Development and use of interface-capturing methods for investigation of surfactant-covered drops in electric fields

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Thesis for the degree of philosophiae doctor

Faculty of Engineering Science and Technology

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Abstract

This thesis investigates the development and use of interface-capturing methods for detailed simulations of surfactant-covered drops in electric fields.

A mathematical model is established for the full hydrodynamic behavior of the drops, including both electric forces caused by an applied electric field and forces due to the non-uniform surface tension caused by the presence of surfactants. Equations for the electric field and for the coupled evolution of surfactants are investigated. Both the level-set method and the phase-field method are used. For the level-set method, the ghost-fluid method which treats discontinuities across the interface in a sharp manner is considered and compared to the conceptually simpler continuous surface-force method. For the phase-field method, sophisticated numerical approaches including nonlinear multigrid methods on block-structured adaptive grids are used to enable simulations in full 3D.

Several physical configurations are examined. It is shown how an electric field can suppress the partial coalescence phenomenon occurring when a drop coalesces with an interface. It is demonstrated that the presence of a surfactant can considerably slow down a sedimenting drop due to inhibition of internal circulation. Conversely, an electric field speeds up the sedimentation due to stretching which leads to reduced drag. The deformation of a surfactant-covered leaky dielectric drop in an electric field is studied, and rich deformation behavior due to the complex interaction between the electric field and the surfactant is demonstrated. Finally, full 3D simulations of a drop in shear flow are performed, with particular emphasis on the influence of a soluble surfactant. It is shown that for the insoluble case, the drop can break up at a later time compared to a clean drop, while for the soluble case, the drop can break up at a later time.

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Preface

The present work was initiated as part of the research project "Electrocoalescence – Criteria for an efficient process in real crude oil systems"; coordinated by SINTEF Energy Research. The project is supported by The Research Council of Norway, under the contract no: 16046/530, and by the following industrial partners: Aker Solutions AS, BP Exploration Operating Company Ltd, Hamworthy Technology & Products AS, Petroleas, Saudi Aramco, Shell Technology Norway AS and Statoil ASA.

I would like to thank my supervisor, Professor Inge R. Gran, for trusting me to pursue my own ideas and thoughts. Thanks are also due to my co-supervisor, Dr. Svend Tollak Munkejord, for always having an open door, an open ear and an open mind. Many thanks to the rest of the electrocoalescence project members and partners for interesting discussions.

I am indebted to Professor John Lowengrub for inviting me to University of California, Irvine. My stay at UC Irvine was enlightening and enjoyable both from a personal and a professional perspective. I also extend thanks to all the people at Lowengrub’s lab who contributed to the work, Fang Jin, Fan Wang, Peng Song, Steven Wise, Xiangrong Li, Zhengzheng Hu and to the rest of the people there for welcoming me.

The financial support received from the Leiv Eriksson mobility programme is gratefully acknowledged. I am also grateful from the support from the Fulbright Foundation, in particular for their invaluable aid in all the practical matters of going abroad and for the inspiring Philadelphia Fulbright Seminar.

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1.1 Background

Oil extracted from offshore oil wells typically contains a significant amount of water. As a result of the oil-water mixture passing through valves and pumps, this water takes the form of small drops, see Figure 1.1 for an example. Since the density of water is larger than that of the oil, it is common to remove the water by sedimentation, where the oil-water mixture is placed in large separation tanks and the water drops eventually fall to the bottom of the tank and is extracted. There is a trend towards moving oil production to floating vessels, called floating production, storing and offloading (FPSO) units. These units have restricted space, so the large separation tanks are problematic. Also, due to uncertainties in future oil production, there is a push towards developing heavier, more viscous oils. These issues create a need for more efficient, and more compact separation units.

In order to understand the separation process, it is instructive to consider a single, small water drop falling through a viscous oil. An approximation of the terminal velocity of such a drop is given by Stokes’ law:

\[ V_t = \frac{\Delta \rho g D^2}{18 \mu} \]

(1.1)
Here, $\Delta \rho$ is the density difference between water and oil, $g$ is the gravitational acceleration, $D$ is the diameter of the drop and $\mu$ is the viscosity of the oil. This formula makes it clear that for heavy, viscous oils and small water drops, the sedimentation process can be very time consuming. It is also evident that to speed up the process, the parameter that has the most significant impact on the falling velocity is the drop diameter. Hence, the most efficient way to speed up the sedimentation process is to obtain larger drops by drop coalescence. This simple observation is utilized in electrostatic coalescers. Due to the large difference in electrical conductivity between salt water and oil, the water behaves as a conductor and the oil as an insulator. When an electric field is applied to a water-in-oil mixture, the water drops are polarized as illustrated in Figure 1.2. This leads to attractive forces between the water drops, which again lead to coalescence.

A drop coalescence event can typically be divided into three stages. The first is drop approach, where the drops are brought into contact. The second is film-thinning, where the thin oil film between the drops is squeezed out by the approaching interfaces. The third and final stage is film rupture and coalescence. To see at which of stage the electric field has greatest influence, it is elucidating to approximate the two drops as dipoles. This leads to a simple expression for the force between them (see e.g. Klingenberg et al. (1991)),

$$ F = \frac{24\pi\varepsilon E R^2}{\varepsilon_0} $$

(1.2)

where $s$ is the permittivity of the oil, $E$ is the electric field magnitude, $R$ is the drop radius and $h$ is the distance between the drops. Due to the $h^-4$ term, we understand that the drops need to be very close in order for the electric forces to have a significant impact. Therefore, the electric field mainly speeds up

The water drops appear black due to the image-capturing technique.

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the film-thinning process, and other forces are needed to bring the drops into contact. In modern commercial electrocoalescers, the electrodes are typically placed where the flow is turbulent. The turbulent forces increase the collision frequency, and the electric forces increase the probability of coalescence during a collision event.

Another factor that is important during the film-thinning process, is the presence of surface-active agents (surfactants). Surfactants are amphiphilic organic compounds which are naturally present in the crude oil, and can be adsorbed at the oil-water interface. The presence of surfactants reduce the surface tension of the interface, and this can in turn significantly impact the film-thinning process. When two drops approach each other, as illustrated in Figure 1.3, surfactant molecules will be swept from the tip of the drop. This will create a surface-tension gradient, which gives rise to tangential stresses along the interface. These stresses will reduce the internal circulation in the drop and inhibit the drainage of the intermediate oil film. It has been observed experimentally in Ha and Yang (1998) and it was found that the presence of surfactants affected both the amount of deformation and the mode of breakup.

In order to obtain a deeper understanding of the electrocoalescence process,
this work sets out to establish mathematical models for describing the above processes. It is also necessary to develop the numerical methods needed to solve the mathematical models in an accurate and efficient manner.

1.2 Relevance to other areas
It is important to emphasize that the present work has relevance reaching beyond just the problem of electrocoalescence. The models and methods developed here can easily be applied to a multitude of other interesting areas.

Electric fields are used to control or modify two-phase flows in several different areas. These include enhanced heat transfer in heat exchangers (e.g. Lasbalderdecha et al. (2007)), drop generation in inkjet printers (e.g. Yu et al. (2005); Shin et al. (2004)) and drop manipulation on lab-on-a-chip devices (e.g. Link et al. (2006); Cristini and Tan (2004)).

The topic of surfactants is also important in other areas. Besides their impact on drop break-up and coalescence (e.g. Hu et al. (2000); Hudson et al. (2003); Leal (2004); Hameed et al. (2008)), surfactants play important roles in vortex pair interaction (e.g., Tryggvason et al. (1992); Hirs and Willmarth (1994)), fingering (e.g. Troian et al. (1999); Matar and Troian (1999)) and are also important in biomedical applications (e.g. Singh and Cameotra (2004)) and in the food industry (e.g. Nitschke and Costa (2007)).

Solving the surfactant dynamics can be generalized to the problem of solving an equation along a general, moving interface and where the bulk dynamics and interface dynamics are coupled. Problems where this is important include biomembranes where transmembrane proteins play an important role in intra- and extra- cellular dynamics (e.g. Kockelkoren et al. (2003); Allain and Amar (2008)), surfactants play important roles in vortex pair interaction (e.g., Tryggvason et al. (1992); Hirs and Willmarth (1994)), fingering (e.g. Troian et al. (1999); Matar and Troian (1999)) and are also important in biomedical applications (e.g. Singh and Cameotra (2004)) and in the food industry (e.g. Nitschke and Costa (2007)).

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(2008); Levine and Rappel (2005); Gomez-Marin et al. (2007), epitaxially grown thin films where adsorbing/desorbing adatoms affect the dynamics and coarsening of the thin film (e.g. Fried and Gurtin (2004); Stocker and Voigt (2008); Li et al. (2009a)), and electrochemical dissolution of binary alloys where one component is removed selectively and dissolved in an electrolyte solution (e.g. Erlebacher et al. (2001); Eilks and Elliott (2008)).
Mathematical modelling and numerical methods

Essentially, all models are wrong, but some are useful.

George E. P. Box

Today you are in an entirely different situation. You don’t have to put the problem on a Procrustean bed and mutilate it before you attack it numerically.

Peter Lax - winner of the Abel Prize 2005

In this chapter, a brief overview of the mathematical models and numerical methods employed in this work are given. The flow dynamics in a many industrial processes covers a wide range of scales, and it is impossible to include all scales in a single model. Therefore, a multiscale approach to modelling is envisioned, where different models suitable for each scale are used together. Figure 2.1 shows an illustration of such a modelling hierarchy for the electrocoalescence process. At the microscale, interface-tracking/capturing methods are employed. These methods are capable of accurately resolving the movement of the drops and the deformation of the interfaces. As demonstrated in Cristini and Tan (2004), these methods are ideal for studying breakup and coalescence phenomena. The level of detail of interface-capturing techniques can in many cases provide information that is not immediately available from experiments. However, they also require high grid resolutions, so the number of drops that can be simulated is limited to small systems. Typically, only one or two drops can be simulated within reasonable times on a single workstation.

In discrete particle methods, each drop is modelled as a spherical particle, and force relationships between these particles are used to advance the solution in time. This simplified arrangement allows for more drops to be simulated. In Melheim (2007), electrocoalescence was simulated using 1 x 10^6 drops. The quality of such a simulation is obviously highly dependent on the accuracy of the models used to represent the forces between the particles.

Even larger systems may be taken into consideration using multi-fluid methods. Here, only the averaged effect of drops are taken into account. This gives rise to unknown terms in the flow models, which need to be modelled to obtain the models used to represent the forces between the particles.

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2. Mathematical modelling and numerical methods

2.1 Mathematical formulation

Consider a domain $\Omega \subset \mathbb{R}^3$, which contains a closed interface, $\Gamma$. The interior of the interface is $\Omega_1 \subset \Omega$, and the exterior is $\Omega_2 \subset \Omega$. See Figure 2.2 for an illustration. The interface is allowed to move, deform, and even change topology. A complete mathematical model for this problem includes equations governing the flow and appropriate interface relations accounting for discontinuities at the interface. These are considered next.

2.1.1 Flow equations

We assume that the flow is governed by the Navier-Stokes equations in each phase, with additional terms accounting for interfacial-tension forces and a closed system. Again, the quality of such a simulation is dependent on the accuracy of the models used.

To derive the models needed for discrete-particle methods and multi-fluid methods a combination of theory and experiments are needed. Theoretical considerations and insight into the physical phenomena can provide a good starting point, and experiments can be used to find unknown constants or to tweak the model parameters. There is a two-way interaction between experiments and numerical simulations. Simulations can provide insight that can assist in designing useful experiments, and results from experiments can aid in developing more accurate simulation tools. The purpose of this work is to develop representative mathematical models and accurate interface-capturing methods for simulating the electroosmotic process at the microlevel. In particular, models and methods suitable for studying the combined effect of an electric field and surface-active agents are considered.

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electric forces. The Navier–Stokes equations are
\[ \rho \left( \frac{\partial u}{\partial t} (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = -\nabla p + \nabla \cdot (\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) + \mathbf{f}_c + \mathbf{f}_e, \]
\[ \nabla \cdot \mathbf{u} = 0, \quad (2.1) \]
where \( \rho \) is the density, \( \mathbf{u} \) is the velocity, \( p \) is the pressure and \( \mu \) is the dynamic viscosity. The effect of an interface, \( \Gamma \), in the domain results in a singular surface force which can be expressed by
\[ f_c(x,t) = \int_{\Gamma} F(s,t) \delta(x - X(s,t)) \, ds, \]
\[ (2.2) \]
where \( s \) is the arc-length, \( X(s,t) \) is the parametrization of the interface, \( x \) is the spatial position and \( \delta \) is the Dirac delta function. \( F \) is given by
\[ F = \gamma \kappa \mathbf{n} + \nabla \gamma. \]
\[ (2.3) \]
Here, \( \gamma \) is the interfacial tension, \( \kappa \) the curvature and \( \mathbf{n} \) is the inward pointing unit normal vector. The surface gradient operator, \( \nabla \Gamma \), can be written as
\[ \nabla_{\Gamma} = (I - \mathbf{n} \otimes \mathbf{n}) \nabla. \]
\[ (2.4) \]
The first term on the right-hand side of Equation (2.3) accounts for the capillary force which acts perpendicularly to the drop interface. This force is present at

Figure 2.2: Illustration of the mathematical domain.
all liquid interfaces. The second term is an additional force due to gradients in the interfacial tension, which can occur if surfactants are present on the interface. This force acts tangentially to the interface. The electric force is given by the divergence of the Maxwell stress tensor, \( f_e = \nabla \cdot \mathbf{S} \), where

\[
\mathbf{M} = \varepsilon_0 E E + \varepsilon I I .
\]  

(2.5)

Here, \( E \) is the electric field and \( I \) is the identity tensor. We assume perfect dielectric materials with no free charges. A conducting drop in an insulating medium, which is the case for a water drop in oil, can then be approximated by setting \( \varepsilon_0 \gg \varepsilon_{\text{oil}} \).

With these assumptions, the electric potential, \( \Phi \), can be calculated from the following Laplace equation:

\[
\nabla \cdot (\varepsilon_0 \nabla \Phi) = 0,
\]  

(2.6)

The electric field can then be calculated as

\[
E = -\nabla \Phi.
\]  

(2.7)

With the above assumptions, \( \nabla \cdot \mathbf{M} = 0 \) everywhere except at the interface. Next, we assume that the interface is covered by surfactants, and we let \( f \) denote the surfactant concentration defined on the interface. \( \Gamma \) is the surface elasticity parameter and expresses the sensitivity of the interfacial tension to changes in the surfactant concentration. For a dilute surfactant, the above expression can be simplified to give a linear equation,

\[
y(f) = y_0 - \Gamma f.
\]  

(2.9)

This expression is often used in the literature. A comparison between these two expressions is given in Figure 2.3. It is evident that the linear equation of state is a good match at low concentrations, but fails to reproduce the steep gradient at higher concentrations. The non-linear equation of state is used for all simulations in this work.

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Assuming that $f$ may be extended off $\Gamma$, the sharp-interface representation of the evolution of the surface surfactant is given by (see e.g. Xu and Zhao (2003))

$$\frac{\partial f}{\partial t} = \nabla \cdot (\mathbf{u} f - n \cdot \nabla f) + D_f \mathbf{\nabla}^2 f - \kappa \mathbf{n} \cdot \nabla f + j_f,$$  

(2.10)

where $D_f$ is the diffusion coefficient. The source term, $j_f$, accounts for adsorption and desorption of surfactant and is given by

$$j(f,F) = r_a F_s (f_s - f) - r_d f.$$  

(2.11)

Here, $r_a$ and $r_d$ are adsorption and desorption coefficients, respectively, and $F_s$ is the surfactant concentration immediately adjacent to the surface.

Now, assume that $f$ is soluble in $\Omega_s$, but not in $\Omega_b$. Let there be a bulk concentration, $F$, in $\Omega_b$, which is governed by

$$\frac{\partial F}{\partial t} + \mathbf{\nabla} \cdot (\mathbf{u} F - n \cdot \nabla F) = D_f \mathbf{\nabla}^2 F,$$  

(2.12)

with the boundary condition at $\Gamma$

$$D_f \mathbf{\nabla} \cdot n = -j_f \text{ on } \Gamma.$$  

(2.13)

Here, $D_f$ is the diffusion coefficient in the bulk.

The equations for the surfactant on the interface and in the bulk are coupled through the source term, $j_f$. In order to simplify the mathematical representation, let $\delta$ be the surface delta function such that

$$\int_{\Gamma} f \, dt = \int_{\Gamma} f \delta \, dt,$$  

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$$\int_{\Gamma} f \, dt = \int_{\Gamma} f \delta \, dt.$$  

(2.14)
Also, let $H$ be the Heaviside function,
\[
H = \begin{cases} 
1 & \text{in } \Omega_i, \\
0 & \text{in } \Omega_o.
\end{cases}
\]  (2.15)

The equation for the interfacial surfactant, Equation (2.10), can now be extended to the general domain $\Omega$ (see e.g. Rätz and Voigt (2006)),
\[
\frac{\partial}{\partial t} (f \delta) + \nabla \cdot (f \delta \mathbf{u}) = D \nabla \cdot (\nabla \Phi f + \delta f),
\]  (2.16)
The formulation given by Equation (2.16) is considerably simpler than the sharp-interface formulation.

Similarly, the bulk concentration can be generalized to the general domain by
\[
\frac{\partial}{\partial t} (f M) + \nabla \cdot (f M \mathbf{u}) = D \nabla \cdot (f \nabla \Phi M + \delta M),
\]  (2.17)
where the boundary condition has been included using the approach from Li et al. (2009b). By introducing numerical regularizations of the delta function and Heaviside function, the much simpler mathematical expressions can be used to evolve the surfactant concentrations.

### 2.1.2 Interface relations

The formulation given by Equation (2.16) includes the jump conditions as
\[
\left[ u \right] = 0,
\]  (2.18)
\[
\left[ p \right] = -2\left[ \mu \nabla \cdot \mathbf{u} \right],
\]  (2.19)
\[
\left[ \nabla \cdot \mathbf{u} \right] = 0,
\]  (2.20)
\[
\left[ \nabla \cdot (\nabla \Phi M) \right] + \left[ \nabla \cdot (\nabla \Phi f) \right] = 0,
\]  (2.21)
\[
\left[ (\nabla \cdot (\nabla \Phi f) \right] = 0,
\]  (2.22)
\[
\left[ \nabla \cdot (\nabla \Phi M) \right] = 0.
\]  (2.23)

Also, let $H$ be the Heaviside function,
\[
H = \begin{cases} 
1 & \text{in } \Omega_i, \\
0 & \text{in } \Omega_o.
\end{cases}
\]  (2.15)

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\frac{\partial}{\partial t} (f \delta) + \nabla \cdot (f \delta \mathbf{u}) = D \nabla \cdot (\nabla \Phi f + \delta f),
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### 2.1.2 Interface relations

The variation in physical properties in the two domains gives rise to discontinuities across the interface which need to be considered to complete the model. The jump conditions for the two-phase problem without electric fields can be found in e.g. Kang et al. (2000). In Hansen (2005); Bjørklund (2009) these are extended to include electric fields, and in Løvberg (2008) the Marangoni stresses are included. Here, we summarize the jump conditions as
\[
\left[ u \right] = 0,
\]  (2.18)
\[
\left[ p \right] = -2\left[ \mu \nabla \cdot \mathbf{u} \right],
\]  (2.19)
\[
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\]  (2.22)
\[
\left[ \nabla \cdot (\nabla \Phi M) \right] = 0.
\]  (2.23)
2.2 Numerical methods

With the complete models in place, the question remains how to tackle them numerically. In particular, how to address the interface is the major challenge, and this will be considered in the next section.

2.2.1 The level-set method

In this work, the equations from the previous sections are solved using the finite-difference method on Cartesian grids. Standard discretization methods from the literature are employed, and more details can be found in the individual papers. This chapter will focus on how the interface is represented and how the boundary conditions between the two phases are captured. Two approaches are considered, the level-set method and the phase-field method. Both are interface-capturing methods, which means that instead of tracking the interface explicitly using a surface mesh, it is captured implicitly by an auxiliary function defined in the entire domain. This leads to a significantly simpler implementation, since Cartesian grids can be used and topological changes are handled automatically.

In the level-set method (see e.g. Sussman et al. (1994); Osher and Fedkiw et al. (1994); Osher and Fedkiw (b))

Figure 2.4: Illustration of the level-set function representing a drop with radius 0.15.

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(2.28), the interface is defined implicitly by the zero level set
\[ \Gamma = \{ x \mid \phi(x) = 0 \}, \] (2.24)
where \( \phi \) is the level-set function, which denotes the signed distance to the interface. An example of how the level-set function looks for a drop is given in Figure 2.4. The level-set function moves with the interface velocity \( u_{\text{int}} \) according to
\[ \frac{d \phi}{dt} + u_{\text{int}} \nabla \cdot \phi = 0. \] (2.25)
Note that this equation is a pure advection equation, and hence accurate numerical schemes must be used to solve this equation. Additionally, to discretize this equation numerically, the interface velocity must be extended off the interface. Adalsteinsson and Sethian (1999) showed that the velocity could be extrapolated orthogonally from the interface by solving
\[ \frac{d \phi}{d t} + \nabla (\phi^n \cdot \nabla \phi) = 0, \] (2.26)
where \( S \) is a sign function given by
\[ S(\phi) = \frac{\phi}{\sqrt{\phi^2 + \Delta \Delta \phi^2}}, \] (2.27)
As the level-set function is advected, it will not remain an exact distance function due to numerical errors. This can be alleviated using reinitialization procedures, that attempt to keep the interface position intact while resetting the level-set function to a distance function. The standard level-set reinitialization procedure is used here, that is we solve the additional equation
\[ \frac{d \phi}{d t} + \nabla (\phi^n (|\nabla \phi| - 1)) = 0, \] (2.28)
An attractive feature of the level-set method is the simple access to geometrical properties, in particular the normal vector and the curvature. With the level-set function as a signed distance function, the normal vector can be calculated as
\[ n = \nabla \phi \left( \begin{array}{c} \phi \end{array} \right), \] (2.29)
and the curvature as
\[ \kappa = \nabla \cdot \frac{\nabla \phi}{|\nabla \phi|}, \] (2.30)
The density, viscosity and permittivity are discontinuous across the interface. These are handled in two different ways in this work. The simplest and most common method is the continuous surface force (CSF) method, introduced by Brackbill et al. (1992), where the singular surface force is smoothed across a narrow region.

\[ f_c = \gamma \kappa H \nabla H \cdot (\nabla \chi) \theta_h, \] (2.31)

where \( H \) is the regularized Heaviside function, defined as

\[ H(\phi) = \begin{cases} 0 & \phi < -c \\ \frac{1}{2} + \frac{1}{2} \sin \left( \frac{\pi \phi}{2c} \right) & |\phi| \leq c \\ 1 & \phi > c \end{cases} \] (2.32)

Here, \( c \) is the smearing width. In this work, the interface is smeared across three grid cells, i.e. \( c = 1.5h \), where \( h \) is the grid spacing. The regularized surface delta function, \( \delta_h \), is defined as

\[ \delta_h(\phi) = \frac{\phi - c}{2} + \frac{1}{2} \sin \left( \frac{\pi \phi}{2c} \right) \] (2.33)

The physical properties are also smoothed according to

\[ \rho(\frac{\partial H}{\partial t}) = \rho \frac{\partial H}{\partial t} + (1 - \theta_h) \rho \] (2.34)

\[ \mu(\frac{\partial H}{\partial t}) = \mu \frac{\partial H}{\partial t} + (1 - \theta_h) \mu \] (2.35)

\[ \frac{1}{\varepsilon} \frac{\partial H}{\partial t} = \frac{1}{\varepsilon} \frac{\partial H}{\partial t} + (1 - \theta_h) \frac{1}{\varepsilon} \] (2.36)

It was shown by Tomar et al. (2007) that using a harmonic mean for the electrical properties was beneficial over an arithmetic mean. Note that in principle, the above regularizations of the delta function and Heaviside function could be used to solve the surfactant equations from the previous section. However, this was found not to work very well, which is believed to be because these regularizations are not accurate enough. Recently, there has been a lot of work on finding more accurate representations, for instance Smereka (2006); Towers (2007); Min and Gibou (2008), which may lead to better results. In this work, only an insouible, interfacial surfactant was considered together with the level-set method, and the sharp-interface representation given by Equation (2.10) was solved directly. This is also the approach taken in Xu and Zhao (2003); Xu et al. (2006).

