU^2). As such a regime is rarely attained in practice, we focus here on the case where viscous effects balance tangential forces, and proceed to examine the resulting mixing.

Any asymmetry generates some degree of mixing within the drop. If the two drops have different sizes, the smaller drop has a greater internal pressure than the larger one, which may result in a vortex ring being pushed from the small into the large drop. However, for the Ohnesorge number we consider in this study, Oh ≥ 0.005, size discrepancies are not found to generate significant mixing, as shown in Fig. 2(a). We restricted our study to drops of initial size ratio greater than 0.6, since smaller drops would result in partial coalescence [22].

In contrast, a much more significant rearrangement is generated by drops of different surface tension, Figs. 2(b)–2(d). In the presence of relatively weak Marangoni effects, $R_\sigma \leq 0.2$ for Oh $= 0.02$, the observed mixing appears to always follow a similar sequence, the only effect of varying R_σ being to determine the speed of the flow. First, coalescence occurs and the drops become a single larger oscillating drop, before any significant mixing has taken

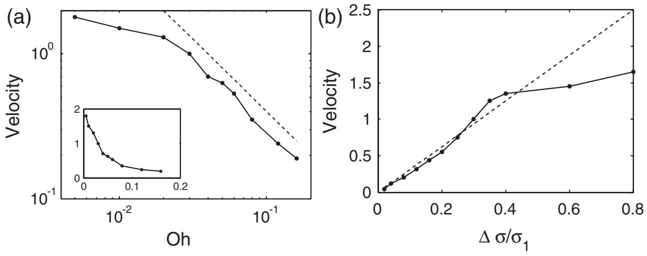

FIG. 1. (a) Dependence on a log scale (linear in inset) of the dimensionless tangential velocity on the Ohnesorge number with $R_\sigma = 0.4$. The dashed line has slope -1. (b) Tangential velocity dependence on R_σ, with Oh $= 0.02$.

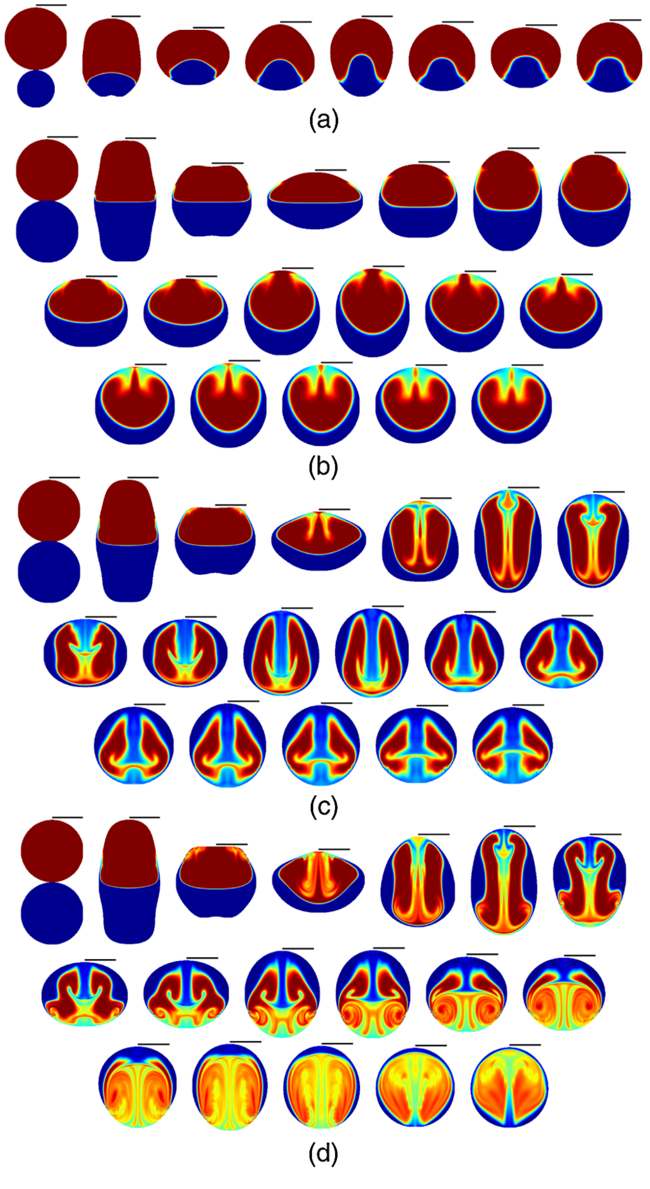

FIG. 2 (color online). (a) Coalescence of drops with size ratio 0.6, identical surface tensions, and Oh $= 0.02$. (b), (c), and (d) Coalescence of equal size drops at Oh $= 0.02$, with $R_\sigma = 0.04$ (b), $R_\sigma = 0.24$ (c), and $R_\sigma = 0.4$ (d). Images are $\tau = \sqrt{\rho R^3/\sigma}$ apart, and the black lines are one initial radius long.

