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# Numerical modeling of drop coalescence in the presence of soluble surfactants

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ABSTRACT

The paper presents a numerical method for simulation of the effect of a soluble surfactant on the last stage of the drop coalescence (film formation, drainage and rupture). An axisymmetric interaction between drops is studied at small capillary and Reynolds numbers and small surfactant concentrations. The hydrodynamic part of the mathematical model includes the Stokes equations in the drop phase and their lubrication approximation in the gap between the drops (film phase), coupled with velocity and stress boundary conditions at the interfaces. The surfactant is considered soluble in both (drop and film) phases and the distribution of the surfactant concentration is governed by a convection–diffusion equation. A convection–diffusion equation is also used to model the distribution of the surfactant on the interfaces. The concentration in both phases is coupled with that on the interfaces via the adsorption isotherm and the fluxes between the interface and the bulk phases. The hydrodynamic and concentration parts of the mathematical model are related via the advection of the surfactant in the fluid phases and on the interfaces. On the other hand, a non-uniform surfactant concentration on the interfaces leads to a gradient of the interfacial tension which in turn leads to an additional tangential stress on the interfaces (Marangoni effects). For the flow in the drops a simplified version of Boundary integral method is used. Finite difference method is used for the flow in the gap, the position of the interfaces and the distribution of surfactant concentration on the interfaces, as well as in the fluid phases. Different approaches are used for an optimization of the numerical algorithm: Non-uniform meshes for space discretization in both ($r$ and $z$) directions; Explicit and implicit first and second order time integration schemes with automatically adaptive time steps; A multiple time step integration scheme that can decrease significantly the computational time without loss of accuracy. Tests and comparisons are performed in order to investigate the accuracy and stability of the different numerical schemes.



## 1. Introduction

Drop coalescence is important to many natural and man made processes. A typical example is the process of emulsification where as a result of mixing of immiscible fluids droplets of size of micrometers, or smaller, are dispersed in a liquid matrix, forming an emulsion. Emulsions are of practical importance for many industrial applications, e.g. food and paint production, composite materials, pharmaceutics, petroleum, etc. The main difficulty for investigation (experimental or theoretical) of the process, and the emulsions itself, is the presence of several scales: the mixer of scale of meters; the drops of

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scale of micrometers; the film region (gap between the drops) with a thickness of order of nanometers. Recently population balance models (see, for example, [1,2]) were successfully used for studying of emulsification. To overcome the difficulties related with the different scales the different subprocesses are considered separately in these models: flow in the mixer; drop deformation and breakup; drop coalescence, including film formation, its drainage and finally film rupture. The process of droplet breakup can be well described theoretically [3], whereas modeling of the coalescence dynamics is more difficult. This is because the drop coalescence involves interaction of two drops/bubbles, formation and drainage of a relatively stable film of order of nanometers.

In the framework of the population balance models the coalescence of two drops can be split conceptually into three elements (see, for example, [4]):

1. The external flow field, governing the frequency, strength and duration of collisions;
2. The process of film formation and drainage;
3. The destabilization of the film by van der Waals and other intermolecular forces, leading to rupture.

The first element furnishes the initial and boundary conditions for the second, which in turn provides those for the third element.

While reasonable first approximations for the collision frequency, force and duration, as well as for the critical film-rupture thickness can be derived in many cases, film drainage is particularly sensitive to the details of the system concerned. Small tangential stresses exerted on the film by the dispersed phase or by interfacial tension gradients translate into large forces per film volume, which strongly affects drainage rates. In pure liquid–liquid systems, exhibiting constant interfacial tension, the only tangential stresses are those exerted by the dispersed phase, arising from the internal motion within the drops. Most practically occurring fluid–liquid dispersions, however, contain surface-active materials, either by accident or design, that can strongly affect the drop and bubble coalescence (see for example [5] and references therein). It has long been realized that this sensitivity derives from the fact that minor variations in interfacial/surface tension, associated with small variations in the surfactant concentration, produce additional tangential stresses that translate into significant forces per unit volume of the film, thereby modifying film drainage rates.

The present paper solves the fully coupled flow and interface equations governing drainage and rupture of the film between interacting drops, together with those governing the surfactant transport and interfacial tension, at the following assumptions:

(a) Axisymmetric drop approach, under a small constant interaction force (small deformation);
(b) A nonionic surfactant;
(c) A low surfactant concentration.

For a discussion about the limitations imposed by the above restrictions see [5].

Numerical solutions of the equations governing film drainage are available in the case of pure liquids [6–11]. The effect of insoluble surfactants is also investigated intensively: on the film drainage [12,5,13–15]; on the interaction between surfactant covered spherical drops [16,17]. The influence of inter-phase mass transfer on the film drainage is studied numerically in [18–20].

The primary objective of the present paper is to develop a numerical procedure for solving the fully coupled system of equations governing the hydrodynamics and the surfactant transport in both phases as well as on the interface. The present study is an extension of previous works, where surfactants soluble only in one of the phases are considered: in the film phase [21] or in the drop/dispersed phase [22].

In the following section, the equations governing the film drainage and rupture in the absence of surface active species are extended to incorporate the influence of a surfactant soluble in both phases. In Section 3 the mathematical model is written in terms of transformed variables, making use of the simplifications provided by the limitation to low surfactant concentrations and small deformation. The numerical method is presented in Section 4. It consists of finite-difference schemes: explicit for the film and the interfacial convection–diffusion equation and hybrid (explicit/implicit) for the equations governing the convection–diffusion in the drop and film phases. A boundary integral method is used for the Stokes equations in the drop phase. In Section 5, results are presented and discussed. Finally, the conclusions are presented in Section 6.

## 2. Mathematical formulation

We consider two drops of one and the same Newtonian liquid interacting along the line of their centers under a given interaction force or velocity in another immiscible Newtonian fluid, see Fig. 1. Here $\mu$ is the drop viscosity, $h(r,t)$ is the film thickness, $t$ denotes time. The surfactant concentrations in the film and in the drop phase are $C(r,z,t)$ and $C_d(r,z,t)$ respectively. In the present paper the drops are considered to approach each other at specified velocity $V(t)$, which is adjusted during the drainage process to maintain a constant interaction force. The same procedure can, however, be used for time-dependent approach velocities, including force–time relationships representative of actual drop collisions.

The model is simplified by a number of approximations, which are valid in the limit of gentle collisions (film radius $a$ is much smaller than drop radii $R_i$) and which have been discussed in [5]. In addition, the influence of both inertia and viscous normal stresses on the film flow and on the adjacent flow in the drops is supposed to be negligible—an approximation that