The second method of handling the discontinuities is the ghost-fluid method (GFM) (see e.g. Fedkiw (1999)). Here, instead of smearing out the discontinuities,
they are handled in a sharp manner by employing the interface relations. This gives a more accurate numerical method, at the expense of a more complex implementation. The basic principle of the method will be illustrated by considering the discretization of the following 1D Poisson equation:

$$\frac{d^2 u}{dx^2} + f(x) = 0.$$  \hspace{1cm} (2.37)

The GFM requires jump conditions, which are relations between the physical quantities on each side of the interface. In the following, the interfacial jump is denoted by $[u] = u^+ - u^-$, where superscript $+$ denotes the side of the interface where $\phi$ is positive, and superscript $-$ denotes the side of the interface where $\phi$ is negative. For the purpose of this section, we assume that the interface conditions are given by

$$[u] = a$$  \hspace{1cm} (2.38)

$$\frac{du}{dx} = b.$$  \hspace{1cm} (2.39)

We also assume that $\beta$ is constant in each phase. Suppose that we have the condition given in Figure 2.5, where an interface is located between $k$ and $k+1$. The standard, second-order discretization of Equation (2.37) is

$$h u_{k-1} + 2 u_k - h u_{k+1} = f_k.$$  \hspace{1cm} (2.40)

This discretization gives second-order accuracy if $f$ and $u$ are smooth functions. But here, because of the discontinuity between points $k$ and $k+1$, there will be

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2.2. Numerical methods

an error at the interface, which will smear the discontinuity. Instead, we would
like to use the value at the interface, i.e.
\[ \beta \frac{\partial u}{\partial x} - \beta \frac{\partial u_k}{\partial x} = f_k. \]  
(2.41)

Here, \( \theta \) is the normalized distance to the interface,
\[ \theta = \frac{x_l - x_k}{\Delta x}. \]  
(2.42)
The main idea of the GFM is to use the jump conditions to find an approximation
of the interfacial value. Discretizing the second jump condition, Equation (2.39),
gives
\[ \beta \frac{u_{k+1} - u_k}{\Delta x} - \beta \frac{u_k - u_{k-1}}{\Delta x} = b. \]  
(2.43)
We can now find the approximated value at the interface by using the first jump
condition, Equation (2.38):
\[ u_l = \frac{\beta \theta u_{k+1} + \beta \theta u_k - \beta \theta u_{k-1}}{\beta \theta + 1}. \]  
(2.44)
Finally, this can be inserted into Equation (2.41) to give the following symmetric
discretization:
\[ \frac{\beta (u_{k+1} - u_k) - \beta'(u_k - u_{k-1})}{\Delta x^2} = f_k \frac{\hat{\beta} a}{\Delta x^2}, \]  
(2.45)
where \( \hat{\beta} \) is defined as
\[ \hat{\beta} = \frac{\beta' \beta''}{\beta'' + 1}. \]  
(2.46)
This method can be applied in a dimension-by-dimension fashion, so an exten-
sion to two or three dimensions is straightforward.

2.2.2 The phase-field method

The phase-field method is used in a lot of different areas. For an overview of
its use in fluid mechanics, see e.g. Anderson et al. (1998) and Jacqmin (1999). In
the phase-field method, the interface is defined implicitly through a phase-field
function, \( \phi \), which is 1 in \( \Omega \) and varies rapidly but smoothly to 0 in \( \Omega_2 \). More
precisely, the phase-field function is taken as
\[ \phi(x,t) = \frac{1}{2} \left[ 1 - \tanh \left( \frac{\phi(x,t)}{\Delta x} \right) \right]. \]  
(2.47)

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\[ \hat{\beta} = \frac{\beta' \beta''}{\beta'' + 1}. \]  
(2.46)
This method can be applied in a dimension-by-dimension fashion, so an exten-
sion to two or three dimensions is straightforward.
where $c$ is a small parameter related to the interface thickness. An example of how the phase-field function looks for a drop is given in Figure 2.6. Here, the radius of the drop is 0.15, and the interface thickness parameter is 0.01. As is evident from the figure, the phase-field function can in the context of two-phase flow be interpreted as a concentration.

To advect the phase-field function, a Cahn-Hilliard equation is solved,

$$\frac{\partial c}{\partial t} + \nabla \cdot (c \nabla \mu) = \nabla \cdot (M(c) \nabla \mu),$$  

(2.48)

$$\mu = g'(c) - c^2 \nabla^2 c,$$  

(2.49)

where $M = \sqrt{c(1-c)c'}$ is a mobility function and $g = c^2(1-c)c'/4$ is a double well potential. $\mu$ is called the chemical potential and $c$ is a small parameter related to the interface thickness. Note that the above equation system is fourth-order and non-linear, which requires specialized numerical methods to solve in an efficient manner.

Since the phase-field method uses a diffuse interface similar to the CSF method, regularizations of the surface delta function and Heaviside function are needed. In the phase-field context, several definitions of the delta function are available from the literature. In this work, the approximation from Rätz and Voigt (2006),

$$\delta B(c) = \frac{2}{\sqrt{\pi}} c^2(1-c)^2,$$  

(2.50)

is used for the surface equation. For the surface-tension term and the boundary condition in the bulk equation, the approximation

$$\delta B = |\nabla c|,$$  

(2.51)

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is used. This is to avoid any scaling of the equations. In the surface equation, the constants in Equation (2.50) cancel out in the discretized equations. The regularized Heaviside function, is simply taken as \[ H(c) = 1 - c. \] (2.52)

2.2.3 Discussion

The level-set method and the phase-field method share many similarities, in particular when the level-set method is used in conjunction with the CSF method for handling the interface discontinuities. In fact, some works exist that borrow from both methods. For instance, in Olsson and Kreiss (2005), a level-set method is designed that uses an interface profile similar to the phase-field function. Artificial compression is then used to keep the shape and width of the profile constant which leads to a conservative scheme with respect to mass conservation. In Kronbichler and Kreiss (2008), a hybrid method was studied where the level-set method was used for external flow, while the phase-field method was used to capture contact-line dynamics near solid boundaries. One of the key advantages of the phase-field method is that no artificial compression or renormalization is needed, these effects are already incorporated in the Cahn-Hilliard equation. Another advantage is that the phase-field method is more flexible with respect to complex physical effects. The diffuse interface in the phase-field method can be viewed as a layer that stores a mixing energy that gives rise to interfacial tension. The use of this energy formulation makes it easy to include more complex physical effects. For instance, the phase-field method was used to include viscoelasticity in Yu et al. (2005), contact-line dynamics in Kronbichler and Kreiss (2008) and bending energy in the context of vesicle membranes in Lowengrub et al. (2009). Another attractive feature of the phase-field method is that it is possible to derive thermodynamically consistent models, see e.g. Anderson et al. (1998), Penrose and Fife (1990). In this work, the method is used to handle the problem of coupling the bulk surfactant to the interfacial surfactant. This does not require any energy considerations, but the approach takes advantage of the phase-field method’s ability to incorporate complex boundary conditions on the interface in a simple manner.

However, the complexity of the Cahn-Hilliard equation makes it difficult to handle numerically. The use of a diffuse interface layer also makes the method less accurate and cost effective for certain problems compared to the level-set method. In other words, both numerical approaches used in this work are useful, but their advantages and disadvantages should be taken into account when deciding which method to use for a particular problem.

2.2. Numerical methods

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In this paper, a thorough evaluation of the accuracy of the ghost-fluid method in the context of electric fields is given. The method is compared both against theoretical results and the simpler continuous surface-force method. Such an evaluation was found lacking from Hansen (2005), where the use of the ghost-fluid method for problems involving electric fields was first introduced. The paper also extends the 2D method presented in Hansen (2005) to a more physically relevant axisymmetrical geometry. Figure 3.1 demonstrates the sharp-interface behavior of the GFM and the higher accuracy compared to the CSF method.

The main contribution of this work is six articles published in peer-reviewed journals and conferences. In this section, a brief summary of each paper is given.

**Paper A - Sharp interface simulations of drop deformation in electric fields**

**Co-author: Svend Tollak Munkejord**

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Figure 3.1: (a) shows the ghost-fluid method applied to a horizontal interface test case. The pressure in the y-direction for a calculation with 10 grid points is compared to the exact solution. Note that the discontinuity in pressure is sharply resolved. (b) shows a comparison of the deformation of a drop in an electric field between theoretical values and the CSF method and the GFM. Note that the GFM is closer to the theoretical values.
When no electric field is applied, partial coalescence may occur, where a small portion of the drop does not coalesce but remains dispersed in the continuous phase. It has been shown experimentally in e.g. Allan and Mason (1962) that when an electric field is applied, this partial coalescence is suppressed. This paper investigates the problem numerically using the previously validated method. First, excellent agreement with experiments for a case without electric fields is demonstrated. Then, it is shown that the results with an applied electric field is in qualitative agreement with the experimental observations, and a physical explanation of the process is suggested. A figure from the paper demonstrating the difference with and without an electric field is shown in Figure 3.2.

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Figure 3.2: Comparison of the neck thickness and drainage rate with and without an electric field.

(a) No electric field (b) Applied electric field, $Bo = 0.1$

Figure 3.2: Comparison of the neck thickness and drainage rate with and without an electric field.

(a) No electric field (b) Applied electric field, $Bo = 0.1$
Paper C - Sharp interface simulations of surfactant-covered drops in electric fields

Co-authors: Karl Ynge Lervåg and Svend Tollak Munkejord

In this paper, a model for surfactants is introduced. To the authors’ knowledge, this is the first time the ghost-fluid method has been applied to the surfactant problem. The model is validated and used to study a falling drop. It is shown that the surfactant generally reduces the deformation and the terminal velocity of the drop. The reduction is most pronounced in the nearly spherical regime where the drop behavior is similar to a solid sphere due to the interface immobilization caused by the presence of a surfactant. This is shown in Figure 3.3. The electric field increases the terminal velocity by stretching the drop in the direction of the electric field which reduces the drag on the drop. This effect is largest for the surfactant-covered drop, which is deformed more due to the lower average interfacial tension.

Figure 3.3: Low Re drop. Streamlines and velocity vectors in a coordinate system moving with the drop centroid. Note how the internal circulation is completely stopped in the contaminated case, making the drop behave like a solid particle.
Paper D – Influence of surfactant on drop deformation in an electric field
Co-author: Svend Tollak Munkejord

This paper investigates the influence of surfactants on the deformation of a drop in an electric field. Instead of assuming a conducting drop and an insulating continuous phase, we extend the model to support a finite conductivity in both phases. This gives a much wider range of deformation behaviors and correspondingly interesting surfactant influence. The deformation can be both prolate and oblate, depending on the ratio of conductivities and permittivities. Additionally, the direction of the induced circulation can be both clockwise and counter-clockwise for the prolate shapes. It was found that for prolate deformation and counter-clockwise circulation, the presence of surfactant leads to greater deformation at low surfactant concentrations. At high surfactant concentrations and high electric capillary numbers, however, the effect of surfactant dilution becomes stronger than the effect of reduced interfacial tension at the tips, and the deformation decreases. For prolate deformation and clockwise flow, the surfactants are swept in the opposite direction, and cause a reduction in deformation. For oblate deformation, which always gives clockwise flow, the results are similar to that of prolate deformation and counter-clockwise flow. Deformation is increased until dilatational effects start to dominate. However, this occurs earlier here, since the surfactant is not concentrated at the tips, but instead spread out over the equator of the drop. Finally, it was shown that for smaller viscosity ratios, the influence of surfactant is stronger, since the relative importance of the Marangoni stresses becomes higher. Figure 3.4 shows the deformation as a function of electric capillary number for various surfactant coverages at a low viscosity ratio.

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Figure 3.4: Deformation as a function of electric capillary number for various surfactant coverages at viscosity ratio $\mu = 0.1$. Note that for case A, surfactant leads to more deformation, for case B surfactant leads to less deformation while for case C, the deformation is negative (oblate deformation instead of prolate) and surfactant leads to more deformation.
This paper introduces changes in both mathematical modelling and numerical methods. Instead of restricting the surfactant to the interface, we couple the interfacial surfactant concentration to a concentration in the bulk. This is a more physically realistic model. Instead of using the level-set method to capture the interface, the phase-field method is employed. These share many similarities, but the phase-field method makes it easier to handle the complexity of the coupled bulk/interface problem.

The model is solved using semi-implicit time discretization and block-structured adaptive grids for the spatial discretization. The semi-implicit time discretization allows longer time steps to be taken, and the adaptive grids limit high resolution grids to regions of interest. Additionally, a non-linear multigrid method is used to solve the equation systems arising at every time step. All these improvements lead to a much more efficient numerical method, suitable for full 3D simulations.

The paper introduces the numerical method, proves the convergence of the method and demonstrates the accuracy and efficiency of the method on multiple test cases. Figure 3.5 shows one of these test cases, the deformation of a 3D drop in a deformation field.
Figure 3.5: Sphere in 3D deformation field. Illustration of the adaptive grids and interfacial surfactant concentration. Inside the black boxes, the grid spacing is $h = 1/64$, inside the red boxes $h = 1/128$ and inside the green boxes $h = h_{\text{min}} = 1/256$. 

(a) Adaptive grid
(b) Interfacial surfactant concentration
Paper F – A diffuse-interface method for two-phase flows with soluble surfactants
Co-authors: John Lowengrub, Peng Song and Axel Voigt

In this paper, the phase-field method introduced in the previous paper is coupled to a flow solver. The method is validated, and used to study the influence of surfactant solubility on a drop in shear flow in both 2D and 3D. It is shown that the deformation of a drop with soluble surfactant in general lies between that of a clean drop and that of a drop covered with insoluble surfactant. However, for the breakup of a drop, it is shown that for the insoluble case, the drop can break up at an earlier time compared to a clean drop, while for the soluble case, the drop can break up at a later time. Figure 3.6 shows the breakup of the drop with soluble surfactant.
Figure 3.6: Three-dimensional simulation of a drop in shear flow with soluble surfactant. The left column shows the drop shape with the surface colored according to the interface surfactant concentration. The right column shows a slice of the bulk surfactant concentration along the $x$-axis.
Conclusions and recommendations for further work

The more I learn, the more I learn how little I know.

Socrates (407 BC–399 BC)

The more you know, the less you understand.

Laozi

In addition to the conclusions given in each separate paper, some general conclusions can be drawn. The contributions made in this work can be divided into three parts, mathematical modelling, numerical methods and investigation of physics.

First, consider the mathematical models. The models include the full Navier-Stokes equations in each phase, with additional terms accounting for the effect of an electric field and the effect of non-uniform surface tension. Equations for the electric field and the coupled evolution of surfactant on the interface and in the bulk were also considered. Several extensions to the model are possible. In particular, for high concentrations of surfactant, an aggregate may form on the interface. This film can be expected to behave in a viscoelastic manner. Models for drops with viscoelastic membranes have been developed for the study of biological flows and could also be considered for the present problem. Another issue not discussed in this work is the presence of close-range forces when two interfaces get close together, for instance the attractive van der Waals force. In particular, steric repulsion forces may become important when aggregates form causing a physical barrier against coalescence. In general, although such forces have in some cases been considered in conjunction with interface-capturing methods, the usefulness of this could be questioned since these forces become important at length scales below what can typically be resolved with the current numerical methods. This suggests a study at a lower level than the interface tracking/capturing level, perhaps using molecular dynamics methods.

Next, consider the numerical methods. This work has investigated the use of interface-capturing methods for multiphysics problems. Both the level-set method and the phase-field method were used, and both were found capable of handling the complex mathematical models considered. Although not tested explicitly in this work, it is expected that the accuracy of the phase-field method

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performs relatively similar to the CSF level-set method. As shown in papers A and C, the GFM is more accurate than the CSF method. This comes at the expense of a more complex implementation. In particular, implementing a semi-implicit solver for the GFM, as was done with the phase-field method, would be very difficult. It could be interesting to investigate a compromise where the simpler terms are treated using GFM and the more complex with CSF. The advantage of a semi-implicit scheme is the removal of a particularly stringent restriction on the time step where the time step is inversely proportional to the square of the grid spacing. This restriction makes accurate simulations of small, viscous drops very time consuming, particularly for very high resolution during a coalescence or breakup event. The block-structured, adaptive grid used here with the phase-field method helps alleviate this problem. However, only a serial implementation was developed for this work. A parallelization of the code would allow the study of more complex arrangements of drops.

Finally, consider the investigation of physics. It was shown how an electric field can suppress the partial coalescence phenomenon occurring when a drop coalesces with an interface. Next, it was demonstrated that the presence of a surfactant can considerably slow down a sedimenting drop due to inhibition of internal circulation. Conversely, an electric field speeds up the sedimentation due to stretching which leads to reduced drag. Next, the deformation of a surfactant-covered leaky dielectric drop was studied. This is not immediately useful with respect to a water-in-oil emulsion, since the conductivity of water is always several orders of magnitude higher than crude oil, but is interesting for other applications. It was shown that the presence of surfactant could lead to both more deformation and less deformation depending on the fluid properties due to the complex interaction between the electric field and the surfactant. For example, it was shown that a drop of a dielectric fluid, with particular emphasis on the influence of a soluble surfactant. It was shown that the deformation of a drop with soluble surfactant in general lies between that of a clean drop and that of a drop covered with a dielectric surfactant. However, for the breakup of a drop, it was shown that for the insoluble case, the drop can break up at a later time compared to a clean drop, while for the soluble case, the drop can break up at a later time. In general, the usefulness of the presented methods for studying drop dynamics in great detail was demonstrated. Opportunities for future work are plentiful. A parallel implementation of a small parameter set was considered in this work, so more in-depth studies of the same setups would be interesting. Further, simulations of drops colliding in external flows would be particularly elucidating. This would be an important step.
towards developing models higher up in the multiscale modelling hierarchy. There has been a lot of work in the literature on drop collisions in compressional flows and shear flows. However, little work has been done for an applied electric field, so this would be a natural starting point for further investigations.


computer simulation of turbulent electrocoalescence


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Sharp interface simulations of drop deformation in electric fields
Teigen, K.E, Munkejord, S.T., IEEE Transactions on Dielectrics and Electrical Insulation. Volume 16, Number 2 (2009), 475-482
### 1 INTRODUCTION

**Electrohydrodynamic** Flows are in general very complex due to the interactions between electric forces and fluid dynamics, and analytical results are limited to simplified setups. The addition of more than one phase to the system further complicates the analysis. This inherent complexity underscores the use of numerical methods to gain additional insight into the physical phenomena.

Early numerical simulations of electrohydrodynamics typically assume either either Poiseuille flow or inviscid flows, which makes it possible to formulate the problem using integral equations. These equations can be solved analytically using the boundary-layer method (BEM). In [1], the deformation of a drop was studied using this approach, and in [2] the interaction between drop pairs was investigated. In [3] and [4], a finite-difference method which allowed solutions at finite Reynolds numbers was employed to study drop deformation in electric fields. It concluded that while the creeping-flow assumption was valid for low drop deformation, it was not able to predict phenomena occurring for higher deformations.

The methods mentioned so far do not take into account topological changes, e.g., the merging and breakup of drops. Recently, numerical methods have been developed that allow such topological changes. In the seminal paper [5], a front-tracking method was presented that uses a set of connected markers to represent the interface. The handling of topological changes is in a fairly complex. First, a search has to be made among the front elements to identify situations where a topology change is needed. Then, the elements have to be updated to account for the change. Additionally, when the interface is stretched, restructuring of the interface is necessary to maintain sufficient accuracy. This is a complicated process, especially in three dimensions. The jumps in a physical property across the interface is handled using a smeared interface. In [6], the front-tracking method was extended to account for electric fields, and the distribution of drops in a channel was investigated. This study, however, did not take the merging of colliding drops into account. In [7] and [8], a finite-difference method which allowed solutions at finite Reynolds numbers was employed to study drop deformation in electric fields. It concluded that while the creeping-flow assumption was valid for low drop deformation, it was not able to predict phenomena occurring for higher deformations. The methods mentioned so far do not take into account topological changes, e.g., the merging and breakup of drops. Recently, numerical methods have been developed that allow such topological changes. In the seminal paper [5], a front-tracking method was presented that uses a set of connected markers to represent the interface. The handling of topological changes is fairly complex. First, a search has to be made among the front elements to identify situations where a topology change is needed. Then, the elements have to be updated to account for the change. Additionally, when the interface is stretched, restructuring of the interface is necessary to maintain sufficient accuracy. This is a complicated process, especially in three dimensions. The jumps in a physical property across the interface is handled using a smeared interface.

**Numerical analysis, electrohydrodynamics, dielectric materials, finite difference methods, hydrodynamics, interface**

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However, the resulting interface is diffusive, i.e. it is a transitional region where the jumps in physical properties occur. In [7] and [8], a finite-difference method which allowed solutions at finite Reynolds numbers was employed to study drop deformation in electric fields. It concluded that while the creeping-flow assumption was valid for low drop deformation, it was not able to predict phenomena occurring for higher deformations. The methods mentioned so far do not take into account topological changes, e.g., the merging and breakup of drops. Recently, numerical methods have been developed that allow such topological changes. In the seminal paper [5], a front-tracking method was presented that uses a set of connected markers to represent the interface. The handling of topological changes is fairly complex. First, a search has to be made among the front elements to identify situations where a topology change is needed. Then, the elements have to be updated to account for the change. Additionally, when the interface is stretched, restructuring of the interface is necessary to maintain sufficient accuracy. This is a complicated process, especially in three dimensions. The jumps in a physical property across the interface is handled using a smeared interface.

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The accuracy of this approach was not evaluated directly. Some discrepancies in the induced flow field compared to theory for a drop in an electric field were found, and those were attributed to the use of a diffuse interface.

A third method that has recently been used for simulating electrohydrodynamic flows is the coupled level-set and volume-of-fluid (CLSVOF) method [9, 10]. In the level-set method [9, 10], the surface is described via an implicit function. In this method, the interface is approximated using sharp discontinuities. The CLSVOF method combines the advantages of the two methods, and eliminates some of the disadvantages. The method was used in [11] to investigate electrohydrodynamic effects on film boiling in perfect mass conservation.

Here, \( \rho \) is the density, \( \mathbf{v} \) is the velocity vector, \( \mathbf{e} \) is the unit normal vector, \( \kappa \) is the surface tension, and \( \mathbf{n} \) is the unit normal vector. In this approach, a surface-force (CSF) approach was used to handle surface-tension forces and electric forces: in this approach, a Halsine function is used to ensure the properties in a region around the interface. It is shown that by using a modified approach to the smearing of electrical properties, the accuracy was improved considerably.

The method used in the present work was proposed in [13, 14], and also uses the level-set method to capture the interface, but instead of using a Halsine function to handle the discontinuity, the ghost-fluid method (GFM) [15,16] is used. The ghost-fluid method modifies the numerical instabilities near the interface to directly take the discontinuity into account. This gives improved accuracy in the computation of surface forces. The high accuracy also makes it easy to implement.

In the method of the ability to simulate drop oscillations, drop breakup, and drop merging due to electrohydrodynamic effects on film boiling in perfect mass conservation.

It is possible to employ the modified approach to the smearing of electrical properties to simulate a drop complex due to jumps in tangential stresses across the interface, and hence beyond the scope of this work.

**2 GOVERNING EQUATIONS AND NUMERICAL METHODS**

The method used in the present work was proposed in [13, 14], and also uses the level-set method to capture the interface, but instead of using a Halsine function to handle the discontinuity, the ghost-fluid method (GFM) [15,16] is used. The ghost-fluid method modifies the numerical instabilities near the interface to directly take the discontinuity into account. This gives improved accuracy in the computation of surface forces. The high accuracy also makes it easy to implement.

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the relative permittivity of the fluid. The electric field can then be calculated as:

\[ \mathbf{E} = \nabla \phi - \mathbf{v} \times \mathbf{B} \]  

and the Maxwell stress tensor as

\[ \mathbf{M} = \varepsilon \mathbf{E} \times \mathbf{B} \]  

Here, \( \mathbf{E} \) is the identity tensor. With the above assumptions, \( \mathbf{M} \) everywhere except at the interface.

2.3 INTERFACE CAPTURING

The interface is captured using the level-set method [9,10]. This method allows accurate computation of the evolution of an interface, along with automatic handling of topological changes. The ghost-fluid method [11,16] is used to calculate discontinuities across the interface into account. This method handles the jumps in physical properties directly in the numerical stencils, without the need for any mapping of properties.