place. Tangential flows then partially mix the interior. Motion then comes to a halt shortly after the entire surface of the drop becomes covered with the fluid of smaller surface tension [Fig. 2(b)], resulting in a one-time reconfiguration of the fluid inside the drop. For moderate Marangoni effects, $0.2 < R_\sigma \leq 0.36$, the internal flow generated by the confluence of the surface flow is sufficiently strong to create a central jet which reaches the lower end of the drop and then flares out [Fig. 2(c)]. This induces a more complicated distribution of fluids 1 and 2, and thus better mixing. Finally, if $R_\sigma > 0.36$, the time scale of coalescence and that of the mixing generated by Marangoni flows are comparable, and even more complicated interactions take place [Fig. 2(d)]. More importantly, the central jet is so vigorous that high surface tension fluid is pushed back onto the interface even well after coalescence has begun. This generates new tangential flows, inducing vortical motion within the drop, which results in much more complete mixing.

We now turn to study drops flowing in a cylindrical tube where a pressure gradient generates a steady flow. We first compute the steady state velocity in and around a drop of uniform composition, assuming periodic conditions in the streamwise direction. Once steady state is achieved, we replace half of the drop with a fluid of different composition and observe the resulting mixing. Such systems are fully described by R_σ, a capillary number, $\mathrm{Ca} = U\rho\nu/\sigma_1$, where U is the average velocity in the pipe, a Reynolds number, $\mathrm{Re} = UR/\nu$, and a Péclet number $\mathrm{Pe} = UR/\kappa$, which we keep constant.

A number of mixing apparatus rely on geometric designs that induce pseudochaotic motion within the drops (see [11] for a review). The time scale associated with such mixing is $t_g \approx R/U(R_t/R)^2$, where R_t is the tube radius and R the drop radius. The mixing results from velocity differences across the drop, hence the term $(R_t/R)^2$. The time scale of surface tension-driven mixing is unaffected by the mean flow in which the drop lies, so in the viscous regime, we have $t_t = R/U_t \approx 20R\rho\nu/\Delta\sigma$. The ratio of those time scales is $t_s/t_g \approx 20\mathrm{Ca}/R_\sigma(R/R_t)^2$. In experiments, the capillary number must be kept small (less than 0.1) to avoid drop breakup, and a typical value is 0.005 [23,24]. The ratio R/R_t is typically close to unity, though always less than one. For the mixing induced by the surface tension mismatch to be dominant, the system must then be such that

$$\frac{\sigma_1 - \sigma_2}{\sigma_1} = R_\sigma > 20\left(\frac{R}{R_t}\right)^2 \mathrm{Ca} = 20\left(\frac{R}{R_t}\right)^2 \frac{\rho\nu U}{\sigma_1}. \qquad (1)$$

Note that for small drop velocities, the mixing due to Marangoni effects is more likely to become dominant. Numerical simulations confirm that tangential flows due to surface tension variations overcome the inner circulation present in flowing drops when this criterion is met.

Figure 3 illustrates the mixing between the front and back regions of a drop in a straight cylindrical tube for even, Fig. 3(a), and uneven surface tensions, Figs. 3(b) and 3(c). We note that the mixing pattern is significantly different depending on whether the tangential flow generated by the surface tension mismatch accentuates or opposes the circulation generated by the mean flow in the pipe. If the initial tangential motion is aligned with that of the inner

