SURFACTANT EFFECTS ON BUOYANCY-DRIVEN COALESCENCE OF SPHERICAL DROPS

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Summary Collision efficiencies are calculated by a trajectory analysis for two contaminated spherical drops in buoyancy at low Reynolds number. The full convective-diffusion equation for the surfactant surface concentration is solved by expansion in spherical harmonics with Lamb's singular series used for the velocity field. A highly efficient algorithm is developed to allow very small surface separations.

INTRODUCTION

Whether present by design or by accident, surfactants are nearly ubiquitous. A proper understanding of the effect of surfactants on the behavior of emulsions, a problem of enormous everyday significance, requires fundamental investigation into their role in the interactions of two or more drops. We consider motion due to gravity of two spherical drops of one liquid immersed in a second immiscible liquid in the presence of bulk-insoluble surfactant when the Reynolds number $Re = \rho_e V_2^{(0)} a_2/\mu_e$ is small. Because the drops do not deform, the capillary number $Ca = \mu_e V_2^{(0)}/\sigma$ is zero. As shown in Fig. 1, the quantities ρ_e and μ_e are the surrounding liquid density and viscosity, respectively, and σ is the interfacial tension, where dimensionless parameters are based on the larger drop radius, a_2.

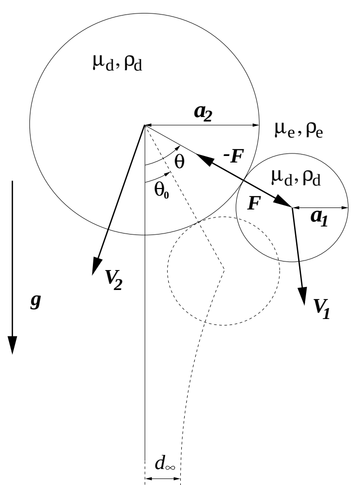

Figure 1. Relative trajectory of two contaminated drops in buoyancy.

Although analytical values for the isolated velocity of the larger drop $V_2^{(0)}$ are not possible in buoyancy for arbitrary surfactant surface coverage in Stokes flow, scaling values can be used. For typical uncontaminated hydrosol systems, Re and Ca are both small, when the drop radius is $O(10 - 50\ \mu\text{m})$.

In the current work, collision efficiencies are determined for two contaminated spherical drops. In an arbitrary trajectory, as in Fig. 1, the drops have an initial horizontal offset d_∞ when well separated, and when the larger drop catches up to the smaller one, the drops will either collide and coalesce, or eventually separate. The collision efficiency E_{12} is determined through the critical horizontal offset d_∞^* demarcating trajectories which lead to coalescence and separation, as follows:

$$E_{12} = \left[d_\infty^*/(a_1 + a_2)\right]^2 , \qquad (1)$$

where a_1 is the smaller drop radius.

NEARLY UNIFORM SURFACE COVERAGE

Previous work to determine collision efficiencies for two contaminated spherical drops in linear flows [1] and buoyancy [2] has focused on the special case of small deviation from uniform surfactant coverage. In this limiting case, the only effect of the surfactant is on the tangential stress boundary condition, and it is not necessary to solve the convective-diffusion equation for the surfactant concentration. Moreover, the problem remains linear and can be solved by decoupling motion normal and parallel to the drops' line of centers to determine mobility functions.

In Figure 2, the gravitational collision efficiency for nearly uniform coverage is graphed versus the drop-to-medium viscosity ratio at a fixed drop-radius ratio of 0.5 for various values of the retardation parameter $A = B\Gamma_0 a_2/(\mu_e D_s)$, where $B = -\partial\sigma/\partial\Gamma$ is assumed constant, D_s is the surface diffusivity, and Γ_0 is the initial surfactant concentration [2]. An interesting feature of Fig. 2 is that E_{12} increases slightly with viscosity ratio $\hat{\mu}$ at large A and moderate $\hat{\mu}$ because the coefficients for the rotational term in Lamb's singular solution are independent of the presence of surfactant.

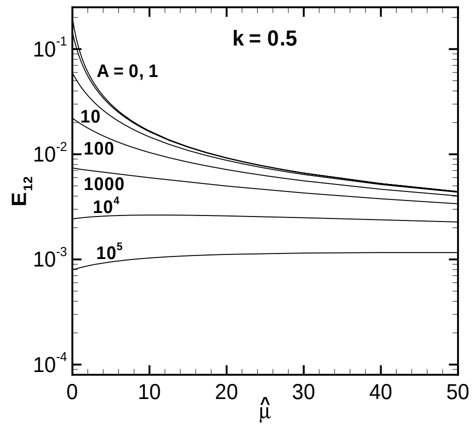

Figure 2. Collision efficiency E_{12} as a function of the drop-to-medium viscosity ratio $\hat{\mu} = \mu_d/\mu_e$ with size ratio $k = a_1/a_2$ = 0.5 at various values of the retardation parameter A for two contaminated spherical drops in buoyancy in the limit of nearly uniform surface coverage. Adapted from [2].

ARBITRARY SURFACE COVERAGE

In general, scaling [1] shows that nearly uniform surface coverage is often a satisfactory assumption for spherical drops. However, when the drops are in close approach, the squeezing flow can cause significant deviation in the surfactant concentration, a fact ignored in earlier studies. Moreover, the solutions of [1,2] show that collision efficiencies depend on the retardation parameter $A = MaPe_s$, where $Ma = B\Gamma_0/(|\rho_e - \rho_d|ga_2^2)$ with g being the magnitude of the gravitational acceleration is the Marangoni number, and $Pe_s = A/Ma$ is the surface Péclet number. On the other hand, existing experiments for small drops in shear flow [3] demonstrate a more complex dependence, with E_{12} being a function of Ma and Pe_s separately. In addition, if the surfactant concentration is dilute [4], redistribution is possible even for larger separations. Therefore, we solve the full time-dependent convective-diffusion equation for the surfactant surface concentration Γ:

$$\frac{\partial \Gamma}{\partial t} = -\nabla_s \cdot (\Gamma \mathbf{u_s}) + \frac{1}{Pe_s}\nabla_s^2 \Gamma, \tag{2}$$

where $\mathbf{u_s}$ is the interfacial velocity and ∇_s is the surface gradient operator. The advantage of our less restrictive solution is that it has very few non-dimensional parameters, making it easy to compare with experiments and avoiding the many additional dimensionless quantities of bulk-soluble surfactant models.

The expansion of the solution of the surfactant equation into spherical harmonics is done similar to [4], which considers single-drop rheology. With surfactant concentration expanded into spherical harmonics, the velocity field is sought *via* Lamb's singular series; boundary conditions are satisfied using biconjugate-gradient iterations to solve the resulting series of nonlinear ordinary differential equations and rotation-based reexpansions of Lamb's series for maximum efficiency [5]. In this problem, it is crucial to extend the dynamical simulation to very small surface separations, with a large number of 3D harmonics/multipoles in the expansions, which requires a highly efficient algorithm. It is anticipated that, under conditions when the surfactant concentration remains nearly uniform when the drops are well separated, significant deviation in coverage may occur in the region of close approach for weak diffusion, causing the interfaces to become immobile. Film drainage would be retarded, considerably decreasing the collision efficiency from spherical-drop results for nearly uniform coverage [2].

References

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