The interface is defined by the zero level set

\[ \phi(x) = 0 \]  

and is evolved by

\[ \frac{d\phi}{dt} = V \cdot \mathbf{n} \]  

Here, \( V \) denotes the signed distance to the interface, \( \mathbf{n} \) is the velocity on the interface, and \( V \) is not readily available, but in [17] it was shown that this velocity could be obtained by computing the velocity orthogonally from the interface. This is achieved by solving

\[ \frac{d\phi}{dt} = \frac{V}{\|\nabla \phi\|} \frac{\nabla \phi}{\|\nabla \phi\|} \cdot \mathbf{n} \]  

where \( \phi \) is a pseudotime and \( \mathbf{n} \) is a sign function. Here,

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Reinitialization is performed every second time step. One of the advantages with the level-set method is the easy calculation of normal vectors and curvature. The unit normal vector can be found as

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Here, \( V \) denotes the signed distance to the interface, \( \mathbf{n} \) is the velocity on the interface, and \( V \) is not readily available, but in [17] it was shown that this velocity could be obtained by computing the velocity orthogonally from the interface. This is achieved by solving

\[ \frac{d\phi}{dt} = \frac{V}{\|\nabla \phi\|} \frac{\nabla \phi}{\|\nabla \phi\|} \cdot \mathbf{n} \]  

where \( \phi \) is a pseudotime and \( \mathbf{n} \) is a sign function. Here,

\[ V = \frac{d\phi}{dt} \]  

and is evolved by

\[ \frac{d\phi}{dt} = \frac{V}{\|\nabla \phi\|} \frac{\nabla \phi}{\|\nabla \phi\|} \cdot \mathbf{n} \]  

Reinitialization is performed every second time step. One of the advantages with the level-set method is the easy calculation of normal vectors and curvature. The unit normal vector can be found as

\[ \mathbf{n} = \frac{\nabla \phi}{\|\nabla \phi\|} \]  

and the curvature as

\[ \kappa = \frac{\|\nabla^2 \phi\|}{\|\nabla \phi\|^3} \]
Finally, this can be inserted into (2.20) to give the following
symmetric discretization:
\[
\frac{1}{\Delta y} \left( \frac{\partial}{\partial y} \left( \alpha \frac{\partial \phi}{\partial y} \right) \right) = -\frac{1}{\epsilon_y} \frac{\partial}{\partial y} \left( \frac{\partial \phi}{\partial y} \right)
\]
(2.23)
where \( \phi \) denotes the computational value of the \( y \)-coordinate.

3 METHOD EVALUATION

This section compares results from the CFD approach used in [12] and [11] with results from the sharp-interface method used here. The first test case is a horizontal interface in an electric field. The test case is excellent for evaluating the handling of the discontinuity in electric properties, and was considered in both [12] and [11]. In [11], an artificial mean was used to find the smoothed electric permittivities, while in [12], it was shown that using a harmonic mean gives significantly better results. In this section, these results are compared to the results obtained with the ghost-field method. The equation for the electric potential is a Laplace equation with constant coefficients in each phase. This equation can be solved by noting that the potential is continuous across the interface (equation (2.26)).

\[
\nabla \cdot \left( \frac{\rho_s}{\epsilon} \nabla \Phi \right) = \rho_i
\]
(2.26)

The jump in velocities are
\[
[U] = \begin{pmatrix} u \cr w \end{pmatrix}
\]
(2.27)

3.1 HORIZONTAL INTERFACE IN AN ELECTRIC FIELD

An interface is placed between two parallel plates, the upper medium has permittivity \( \epsilon_u \), and the lower medium has permittivity \( \epsilon_l \). The upper plate is given a potential \( \Phi_u \) while the lower plate is grounded. This configuration is illustrated in Figure 2. This test case is excellent for evaluating the handling of the discontinuity in electric properties, and was considered in both [12] and [11]. In [11], an artificial mean was used to find the smoothed electric permittivities, while in [12], it was shown that using a harmonic mean gives significantly better results. In this section, these results are compared to the results obtained with the ghost-field method.

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The evolution in time for the Navier-Stokes equations, the electric field equation and the velocity extrapolation is performed using a four-step, third-order, stability preserving SSP-RK method [11] with a strong second order SSP RK method employed for the computation of the electric field equation. The equation is spatially discretized on a staggered grid, with scalar values stored in cell centers and vector values stored on cell boundaries. The convective terms are discretized using the fifth order Weighted Essentially Non-Oscillatory (WENO) scheme [19], and viscous terms are discretized using standard second-order central differences.

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We now analyze the accuracy of the ghost-fluid method for this test case. The chosen physical parameters along with the computed analytical solutions are given in Table 1, and are equivalent to those used in [12].

The ghost-fluid method uses an extremal value for the electric potential around a dielectric sphere in an electric field, which means that the electric potential is significantly better than the CSF method for this particular case.

Table 1. Physical properties and analytical values for the horizontal-interface test case.

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<thead>
<tr>
<th>Quantity</th>
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<tbody>
<tr>
<td>Permittivity 1, $\varepsilon_1$</td>
<td>60</td>
</tr>
<tr>
<td>Permittivity 2, $\varepsilon_2$</td>
<td>1</td>
</tr>
<tr>
<td>Potential difference, $\Psi$</td>
<td>100</td>
</tr>
<tr>
<td>Electric field 1, $E_1$</td>
<td>$-2.816 + j10$</td>
</tr>
<tr>
<td>Electric field 2, $E_2$</td>
<td>$-1.971 + j10$</td>
</tr>
<tr>
<td>Pressure jump, $\Delta p$</td>
<td>$1$</td>
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</table>

The ghost-fluid method uses for calculating the gradient of the potential and for the discretization of the pressure equation, as again we expect an exact solution for all grid sizes for this particular test case. Figure 3 shows the computed solutions of the electric field and the pressure, respectively, together with the analytical solution, for a grid with 10 points. The relative error for the value of the electric field was $2.2 \times 10^{-6}$, which means that the electric potential is significantly better than the CSF method for this test case.

The horizontal-interface test case. The electric field in the $x$-direction, scaled by the exact solution for phase 1, for a calculation with 10 grid points.

3.2 A SPHERICAL DROP SUBJECT TO AN ELECTRIC FIELD

This test case serves to assess the accuracy of the ghost-fluid method for an axisymmetric problem. Finding the potential around a dielectric sphere in an electric field is a classical problem in electrodynamics (see e.g. [20]), with the analytical solutions for phase 1, together with the error in the pressure jump, [12] report $\psi_{\text{num}} = 1.6959 \times 10^{-3}$, which means that the electric potential is significantly better than the CSF method for this test case.

The horizontal-interface test case. The electric field in the $x$-direction, scaled by the exact solution for phase 1, for a calculation with 10 grid points.

Table 2. Physical properties and analytical values for the horizontal-interface test case.

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$$\psi(r, \theta, \phi) = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \left( \frac{\varepsilon_2}{\varepsilon_1} \right)^{1/2} \frac{1}{r} \left( \frac{\varepsilon_2}{\varepsilon_1} \right)^{1/2} \sin \theta \cos \phi$$

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is the permittivity ratio \( \varepsilon \) between the drop and the surrounding medium. The electric field is then

\[ E_{\text{field}}(r) = \frac{1}{\varepsilon} \frac{P}{4\pi r^2} \]

(3.6)

Note that this is the electric field in the collection and direction, but defined using \( \varepsilon \) and \( \sigma \) for the purpose of a more compact presentation. These values can be employed to those found by the present algorithm by taking only one time step, so that there is no contribution of the values. The physical properties used for the test case is given in Table 2. A domain size of \( 30^3 \) was used. The error in the potential, together with the convergence behavior, is given in Table 3. The order of convergence is defined as

\[ |E_b| = E_b(r) - |E_b| \]

(3.7)

Where \( E_b \) is the error on a grid with \( N \) grid points. The error is low even for small grid sizes, and the convergence is that expected of the ghost-fluid method.

Figure 6 shows a comparison of the potential contour lines for the analytical and numerical results. Figure 7, which shows is the permittivity ratio \( \varepsilon \) between the drop and the surrounding medium. The electric field is then

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<td>Initial electric field, ( E_0 )</td>
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In [12], they computed the pressure jump across the interface along the \( y \)-axis, where the jump is pressure is the highest, in the theoretical result. The pressure jump is given by equation (2.26), which for the particular problem becomes

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If an electric field is applied to an initially spherical drop in a matrix fluid of different permittivity, the drop will deform. As explained in [2], a perfect dielectric droplet will always stretch in the direction of the electric field, the elongation depends on the permittivity ratio \( \varepsilon \), and the ratio between electric forces and capillary forces, expressed by the electric-field-induced deformation factor \( \alpha_{e} \).

An expression for the study of the deformation was found in [22], by an energetic approach. Good agreement with finite-element computations was reported. The expression can be written as:

\[
\frac{\alpha_{e}}{\alpha_{e}} = \left( \frac{\varepsilon_{e}}{\varepsilon_{m}} \right)^{2} - 1
\]

For permittivity ratios above approximately 28, the droplet is no longer single-valued, and hysteresis may occur. The parametric range that allows hysteresis is very narrow, 20 < \( \varepsilon \) < 25. For other values, the droplet shape is unstable, and the drop will begin to evert small drops from its tips to lower its value and finally remain a stable value. A series of numerical calculations were performed to compare the numerical method to the above theoretical model. To avoid having to run the simulations to steady state, the simulations were run for one oscillation period with condolences equal to zero, and the average between the maximum and the minimum values was computed. The numerical convergence behavior is similar for the two methods. The error is nearly equal to that reported in [12] for \( \varepsilon = 10 \).

The prolate shape is induced when \( \varepsilon_{w} < \varepsilon_{m} \) and \( \varepsilon_{e} > 1 \). As explained in [2], a perfect dielectric droplet will always stretch in the direction of the electric field, the elongation depends on the permittivity ratio \( \varepsilon \), and the ratio between electric forces and capillary forces, expressed by the electric-field-induced deformation factor \( \alpha_{e} \).

An example of the induced flow field is given in Figure 9. This is when the flow field reaches a maximum, just before the surface-tension forces begin reversing the flow. Note that the electric force is highest towards the pole of the drop. For high field strength, this can lead to axial instabilities, as shown in [22]. The flow field tends to zero as the droplet reaches its equilibrium shape. This shows the superiority of the sharp-interface approach compared to the smeared-interface approach. The convergence behavior is similar for the two methods.

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A comparison between the theoretical values and the computational values for the ratio of the semi-major and the semi-minor axes is given in Figure 8. The CFL results are computed using the approach from [11], with permittivities approximated using harmonic mean. The results for the ghost-fluid method are significantly closer to the theoretical predictions than the results for the CFL approach.

Since the electric field is abruptly applied \( \varepsilon_{w} \), inertia will cause the drop to overshoot the asymptotic value for the velocity, and then oscillate around this value until the viscous effects have damped out the motion. This overshoot may cause the drop to become unstable at values lower than those predicted by equation (3.9). For the values used here, the theoretical expression predicts breakup by \( x = 1.34 \) when using the ghost-fluid method.

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will then no longer be a function of just ρ, u, and T, but also depend on the viscosity and density of the two media. Investigating such a criterion is beyond the scope of this work.

4 CONCLUSION

This work presented an evaluation of a sharp-interface approach to simulating two-phase, electrohydrodynamic flows. The sharp-interface method was shown to give significant improvements in accuracy compared to standard methods.

The generality of the method allows it to be used in a wide range of problems involving two-phase flows and electric fields. The inherent handling of topological changes makes the method attractive for problems involving breakup or coalescence, for instance film boiling and emulsion stability.

Only perfect dielectric fluids were considered in this work. A natural extension is to apply the method to the highly dielectric model. This will be presented in a future work.

ACKNOWLEDGMENT

The authors thank Jan Vincenz for insightful discussions regarding the Lattice-Boltzmann method. Further, the constructive comments of the referees have improved the article.

REFERENCES

A COMPUTATIONAL STUDY OF THE COALESCENCE PROCESS BETWEEN A DROP AND AN INTERFACE IN AN ELECTRIC FIELD

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NTNU, Department of Energy and Process Engineering, 7491 Trondheim, Norway

Knutert@gmail.com
μ

ρ

ε

NOMENCLATURE

ABSTRACT

The coalescence process between a drop and an interface may not be determinative, but result in the creation of a smaller secondary drop. This process may be repeated several times before the coalescence is complete. Experiments have shown that an electric field can suppress this phenomenon and give coalescence in a single stage. In this paper, the influence of an electric field on the partial coalescence process is studied using numerical simulations. The simulations shows that the electric field reduces the time from pinch-off to a secondary drop to recoalescence, and essentially gives single-stage coalescence. A single-stage coalescence event is presented in detail, and the scalings provided for coalescence. The results support arguments from the literature that single-stage coalescence is caused by an increased downward momentum due to electrostatic attraction.

Keywords: Coalescence, electrocoalescence, electricity, dropletics, level-set method, ghost-fluid method

1. Direct drop function
2. Electric potential [V]
3. Interface
4. Carvusin [-1]
5. Level-set function
6. Dynamic viscosity [Pa s]
7. Velocity ratio
8. Relative permittivity
9. Vacuum permittivity (0.85 × 10^-12 [F/m])
10. Permittivity ratio
11. Density [kg/m^3]
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A COMPUTATIONAL STUDY OF THE COALESCENCE PROCESS BETWEEN A DROP AND AN INTERFACE IN AN ELECTRIC FIELD

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μ

ρ

ε

NOMENCLATURE

ABSTRACT

The coalescence process between a drop and an interface may not be determinative, but result in the creation of a smaller secondary drop. This process may be repeated several times before the coalescence is complete. Experiments have shown that an electric field can suppress this phenomenon and give coalescence in a single stage. In this paper, the influence of an electric field on the partial coalescence process is studied using numerical simulations. The simulations shows that the electric field reduces the time from pinch-off to a secondary drop to recoalescence, and essentially gives single-stage coalescence. A single-stage coalescence event is presented in detail, and the scalings provided for coalescence. The results support arguments from the literature that single-stage coalescence is caused by an increased downward momentum due to electrostatic attraction.

Keywords: Coalescence, electrocoalescence, electricity, dropletics, level-set method, ghost-fluid method

1. Direct drop function
2. Electric potential [V]
3. Interface
4. Carvusin [-1]
5. Level-set function
6. Dynamic viscosity [Pa s]
7. Velocity ratio
8. Relative permittivity
9. Vacuum permittivity (0.85 × 10^-12 [F/m])
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### GOVERNING EQUATIONS AND NUMERICAL METHODS

**Electric fields are currently being employed to speed up the separation of water from oil in offshore fields.** An electric field increases the capillary force between water drops which again enhances the settling process. Numerical simulations indicate that the capillary force is an important factor in the separation process. The partial coalescence phenomenon was made widely known by Charles and Mason (1960a) and Mason (1960b). They attributed the phenomenon to a static Rayleigh–Plateau instability, and proposed a criterion for partial coalescence based on the viscosity ratio. Moreover, in Blachnik and Bjugham (1988), it was demonstrated that the Rayleigh–Plateau instability could not be the cause of the instability, and instead proposed a propagation of capillary waves on the tip of the droplet as the dominating mechanism. A detailed study of the propagation of those capillary waves was made in Gitis et al. (2007), and it was concluded that other viscous mechanisms also play an important role in the process.

In Thoroddsen and Takehara (2000), partial coalescence was observed in a co-current flow which is higher than the critical one in Mason and Charles (1988). Blachnik and Bjugham (1988) and Stein et al. (2000) made an extensive parametric study using numerical simulations, and found an expression for the critical Ohnesorge number based on the viscosity ratio. However, they did not consider larger Bond numbers, so a universal criterion for the occurrence of partial coalescence remains elusive.

**In this work, all equations are solved in an axisymmetric geometry, so the divergence theorem and Laplace equation are not needed.**

**Electric forces**

We assume perfect electric materials with no free charge. In Allan and Mason (1961), it was concluded that single-stage coalescence was a static Rayleigh–Plateau instability, and gave a criterion for the occurrence of partial coalescence based on the Ohnesorge number and the Bond number. However, they did not consider larger Bond numbers, so a universal criterion for the occurrence of partial coalescence remains elusive.

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that the ionic strength of the aqueous solution had lit-
ttle influence on the coalescence process. Furthermore, Brown and Hanson (1985) found that it is the electric
field at the interface, rather than the charge it carries, that is dominating the process.
With these assumptions, the electric potential $\phi$ can be calculated from the following Laplace equation:

$$\nabla^2 \phi(x) = 0,$$

which is solved numerically to keep the level-set function as a signed distance function throughout the computation. This is accomplished by solving

$$\nabla \cdot (\nabla \phi(x) + \nabla \phi(x)) = \nabla \cdot (\nabla \phi(x) + \nabla \phi(x)),$$

where $\nabla \cdot$ is the divergence operator.

The reinitialization is performed every second time step. The scheme used to handle the discon-

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$$\nabla \cdot (\nabla \phi(x) + \nabla \phi(x)) = \nabla \cdot (\nabla \phi(x) + \nabla \phi(x)),$$
1. Solve Equation (6) for the electric potential
2. Calculate electric field and electric forces using Equations (7)-(9)
3. Calculate a temporary vector field with Equation (20)
4. Solve Equation (21) to find the pressure
5. Calculate the final velocity field using Equation (22)
6. Evaporate the velocity from the previous time step by solving Equation (11)
7. Update the level-set function with Equation (16), using the antipodal velocities
8. Reinitialize the level-set function by solving Equation (13)

### Dimensionless groups

In Yue et al. (2006) the following four dimensionless groups were used to describe the partial coalescence phenomenon: The Ohnesorge number, relating viscous forces to interfacial tension forces

\[ \frac{\sigma}{\rho g D^2} \]

The Bond number, relating gravitational forces to interfacial tension forces

\[ \frac{\rho g D^2}{\sigma} \]

The density ratio

\[ \frac{\rho_1}{\rho_2} \]

The viscosity ratio

\[ \frac{\mu_1}{\mu_2} \]

Here, the subscripts 1 and 2 denote the drop and the matrix phase, respectively. \( D \) is the diameter of the drop and \( e \) is the interfacial tension between the two phases. The addition of an electric field gives three new variables in the system, the initial electric field \( E_0 \) and the permeability ratio \( \epsilon_{b1} \) and \( \epsilon_{b2} \). This calls for two new dimensionless variables to properly describe the system. Hence, we choose the electric Bond number, relating electric forces to interfacial tension forces

\[ \frac{\sigma}{\rho g D^2 \epsilon_{b1}} \]

and the electric Ohnesorge number, relating viscous forces to interfacial tension forces

\[ \frac{\sigma}{\rho g D^2 \epsilon_{b1} \epsilon_{b2}} \]

A series of calculations on varying grid sizes were performed to validate the model against published data. The numerical parameters for the turbulence model are given in Table 1. For these values, the asymptotic expression gives

\[ \frac{\sigma}{\rho g D^2 \epsilon_{b1} \epsilon_{b2}} \approx 3 \times 10^{-3} \]

Comparison with experiment

In Yue et al. (2006), an experiment was performed of a water droplet merging with an interface between 20% ethanol and air. The dimensionless numbers were calculated as

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A schematic of the geometry for the numerical simulation is shown in Figure 1, and only the right half is actually part of the computational domain.

RESULTS AND DISCUSSIONS

In this section, the evolution of an initially spherical drop subjected to an electric field is discussed. Calculations were performed using the same numerical setup and physical properties as in the previous section, but now a potential difference is applied between the upper and lower boundary. Additional forces during the approach of the drop are the electrical forces due to the electric field, in contrast to the previous section, where the purpose of this study is to examine the actual coalescence process, and not the reduction in rest time.

Figure 3 shows snapshots from the experiment performed in Chen et al. (2006), and Figure 4 shows the computable snapshots from the numerical calculation. The simulation is capable of reproducing the partial coalescence process, and also captures the evolution of the interface with quantitative precision. In particular, the numerical method is capable of predicting the evolution of the capillary waves, indicated by arrows in Figure 4.

Table 2: Physical properties of the partial coalescence experiment performed by Chen et al. (2006).

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Figure 4: Illustration of the stretching of an initially spherical drop when an electric field is applied.

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Effect of the electric Bond number

Figure 6 shows the time interval from pinch-off to coalescence of the secondary drop, denoted \( \tau_0 \), for different electric Bond numbers. The interval decreases until single-stage coalescence is obtained at \( \text{Be} \approx 0.1 \). This result is equivalent to that observed in Allen and Mason (1965). Single-stage coalescence is furthermore limited to a range of electric Bond number, until pinch-off occurs again at \( \text{Be} \approx 0.15 \). The increase in electric field strength at higher field strengths was not observed by Allen and Mason (1961) or Eow and Ghadiri (2003). However, recent experiments (Hollins 2008) confirm that this behavior may occur.

Snapshots from the entire calculation for \( \text{Be} = 0.1 \) is given in Figure 7. The potential drop across the drop and the upper part of the column is nearly constant during the emptying. With an electric field applied, the height decreases rapidly to a low value of \( \text{Be} \approx 0.1 \). The actual pinch-off in Figure 5, (a), corresponds to in Figure 7. The liquid bridge becomes thinner with an applied electric field, and the capillary forces are too small to give the necessary downward momentum to prevent pinch-off.

Figure 8 shows that the pressure inside the drop is higher when an electric field is applied. This is what causes the thickening and prevents pinch-off.

Effect of the permittivity ratio

Three simulations were performed at different permittivity ratios. The time from pinch-off to recoalescence is plotted in Figure 10. It is evident that for much lower or higher than that used in the previous section, the coalescence becomes multi-staged again.

Figure 6: Time from pinch-off to recoalescence of sec- ondary drop for varying electric Bond number. For intermediate range of electric Bond numbers, the coales- cence is single-stage.

For a low permittivity ratio, the increased stretching of the drop overcomes the effect of the dominant momentum, which causes pinch-off to occur.

CONCLUSIONS

This article presented a computational investigation of the partial coalescence phenomenon, with and without electric fields applied. It was shown that the natural model is capable of reproducing a partial coalescence event with near quantita- tive precision in the absence of electric fields. For the calculations with an applied electric field, the natural model was able to reproducibly reproduce trends reported in the literature. In particular, suppression of the partial coalescence at higher field strengths was not observed by Allen and Mason (1961) or Eow and Ghadiri (2003). However, recent experiments (Hollins 2008) confirm that this behavior may occur.

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Snapshots from the entire calculation for \( \text{Be} = 0.1 \) is given in Figure 7. The potential drop across the drop and the upper part of the column is nearly constant during the emptying. With an electric field applied, the height decreases rapidly to a low value of \( \text{Be} \approx 0.1 \). The actual pinch-off in Figure 5, (a), corresponds to in Figure 7. The liquid bridge becomes thinner with an applied electric field, and the capillary forces are too small to give the necessary downward momentum to prevent pinch-off.

Figure 8 shows that the pressure inside the drop is higher when an electric field is applied. This is what causes the thickening and prevents pinch-off.

Effect of the permittivity ratio

Three simulations were performed at different permittivity ratios. The time from pinch-off to recoalescence is plotted in Figure 10. It is evident that for much lower or higher than that used in the previous section, the coalescence becomes multi-staged again.

Figure 6: Time from pinch-off to recoalescence of sec- ondary drop for varying electric Bond number. For intermediate range of electric Bond numbers, the coales- cence is single-stage.

For a low permittivity ratio, the increased stretching of the drop overcomes the effect of the dominant momentum, which causes pinch-off to occur.

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Snapshots from numerical simulation with $D = 1.1 \text{ mm}$, $Be = 0.0995$, $Oh = 0.0067$, and $Bo = 0.1$, demonstrating single stage coalescence. The time interval is $\Delta t = 7.75 \times 10^{-4}$ s, and the contour lines show the electric potential with a 10 V interval. The potential in the aqueous phase is close to uniform, due to the high relative permittivity.

Figure 7: Snapshots from numerical simulation with $D = 1.1 \text{ mm}$, $Be = 0.0995$, $Oh = 0.0067$, and $Bo = 0.1$, demonstrating single stage coalescence. The time interval is $\Delta t = 7.75 \times 10^{-4}$ s, and the contour lines show the electric potential with a 10 V interval. The potential in the aqueous phase is close to uniform, due to the high relative permittivity.