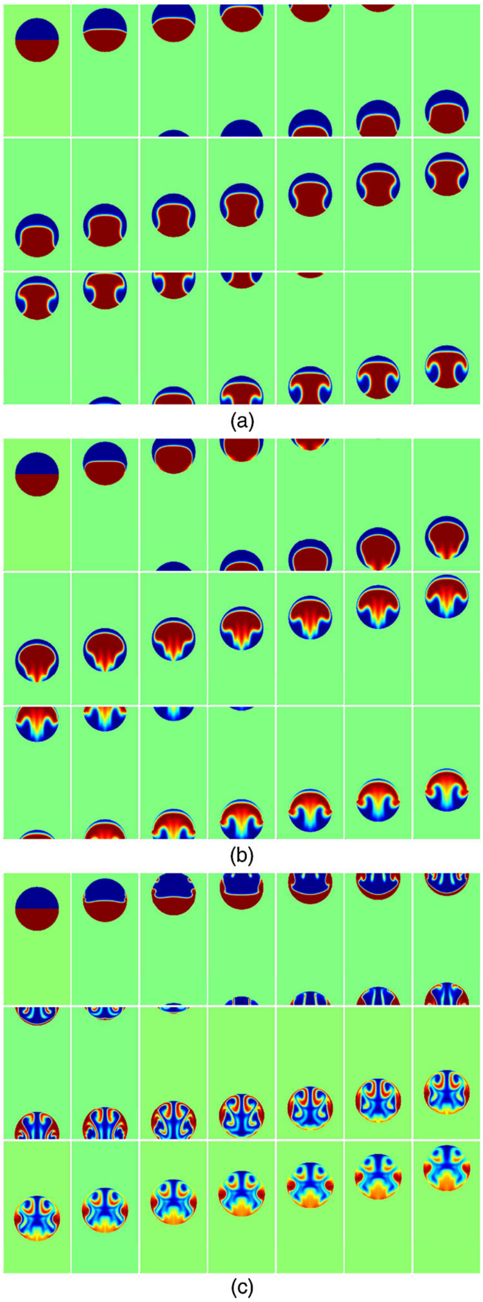

FIG. 3 (color online). Simulations of a flowing drop with $R/R_t = 2/3$, $\mathrm{Ca} = 2.5 \times 10^{-4}$, $\mathrm{Re} = 1.5$, and $\mathrm{Pe} = 0.15$. In (a) $R_\sigma = 0$, in (b) $R_\sigma = 0.05$, and in (c) $R_\sigma = -0.05$. Positive values of R_σ correspond to tangential flow opposing the drop motion. Images are $\Delta t = 0.035R/U$ apart.

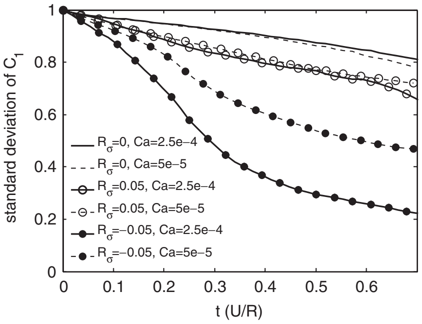

FIG. 4. Standard deviation of C_1 within the drop (measure of mixing) as a function of time for various R_σ and Ca. The cases with $\mathrm{Ca} = 2.5 \times 10^{-4}$ are those shown in Fig. 3.

circulation [Fig. 3(b), $R_\sigma > 0$], the drop accelerates and the early stages of mixing occur faster. However, after the initial mixing, the fluid of lower surface tension quickly covers the entire drop surface, and the flow inside the drop returns to that of a drop of homogeneous composition [25]. If the initial tangential flow is opposite the inner circulation, the drop is slowed [Fig. 3(c), $R_\sigma < 0$]. The shear along the interface is then enhanced, occasionally leading to the detachment of some fluid from the interface. The complicated flow pattern resulting from the competition between external viscous stresses and surface tension mismatch yields much more complete mixing.

Figure 4 shows the extent of the mixing within the drops showed in Fig. 3, as well as within similar drops with smaller Ca. We use as a measure of mixing the standard deviation of the distribution of C_1, normalized by its initial value. All drops become mixed owing to the inner circulation present in any flowing drop. The presence of Marangoni stresses slightly accelerates this process when the tangential flow is aligned with that circulation, but the effect remains modest. However, if the tangential flow is opposite the inner circulation and is sufficiently strong, the mixing is both faster and more complete. Drops of smaller Ca, or larger surface tension difference, exhibit even quicker mixing, as the tangential flow is faster and its effects persist even after the drop is covered with the fluid of low surface tension.

In conclusion, our simulations demonstrate that significant mixing may be induced within drops by surface tension gradients. Stationary coalescing drops can be mixed thoroughly if the time scale of tangential flow is comparable to that of coalescence. For flowing drops in a tube, significant mixing may be obtained even for small Reynolds numbers. The time scale of tangential flow generated by surface tension differences is $t_m \sim 20R\rho\nu/\Delta\sigma$, which is comparable or faster than that of mixing by geometrical devices in microfluidic networks. The extent of the mixing depends on the capillary number of the drop, with more viscous drops being more resistant to mixing. We note that if surface tension gradients are generated perpendicular to the mean flow, mixing may also be generated, but the drop will then be displaced laterally and approach the sidewall, potentially coming into contact with the solid substrate, an undesirable result.

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