Figure 8: Contour plot of relative pressure at $t = 4.0 \times 10^{-5}$ s, with and without an electric field. The electric field gives a higher pressure inside the drop, due to the additional electric forces at the interface.

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numbers, electric Bond number, and permeability ratios. These short simulations of the approach of the drop.

Finally, the influence of impurities on the interface has not been taken into account in the numerical modeling.

Such impurities may cause surface tension gradients which give rise to additional forces that may modify the coalescence behavior. However, recent experiments (Kluss 2000) performed with water drops in real crude oil show the same qualitative behavior as the results presented here.

ACKNOWLEDGEMENTS

This work is funded by the project ‘Electrocoalescence – Criteria for an efficient process in real crude oil systems’, co-funded by SINTEF Energy Research. The project is supported by The Research Council of Norway, under the contract no. 169466/S30, and by the following industrial partners: Ardex AS, Aker Kværner Process Systems AS, StatoilHydro ASA, BP Exploration Operating Company Ltd, Shell Technology Norway AS, Kjetilseth.

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REFERENCES


Hillero, S. M. Personal communication, 2008.


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Sharp interface simulations of surfactant-covered drops in electric fields

Teigen, K.E, Lervåg, K.Y., Munkejord, S.T.,
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SHARP INTERFACE SIMULATIONS OF SURFACTANT-COVERED DROPS IN ELECTRIC FIELDS
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Key words: fluid dynamics, multiphase flow, surfactant, level-set method, sharp interface, ghost-fluid method

Abstract. A level-set method for computations of interfacial flows with insoluble surfactants with electric fields is presented. The discontinuities at the interfaces are captured in a sharp manner using the ghost-fluid method. The accuracy of the method is tested and compared to the standard level-set method. The method is then used to study the combined effect of insoluble surfactants and electric fields on the motion and deformation of a falling drop. It is found that the surfactant generally reduces the deformation and the terminal velocity of the drop. This reduction is most pronounced in the nearly spherical regime where the drop behavior is similar to a solid sphere due to the interface immobilization caused by the presence of a surfactant. The electric field increases the terminal velocity by stretching the drop in the direction of the electric field. This effect is largest for the surfactant-covered drop, which is deformed more due to the lower average interfacial tension.

1 INTRODUCTION

The presence of surface-active agents (surfactants) at fluid interfaces can have a considerable effect on flow dynamics. Surfactants are amphiphilic organic compounds, which can be adsorbed at liquid-gas or liquid-liquid interfaces. The presence of surfactants typically alters the interface dynamics by a reduction in the interfacial tension. An inhomogeneous distribution of surfactants produces gradients in interfacial tension, which again gives rise to tangential forces along the interface. Through this so-called Marangoni effect, surfactants can play an important role in several physical phenomena, for instance vortex pair interaction in emulsions. In some oil fields, heavy oil with high viscosity combined with surface-active

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components like surfactants and emulsion make it hard to extract the water using traditional sedimentation processes. In order to accelerate the sedimentation process, an electric field can be applied to the emulsion.\(^2\) This will introduce attractive forces between the water drops, which increase the coalescence rate and thereby also the sedimentation rate. Both the influence of surfactants and electric fields on drops have been studied numerically.\(^2\) However, to the authors' knowledge, there is no first numerical study of the combined effect of surfactant and electric fields. The available numerical methods for detailed simulations of two-phase flows can roughly be divided into two categories: interface-tracking and interface-capturing methods. In interface-tracking methods, the separate grid is used for the interface, or a set of interconnected points to mark the interface. Examples of methods which have been applied to both surfactants and electric fields include the boundary-integral method\(^{5,12,13}\), and the front-tracking method\(^{4,14,15}\). In general, interface-tracking approaches can be made very accurate, but can be relatively complicated to implement, especially in three dimensions and for problems involving topological changes.

In interface-capturing methods, the interface is not tracked explicitly, but is instead implicitly defined through a regularization of the interface. This means that the evolution of the interface is handled independently of the underlying grid, which greatly simplifies grid generation and handling of topological changes. Well known methods in this category include the volume-of-fluid method\(^{16,17}\), the phase-field method\(^{18,19}\), and the level-set method\(^{20,21,22}\). Other novel methods are the lattice-Boltzmann method with electric fields\(^2\) and the smoothed particle hydrodynamics method with soluble surfactants\(^2\).

In this paper, we build upon the previous work of Xu et al.\((2006)\)\(^{23}\), and use the level-set method to represent the interface. However, instead of using the immersed-interface method\(^{24}\) (IIM) to handle discontinuities across the interface, we employ the ghost-fluid method\(^{(4,25)}\) (GFM). For the case of constant coefficients in the jump conditions, the GFM is a lower order version of the IIM. The main disadvantage of the IIM is that discontinuity relations for higher-order derivatives must be developed and implemented. For more complex physical systems, these may not be available a priori, in which case an iterative method has to be used to calculate the discontinuities, leading to a more complex implementation and a more expensive computation. The GFM has the advantages that it is more accurate than the standard level-set method based on a diffuse interface, the so-called continuous surface force (CSF) method, while remaining computationally efficient and relatively easy to implement for both two- and three-dimensional problems. A ghost-fluid method for electric fields was presented in Hansen\((2008)\)\(^{26}\), and we use the same methodology here.

The paper is organized as follows. In Section 2, we state the governing equations and briefly discuss the numerical method. In Section 3 we present simulations demonstrating the capabilities of the method. We first compare the accuracy to a diffuse-interface method using a test case with an available analytical solution, then we present simulations of a components-like surfactants and emulsion make it hard to extract the water using traditional sedimentation processes. In order to accelerate the sedimentation process, an electric field can be applied to the emulsion.\(^2\) This will introduce attractive forces between the water drops, which increase the coalescence rate and thereby also the sedimentation rate. Both the influence of surfactants and electric fields on drops have been studied numerically.\(^2\) However, to the authors' knowledge, there is no first numerical study of the combined effect of surfactant and electric fields. The available numerical methods for detailed simulations of two-phase flows can roughly be divided into two categories: interface-tracking and interface-capturing methods. In interface-tracking methods, the separate grid is used for the interface, or a set of interconnected points to mark the interface. Examples of methods which have been applied to both surfactants and electric fields include the boundary-integral method\(^{5,12,13}\), and the front-tracking method\(^{4,14,15}\). In general, interface-tracking approaches can be made very accurate, but can be relatively complicated to implement, especially in three dimensions and for problems involving topological changes.

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2 GOVERNING EQUATIONS AND NUMERICAL METHODS

The full Navier–Stokes equations are solved in each phase, and the interface between the two phases is captured using the level-set method. The ghost-fluid method is used to treat discontinuities across the interface in a sharp manner.

2.1 Flow equations

The flow is governed by the incompressible Navier–Stokes equations, with added terms for interfacial-tension forces and electric forces:

$$\rho \left( \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = -\nabla p + \nabla \cdot (\mathbf{g} \rho) - \nabla \cdot \mathbf{F} + \mathbf{F}_s + \mathbf{F}_e,$$

where $\mathbf{F}$ is the force due to the presence of an electric field. The effect of an interface, $\Gamma$, in the domain results in a singular interfacial force which can be expressed by

$$\mathbf{F}_s(x,t) = \int_{\Gamma(x,t)} \mathbf{f}_{s,\mathbf{x}}(x-X_s(t)) \, ds,$$

where $s$ is the arclength, $X_s(t)$ is the parametrization of the interface, $x$ is the spatial position and $\mathbf{x}$ is the Dirac delta function. For the present problem, $\mathbf{F}_s$ is given by

$$\mathbf{F}_s = -\nabla \cdot \mathbf{F}_s.$$

The first term accounts for the normal capillary force due to interfacial tension. Here, $\sigma$ is the coefficient of interfacial tension, $\kappa$ is the curvature and $n$ is the outward pointing unit normal vector. The second term is the Marangoni force, which is caused by gradients in the interfacial tension and acts tangentially to the interface. The interfacial gradient, $\nabla_T$, is given by

$$\nabla_T = (I - nn\nabla),$$

where $I$ is the identity tensor.

2.2 Surfactants

Graduates in the interfacial tension occur due to the presence of an insoluble surfactant on the interface. The dynamics of the surfactant concentration, $f$, is governed by

$$\frac{\partial f}{\partial t} + \nabla \cdot (\mathbf{u} f) = -D_1 (\nabla^2 f - \nabla \cdot \nabla f) - \sigma (\nabla \cdot \mathbf{u} f) + \mathbf{f}(\sigma_{\kappa} \nabla \cdot \mathbf{u} f),$$

where $D_1$ is the coefficient of interfacial tension, $\kappa$ is the curvature and $n$ is the outward pointing unit normal vector. The second term is the Marangoni force, which is caused by gradients in the interfacial tension and acts tangentially to the interface. The interfacial gradient, $\nabla_T$, is given by

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where \( D_s \) is the surfactant diffusion coefficient. We employ the Langmuir equation of state to relate the interfacial tension and surfactant concentration,

\[
\sigma(f) = \sigma_0 \left[ 1 + \beta \ln \left( 1 - \frac{f}{f_0} \right) \right]
\]

(6)

Here, \( \beta = R f_m / \sigma_0 \) is the interface elasticity number, which is a measure of the sensitivity of interfacial tension to surfactant concentrations, \( f_m \) is the maximum surfactant packing, \( R \) is the universal gas constant, \( T \) the temperature and \( \sigma_0 \) is the interfacial tension of a clean interface.

In this paper, we will assume that the surfactant is restricted to the interface, i.e. it will not be able to dissolve into the surrounding fluid. Surfactants behave as insoluble monolayers in two limits. The first corresponds to dilute bulk concentrations, for which the diffusion flux from the bulk is slow compared to the interface convection flux. The second limit corresponds to slow adsorption-desorption exchange, which can occur in aqueous systems with long-chained surfactants. Since we assume that the surfactant is insoluble, it is only defined on the interface.

In order to solve the evolution equation numerically, we must therefore first extend the surfactant concentration off the interface. This is accomplished by solving

\[
\frac{\partial f}{\partial \tau} + S(\phi) m \cdot \nabla f = 0
\]

(7)

Here, \( S(\phi) \) is a sign function given by

\[
S(\phi) = \frac{\phi - \phi_0}{\sqrt{\phi_0^2 - \phi^2}}
\]

(8)

Note that this equation is hyperbolic, so it is not necessary to solve it to steady state, since only the information a few grid points away from the interface is relevant.

2.3 Electric forces

We want to model a conductive drop in an otherwise dielectric medium, for instance a water drop in oil. This can be achieved by assuming perfect dielectric materials with no free charges, and then choosing a high permittivity ratio between the two phases. With these assumptions, the electric force is given by

\[
F_e = -\nabla M
\]

(9)

where \( M \) is the Maxwell stress tensor,

\[
M = \varepsilon_0 \varepsilon \left( \nabla E \cdot \nabla E \right) I
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Here, \( E \) is the electric field. With the above assumptions, \( \nabla \cdot \mathbf{E} = 0 \) everywhere except at the interface. The electric field is divergence free, such that
\[
\mathbf{E} = -\nabla \Phi, \tag{11}
\]
where \( \Phi \) is the electric potential. The electric potential is found from the following Laplace equation:
\[
\nabla^2 \Phi = 0. \tag{12}
\]

### 2.4 Interface capturing

The interface is captured using the level-set method[20,30]. This method allows accurate computation of the evolution of an interface, along with automatic handling of topological changes. The ghost-fluid method[13,30] (GFM) is used to take discretizations across the interface into account. This method handles the jumps in physical properties directly in the numerical stencil, without the need for any averaging of properties.

The GFM requires jump conditions, which are relations between the physical quantities on each side of the interface. The jump conditions for the present problem are:

\[
\begin{align*}
|\mathbf{u}| &= 0, \tag{13} \\
|\mathbf{p}| &= 2 \rho_0 |\mathbf{u} + n \cdot \mathbf{J}| = \rho_0 |\mathbf{u} + n \cdot \mathbf{J}|, \tag{14} \\
|\nabla \mathbf{u}| &= \left[ \rho_0 |\nabla \mathbf{u}| + \rho_0 n \cdot \nabla \mathbf{J} \right], \tag{15} \\
\nabla \cdot \mathbf{u} &= \left( \nabla \cdot \mathbf{u} + \tau \cdot \mathbf{u} + n \cdot \nabla \mathbf{J} \right), \tag{16} \\
\nabla \cdot \mathbf{J} &= 0. \tag{17} \\
\n\rho_{\text{gas}} \mathbf{J} &= \Phi, \tag{18}
\end{align*}
\]

A well-known issue with the level-set method is that it does not conserve mass. The more accurate ghost-fluid discretization somewhat alleviates the problem, but for long-running simulations it is still an issue. In particular, since we use an explicit time-integration method in this work, simulations at low Reynolds numbers (i.e. highly viscous fluids) suffer from severe mass loss. We therefore introduce a simple mass correction scheme for these simulations. At each time step, we add a constant, \( \alpha \), to the level-set function, where \( \alpha \) is found by solving the equation
\[
\int \mathcal{H}(\phi + \alpha)d\Omega = \int \mathcal{H}(\phi)d\Omega. \tag{19}
\]
Here, \( \phi \) is the initial level-set function. The effect of this correction scheme is to add any lost mass back globally over the entire drop. Since mass loss typically occurs in regions of high curvature and low resolution, this scheme works well for low Reynolds number simulations.
drops, which tend to remain nearly spherical. We note that more sophisticated approaches for dealing with the mass loss exist. These include coupling with Lagrangian particles, while a second-order SSP RK method is employed and using modified advection procedure.

2.5 Numerics

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3.1 Bubble rising due to thermocapillary effects

As a test case for the implementation of the interfacial-tension force, we will simulate the thermocapillary migration of a bubble. It is well known that due to the dependence of interfacial tension on temperature, there will be a discontinuity in the tangential stresses across the interface for a bubble in a temperature gradient[39]. The result is a motion of the drop in a direction that will reduce its interfacial free energy. The flow at the interface will be from the warmer to the cooler pole of the bubble, and therefore, the bubble will move

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in the direction of the warmer pole. This motion is known as thermocapillary migration. We assume that the temperature varies as

\[ T(x, t) = \frac{L}{c} = \frac{L}{\Delta T} \tag{20} \]

where \( L \) is the domain height, and the relationship between temperature and interfacial tension is

\[ \sigma(z) = \sigma_0 e^{-\frac{L}{2}} \tag{21} \]

We assume that the pressure in the surrounding fluid is zero. Then the pressure inside the bubble is given by

\[ p(z) = 2\sigma(z) \tag{22} \]

where \( R \) is the bubble radius. For a viscous bubble in a linear temperature gradient, an approximation for the terminal rise velocity \( u \)

\[ V_{\text{TH}} = \frac{2(\rho_0 H L - \Delta \rho_0 \sigma_0\mu_0)\mu_0}{(5\eta_0 + 9\eta_0)} \tag{23} \]

Here, we choose a domain size \( 5.5 \times 15 \) and parameters \( \mu_0 \approx 0.2 \mu_0, R = 0.5 \), \( \eta_0 = 1.5 \), \( \mu_0 = 10 \), and parameters \( \mu_0 \approx 0.2 \mu_0, R = 0.5 \), \( \eta_0 = 1.5 \), \( \mu_0 = 10 \). Gravity effects are neglected. According to Eq. (23), this should give a Reynolds number of \( Re = 0.0444 \), which is well within the creeping flow regime for which the equation is valid.

Next, we compare the GFM and the CSF method with respect to Eq. (22) for the pressure. \( V_1 \) shows a close-up of pressure contours inside the bubble. In Fig. 1h, the pressure along the vertical center line is compared to the analytical result for both the GFM and the CSF method for \( Re = 10 \). We see that with the GFM, the jump in pressure at the interface is treated in a sharp manner, and that the pressure inside the bubble is accurately captured. For the CSF, however, the discontinuity is smeared out, and the jump in pressure is over-predicted. In Table 1, the relative error of the pressure in the bubble center is given together with convergence rates for the GFM. The error decreases in a first-order fashion, which is consistent with other results obtained with the GFM.\(^3\)

Next, we compare the simulated rise velocity to Eq. (23). The computational rise velocity was calculated with

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Figure 1: Pressure after one time step for a bubble rising in a linear surfactant gradient.

(a) Pressure contours after one time step.
(b) Pressure along vertical centerline compared to analytical result, Eq. (22).

Figure 2: Velocity field at steady state and rise velocity versus time for the thermocapillary migration test case.

(a) Velocity vectors at steady state.
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Table 1: Thermocapillary migration test case. Error and convergence for the pressure inside the bubble after one time step.

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<tbody>
<tr>
<td>10</td>
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Table 2: Parameters for falling drop at low Reynolds number

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3.2 Falling drop at low Reynolds number

We now consider a drop falling in a gravity field at a low Reynolds number. The parameters chosen are given in Table 2. In terms of dimensionless numbers, these pa-

The velocity field around the bubble at steady state is shown in Fig. 2a for a grid spacing of R/h = 10. The figure is in good agreement with results from the literature.25,26. Fig. 2b shows the normalized rise velocity for both the GFM and the CSF method. After an initial acceleration phase, the velocity approaches the theoretical prediction asymptotically. We observe that the results for the GFM is closer to the theoretical value. However, the accuracy is surprisingly good for both methods considering the relatively coarse grid used. For the GFM, the difference between the theoretical rise velocity and the computed at t = 0.6 s is 2.38%, while for the CSF method, the difference is 3.31%.

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We now consider a drop falling in a gravity field at a low Reynolds number. The parameters chosen are given in Table 2. In terms of dimensionless numbers, these pa-
For the simulations, we choose a domain size of 16 × 10^3 s. The simulated terminal velocity is reduced to \( V_T = 0.96 \times 10^{-3} \text{ m/s} \), which gives \( \frac{V_T}{\text{HR}^0} = \frac{2}{3} \sqrt{\frac{2}{\rho g R}} \), or \( \text{Re} = 0 \times 10^3 \text{ s}^{-1} \), an increase over the clean drop. The reason for this becomes evident by looking at the velocity profiles given in Figure 3. For the contaminated drop, the internal circulation nearly disappears, and the drop behaves close to a rigid particle. The Stokes formula for a rigid, spherical particle in creeping flow, \( V_T = \frac{2 \sigma}{\rho g R} \), gives \( V_T = 1.30 \times 10^{-3} \text{ m/s} \), which is close to the terminal velocity for the contaminated drop. Again, the discrepancy is attributed to the bounded domain.

We then consider the effect of an electric field. The drop is allowed to reach a steady state before the electric field is switched on. The strength of the electric field can be characterized by the electric capillary number, \( \text{Ca} = \frac{e^2}{\rho g R^2} \). A conductive drop submitted to an electric field becomes unstable when \( \text{Ca} = 0.41 \times 10^{-4} \). However, here the gravitational forces will act to stabilize the drop, allowing the use of an even higher \( \text{Ca} \). We choose \( \text{Ca} = 0.45 \), which gives \( e = 8 \times 10^{-3} \text{ V/s} \). Figure 5a illustrates the drop shape for the clean drop, along with electric field lines and velocity vectors. The drop clearly stretches into a prolate shape. This more streamlined profile gives a reduction in drag and hence a higher terminal velocity. The terminal velocity was calculated to be \( V_T = 1.90 \times 10^{-3} \text{ m/s} \), an increase over the clean drop without an electric field. The aspect ratio of the drop is 0.77, while theory predicts gives \( V_T = 1.70 \times 10^{-3} \text{ m/s} \), which is close to the terminal velocity for the contaminated drop. Again, the discrepancy is attributed to the bounded domain.

Figure 4a shows the surfactant concentration as a function of the arc length, \( \epsilon \), measured in the counterclockwise direction. The surfactant concentration takes the shape of an S-curve, and hence the Marangoni stresses are evenly distributed across the drop. The consequence of this is illustrated in Figure 4b, which shows the interface velocity for both the clean and the contaminated drop. The interface velocity of the contaminated drop is greatly reduced across the entire drop interface. We then consider the effect of an electric field. The drop is allowed to reach a steady state before the electric field is switched on. The strength of the electric field can be characterized by the electric capillary number, \( \text{Ca} = \frac{e^2}{\rho g R^2} \). A conductive drop submitted to an electric field becomes unstable when \( \text{Ca} = 0.41 \times 10^{-4} \). However, here the gravitational forces will act to stabilize the drop, allowing the use of an even higher \( \text{Ca} \). We choose \( \text{Ca} = 0.45 \), which gives \( e = 8 \times 10^{-3} \text{ V/s} \). Figure 5a illustrates the drop shape for the clean drop, along with electric field lines and velocity vectors. The drop clearly stretches into a prolate shape. This more streamlined profile gives a reduction in drag and hence a higher terminal velocity. The terminal velocity was calculated to be \( V_T = 1.50 \times 10^{-3} \text{ m/s} \), an increase over the clean drop without an electric field. The aspect ratio of the drop is 0.77, while theory predicts...
Figure 3: Low Re drop. Streamlines and velocity vectors in a coordinate system moving with the drop centroid. Velocity vectors are plotted at every other grid point.

Figure 4: Low Re drop. Surfactant concentration and interface velocities as functions of arc length.
a minimum aspect ratio of 0.528. Since we have an electric field stronger than the predicted critical value for a stationary drop, this demonstrates the stabilizing effect of the gravitational force.

The contaminated drop with an electric field is shown in Figure 5b. For this drop, the terminal velocity has increased to \( v_T = 1.09 \times 10^{-5} \text{ m/s} \), compared to the contaminated drop without an electric field. This increase in terminal velocity is much larger than for the clean drop, which is caused by the lower average surface tension yielding a higher degree of stretching. An aspect ratio of 0.708 is calculated for the contaminated drop compared to 0.770 for the clean drop.

Finally, we observe that the electric field lines are close to perpendicular to the interface at the drop interface, and that the electric field magnitude is close to zero inside the drop. This indicates that our method of approximating a conductive drop in a dielectric medium by simulating a dielectric/dielectric system with high permittivity ratio is satisfactory.

### 3.3 Falling drop at high Reynolds number

We now consider a drop at a relatively high Reynolds number. We use the same parameters as above, with the exception of a higher radius, \( R = 5.15 \times 10^{-7} \), and a lower matrix viscosity, \( \nu_2 = 0.19 \), to achieve a higher Reynolds number. The dimensionless parameters for this case become \( E_0 = 6.64 \text{ and } \nu_1 = 1.05 \times 10^{-5} \). For a clean drop, the calculated terminal velocity was \( v_T = 0.014 \text{ m/s} \) which gives \( Re = 67.4 \). An experiment performed with the same parameters gave \( Re = 67.3^{10} \), which very close to the simulated value.

Since the viscosity of the matrix fluid is lower in this case, we expect the boundaries a minimum aspect ratio of 0.528. Since we have an electric field stronger than the predicted critical value for a stationary drop, this demonstrates the stabilizing effect of the gravitational force.

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(a) Clean  
(b) Contaminated

Figure 6: High Re drop. Streamlines and velocity vectors in a coordinate system moving with the drop centroid. Velocity vectors are plotted at every other grid point.

to have less influence for this drop. The excellent agreement with the experiment indicates that this is indeed the case. Figure 6a shows the drop shape and velocity pattern. At this higher Re, the drop deforms into an ellipsoidal shape, and a vortex is formed behind the drop.

We then add surfactants to the system. It is well known that for contaminated drops or bubbles moving at higher Reynolds numbers through an otherwise stagnant fluid, the surfactants will be swept to the rear of the drop. This will create a region where the interface is nearly immobile due to the resulting high Marangoni stresses, while the front of the drop will be surfactant-free and mobile. The immobile region is often denoted the stagnation cap. Several models have been developed which relate the cap angle to e.g. the drag coefficient. The numerical method used here requires no assumption of a stagnation cap, and no a priori estimate of the cap angle is necessary.

The resulting drop shape and velocity pattern for the contaminated drop is given in Figure 6b. It is evident that the deformation is smaller than for the clean drop. Additionally, we see that the center of the internal vortex has moved closer to the front, and that the trailing vortex is larger for the contaminated drop. This results in a lower terminal velocity of $V_T = 0.119$ m/s compared to $V_T = 0.131$ m/s for the clean drop. This is a much lower difference than for the low Re drop.

The surfactant concentration is shown in Figure 7a. Here, the gradient in the surfactant concentration does not vary smoothly like for the low Re drop. Instead, there is no surfactant at the tip of the drop, followed by a sharp jump in concentration towards the back of the drop. This jump in concentration will effectively immobilize this part of the drop.

Knut Erik Teigen, Kari Yngve Lervåg and Svend Tollak Munkejord

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Figure 7: High Re drop. Surfactant concentration and interface velocities as functions of arc length.

The evolution of the drop is shown in Figure 9, with the drop revolved around the $z$-axis and colored according to the surfactant concentration. When the electric field is switched on, the back of the drop starts to stretch, while the front of the drop remains stable. Eventually, the stretched part develops a pointed tip and we see the formation of a small drop on the tip. It has been shown both experimentally and numerically that conductive drops become pointed and starts emitting small drops from the tips. An active drop becomes pointed and starts emitting small drops from the tips. Eventually, the stretched part develops a pointed tip and we see the formation of a small drop on the tip. It has been shown both experimentally and numerically that conductive drops become pointed and starts emitting small drops from the tips.

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interesting observation is that as the tip starts to form, surfactant is swept from the tip and towards the middle of the drop. The drop formed at the tip has a very low concentration of surfactants. This is a fundamentally different process from surfactant-covered drops being stretched in extensional flows or shear flows. For these flows, surfactant is swept to the drop tips and contributes to the tip-streaming process. This creates small drops with high surfactant concentrations which consequently are very stable. The present simulations suggest that this is not the case for drops broken due to electric fields. Another interesting phenomenon suggested by the experimental results of Ha & Yang \cite{Ha2008} is that the presence of a surfactant can cause the break-up mode to change from bubble-end formation to tip-streaming. The proposed physical mechanism was the same as for drops in shear flows. Again, our numerical results suggest that this may not be the correct explanation for the observed behavior.

4 CONCLUSIONS

A level-set method for computations of interfacial flows with insoluble surfactants and electric fields was presented. It was shown that the method is more accurate than the standard level-set method at handling the pressure jump at the interface. Currently, the method only handles insoluble surfactants. A natural extension of the method is to include solubility. For instance, the method proposed in Trögn et al. \cite{Trogneux2020} for the phase-field method is also applicable to the level-set method.

The method was used to study an axisymmetric drop falling in an otherwise quiescent fluid. It was found that the surfactant reduced the deformation and the terminal velocity of the drop shows velocity vectors in a coordinate system moving with the drop centroid. Velocity vectors are plotted at every other grid point.

Figure 8: High Re drop with electric field. The left part of the drop shows streamlines of the electric field and contours colored by the electric field magnitude. The right part of the drop shows velocity vectors in a coordinate system moving with the drop centroid. Velocity vectors are plotted at every other grid point.

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of the drop. The reduction was most pronounced at low Reynolds number, where the drop remains spherical. Here, the surfactant-covered drop behaves similarly to a solid sphere. These results are in agreement with experiments and simulations in the literature. The effect of an electric field was mainly to increase the terminal velocity. This is due to the drop stretching in the direction of the electric field, which gives a larger projected interface area and hence lower drag. This effect was also more evident at lower Reynolds numbers, which was attributed to lower convection forces which allowed the drop to stretch more. The effect of an electric field on the contaminated drop was also to increase the terminal velocity. However, the effect was slightly higher here, due to the overall lower interfacial tension of the contaminated drop which gives a lower resistance to deformation. Only two different drops were investigated in this study, and the surfactant parameters and electric fields were not varied. It would be instructive to investigate a wider range of drop shapes, and study the influence of the surfactant parameters and electric fields in more detail. In particular, the observed behavior of an unstable drop is fundamentally different from previous results for drops in extensional flows or shear flows, and this warrants further studies.

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Figure 9: Behavior of contaminated drop above the critical field strength. The drop surface is colored according to surfactant concentration. The first frame shows the drop before the electric field is switched on. The subsequent frames are at times 0.7, 1.0, 1.3, 1.4 and 1.7 seconds after the field has been switched on.

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Influence of surfactant on drop deformation in an electric field

Teigen, K.E, Munkejord, S.T.,
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Influence of surfactant on drop deformation in an electric field
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The deformation of a surfactant-covered, viscous drop suspended in a viscous fluid under the influence of an electric field is investigated using numerical simulation. The bulk Navier-Stokes equations are solved in both fluid phases, and the motion of the interface and the interfacial discontinuities are handled using the level set method. The level-set method is used to track the surfactant concentration by means of the following equation:

\[ \frac{\partial C}{\partial t} + \nabla \cdot (C \mathbf{u}) = 0 \]

where \( C \) is the surfactant concentration and \( \mathbf{u} \) is the velocity field. The motion of the interface is then determined by integrating the normal component of the net surface force, which is given by the following equation:

\[ \mathbf{F}_{\text{surf}} = \int_{\Gamma} \mathbf{t} \cdot \mathbf{F}_{\text{surf}} \, d\Gamma \]

where \( \mathbf{F}_{\text{surf}} \) is the surface force density and \( \mathbf{t} \) is the outward normal to the interface. The surface force density is given by the following equation:

\[ \mathbf{F}_{\text{surf}} = \sigma \mathbf{n} \times \mathbf{E} - \frac{1}{2} \mathbf{n} \cdot \mathbf{E} \mathbf{E} \cdot \mathbf{n} + \mathbf{E} \cdot \mathbf{F}_{\text{int}} \]

where \( \sigma \) is the interfacial tension, \( \mathbf{E} \) is the electric field, and \( \mathbf{F}_{\text{int}} \) is the interfacial tension force density, which is given by the following equation:

\[ \mathbf{F}_{\text{int}} = \frac{1}{2} \sigma \nabla_{\Gamma} \cdot \mathbf{v} \]

where \( \nabla_{\Gamma} \cdot \mathbf{v} \) is the divergence of the interfacial velocity. The interfacial velocity is given by the following equation:

\[ \mathbf{v} = \mathbf{u} - \mathbf{v}_d \]

where \( \mathbf{u} \) is the velocity field and \( \mathbf{v}_d \) is the velocity of the drop. The drop velocity is given by the following equation:

\[ \mathbf{v}_d = \frac{1}{2} \mathbf{u} + \mathbf{u} \times \frac{1}{2} \nabla_{\Gamma} \cdot \mathbf{v} \]

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ulicant-covered drop in an electric field using numer-
cal simulations. In Section III we give the mathematical for-
mation of the problem and present our numerical method.
In Section III we investigate the study state has-
formation for different configurations of electrical prop-
ties and the influence of surfactants. Concluding remarks
and proposals for future work are given in Section V.

II. MATHEMATICAL MODEL AND NUMERICAL
METHOD

A. The level-set method

We consider a system of two immiscible phases sepa-
ated by an interface. In this section we introduce the level-set
method to capture this interface, which allows handling of the
 discontinuities at the interface in a simple and accurate
manner.

In the level-set method, the interface is defined impli-
dely by the zero level-set, i.e.,

\[ \phi(x, t) = 0, \]

where \( \phi(x, t) \) is the level-set function, which denotes the signed
distance to the interface.

The level-set function moves with the interface velocity \( u_n \) according to

\[ \frac{\partial \phi}{\partial t} + u_n \cdot \nabla \phi = 0. \]

To allow this equation to be solved numerically, the inter-
face velocity is extracted from the interface. Advancements and
Sethian\(^4\) showed that the velocity could be extrap-
olated orthogonally from the interface by solving

\[ \frac{\partial \phi}{\partial t} = \frac{\partial \phi}{\partial t}^\omega + \frac{\partial \phi}{\partial t}^\gamma, \]

where \( \frac{\partial \phi}{\partial t}^\omega \) is the regularized Heaviside function, defined as

\[ H_\epsilon(x) = \begin{cases} 1 & \text{if } x > 0, \\ 0 & \text{if } x < 0, \end{cases} \]

and the regularized Heaviside function, defined as

\[ H_\epsilon^\omega(x) = \frac{1}{\epsilon} \int_0^x H_\eta(y) \, dy, \]

with \( \epsilon \) being the smoothing width. We employ a smearing
width of \( \epsilon = 1 \) in this work.

The standard level-set reinitialization procedure is used to keep the level-set function as a signed distance
function throughout the computation. This is accom-
plished by solving

\[ \frac{\partial \phi}{\partial t} = \frac{\partial \phi}{\partial t}^\omega + \frac{\partial \phi}{\partial t}^\gamma, \]

where \( \frac{\partial \phi}{\partial t}^\gamma \) is the regularized delta function, defined as

\[ \delta_\epsilon^\gamma(x) = \frac{1}{\epsilon^2} \int_0^1 \frac{1}{|c \cdot n|} \, dc. \]

Reinitialization is performed every other time step.

With the level-set function as a signed distance
function, the normal vector (normed) can be calculated as

\[ n = \frac{\nabla \phi}{|\nabla \phi|}. \]

and the curvature as

\[ \kappa = \nabla \cdot \frac{\nabla \phi}{|\nabla \phi|^2}. \]

The density, viscosity, permeability and conductivity are

dimensional properties across the interface. We smooth these
properties over a narrow transition region using

\[ \rho_\epsilon(x) = \rho(1 - \frac{|x|}{\epsilon}), \]

\[ \mu_\epsilon(x) = \mu(1 - \frac{|x|}{\epsilon}), \]

\[ \kappa_\epsilon(x) = \kappa(1 - \frac{|x|}{\epsilon}), \]

\[ \sigma_\epsilon(x) = \sigma(1 - \frac{|x|}{\epsilon}). \]

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The electric force is given by the divergence of the Maxwell stress tensor, $f = \nabla \cdot \mathbf{E}$, where

$$M = \frac{\varepsilon_0}{\text{Ohnesorge number}} \frac{\mathbf{E} \cdot \mathbf{E}}{\mathbf{E} \cdot \mathbf{E}}$$

Here, $E$ is the electric field. We assume that the fluids are locally dielectric, that is, we assume that the volume charge reaches a steady state in a much shorter time than the fluid. This means that the electric force for charge conservation

$$\mathbf{D} = \varepsilon_0 \nabla \phi$$

Next, we analyze the second equation for the electric field. We analyze the dynamic effect of a possible membrane on the electric field.

$$\sigma = \varepsilon_0 \nabla \cdot \mathbf{E}$$

C. Non-dimensionalization

We solve the above equations in their dimensional form, but express the results in terms of relevant non-dimensional quantities. To cast the mathematical model in non-dimensional form, we introduce the following non-dimensional variables, denoted with a *:

$$x^* = \frac{x}{L}, \quad t^* = \frac{t}{T}, \quad f^* = \frac{f}{f_0}, \quad \mathbf{E}^* = \frac{\mathbf{E}}{E_0}, \quad \mathbf{D}^* = \frac{\mathbf{D}}{D_0}, \quad \phi^* = \frac{\phi}{\phi_0}, \quad \sigma^* = \varepsilon_0 \frac{\nabla \cdot \mathbf{E}}{E_0}$$

Here, $E_0$ is the electric field scale, which is the dimensionless electric field scale, and $\mathbf{E}_0$ is the electric field vector.

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Here, $E_0$ is the electric field scale, which is the dimensionless electric field scale, and $\mathbf{E}_0$ is the electric field vector.
Finally, the velocity field is calculated with
\[ \nabla \cdot \mathbf{v} = \frac{\partial p}{\partial t} + \mathbf{f} \cdot \nabla \mathbf{u} \] (32)

Finally, the velocity field is calculated with
\[ \mathbf{v} = \nabla \times \mathbf{a} \] (33)

III. RESULTS AND DISCUSSION

Finally, we discuss the influence of surfactants on the transient deformation of a conductive drop when the electric field is so high that no steady-state solution exists.

The computational domain is illustrated in Fig. 1. The simulations are performed in an anisotropic, cylindrical coordinate system, where the axis of symmetry is aligned with the electric field. Additionally, it is assumed that the fluid mechanics are symmetric about the z-axis, while the electric problem is antisymmetric. This means that the simulations are only performed in one quadrant of the drop, which reduces the computational complexity.

We first present a comparison with theoretical results for the steady-state deformation of a drop in an electric field. Then, we present results for the steady-state deformation of a conductive drop for various electric properties. Finally, we discuss the influence of surfactants on the transient deformation of a conductive drop when the electric field is so high that no steady-state solution exists.

A. Comparison with small-deformation theory for clean drops

In the limit of small perturbations, an expression for the deformation of a baby-decorated drop in a baby-decorated liquid was derived by Taylor\(^{26}\) in the first order, and later extended to second order by Ajayi\(^7\). This

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The evolution in time is calculated using a fourth-order, strong-stability-preserving (SSP) Runge-Kutta (RK) method\(^{5,11}\). This method is also used for the level-set equation and the surfactant equation, while a four-step second-order SSP RK method is employed for the reinitialization of the level-set equation and extrapolation of the velocity field and surfactant.

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can be written as

$$B = \frac{1}{\mu} \left[ \ln \left( \frac{C_1}{C_2} \right) \right]$$

where $C_1$ and $C_2$ are the drop extensions along the $x$- and $y$-axes, respectively. The coefficients $C_1$ and $C_2$ are given by

$$C_1 = \frac{\sigma}{\beta}$$

and

$$C_2 = -\frac{\sigma}{\beta}$$

Here, $\sigma$ denotes the ratio between phase 1 and phase 2. The form of deformation is given by $B$. If $B = 0$, the drop will have a $\beta$-shape. If $B < 0$, the drop will have an $\alpha$-shape. If $B > 0$, the drop will have a $\beta$-shape. If $B = 0$, the drop will have an $\alpha$-shape.

**Influence of surfactants on steady-state deformation**

We now turn our attention to the steady-state deformation of a drop with a surfactant present on the interface.

**TABLE I. The parameters used for validation of the electric flow, together with the predicted deformation types and flow patterns.**

<table>
<thead>
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<th>Case</th>
<th>$\epsilon$</th>
<th>$\sigma$</th>
<th>$\beta$</th>
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<th>$\gamma$</th>
<th>$\delta$</th>
<th>Flow patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>Distorted C</td>
</tr>
<tr>
<td>B</td>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>Distorted C</td>
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<tr>
<td>C</td>
<td>2.0</td>
<td>0.5</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>Distorted C</td>
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</tbody>
</table>

**TABLE II. The parameters used for validation of the electric flow, together with the predicted deformation types and flow patterns.**

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</table>

**Influence of surfactants on steady-state deformation**

We now turn our attention to the steady-state deformation of a drop with a surfactant present on the interface.

**TABLE IV. The parameters used for validation of the electric flow, together with the predicted deformation types and flow patterns.**

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**Influence of surfactants on steady-state deformation**

We now turn our attention to the steady-state deformation of a drop with a surfactant present on the interface.

**FIG. 2. A map of the different induced flow patterns and deformations for $r_1 = 1$.**

**FIG. 3. Comparison of numerical results (solid) and the small deformation theory of Taylor (dashed line) and Ajayi (gold line) for the parameters given in Table 1.**

**FIG. 4. Comparison of numerical results (solid) and the small deformation theory of Taylor (dashed line) and Ajayi (gold line) for the parameters given in Table 1.**

**FIG. 5. Comparison of numerical results (solid) and the small deformation theory of Taylor (dashed line) and Ajayi (gold line) for the parameters given in Table 1.**

**FIG. 6. Comparison of numerical results (solid) and the small deformation theory of Taylor (dashed line) and Ajayi (gold line) for the parameters given in Table 1.**
1. Case A

We first study the effect of surfactants on the system with probe deformation and counter-clockwise flow. The deformation as a function of electric capillary number for different surfactant coverages is shown in Fig. 5. For low $\text{Ca}_{\text{S}}$, higher surfactant concentration led to higher deformation. This is due to the induced flow from the electric field, which leads to a sharper transition near the tip of the drop, as shown in Fig. 7(c). This will transfer surfactant to the tip of the drop and increase the interfacial tension, which leads to more uniform surfactant profiles. The gradient is low, this only leads to modest gradients in the interfacial tension than for the low concentrations, the concentration at the tips approaches the maximum surfactant packing. This leads to larger gradients in the interfacial tension for the low concentration, and correspondingly higher Marangoni stresses which lead to higher Reynolds number. A balance between the normal interfacial tension force, the hydrodynamic pressure and the electric pressure, the drop expands more to yield a higher mean curvature. However, as the drop is stretched further, the average interfacial tension increases due to dilution of the surfactant. This will act to reduce deformation, and eventually the effect becomes stronger than the effect of reduced interfacial tension at the tips, leading to less deformation. This is clearly seen for $\text{Ca}_{\text{S}} = 0.5$ in the figure. At low $\text{Ca}_{\text{S}}$, the deformation is higher than for the lower $\text{j}_1$ numbers, but at high $\text{Ca}_{\text{S}}$, it becomes lower.

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In Figure 6 we illustrate the drop shapes and velocity patterns for electric capillary numbers 0.3, 0.8 and 1.2, and for a clean and surfactant-covered drop. We immedi-
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3. Conclusion

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FIG. 9. (Color online) Case A. Deformation as a function of electric capillary number for various surfactant coverages.

2. Case B

Here, we consider the case where the drop deforms in a prolate fashion, but the induced flow is from the poles to the equator. The deformation as a function of electric capillary number for different surfactant coverages is shown in Fig. 10. We see that a higher concentration of surfactant consistently gives a lower degree of deformation. The reason for this is that new surfactant is swept towards the equator instead of the poles. The interfacial tension will therefore become higher at the tips, and give a larger resistance against deformation than for a clean drop.

Note that the deformation is relatively low for the C8z considered here. We would expect that dilatational effects would occur here as well for higher deformations. However, for this case these effects would only give an even lower deformation, further increasing the difference between the clean and surfactant-covered drops. We would also expect, as we will see in the next section, that the dilatational effects would occur sooner than for case A. This is because when surfactant is swept towards the equator instead of towards the poles, it will be spread over a larger surface area and thereby contribute less to:

FIG. 8. (Color online) Case A. Deformation as a function of electric capillary number for various surfactant coverages.

FIG. 7. (Color online) Case A. Interfacial tensions along the interface for various surfactant coverages.

FIG. 6. Case A. Drop deformation and induced flow pattern. The right quadrant shows the clean drop and the left quadrant shows the surfactant-covered drop with $\gamma_0 = 0.7$. The velocity scale is different in the three figures.

Here, we consider the case where the drop deformation in a prolate fashion, but the induced flow is from the poles to the equator. The deformation as a function of electric capillary number for different surfactant coverages is shown in Fig. 10. We see that a higher concentration of surfactant consistently gives a lower degree of deformation. The reason for this is that new surfactant is swept towards the equator instead of the poles. The interfacial tension will therefore become higher at the tips, and give a larger resistance against deformation than for a clean drop.

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FIG. 8. (Color online) Case A. Deformation as a function of electric capillary number for various surfactant coverages.

FIG. 7. (Color online) Case A. Interfacial tensions along the interface for various surfactant coverages.

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FIG. 8. (Color online) Case A. Deformation as a function of electric capillary number for various surfactant coverages.

FIG. 7. (Color online) Case A. Interfacial tensions along the interface for various surfactant coverages.

FIG. 6. Case A. Drop deformation and induced flow pattern. The right quadrant shows the clean drop and the left quadrant shows the surfactant-covered drop with $\gamma_0 = 0.7$. The velocity scale is different in the three figures.
Next, we consider the case of oblate deformation, with induced flow from the poles to the equator. The deformation is a function of electric capillary number for different surfactant coverages is shown in Fig. 11. For the chosen parameter set, we see that the deformation is almost negligible for low surf. With surf, as shown in the closeup in Fig. 11(b), the deformation is slightly larger in magnitude, but the concentration is the same. This is again because surfactant is swept towards the drop equator by the induced flow, and the resulting low interfacial tension here gives a corresponding lower resistance to higher deformation. The change in deformation is lower because the surfactant is spread across the equator instead of concentrated at the tips. This also means that the relative effect of dilatation will occur earlier than for case A. This can be seen at higher surf (Case B) in Fig. 11. For higher surf (Case B) compared to case A, the difference in deformation is lower because the surfactant is spread across the equator instead of concentrated at the tips.

IV. CONCLUSIONS

A fixed model for the chosen viscosity ratio, with induced flow from the poles to the equator. The deformation is a function of electric capillary number for different surfactant coverages is shown in Fig. 11. For the chosen parameter set, we see that the deformation is almost negligible for low surf. With surf, as shown in the closeup in Fig. 11(b), the deformation is slightly larger in magnitude, but the concentration is the same. This is again because surfactant is swept towards the drop equator by the induced flow, and the resulting low interfacial tension here gives a corresponding lower resistance to higher deformation. The change in deformation is lower because the surfactant is spread across the equator instead of concentrated at the tips. This also means that the relative effect of dilatation will occur earlier than for case A. This can be seen at higher surf (Case B) in Fig. 11. For higher surf (Case B) compared to case A, the difference in deformation is lower because the surfactant is spread across the equator instead of concentrated at the tips.

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covered drop, and thereby increase the difference between the clean and surfactant-covered flow.

For dilute deformation, which almost gives dilute flow, the results are similar to that of planar deformation and some clockwise rotation. A limit to the influence of surfactant is stronger, since the relative importance of the Marangoni stresses becomes higher.

In this work, only steady-state deformation was considered. At high electric capillary numbers, no steady-state states exist and the drop will stretch further and eventually break up. It would be of interest to investigate the influence of surfactants on the breakup behavior. In particular, for a conductive drop in an otherwise dielectric medium, the influence of surfactant may be important even though it has no influence on the steady-state deformation. The presented numerical method is applicable to such a study as well.

ACKNOWLEDGMENTS

This work is funded by the project “Electrohydrodynamics of Flowers: An Exploration into their...”, co-funded by NIMW. The focus of this work is to study the influence of surfactants on the dilatational stress state of a drop.


A DIFFUSE-INTERFACE APPROACH FOR MODELING TRANSPORT, DIFFUSION AND ADSORPTION/DESORPTION OF MATERIAL QUANTITIES ON A DEFORMABLE INTERFACE

KNUT ERIK TEIGEN, XIANGGONG LI, JOHN LOWENGRUB, FAN WANG, AND AXEL VOIGT

Abstract. A method is presented to solve two-phase problems involving a material quantity on an interface. The interface can be advected, stretched, and change topology, and material can be adsorbed to and desorbed from it. The method is based on the use of a diffuse interface framework, which allows a simple implementation using standard finite-difference or finite-element techniques. Here, finite-difference methods are used to discretize the linearized, approximated, variational equation and the resulting equations are solved using a non-linear multigrid method. Interface flow with soluble surfactants is used as an example of the application of the method, and several test cases are presented demonstrating its accuracy and convergence.

Key words. Partial differential equations, diffuse interface, interfacial dynamics, complex geometry, adsorption, desorption, surfactant diffusion.

AMS subject classifications. 35Q35, 35K05, 35K57, 65Z05, 65M06, 65M50, 65M55, 76Txx, 82C24

1. Introduction

Many problems in the biological, physical, and engineering sciences involve systems of equations that need to be solved in evolving domains with complex shapes. In addition, the solutions in the bulk domain may couple with the surface through adsorption of mass from the bulk to the surface and desorption from the surface to the bulk. Furthermore, the evolution of the domain boundary may depend on the distribution of the surface concentration through the modification of interfacial forces. Surfactants are a classic example where the amphiphilic organic compounds may adsorb to and desorb from a liquid/liquid or liquid/gas interface and lower the surface tension on the interface. Thus, inhomogeneous distribution of surfactants produces Marangoni forces — tangential forces along the interface — that affect the dynamics; surfactants play important roles in vortex pair interaction (e.g., [36, 34], fingering (e.g., [34, 43]), and deep break-up and coalescence (e.g., [35, 36, 48, 42]). Other examples include biomembranes where transmembrane proteins play an important role in intra- and extra-cellular dynamics (e.g., [17, 74, 51, 29]), epithelial cells (e.g., [10], 68, 11), protein and lipid singularities, and extra-cellular dynamics (e.g., [75]). Other examples include biomembranes where transmembrane proteins play an important role in intra- and extra-cellular dynamics (e.g., [17, 74, 51, 29]), epithelial cells (e.g., [10], 68, 11), protein and lipid singularities, and extra-cellular dynamics (e.g., [75]). Other examples include biomembranes where transmembrane proteins play an important role in intra- and extra-cellular dynamics (e.g., [17, 74, 51, 29]), epithelial cells (e.g., [10], 68, 11), protein and lipid singularities, and extra-cellular dynamics (e.g., [75]). Other examples include biomembranes where transmembrane proteins play an important role in intra- and extra-cellular dynamics (e.g., [17, 74, 51, 29]), epithelial cells (e.g., [10], 68, 11), protein and lipid singularities, and extra-cellular dynamics (e.g., [75]).
When solving equations in complex domains (e.g., amphiphilic nature of surfactants). The available numerical methods for solving these problems can roughly be divided into two categories: interface tracking and interface capturing methods. Interface tracking methods use either Lagrangian approaches or Eulerian approaches. Lagrangian approaches are typically very accurate, but can be relatively complex to implement, especially in three dimensions and for problems involving topological changes. Eulerian approaches are typically very accurate, but are not ideal for solving problems with topological changes.

In interface capturing methods, the interface is not tracked explicitly, but instead is implicitly defined through a regularization of the interface. This means that the solution of the problem can be done independently of the underlying grid, which greatly simplifies grid generation, and handling of topological changes. For example, a volume-of-fluid (VOF) method for insoluble surfactants was developed in [77]. A more general method which allows non-linear equations of state for surface concentration may only be soluble in either the exterior or interior of the domain (e.g., amphiphilic nature of surfactants). The available numerical methods for solving these problems can roughly be divided into two categories: interface tracking and interface capturing methods. Interface tracking methods use either Lagrangian approaches or Eulerian approaches. Lagrangian approaches are typically very accurate, but can be relatively complex to implement, especially in three dimensions and for problems involving topological changes.

The diffuse-interface, or phase-field, method represents yet another approach for simulating solutions of equations in complex domains. For example, we follow here, the complex domain is represented implicitly by a phase-field function, which is an approximation of the characteristic function of the domain. The boundary of the domain can thus be represented as an isosurface of the phase-field function rapidly transitions from one inside the domain to zero in the exterior of the domain. The boundary of the domain can thus be represented as an isosurface of the phase-field function.
the phase-field function. The bulk and surface PDEs are then extended on a larger, regular domain with additional terms that approximate the advection-diffusion flux boundary conditions and source terms for the bulk and surface equations respectively. Standard finite-difference or finite-element methods may be used. Here, we focus on a finite difference approach.

The diffuse interface method, which has a long history in the theory of phase transitions dating back to van der Waals [e.g., 79, 3], was used in [6] to study diffusion inside a cell with non-Neumann boundary conditions at the (stationary) cell boundary (see also [8, 9], and later was used to simulate electrical double layers in a cell [21]). This approach has been extended [51] to simulate coupled bulk diffusion with an ordinary-differential equation description of reaction-kinetics on the bounding surface of a stationary domain to simulate membrane-bound Turing patterns.

More recently, general diffuse-interface methods have been adapted for solving PDEs on stationary surfaces [73], evolving surfaces [13, 14, 16, 17], and for solving PDEs on complex evolving domains with Dirichlet, Neumann and Robin boundary conditions [54].

As shown in the previous paragraphs, bulk/surface problems are important in a wide range of areas. Here, we combine and refine previous work on diffuse-interface methods to develop a new method for solving coupled bulk/surface problems on general, evolving domains. The method is very simple compared to other methods, and can handle advection, diffusion and adsorption/desorption in a straightforward manner.

Matched asymptotic expansions are used to demonstrate that the diffuse interface system converges to the original sharp interface equations as the interface thickness tends to zero. The use of a non-linear multigrid method and block-structured, adaptive grids also make the method computationally efficient. We present several test cases demonstrating the accuracy and convergence of the proposed method.

The paper is organized as follows. In section 2, the governing equations for the surface concentration and the bulk concentration are introduced, and the interface representation presented. Section 3 presents an asymptotic analysis of the proposed method. Section 4 then details the numerical implementation. In section 5, the performance of the numerical method is evaluated on a set of test cases. Finally, section 6 contains conclusions and discussions of future work.

2. Mathematical formulation

2.1. Governing equations

Consider a domain $\Omega \subset \mathbb{R}^d$, which contains a closed interface $\Gamma$, the inner part of $\Gamma$ is $\Omega_+$ and the exterior is $\Omega_\times$. See figure 2.1 for an illustration. Let $f$ denote a surface concentration defined on $\Gamma$. We suppose that $f$ is extended off $\Gamma$ constant in the normal direction (i.e., $\nabla f \cdot n = 0$) so that $f$ is defined in a neighborhood of $\Gamma$. Then, the sharp interface mass conservation equation is

$$\frac{\partial f}{\partial t} + \nabla \cdot (\nabla f \cdot n) = 0 \quad \text{on } \Gamma,$$

where $u$ is the velocity, $\nabla f = -\nabla u \cdot n$ is the surface gradient, $\mu$ is the normal vector to $\Gamma$ pointing into $\Omega_+$, $D_f$ is the diffusion coefficient, $\rho_f = (\nabla \cdot u) \cdot n$, $u_n = u \cdot n$ is the normal curvature of $\Gamma$ (positives for a sphere), and $j$ is a source term that arises from adsorption to and desorption from $\Gamma$.

$$j = \nabla \cdot F_{\Gamma} f,$$

where $\nabla \cdot F_{\Gamma} f$ is the net flux between $\Gamma$ and the interior of $\Omega$. This flux is the net inward flux due to diffusion into $\Omega_+$ and the net outward flux due to desorption from the surface.$\nabla \cdot F_{\Gamma} f$

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where \( r_j \) and \( r_k \) are adsorption and desorption coefficients, respectively, and \( F \) is the bulk concentration (evaluated immediately adjacent to \( \Gamma \)). Note that in the context of surfactants, the interface may become saturated and instead one may use

\[
j = r_j F (r_k - f) - r_k f. \tag{2.3}
\]

where \( f_{\infty} \) is the maximum interface concentration. An equivalent formulation is

\[
\frac{df}{dt} + \nabla \cdot (n_f r_j (D_f \nabla_f F)) = r_k f. \tag{2.4}
\]

We refer the reader also to [11] for further discussion of formulations involving interfacial transport using constant normal extensions and to [38] for Eulerian formulations of the dynamics of surface concentrations.

Assume that the surface concentration \( f \) is soluble in \( \Omega_0 \), but not in \( \Omega_k \). Then, define the bulk concentration in \( \Omega_k \) to be \( F \), which evolves according to the bulk mass conservation equation

\[
\frac{DF}{dt} + \nabla \cdot (n_f r_j (D_f \nabla_f F)) = r_k f. \tag{2.5}
\]

with the boundary condition at \( \Gamma \)

\[
D_f \nabla F \cdot n = - j \quad \text{on} \quad \Gamma. \tag{2.6}
\]

Note that if the surface concentration were soluble in \( \Omega_k \), then an additional mass conservation equation would need to be passed. Our formulation is sufficiently general to handle this case.

Next, we consider a distribution formulation of equation (2.4) by introducing a surface delta function \( \delta \), such that

\[
\int F \, d\Omega = \int \int f \, d\Omega. \tag{2.7}
\]
where \( \Omega = \Omega \setminus \Omega_h \) (actually the above equation holds for any domain \( \Omega \) that contains \( \Gamma \)). The mass conservation equation may be rewritten accordingly as
\[
\frac{\partial}{\partial t} F(c) + \nabla \cdot (\mathbf{f} \nu) = -\nabla \cdot (\mathbf{D} \nabla \mathbf{f} (c)) + \mathbf{b}.
\] (2.8)
This distribution formulation formally holds in \( \Omega \).

Analogously, the bulk equation (2.5) may be extended to hold in \( \Omega \) in distribution form. Introducing the Heaviside function
\[
H = \begin{cases} 1 & \text{in } \Omega_h, \\
0 & \text{in } \Omega_h^c,
\end{cases}
\] (2.9)
the bulk concentration equation (2.5) and boundary condition (2.6) may be reformulated as
\[
\frac{\partial}{\partial t} (H F u) + \nabla \cdot (- (H F u) c) = \delta_{\Omega (2.8)} \nabla \cdot (H F \nabla f) - \mathbf{b}.
\] (2.10)
where the boundary condition has been included as a singular source term following [54].

2.2. Interface representation. A phase-field function \( c \) may be used to approximate the characteristic function of \( \Omega_h \). Let
\[
\rho(x,t) = \frac{1}{2} \left[ 1 + \tanh \left( \frac{x}{\sqrt{2} \sigma} \right) \right],
\] (2.11)
where \( \sigma \) is a small parameter related to the interface thickness and \( \rho(x,t) \) is a signed distance function to \( \Gamma \) (positive in \( \Omega_h \)).

The position of the interface may be taken to be \( \Gamma(t) = \{ x \in \Omega_h \mid \rho(x,t) = \frac{1}{2} \} \). To evolve \( c \), one may evolve \( v \) by
\[
\frac{\partial v}{\partial t} + \nabla v = 0,
\] (2.12)
where \( w \) is an extension of \( u \) of the interface which is constant in the normal direction [1].

An alternative, an advective Cahn-Hilliard equation can be used,
\[
\frac{\partial c}{\partial t} = \nabla \cdot \mathbf{v} = \nabla \cdot (M(c) \nabla \phi(c)),
\] (2.13)
where \( M(c) \) is a signed distance to \( \Gamma \). The polynomial energy does not constrain the deviation from this interval
\[
E = 4 \int_0^1 \phi(c) | c' |^2 + \frac{\mu}{2} | c' |^4.
\] (2.14)
where \( \mu \) is a chemical potential. Here, we take \( \phi(c) = \frac{1}{2} (c-c_0)^2 - \frac{1}{4} (c-c_0)^4 \) as the double well potential.

Note that this polynomial energy does not constrain \( c \in [0,1] \) but the deviation from this interval is typically \( O(\epsilon) \) at most. Alternative choices (e.g., double-obstacle [6,7] or logarithmic potentials [4]) may be used that do constrain \( c \in [0,1] \). The mobility \( M \) is localized on the interface and is taken to be \( M(c) = \frac{\epsilon c_0^2}{1+|c|^2} \). This equation is fourth-order and nonlinear and thus requires specialized numerical methods to solve in an efficient manner. This is discussed further in section 4.

2.3. Regularized delta and Heaviside functions. In order to evaluate equation (2.8) and equation (2.10) numerically, regularizations of the surface delta function and Heaviside function are needed. In the phase-field context, several definitions of
\[
\frac{\partial}{\partial t} (\delta_{\Omega_h} + \mathbf{v} \cdot \nabla) \left( \frac{1}{2} \left[ 1 + \tanh \left( \frac{x}{\sqrt{2} \sigma} \right) \right] \right) = 0.
\] (2.12)
where \( w \) is an extension of \( u \) of the interface which is constant in the normal direction [1].

An alternative, an advective Cahn-Hilliard equation can be used,
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the delta function are available from the literature. In this work, the approximation from [73],
\[ \delta \approx \frac{\sqrt{3}}{\pi} \delta(x), \quad B(x) = c^2(1 - x^2)^2, \] (2.15)

is used for the surface equation. Note that other choices may be used [17]. For the boundary condition in the bulk equation, the approximation
\[ \delta \approx \frac{\sqrt{3}}{\pi} \delta(x), \quad B(x) = c^2(1 - x^2)^2, \] (2.15)
is used, which avoids additional scaling issues in the equation [53]. Further, the regulated Heaviside function is simply taken to be [53]
\[ H(\epsilon) \approx \epsilon. \] (2.17)

3. Asymptotic analysis
In this section, the method of matched asymptotic expansions is used to provide a formal justification for the diffuse interface approach. To make the system slightly more general, we may add reaction terms to the bulk and surface equations, i.e., \( \dot{R}(f) + D(f) \) may be added to equations (2.18) and (2.19) respectively. In this approach, the domain \( \Omega \) is separated into two regions — the regions for \( \Gamma \) (outer region, i.e., the portions of \( \Omega_1 \) and \( \Omega_2 \) away from \( \Gamma \)) and the region near \( \Gamma \) (inner region).

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and analogously for the other variables. Furthermore, in this coordinate system we have
\[ \frac{\partial \tilde{u}}{\partial \tilde{t}} = -\tilde{\nabla} \cdot \tilde{u} + \tilde{O}(\epsilon), \tag{3.3} \]
\[ \tilde{\nabla} \cdot u_{\text{eff}} = U_{\text{eff}} + O(\epsilon), \tag{3.4} \]
where \( \tilde{U} \) is the leading term of the normal velocity of \( \Gamma \).

3.2. Matching Condition Assumming that there is an overlapping region where both the inner and outer expansion are valid, we may write the outer expansion in the local coordinate system as
\[ (3.8) \]
\[ \hat{u}(x) = (\nabla \cdot u)(x) + \epsilon \hat{u}_0(x) + \epsilon^2 \hat{u}_1(x) + \ldots \]
and analogously for the other variables. Matching the inner and outer expansions in this region, the following matching conditions hold \[16, 71, 22\],
\[ \lim_{\epsilon \to 0} F_\epsilon = \lim_{\epsilon \to 0} F_\epsilon = \hat{F}_\epsilon, \tag{3.11} \]
\[ \lim_{\epsilon \to 0} \nabla F_\epsilon = \lim_{\epsilon \to 0} \partial_x F_\epsilon, \tag{3.12} \]
\[ \lim_{\epsilon \to 0} \partial_r F_\epsilon = 0. \tag{3.13} \]
Analogous matching conditions hold for the other variables.

3.3. Bulk Equation

3.3.1. Outer Expansion The \( \mathcal{O}(\epsilon^3) \) term of equation (2.19) gives:
\[ \frac{\partial \tilde{u}}{\partial \tilde{t}} + \tilde{\nabla} \cdot (\mathcal{F}(\tilde{u}) - \nabla \cdot (D_0 \tilde{F}_{\tilde{u}}) + R_{\tilde{F}_\epsilon}(F_\epsilon)). \tag{3.10} \]
Thus at leading order equation (2.5), with the reaction term, is recovered. To determine the boundary conditions on \( \Gamma \), we match with the inner expansion.

3.3.2. Inner expansion At \( \mathcal{O}(\epsilon^{-3}) \), we obtain
\[ \partial_t (c_D \partial_x F_\epsilon) = 0, \tag{3.11} \]
which implies \( \partial_t F_\epsilon = 0 \). At \( \mathcal{O}(\epsilon^{-1}) \) we obtain
\[ (V_{\text{out}} - V_{\text{in}}) \partial_t (c_D \partial_x F_\epsilon) + (\partial_x F_\epsilon - \sigma_{\text{in}} F_\epsilon) \partial_x C, \tag{3.12} \]
Since \( U_{\text{in}} = V_{\text{in}} \) by the asymptotic analysis of the advective Cahn-Hilliard equation \[58\], \( F_\epsilon \) is independent of \( z \), as we show below, \( F_\epsilon \) is also independent of \( z \), we may integrate equation (3.12) and use that \( \int_{\Gamma_{\epsilon}} f \partial_x \epsilon \, d\Gamma = 0 \), again taken from \[58\], to obtain
\[ \lim_{\epsilon \to 0} \partial_r F_\epsilon = -\left( r F_{\text{in}} - \sigma_{\text{in}} F_{\text{in}} \right) \tag{3.13} \]
Together with equation (3.8), we therefore recover the Neumann boundary condition (2.6) for the outer solution at leading order
\[ \lim_{\epsilon \to 0} \partial_t F_\epsilon = -\left( r F_{\text{in}} - \sigma_{\text{in}} F_{\text{in}} \right), \tag{3.14} \]
where we have set \( f = f_0 \) since \( f_0 \) is independent of \( z \). Next, we turn to the surface concentration equation.

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where we have set \( f = f_0 \) since \( f_0 \) is independent of \( z \). Next, we turn to the surface concentration equation.
3.4. Surface Equation

Here, we only focus on the inner expansion since the equation is localized around the interface. At \( O(\epsilon^{-2}) \), we obtain

\[
\partial_t \begin{bmatrix} D \nabla c_N(a_N) f_N \end{bmatrix} = 0,
\]

which implies \( \partial_t f_N = 0 \), as claimed above. The \( O(\epsilon^{-3}) \) term gives

\[
0 = \partial_t (b_N R(c_N)(a_N) f_N),
\]

where we have used that \( U_N = \bar{U} \). Equation (3.16) implies that \( \partial_t f = 0 \) also. At \( O(\epsilon^0) \), we obtain

\[
\partial_t (b_N R(c_N)(a_N) f_N) + \partial_t (a_N D_R(\nabla c_N)(a_N) f_N) = \partial_t \left( \frac{D_R}{|R|^2} \nabla f_N + \frac{B_N R(c_N)(a_N) f_N}{|R|^2} \right),
\]

(3.17)

Since \( f_N \) is independent of \( z \), we may integrate equation (3.17) in \( z \) from \( -\infty \) to \( +\infty \), and divide by \( \int_{-\infty}^{\infty} b_N R(c_N)(a_N) f_N \) to obtain

\[
\partial_t f + \nabla f = \left( f_N \right) = -\left( \frac{D_R}{|R|^2} \nabla f + \frac{B_N R(c_N)(a_N) f_N}{|R|^2} \right),
\]

(3.18)

where we have taken \( f_N = f_0 = F_0 \) and we also have assumed that \( U_N \) is independent of \( z \) (which implies there is no jump in velocity across \( \Gamma \)) so that we may write \( U_N = u_N \). Thus, equation (2.4), with the reaction term, is recovered at leading order.

4. Numerical methods

This section briefly describes the numerical methods used to solve the above equations. The algorithm follows the one developed in \([77]\). In particular, the equations are discretized using finite differences in space and a semi-implicit time discretization. A block-structured, adaptive grid is used to increase the resolution around the interface in an efficient manner. The nonlinear equations at the implicit time level are solved using a non-linear Adaptive Full Approximation Scheme (AFAS) multigrid algorithm. For a detailed discussion of the adaptive algorithm and the multigrid solver, the reader is referred to \([77]\).

The equations are discretized on a rectangular domain. The surface concentration, the bulk concentration, the phase-field function and the chemical potential are defined at the cell-centers, while the velocity components are defined on cell-edges.

Special care has to be taken for the temporal discretization. The Cahn-Hilliard system is fourth order in space, and requires the use of an implicit method to avoid severe limitations in the time step. Here, Crank-Nicolson type schemes are used \([45]\),

\[
\frac{\phi^{n + 1} - \phi^n}{\Delta t} = \frac{1}{2} \left[ \frac{\left( D_R \partial^2 \phi \right)^{n + 1} + \left( D_R \partial^2 \phi \right)^{n}}{2} \right] + \frac{1}{2} \left[ \frac{\left( D_R \partial^2 \phi \right)^{n + 1} + \left( D_R \partial^2 \phi \right)^{n}}{2} \right],
\]

(4.1)

\[
\phi^{n + 1} = \phi^n - \frac{\Delta t}{\mu} \frac{\partial}{\partial z} \left( \nabla \phi \cdot \nabla \phi \right),
\]

(4.2)

In \([45, 87]\) this approach was shown to be robust and efficient. The equations for

4.4. Surface Equation

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\[
\partial_t \begin{bmatrix} D \nabla c_N(a_N) f_N \end{bmatrix} = 0,
\]

which implies \( \partial_t f_N = 0 \), as claimed above. The \( O(\epsilon^{-4}) \) term gives

\[
0 = \partial_t (b_N R(c_N)(a_N) f_N),
\]

where we have used that \( U_N = \bar{U} \). Equation (3.16) implies that \( \partial_t f = 0 \) also. At \( O(\epsilon^0) \), we obtain

\[
\partial_t (b_N R(c_N)(a_N) f_N) + \partial_t (a_N D_R(\nabla c_N)(a_N) f_N) = \partial_t \left( \frac{D_R}{|R|^2} \nabla f_N + \frac{B_N R(c_N)(a_N) f_N}{|R|^2} \right),
\]

(3.17)

Since \( f_N \) is independent of \( z \), we may integrate equation (3.17) in \( z \) from \( -\infty \) to \( +\infty \), and divide by \( \int_{-\infty}^{\infty} b_N R(c_N)(a_N) f_N \) to obtain

\[
\partial_t f + \nabla f = \left( f_N \right) = -\left( \frac{D_R}{|R|^2} \nabla f + \frac{B_N R(c_N)(a_N) f_N}{|R|^2} \right),
\]

(3.18)

where we have taken \( f_N = f_0 = F_0 \) and we also have assumed that \( U_N \) is independent of \( z \) (which implies there is no jump in velocity across \( \Gamma \)) so that we may write \( U_N = u_N \). Thus, equation (2.4), with the reaction term, is recovered at leading order.

4. Numerical methods

This section briefly describes the numerical methods used to solve the above equations. The algorithm follows the one developed in \([77]\). In particular, the equations are discretized using finite differences in space and a semi-implicit time discretization. A block-structured, adaptive grid is used to increase the resolution around the interface in an efficient manner. The nonlinear equations at the implicit time level are solved using a non-linear Adaptive Full Approximation Scheme (AFAS) multigrid algorithm. For a detailed discussion of the adaptive algorithm and the multigrid solver, the reader is referred to \([77]\).

The equations are discretized on a rectangular domain. The surface concentration, the bulk concentration, the phase-field function and the chemical potential are defined at the cell-centers, while the velocity components are defined on cell-edges.

Special care has to be taken for the temporal discretization. The Cahn-Hilliard system is fourth order in space, and requires the use of an implicit method to avoid severe limitations in the time step. Here, Crank-Nicolson type schemes are used \([45]\),

\[
\frac{\phi^{n + 1} - \phi^n}{\Delta t} = \frac{1}{2} \left[ \frac{\left( D_R \partial^2 \phi \right)^{n + 1} + \left( D_R \partial^2 \phi \right)^{n}}{2} \right] + \frac{1}{2} \left[ \frac{\left( D_R \partial^2 \phi \right)^{n + 1} + \left( D_R \partial^2 \phi \right)^{n}}{2} \right],
\]

(4.1)

\[
\phi^{n + 1} = \phi^n - \frac{\Delta t}{\mu} \frac{\partial}{\partial z} \left( \nabla \phi \cdot \nabla \phi \right),
\]

(4.2)

In \([45, 87]\) this approach was shown to be robust and efficient. The equations for
where, in the above equations, we set \( \delta \Gamma_1 = B(\epsilon_1) \) \( \alpha \) and \( \delta \Gamma_2 = \sqrt{\epsilon_1} \), with \( \alpha \) being a small parameter (\( \alpha \approx 10^{-3} \)) that is used to ensure that diffusion by zero does not occur. The results are found to be quite insensitive to the precise choice of \( \alpha \) provided it is sufficiently small. The operator \( \nabla \) represents the standard second-order finite-difference discretization. The convective terms of the form \( \nabla \cdot \Phi \) are discretized using the third-order WENO reconstruction method \([78, 55] \). The WENO reconstruction method has the advantage that it handles steep gradients well, which may occur in the type of dynamics described in this work. Additionally, fewer grid points are needed to achieve a high order solution. This is particularly important for the efficiency of the adaptive grid, because fewer ghost cell values have to be calculated at the boundaries of each grid block.

Homogeneous Neumann far-field boundary conditions are prescribed for all variables. This is imposed by introducing a set of ghost cells around the domain. These ghost cells are updated before every smoothing operation. The AFAS multigrid algorithm is used to solve the discretized equations at every time step. The full description of the AFAS multigrid method will not be given here, the details can be found in \([57, 56] \) and in the reference text \([56] \). The ideal run-time complexity of this algorithm is optimal, i.e., \( O(N) \) where \( N \) is the number of grid points.

The present implementation achieves this complexity, which is shown in section 5.6.

5. Code validation

5.1. Surface diffusion on a stationary circle

First, a problem without bulk concentration is considered. This tests the validity of the diffuse interface representation of the surface equation, and of the correct implementation of the diffusion term.

Consider a stationary circle of radius \( R \), with an initial surface concentration given by

\[
\theta(\theta) = \frac{1}{2} (1 - \cos \theta),
\]

where \( \theta \) denotes the angle measured in the counter-clockwise direction from the \( x \)-axis. The surface concentration equation can now be written in polar coordinates as

\[
\frac{\partial \theta}{\partial t} = \frac{D}{\alpha} \frac{\partial^2 \theta}{\partial \theta^2} (N\text{.1})
\]

\[
\frac{\partial \theta}{\partial t} = \frac{D}{\sin \theta} \frac{\partial}{\partial \theta} \left( \mu \frac{\partial \theta}{\partial \theta} \right) (N\text{.2})
\]

where \( \theta \) denotes the angle measured in the counter-clockwise direction from the \( x \)-axis. The surface concentration equation can now be written in polar coordinates as

\[
\frac{\partial \theta}{\partial t} = \frac{D}{\alpha} \frac{\partial^2 \theta}{\partial \theta^2},
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\frac{\partial \theta}{\partial t} = \frac{D}{\alpha} \frac{\partial^2 \theta}{\partial \theta^2},
\]

\[
\frac{\partial \theta}{\partial t} = \frac{D}{\sin \theta} \frac{\partial}{\partial \theta} \left( \mu \frac{\partial \theta}{\partial \theta} \right)
\]
with initial condition \( f_0 \) and periodic boundary condition in the \( \theta \)-direction. This equation can be solved analytically, yielding

\[
f(\theta, t) = -\frac{1}{2} \left( 1 - \sqrt{1 - 4\tanh^2 \left( \frac{\sqrt{2\pi} (x-y)}{2\Delta_x} \right)} \right).
\]  

(5.3)

A series of simulations are performed comparing the numerical solution to the analytical solution. The computational domain chosen for the simulations is \([-2,2]\) and a circle with radius \( R = 1 \) is placed in the center of the domain. The phase-field function is initialized by

\[
\varepsilon(x, y) = \left[ 1 - \tanh \left( \frac{\sqrt{2\pi} (x-y)}{2\Delta_x} \right) \right].
\]  

(5.4)

The initial surface concentration is given by the analytical solution, and the time step is \( \Delta t = 1 \times 10^{-2} \).

In the numerical code, the surface concentration is defined at grid points near the interface. To enable a direct comparison with the analytical solution, the concentration at the interface is needed. This is done by using a marching squares algorithm (see e.g. [52]) to generate a set of points at the 0.5 isocontour of the phase-field function. Bilinear interpolation is then used to interpolate the grid values of the surface concentration to these interface points. Note that this will introduce extra uncertainties, so the absolute errors given later may not be exact values. The order of convergence results should not be affected by this.

An example of the adaptive grid is shown in figure 5.1. Clearly, the grid follows the circle shape very well. No significant difference between the solutions on adaptive grids and uniform grids was found for this test case for the same effective resolution. Figure 5.2 shows comparisons between the numerical solution at various times and surface diffusion coefficients. Good agreement is observed. The error in the infinity norm between the interpolated values and the exact values at the interface is given in Table 5.1. The numerical solution converges towards the exact solution in a first order fashion, as predicted by the asymptotic analysis.

### Table 5.1: The error and convergence order for the surface diffusion test case at \( t = 1 \). The interface thickness is defined as \( \epsilon_{\text{min}} \), the minimum grid size.

<table>
<thead>
<tr>
<th>Grid spacing</th>
<th>Error</th>
<th>Order (( l = 10^{-2} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/8</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>1/16</td>
<td>2.35</td>
<td>0.87</td>
</tr>
<tr>
<td>1/32</td>
<td>1.18</td>
<td>0.99</td>
</tr>
<tr>
<td>1/64</td>
<td>0.60</td>
<td>0.98</td>
</tr>
<tr>
<td>1/128</td>
<td>0.30</td>
<td>1.00</td>
</tr>
</tbody>
</table>

5.2. Surface diffusion on an advected circle

Now, the circle in the above test case is put in a constant velocity field, \( v = (0,0) \). The analytical solution is the same, only translated in the computational domain. The computational domain is extended by two in the \( x \)-direction to accomodate the translation.

The initial surface concentration is given in Table 5.1. The numerical solution converges towards the exact solution in a first order fashion, as predicted by the asymptotic analysis.

### Table 5.1: The error and convergence order for the surface diffusion test case at \( t = 1 \). The interface thickness is defined as \( \epsilon_{\text{min}} \), the minimum grid size.

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</thead>
<tbody>
<tr>
<td>1/8</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>1/16</td>
<td>2.35</td>
<td>0.87</td>
</tr>
<tr>
<td>1/32</td>
<td>1.18</td>
<td>0.99</td>
</tr>
<tr>
<td>1/64</td>
<td>0.60</td>
<td>0.98</td>
</tr>
<tr>
<td>1/128</td>
<td>0.30</td>
<td>1.00</td>
</tr>
</tbody>
</table>
The initial and final surface concentration is given in figure 5.3. As shown in Table 5.2, the convergence is first order as in the diffusion only test case. The error is slightly higher due to the additional errors caused by the advection.

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5.3. Surface concentration evolution on an expanding circle

\[ u = \cos \theta, v = \sin \theta, \]

which is illustrated in figure 5.4(a). In the absence of diffusion, the surface concentration is just a function of the circle circumference, so the mass conservation equation reduces to

\[ f(t) = \frac{C_s}{C_i} f_i, \]  

where \( C = 2\pi R \) is the surface area, and subscript 0 denotes the initial condition.

For this test case, the computational domain was set to \( \Omega = [-16,16] \times [-16,16] \) to accommodate the expansion. The initial radius was set to \( R_0 = 1 \), and the initial surface concentration was set to \( f_0 = 0.5 \). Instead of solving the Cahn-Hilliard system, equations (2.13)–(2.14), the phase-field function is evolved analytically for this test case. No significant difference is observed if the interface is evolved according to the Cahn-Hilliard system, as is done below.

Table 5.2: The error and convergence order for the diffusion on a translating circle at \( t = 1 \). The interface thickness is defined as \( \epsilon = 1.6h_{\text{min}} \).

<table>
<thead>
<tr>
<th>Grid spacing</th>
<th>Error (10^-2)</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/8</td>
<td>4.60</td>
<td>-</td>
</tr>
<tr>
<td>1/16</td>
<td>2.47</td>
<td>0.90</td>
</tr>
<tr>
<td>1/32</td>
<td>1.23</td>
<td>1.01</td>
</tr>
<tr>
<td>1/64</td>
<td>0.62</td>
<td>0.99</td>
</tr>
<tr>
<td>1/128</td>
<td>0.31</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Fig. 5.3: The initial and final surface concentration for the advected circle test case.
This test case was introduced in [56] in the context of surfactants, to test the coupling between a bulk concentration and a surface concentration. Consider an initially clean circle of radius $a$ in a domain which contains an initial bulk concentration $F_a$. A simplified version of the source term is used, where mass moves from the bulk to the interface, 

$$ j = r_a F. \quad (5.7) $$

<table>
<thead>
<tr>
<th>Grid spacing</th>
<th>Error ($10^{-2}$)</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.62</td>
<td>-</td>
</tr>
<tr>
<td>1/2</td>
<td>6.60</td>
<td>1.03</td>
</tr>
<tr>
<td>1/4</td>
<td>3.30</td>
<td>1.00</td>
</tr>
<tr>
<td>1/8</td>
<td>1.62</td>
<td>1.03</td>
</tr>
</tbody>
</table>

5.4. Bulk diffusion and bulk-surface mass transfer

This test case was introduced in [56] in the context of surfactants, to test the coupling between a bulk concentration and a surface concentration. Consider an initially clean circle of radius $a$ in a domain which contains an initial bulk concentration $F_a$. A simplified version of the source term is used, where mass moves from the bulk to the interface, 

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<table>
<thead>
<tr>
<th>Grid spacing</th>
<th>Error ($10^{-2}$)</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.6</td>
<td>-</td>
</tr>
<tr>
<td>1/2</td>
<td>6.60</td>
<td>1.03</td>
</tr>
<tr>
<td>1/4</td>
<td>3.30</td>
<td>1.00</td>
</tr>
<tr>
<td>1/8</td>
<td>1.62</td>
<td>1.03</td>
</tr>
</tbody>
</table>
The evolution of the bulk concentration can now be described with the heat equation in an infinite, hollow cylinder,

$$\frac{\partial F}{\partial t} + \frac{\partial F}{\partial r} \frac{1}{r} \frac{\partial F}{\partial r} = \frac{\partial^2 F}{\partial r^2}$$

with boundary conditions

$$\frac{\partial F}{\partial r} \bigg|_{r=R} = r_a F(r=a),$$

$$F(r=0) = F_{in}.$$  \hspace{1cm} (5.9)

where $R$ is the extent of the domain. It is taken to be 4. In lieu of an analytical solution, a fourth-order accurate finite-difference discretization of the above 1D problem is used for comparison to the diffuse-interface solution. The grid size for this problem was chosen high enough to give a resolution independent solution. The physical properties used in the simulations are given in Table 5.4.

A visual comparison between the 1D solution and the diffuse-interface results for the bulk concentration at various time steps is given in figure 5.5(a). Apart from the small errors close to the interface during the early times due to the sharp gradients, the agreement is excellent.

The amount of mass accumulated on the interface can be found from the 1D solution via mass conservation,

$$M_f(t) = M_f(0) - 2\pi \int_0^a F(y) dy,$$ \hspace{1cm} (5.11)

Figure 5.5(b) shows that the diffuse-interface solution is in good agreement with the 1D solution.

The error and convergence for both the bulk concentration and the surface concentration is given in Table 5.5. The error decreases in a second-order fashion. The reason for this is that for this test case, the surface concentration is uniform, so there is no surface diffusion.

Next, the effect of varying the surface diffusion coefficient relative to the bulk diffusion coefficient, $D_f = D/D_f$, is investigated. The initial bulk concentration is set to $F_0(r) = (a_{max} - a) \times 10^{-5}$.

Instead of the previous uniform concentration and we consider both adsorption and desorption. There is a non-uniform adsorption to the interface which gives rise to

$$F_0(r) = (a_{max} - a) \times 10^{-5}.$$ \hspace{1cm} (5.12)

Table 5.4: Values used in the bulk diffusion and bulk-surface mass transfer test case.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius, $a$</td>
<td>1.0</td>
</tr>
<tr>
<td>Adsorption rate, $r_a$</td>
<td>1.0</td>
</tr>
<tr>
<td>Diffusion coefficient, $D_f$</td>
<td>1.0</td>
</tr>
<tr>
<td>Initial bulk concentration, $F_{in}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The evolution of the bulk concentration can now be described with the heat equation in an infinite, hollow cylinder,

$$\frac{\partial F}{\partial t} + \frac{\partial F}{\partial r} \frac{1}{r} \frac{\partial F}{\partial r} = \frac{\partial^2 F}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial F}{\partial r} \right).$$

with boundary conditions

$$\frac{\partial F}{\partial r} \bigg|_{r=R} = r_a F(r=a),$$

$$F(r=0) = F_{in}.$$  \hspace{1cm} (5.9)

where $R$ is the extent of the domain. $R$ is taken to be 4. In lieu of an analytical solution, a fourth-order accurate finite-difference discretization of the above 1D problem is used for comparison to the diffuse-interface solution. The grid size for this problem was chosen high enough to give a resolution independent solution.

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Instead of the previous uniform concentration and we consider both adsorption and desorption. There is a non-uniform adsorption to the interface which gives rise to
diffusion effects on the surface. Additionally, desorption is added to yield more complex dynamics. The radius is set to $r/a = 0.15$ and the drop is centered at $(0.5, 0.5)$. The adsorption and desorption rates are $r_a = r_d = 100$ and the bulk diffusion coefficient is $D_F = 1.0$. Figure 5.6 shows the concentration in the bulk and on the surface at $t = 0.09$ for varying diffusion ratios. A grid spacing of $h = 1/256$ was employed, along with interface thickness $\epsilon = 0.004$. Because of the non-uniform bulk distribution, the adsorption will be higher at the bottom of the circle than at the top. As the surface diffusion coefficient increases, mass is diffused from the bottom to the top of the circle faster, which further reduces the adsorption at the top. This effectively increases the diffusion and leads to a more uniform concentration distribution in the bulk. This is illustrated in figure 5.7, which shows the bulk concentration along $x = 0.5$. The larger surface diffusion also leads to lower total interface concentration, since mass is

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### Table 5.5: The error in the infinity norm and convergence order for the bulk concentration and the accumulated surface mass in the bulk diffusion and bulk-surface mass transfer test case. The interface thickness is $\epsilon = 1.0h_{bulk}$.

<table>
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<tr>
<th>Grid spacing</th>
<th>Bulk concentration Error Order</th>
<th>Surface mass Error Order</th>
</tr>
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<tbody>
<tr>
<td>1/8</td>
<td>11.38</td>
<td>9.66</td>
</tr>
<tr>
<td>1/16</td>
<td>5.21</td>
<td>4.50</td>
</tr>
<tr>
<td>1/32</td>
<td>1.57</td>
<td>2.30</td>
</tr>
<tr>
<td>1/64</td>
<td>0.543</td>
<td>2.22</td>
</tr>
<tr>
<td>1/128</td>
<td>0.0473</td>
<td>0.036</td>
</tr>
</tbody>
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</tr>
<tr>
<td>1/64</td>
<td>0.543</td>
<td>2.22</td>
</tr>
<tr>
<td>1/128</td>
<td>0.0473</td>
<td>0.036</td>
</tr>
</tbody>
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diffusion effects on the surface. Additionally, desorption is added to yield more complex dynamics. The radius is set to $r/a = 0.15$ and the drop is centered at $(0.5, 0.5)$. The adsorption and desorption rates are $r_a = r_d = 100$ and the bulk diffusion coefficient is $D_F = 1.0$. Figure 5.6 shows the concentration in the bulk and on the surface at $t = 0.09$ for varying diffusion ratios. A grid spacing of $h = 1/256$ was employed, along with interface thickness $\epsilon = 0.004$. Because of the non-uniform bulk distribution, the adsorption will be higher at the bottom of the circle than at the top. As the surface diffusion coefficient increases, mass is diffused from the bottom to the top of the circle faster, which further reduces the adsorption at the top. This effectively increases the diffusion and leads to a more uniform concentration distribution in the bulk. This is illustrated in figure 5.7, which shows the bulk concentration along $x = 0.5$. The larger surface diffusion also leads to lower total interface concentration, since mass is

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Fig. 5.6: Bulk concentration and surface concentration for the mass transfer test case with non-uniform initial bulk concentration at $t = 0.08$. From top to bottom, $D = 0.1$, $D = 1.0$ and $D = 10$. 
described back into the bulk.

5.5. Bulk-surface coupling on a perturbed circle. In this test case, the surface evolution on, and the bulk evolution inside, a perturbed circle is considered. The circle is given by

\[ r(\theta) = 1 + 0.1 \cos(3\theta), \]  

and forcing functions are added to the surface and bulk equations so that the exact solution is known. More specifically,

\[ \frac{\partial}{\partial t} \nabla F - f + F + \zeta_1 \text{ on } \Gamma \]  

\[ \frac{\partial}{\partial n} \nabla F - F \zeta_2 \text{ in } \Omega_0 \]  

is solved subject to the boundary condition

\[ \nabla F \cdot \mathbf{n} = f - F \text{ on } \Gamma. \]  

The forcing functions are chosen such that the solution in \( \Omega_0 \) is

\[ F = \frac{1}{4} x^2 + y^2 e^{-3t}, \]  

and the solution on \( \Gamma \) is

\[ f = \left( \frac{1}{2} \frac{\partial F}{\partial n} + \frac{1}{2} \frac{\partial^2 F}{\partial n^2} \right) e^{-3t}. \]

Fig. 5.7: Bulk concentration along \( x = 0.5 \) for three different diffusion coefficient ratios at \( t = 0.08 \). A larger surface diffusion coefficient increases the transport of bulk concentration and gives a more uniform profile.

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dsolved back into the bulk.
The diffuse-interface representation of the above system is
\[ \frac{\partial}{\partial t} (\nabla \cdot \mathbf{B}(c)) = \nabla \cdot (\mathbf{B} \nabla F) - \mathbf{B} \frac{\partial \zeta}{\partial c}, \]
where the Heaviside function is now given by
\[ H(c) = 1 - e^{-\frac{c}{\epsilon}}, \]
instead of equation (2.17) since the bulk concentration is required in \( \Omega_b \) (not in \( \Omega_c \)).

The simulation was run to time \( t = 2.0 \times 10^{-3} \), and the interface thickness was scaled as \( \epsilon = 1.28 \delta_h \). Figures 5.8a and 5.8b show the final solution for the surface concentration and the bulk concentration for a grid spacing of \( \delta_h = 1/128 \). The analytical solutions given by equations (5.17) and (5.18) are compared to the numerical results in figure 5.9. Excellent agreement is observed. In Table 5.6, the respective errors compared to the analytical solutions are listed together with the convergence order. Again, first order convergence results are obtained.

5.6. Bulk-surface coupling in a 2D vortical flow A circle with radius \( r = 0.15 \) is placed at \( x = 0.5, y = 0.75 \) in a domain \( \Omega = [0,1] \times [0,1] \). The circle is advected by a prescribed velocity field defined by the stream function
\[ \Psi = -\cos(x) \frac{1}{2} \sin(x) \sin(y), \]
which gives the individual velocity components as
\[ u = -2\cos(x) \sin(x) \cos(y), \]
\[ v = 2\cos(x) \sin(x) \sin(y), \]
\[ \omega = \frac{1}{2} \sin(2x) \sin(y). \]

Fig. 5.8: The solutions at \( t = 2.0 \times 10^{-3} \) for the bulk-surface coupling on a perturbed circle.

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Fig. 5.8: The solutions at \( t = 2.0 \times 10^{-3} \) for the bulk-surface coupling on a perturbed circle.
The initial condition is illustrated in figure 5.10. This is a demanding test case for both the interface advection and the adaptive grid, because the interface undergoes large deformations. Because of the periodicity of the flow field, it is common to compare the initial solution to the solution after one period. However, with diffusion and adsorption/desorption, the solution is not time-reversible. Here, a comparison with the results from [90] is first considered as a validation case, before simulations with bulk/interface coupling are presented.

For the validation case, the diffusion is set to $D = 10^{-5}$ for the surface concentration, and the evolution of the bulk concentration is not considered. Hence, there is no coupling between the bulk and surface for this test case. The initial surface concentration is $c_i = 1$. An effective grid spacing of $h_{min} = 1/512$ was used along with an interface thickness $\epsilon = 0.002$. Figure 5.11(a) shows the evolution of the interface and the adaptive grid. The grid clearly tracks the interface in an efficient manner, and the

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### Table 5.6: The error in the infinity norm and convergence order for the bulk concentration and the interface concentration in the perturbed circle test case. The interface thickness is $\epsilon = 1/28$.

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<tbody>
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<td>Error (x 10^-4)</td>
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<tr>
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morphology at $t=0.5$ matches that of figure 11(b) in [90]. The surface concentration
along the interface is shown in figure 5.11(b). Due to the complex flow field, mass
is swept to the lower and upper part of the stretching circle. The concentration
is particularly high at the upper part. This profile is in good agreement with
the equivalent figure 11(c) in [90].

Next, the effect of varying the surface diffusion coefficient relative to the bulk
diffusion coefficient, $D_{d_{s}}/D_{d_{b}}$, is investigated. The initial surface concentration
is $f_{0}=10^{-4}$ and the initial bulk concentration is given by the non-uniform profile
$F_{0}=10^{-4}$ $A_{x}$. Additionally, the bulk and interface is coupled, with adsorption coefficient
$\alpha_{s}=100$ and desorption coefficient $\gamma_{s}=200$. The bulk diffusion coefficient is $D_{d_{b}}=0.1$,
while the surface diffusion coefficient is varied. An effective grid spacing of $h_{\text{max}}=1/256$
was employed, along with interface thickness $\epsilon=0.004$. The concentration at $t=0.5$ for the bulk and the interface for three different
diffusion coefficient ratios is shown in figure 5.12. When the surface diffusion coefficient
is low, the main transport mechanism is the convection. Some mass is adsorbed onto
the interface, but the low diffusion coefficient leads to a highly non-uniform profile. As
the surface diffusion coefficient increases, more mass is adsorbed from the upper part
of the domain, where the bulk concentration is high, then diffused along the interface
and finally desorbed in the lower part of the domain. This leads to a more uniform
bulk distribution around the advected circle.

Finally, the effect of the efficiency of the multigrid algorithm and the adaptive grid
was performed on this test case. This was done by comparing the time taken to complete
1000 time steps on several grid sizes on both uniform and adaptive grids. The time
step size was kept constant, and low enough so that the number of V-cycles on each
time step was equivalent for all grid sizes. The results are shown in figure 5.13. Both
the uniform and adaptive run-times increase in a linear fashion, which indicates that
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bulk distribution around the advected circle.
Fig. 5.11: Evolution of a circle in a vortex field, depicted at $t=0, 0.25, 0.5$. The parent grid level has spacing $h = 1/32$, and there are 4 levels of refinement, giving an effective grid spacing of $h_{\text{min}} = 1/512$. 

(a) Adaptive grid and interface morphology.
(b) Surface concentration along the interface.
Fig. 5.12: Bulk concentration and interface concentration at $t = 0.5$ for the vortex test case with non-uniform initial bulk concentration and bulk/interface coupling. From top to bottom, $D = 0.1$, $D = 1.0$, and $D = 10$. 

(a) Bulk concentration  
(b) Surface concentration
uniform simulations, which is a demonstration of the efficiency of block-structured, adaptive grids for these types of simulations.

5.7. Bulk-surface coupling in a 3D deformation field

Finally, a threedimensional test problem is considered. The flow field is the one proposed by [30], which combines a deformation in the $x-y$ plane with one in the $x-z$ plane. The velocity components are

$$
\begin{align*}
  u &= -2\cos \left( \frac{\pi}{h} \right) \sin^3(x) \sin(2y) \sin(2z), \\
  v &= \cos \left( \frac{\pi}{h} \right) \sin(2x) \sin(2y) \sin(2z), \\
  w &= \cos \left( \frac{\pi}{h} \right) \sin(2x) \sin(2y) \sin^3(z),
\end{align*}
$$

and a sphere of radius 0.15 is placed at $(0.35, 0.35, 0.35)$ in a unit cube computational domain. The initial surface concentration is $K_{\text{E}} = 10^{-4}$ and the initial bulk concentration is given by the non-uniform profile $\rho_{\text{bulk}} = 10^{-4}$. Additionally, the bulk and interface is coupled, with adsorption coefficient $\epsilon_a = 100$ and desorption coefficient $\epsilon_d = 200$. The bulk and surface diffusion coefficients are matched with $D_b = D_s = 1$. A grid with spacing $\Delta = 0.12$ at the root level and three levels of refinement is used ($h_{\text{min}} = 1/256$), along with the interface thickness $\epsilon = 0.004$. Figure 5.14(a) shows the evolution of the sphere. The morphology agrees well with figure 29 from [18], where the same problem was solved with the level set method, only without any surface quantities. As the interface stretches, the surface concentration becomes lower. The concentration is higher at the front of the deforming sphere, because of adsorption from the bulk. The bulk concentration increases in the $y$-direction, and the front of the deforming sphere moves through this part, thereby increasing the local concentration on the front. This can be seen from the slice of the bulk concentration, figure 5.14(b), at time 1.0, where the concentration is lower near the local concentration on the front. This can be seen from the slice of the bulk concentration, figure 5.14(b), at time 1.0, where the concentration is lower near the slice of the bulk concentration.
region that the interface has moved through. The middle of the stretched sphere has a much lower concentration, due to the fact that it has experienced a large deformation and is in a region of low bulk concentration.

Figure 5.15 shows a sequence of the block-structured grids used in the simulation. The boxes denote grid level boundaries, so that inside each box the resolution is doubled. This demonstrates that the adaptive grid algorithm also works well for three-dimensional problems.

6. Conclusion
A diffuse-interface method for solving problems involving transport, diffusion, and adsorption/desorption of a material quantity on a deformable interface was presented. The method was shown to perform well on a wide range of test cases. The efficiency of the numerical implementation, using adaptive grids and a multigrid method, was also demonstrated.

The asymptotic analysis suggests, and numerical evidence confirms, that the convergence to the sharp interface system is first order in the interface thickness parameter $\epsilon$. It may be possible to gain second order accuracy in $\epsilon$ by explicitly removing the corresponding term in the asymptotic expansion as can be done in the context of solidification to enable simulations with arbitrary kinetic coefficients [43, 44]. This should be explored.

A natural extension of the method is to couple it to an external flow solver. The ability of the diffuse-interface method to handle complex fluids and interfacial dynamics makes this a very attractive combination. We have currently developed such an algorithm to simulate the dynamics of interfacial flows with soluble surfactants.

Another interesting extension is to couple the method with models of cellular mechanics to simulate cell-polarization and motility.

Finally, this work used a phase-field function to represent the interface. Alternatively, a level-set function could be used instead. Accurate representations of delta functions and Heaviside functions in the levelset context can be found in for example [80, 83, 68].

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Acknowledgment. The authors thank Steven Wise and Fang, for assistance with the numerical code and visualization, and the reviewers, whose comments have improved the paper. KET is funded by the project “Electrocoalescence – Criteria for an efficient process in real oil systems”, coordinated by SINTEF Energy Research. The project is supported by The Research Council of Norway, under the contract no: 160466/S50, and by the following industrial partners: Aibel AS, Aker Solutions AS, BP Exploration Operating Company Ltd, Saudi Aramco, Shell Technology Norway AS, StatoilHydro ASA and Petrolebra. KET also acknowledges support from the Research Council of Norway through IN-BILAT 192532 and from the Fullbright Foundation. The project is supported by The Research Council of Norway, under the contract no: 160466/S50, and by the following industrial partners: Aibel AS, Aker Solutions AS, BP Exploration Operating Company Ltd, Saudi Aramco, Shell Technology Norway AS, StatoilHydro ASA and Petrolebra. KET also acknowledges support from the Research Council of Norway through IN-BILAT 192532 and from the Fullbright Foundation.
Fig. 5.14: Sphere in 3D deformation field. The left column shows the interface and the surface concentration at times 0, 0.5 and 1.0. The right column shows slices of the bulk concentration at the same times and y-positions 0.35, 0.5 and 0.6, respectively.
COUPLED INTERFACIAL AND BULK MASS TRANSPORT

Fig. 5.15: Sphere in 3D deformation field. Illustration of the adaptive grids at times (from top to bottom) 0, 0.5 and 1.0. Two different angles are shown for each time step. Inside the black boxes, the grid spacing is $h=1/64$; inside the red boxes $h=1/128$ and inside the green boxes $h=1/256$.

REFERENCES


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A diffuse-interface method for two-phase flows with soluble surfactants

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\textsuperscript{b}Department of Mathematics, University of California, Irvine, Irvine CA-92697, USA
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Abstract
A method is presented to solve two-phase problems involving soluble surfactants. The incompressible Navier–Stokes equations are solved along with equations for the bulk and interfacial surfactant concentrations. A non-linear equation of state is used to relate the surface tension to the interfacial surfactant concentration. The method is based on the use of a diffuse interface, which allows a simple implementation using standard finite difference or finite element techniques. Here, finite difference methods on a block-structured adaptive grid are used, and the resulting equations are solved using a non-linear multigrid method. Results are presented for a drop in shear flow in both 2D and 3D, and the effect of solubility is discussed.

Key words: Multiphase flows, interfacial dynamics, surfactant, soluble surfactant, surface phase, bulk phase, adsorption, desorption, complex geometry, diffuse interface, phase field, multigrid, adaptive grid, finite difference

1. Introduction
The presence of surface active agents (surfactants) at fluid interfaces can have a considerable effect on flow dynamics. Surfactants are amphiphilic organic compounds, which can be adsorbed at liquid-liquid or liquid-solid interfaces. The presence of surfactant typically alters the interface dynamics by a reduction in the surface tension of the

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A diffuse-interface method for two-phase flows with soluble surfactants

Abstract
A method is presented to solve two-phase problems involving soluble surfactants. The incompressible Navier–Stokes equations are solved along with equations for the bulk and interfacial surfactant concentrations. A non-linear equation of state is used to relate the surface tension to the interfacial surfactant concentration. The method is based on the use of a diffuse interface, which allows a simple implementation using standard finite difference or finite element techniques. Here, finite difference methods on a block-structured adaptive grid are used, and the resulting equations are solved using a non-linear multigrid method. Results are presented for a drop in shear flow in both 2D and 3D, and the effect of solubility is discussed.

Key words: Multiphase flows, interfacial dynamics, surfactant, soluble surfactant, surface phase, bulk phase, adsorption, desorption, complex geometry, diffuse interface, phase field, multigrid, adaptive grid, finite difference

1. Introduction
The presence of surface active agents (surfactants) at fluid interfaces can have a considerable effect on flow dynamics. Surfactants are amphiphilic organic compounds, which can be adsorbed at liquid-liquid or liquid-solid interfaces. The presence of surfactant typically alters the interface dynamics by a reduction in the surface tension of the

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interface. An inhomogeneous distribution of surfactants produces gradients in surface tension, which again gives rise to tangential forces along the interface. Through this so-called Marangoni effect, surfactants can play an important role in several physical phenomena such as vortex pair interaction (e.g., [1]), fingering (e.g., [2]), drop break-up and coalescence (e.g., [3, 4, 5]) and tip-streaming (e.g., [6, 4]).

From a numerical point of view, solving the problem of soluble surfactants is highly challenging. A coupled bulk/surface system of equations must be solved on a moving, complex, deforming domain, which may stretch, break-up or coalesce with other interfaces. Absorption of mass to, and desorption of mass from, the interfaces poses another challenge. Further, the surface concentration may only be soluble in either the exterior or interior of the domain (e.g., amphiphilic surfactants). The available numerical methods for solving these problems can roughly be divided into two categories: interface tracking and interface capturing methods. Interface tracking methods use either a separate grid for the interface, or a set of interconnected points to mark the interface. For example, boundary integral methods use a surface mesh to track the interface. In the context of surfactants, a boundary integral method for studying the effect of insoluble surfactants on drop deformation was developed in [7]. This method was extended to arbitrary viscosity ratios in [8], to 3D in [9] and to soluble surfactants in [10]. See the review [11]. Another tracking method is the front-tracking method (see the review [12]), where a fixed grid is used to compute the flow, while a set of connected marker particles is used to track the interface and any interfacial quantities. A front-tracking method for insoluble surfactants was developed in [13], and this method was extended to handle soluble surfactants in [14] and [15]. A related front tracking method is the immersed boundary method (see the review [16]), which was recently used to simulate interfacial flows with insoluble surfactants [17]. A ghost-cell immersed boundary method was introduced in [18], and was used to study the effects of a diffusion controlled surfactant on a viscous drop injected into a viscous medium [19]. A hybrid level-set/front-tracking approach was used to study the dynamics of capillary waves with insoluble surfactant [20]. Another front-tracking method which combines a finite element methodology with adaptive body-fitted meshes was used to simulate the deformation and break-up of axisymmetric liquid bridges [21] and thin filaments [22] with insoluble surfactants. Very recently, Booty & Siegel [90] developed a hybrid numerical method to simulate bubbles in Stokes flow by combining a boundary integral method with a finite element methodology for a surfactant equation (using a mapped domain) that incorporates a singular perturbation analysis to account for the rapid variation of the bulk surfactant concentration near the interface when the bulk Peclet number is large. In general, interface tracking methods can be made very accurate but can be relatively complicated to implement, especially in three dimensions and for flows involving topological changes.

In interface capturing methods, the interface is not tracked explicitly, but instead is implicitly defined through an auxiliary function (e.g. level-set, color or phase-field function). This means that the solution of the problem can be done independently of the underlying grid, which greatly simplifies the handling of topological changes. For example, a volume-of-fluid (VOF) method (see the review [23]) for insoluble surfactants was developed in [24]. A more general method which

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allows non-linear equations of state for surface tension was later developed in [25].

Very recently, a VOF method was developed for soluble surfactants in the limit of large sorption rates where there is an analytic relationship between the surface and bulk concentrations at the interface [26]. A level-set method [27] for solving the surfactant equation was presented in [28], and later coupled to an immersed-interface external flow solver in [29]. See the review [30] for fluid dynamics applications. An alternative approach for simulating fluid interfaces with insoluble or soluble surfactant was developed dating back to van der Waals (e.g., [31, 32]), using the so-called Arbitrary Lagrangian-Eulerian (ALE) method (see the review [33]) together with a coupled level-set and volume of fluid method. Very recently, surfactant dynamics was simulated using a conservative smooth particle hydrodynamics algorithm [34].

The diffuse-interface, or phase-field, method represents yet another approach for simulating solutions of equations in complex, evolving domains (see the reviews [35, 36]). In this method, which we review here, the complex interface is represented by a phase-field function, which is an approximation of the characteristic function of the drop or matrix fluid domain. The boundary is captured by a diffuse interface layer such that the phase-field function rapidly transits from one inside the domain to zero in the exterior of the domain. The boundary of the domain can thus be represented as an isosurface of the phase-field function. The bulk and surface PDEs are then extended on a larger, regular domain with additional terms that approximate the adsorption-desorption flux boundary conditions and source terms for the bulk and surface equations respectively. Standard finite-difference or finite-element methods may be used. Here, we focus on a finite difference approach.

The diffuse-interface method, which has a long history in the theory of phase transitions dating back to van der Waals (e.g., [37, 35, 36]), has been used to simulate multiphase flows in simple geometries including drop coalescence and break-up, electrowetting, and viscoelasticity (e.g., [38, 39, 40, 41, 42, 43, 44, 45]). In [46], a diffuse interface model is implemented using a lattice Boltzmann scheme to simulate the effect of surfactant adsorption on droplet dynamics, preliminary simulations were performed. The interaction of multiphase flows with complex boundaries has also been investigated using the diffuse interface method including contact line dynamics and the effect of wetting (e.g., [47, 48, 49]). More generally, the interface modeling framework has been extended to solving PDEs on stationary surfaces [30], evolving surfaces [51, 52, 53, 54] and for solving PDEs in complex stationary [55, 56, 57] and evolving domains with Drischler, Neumann and Robin boundary conditions [58]. Extending previous work [56], in [59] it was shown how to solve the coupled bulk/surface problem on general, evolving domains with the diffuse interface method.

Here, we couple the diffuse interface approach from [59] with the solution of the Navier-Stokes equations, and use the method to simulate a drop in shear flow in the presence of a soluble surfactant. The method is very simple compared to previous methods, and can handle advection, diffusion and adsorption/desorption in a straightforward manner. The use of a non-linear multigrid method and block-structured, adaptive grids also make the method computationally efficient. Results are presented for a drop in shear flow in both 2D and 3D, and the effect of surfactant solubility is discussed. As observed allows non-linear equations of state for surface tension was later developed in [25].

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by Milliken and Leal [10] in the context of drop deformation in extensional flows, solubility mitigates many of the surfactant effects by making the surface concentration more uniform. In particular, while an insoluble surfactant can immobilize a surface, solubility may remobilize the surface due to surfactant exchange with the bulk.

The paper is organized as follows. In Section 2, the mathematical formulation of the problem is stated. The governing equations for the interfacial surfactant and the bulk surfactant are introduced, and the interface representation is presented. Section 3 then details the numerical implementation of the mathematical formulation and Section 4 presents some validation test cases of the method. In Section 5, a drop in shear flow is studied in detail and the effect of solubility discussed. Finally, Section 6 provides conclusions and discusses future work.

2. Mathematical formulation

2.1. Governing equations

Consider a domain \( \Omega \subset \mathbb{R}^{3} \), which contains a closed interface, \( \Gamma \). The interior of the interface is \( \Omega_{1} \subset \Omega \), and the exterior is \( \Omega_{0} \subset \Omega \). See Figure 1 for an illustration.

We assume that the flow inside the domain \( \Omega \) is governed by the incompressible Navier–Stokes equations, which in dimensional form are

\[
\rho \left( \frac{\partial \mathbf{u}^\ast}{\partial t} + \mathbf{u}^\ast \cdot \nabla \mathbf{u}^\ast \right) = -\nabla p^\ast + \nabla \left( \mu^\ast \left( \nabla \mathbf{u}^\ast + (\nabla \mathbf{u}^\ast)^T \right) \right) + \mathbf{F}^\ast,
\]

where \( \rho \) is the density, \( \mathbf{u}^\ast \) is the velocity, \( p^\ast \) is the pressure, \( \mu^\ast \) is the dynamic viscosity, and \( \mathbf{F}^\ast \) is the interfacial force, given below in Eq. (5). The density and viscosity can be

\[
\rho = \rho_{0} \quad \mu = \mu_{0} \Omega_{0}
\]

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\rho = \rho_{\ast} \quad \mu = \mu_{\ast} \Omega_{1}
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Figure 1: Illustration of the mathematical domain.

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We will only consider cases where the densities and viscosities are equal in the two phases in this work, but the discontinuity can in general be handled by interpolating their values using an indicator or characteristic function $\chi$ that varies from 0 to 1 across the interface (characterizing function of $O_3$), such that

\begin{align}
\rho' &= \rho(1 - \chi) + \rho\chi \\
\nu' &= \nu(1 - \chi) + \nu\chi.
\end{align}

(2)

In practice, $\chi$ may be smoothed so that the transition from 0 to 1 is steep but finite. An example of a smoothed characteristic function is given in Section 2.3.

We consider the deformation of an initially circular drop of radius $a$, placed in a shear flow of shear rate $\gamma$. Choosing $\delta = a$ as the length scale and $\Gamma = \gamma a^3$ as the time scale, and $\Gamma u$ as the velocity scale, the nondimensional Navier–Stokes equations can be written as

\begin{align}
\frac{\partial}{\partial t} \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u} &= -\nabla p + \frac{1}{Re} \nabla^2 \mathbf{u}, \\
\nabla \cdot \mathbf{u} &= 0,
\end{align}

(4)

where $Re = \rho \gamma a^2 / \mu$ is the Reynolds number, which measures the relative strength of the inertial and viscous forces, and $Ca = \rho \gamma a^2 / \sigma$ is the Capillary number which measures the relative strength of the viscous and surface tension forces, where $\sigma$ is the surface tension of a clean drop. The influence of these parameters on a clean interface has been extensively studied in the literature (e.g., [60, 61, 62, 63]). For example, as the capillary number is increased, the drop will become increasingly elongated. There exists a critical capillary number, above which the drop will no longer attain a steady shape, but continue to stretch until it breaks into smaller droplets. The value of the critical capillary number increases with increasing Reynolds numbers and viscosity ratios $\kappa = \mu_0 / \mu_1$.

Larger viscosity ratios serve to reduce the deformation, and for creeping flow there exists a limit where there is no critical capillary number. However, for flows with higher Reynolds numbers, break-up may still occur, due to inertial forces. In this work, we will only consider flows with moderate Reynolds numbers and viscosity ratios.

The interface force $F^i$ is given by

\begin{align}
F^i &= \nabla \cdot \left( \left( [1 - n] \mathbf{n} \right) \sigma \right).
\end{align}

(5)

Here, $\sigma$ is the interfacial tension, $I$ is the identity tensor and $n$ is the outward pointing unit normal vector. $\mathbf{n}$ is a regularized delta function, to be defined in Section 2.3. Alternatively, one may write

\begin{align}
F^i &= -\delta \mathbf{n} \cdot \nabla \left( \left( [1 - n] \mathbf{n} \right) \sigma \right),
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where $\delta$ is the total curvature and $\nabla \cdot \left( [1 - n] \mathbf{n} \right) \mathbf{u}$ is the surface gradient operator. The first term on the right-hand side is the normal surface tension force, while the second is the tangential (Marangoni) force, which appears due to non-uniform surface tension.

Next, we assume that the interface is covered by surfactants, and we let $f^i$ denote the dimensional surfactant concentration defined on $I$. The presence of a surfactant will

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decrease the surface tension of the interface. We assume that the dependence of the surface tension is governed by the Langmuir equation of state,

$$\sigma'(f') = \alpha_1 + \frac{RT_0}{
\delta_0 \ln \left(1 \left(\frac{f'}{f_0}\right)\right)},$$

(7)

where $\delta_0$ is the ideal gas constant, $T_0$ is the absolute temperature, $f_0$ is the surface tension of a clean interface and $f_0$ is the maximum interfacial surfactant concentration. Let $f_0$ denote the average of $f'$ at time $t = 0$. We define $f' = f' - f_0$ to be the dimensionless surfactant concentration, which gives the dimensionless surface tension

$$\sigma(f) = 1 + \beta \ln \left(1 \left(\frac{f}{f_0}\right)\right),$$

(8)

where $\beta = RT_0/\delta_0$ is the elasticity number and $x = f/f_0$ is the dimensionless surfactant coverage. The elasticity number is a measure of the sensitivity of the surface tension to the surfactant concentration, and thus a larger elasticity number increases the deformation. In this definition, $\beta$ is independent of $x$, see [64].

For low surfactant concentrations, Eq. (8) can be simplified to

$$\sigma(f) = 1 - \beta f,$$

(9)

which is known as the linear equation of state. These two expressions are compared in Figure 2. We see that the expressions are similar for low surfactant concentrations, but deviate significantly for higher concentrations. Also note that for large elasticity numbers and surfactant concentrations close to 1/$\beta$, the non-linear equation of state may give unphysical (negative) values of surface tension. In [15], a minimum surface tension was introduced to alleviate this problem. However, in [65], it was argued that high elasticity numbers rarely occur in real systems. We use Eq. (8) directly for all the simulations in this work and do not encounter negative surface tension.

In [66], the sharp-interface representation of the surfactant mass balance equation is

$$\frac{d f'}{d t} = -\nabla \cdot \nabla f' + f'(u' w' n) \nabla - \nabla \cdot \left(\frac{j}{f'} + D_j \nabla f'\right),$$

(10)

Since

$$\nabla \cdot \nabla f' = -\nabla \cdot \nabla f' + f'(u' w' n) \nabla - \nabla \cdot \left(\frac{j}{f'} + D_j \nabla f'\right),$$

(12)

and

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which is known as the linear equation of state. These two expressions are compared in Figure 2. We see that the expressions are similar for low surfactant concentrations, but deviate significantly for higher concentrations. Also note that for large elasticity numbers and surfactant concentrations close to 1/$\beta$, the non-linear equation of state may give unphysical (negative) values of surface tension. In [15], a minimum surface tension was introduced to alleviate this problem. However, in [65], it was argued that high elasticity numbers rarely occur in real systems. We use Eq. (8) directly for all the simulations in this work and do not encounter negative surface tension.

In [66], the sharp-interface representation of the surfactant mass balance equation is

$$\frac{d f'}{d t} = -\nabla \cdot \nabla f' + f'(u' w' n) \nabla - \nabla \cdot \left(\frac{j}{f'} + D_j \nabla f'\right),$$

(10)

Since

$$\nabla \cdot \nabla f' = -\nabla \cdot \nabla f' + f'(u' w' n) \nabla - \nabla \cdot \left(\frac{j}{f'} + D_j \nabla f'\right),$$

(12)

and

$$\nabla \cdot \left(\frac{j}{f'} + D_j \nabla f'\right) = \nabla \cdot \left(\frac{j}{f'} + D_j \nabla f'\right),$$

(15)

decrease the surface tension of the interface. We assume that the dependence of the surface tension is governed by the Langmuir equation of state,

$$\sigma'(f') = \alpha_1 + \frac{RT_0}{
\delta_0 \ln \left(1 \left(\frac{f'}{f_0}\right)\right)},$$

(7)

where $\delta_0$ is the ideal gas constant, $T_0$ is the absolute temperature, $f_0$ is the surface tension of a clean interface and $f_0$ is the maximum interfacial surfactant concentration. Let $f_0$ denote the average of $f'$ at time $t = 0$. We define $f' = f' - f_0$ to be the dimensionless surfactant concentration, which gives the dimensionless surface tension

$$\sigma(f) = 1 + \beta \ln \left(1 \left(\frac{f}{f_0}\right)\right),$$

(8)

where $\beta = RT_0/\delta_0$ is the elasticity number and $x = f/f_0$ is the dimensionless surfactant coverage. The elasticity number is a measure of the sensitivity of the surface tension to the surfactant concentration, and thus a larger elasticity number increases the deformation. In this definition, $\beta$ is independent of $x$, see [64].

For low surfactant concentrations, Eq. (8) can be simplified to

$$\sigma(f) = 1 - \beta f,$$

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which is known as the linear equation of state. These two expressions are compared in Figure 2. We see that the expressions are similar for low surfactant concentrations, but deviate significantly for higher concentrations. Also note that for large elasticity numbers and surfactant concentrations close to 1/$\beta$, the non-linear equation of state may give unphysical (negative) values of surface tension. In [15], a minimum surface tension was introduced to alleviate this problem. However, in [65], it was argued that high elasticity numbers rarely occur in real systems. We use Eq. (8) directly for all the simulations in this work and do not encounter negative surface tension.

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The equation for the surface surfactant concentration, Eq. (16), can be extended to the general domain $\Omega$ by introducing a surface delta function, $\delta_n$, such that

$$\int_\Gamma \frac{\partial \Gamma}{\partial t} d\Gamma = \int_\Omega f \delta_n d\Omega.$$  \hfill (21)

Eq. (10) is equivalent to

$$\frac{\partial \Gamma}{\partial t} = \alpha \nabla \cdot \Gamma f' (\mathbf{a} \nabla \mathbf{u} - \mathbf{n} \mathbf{u}) = D_f (\nabla^2 \Gamma f' - \mathbf{n} \cdot \mathbf{n} \nabla \Gamma f') + f''.$$  \hfill (16)

The source term, $f''$, is given by

$$f''(\mathbf{F}, \nabla) = r_s f'_s (\mathbf{F} - \mathbf{F}') - r_d f'_d.$$

In this work, we use the full nonlinear form in Eq. (17).

Now, assume that $f'$ is soluble in $\Omega$, but not in $\Omega$. The bulk concentration, $F'$, in $\Omega$, evolves according to

$$\frac{\partial F}{\partial t} = D_f \nabla^2 F - \mathbf{n} \cdot \mathbf{n} \nabla F + f''.$$  \hfill (16)

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Following [59], Eq. (16) can be rewritten in distribution form as
\[
\frac{\partial}{\partial t} (\mathbf{F} \cdot \nabla \delta u) = \mathbf{V} \cdot (\mathbf{F} \cdot \nabla \delta u) = D_f \nabla^2 (\delta \nabla \mathbf{F}) + \delta \mathbf{f}^r.
\] (22)

The formulation given by Eq. (22) is considerably simpler than the sharp-interface formulation.

Similarly, the bulk concentration equation (19) can be extended to \(\Omega\) by using the characteristic function \(\chi\)
\[
\chi = \begin{cases} 
1 & \text{in } \Omega_1; \\
0 & \text{in } \Omega_0.
\end{cases}
\] (23)

In distribution form, Eq. (19) becomes
\[
\frac{\partial}{\partial t} (\mathbf{F} \cdot \nabla \mathbf{f}) + \mathbf{V} \cdot (\mathbf{F} \cdot \nabla \mathbf{f}) = D_f \nabla^2 (\mathbf{F} \cdot \nabla \mathbf{f}) + \delta \mathbf{f}^r.
\] (24)

where the boundary condition has been included using the approach from [58, 59].

Let \(F = \mathbf{F} / \delta\) be the dimensionless surfactant concentration in the bulk fluid, where \(F_r\) average of the initial bulk concentration. Then, Eqs. (22) and (24) can be written in dimensionless form as
\[
\frac{\partial}{\partial t} \mathbf{F} + \mathbf{V} \cdot (\mathbf{F} \cdot \nabla \mathbf{f}) = D_f \nabla^2 (\mathbf{F} \cdot \nabla \mathbf{f}) + \mathbf{f}^r.
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where \(\mathbf{F} = \mathbf{F} / \delta\) is the surface Peclet number, \(\mathbf{F} = \mathbf{F} / \delta\) is the bulk Peclet number and \(\mathbf{F} = \mathbf{F} / \delta\) is the adsorption depth. The dimensionless source term, \(\mathbf{f}\), is given by
\[
\mathbf{f} = \frac{1}{\delta} \mathbf{f}^r.
\] (26)

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The dimensionless parameters are \(\mathbf{F} = \mathbf{F} / \delta\) (Biot number and \(\mathbf{F} = \mathbf{F} / \delta\) (adsorption number). In our simulations, we assume that \(\mathbf{F} = \mathbf{F} / \delta\) are in equilibrium such that \(\mathbf{f} = \mathbf{f}^r = 0\). Consequently, the following relations hold:
\[
k = \frac{1}{\mathbf{F}^r},
\]
\[
h = \frac{\mathbf{F}^r}{\mathbf{F}^r} (1 - x).
\] (28)

An insoluble surfactant may be characterized by \(\mathbf{F} = 0\). The Biot number is the ratio of the desorption rate to the interfacial surfactant convection due to shear. For large Biot numbers, there is strong coupling between the surface and the bulk.
2.2. Interface representation

To represent the interface implicitly, we may either use a level-set function or a phase-field function. For example, taking \( \Gamma(x) \) to be a signed distance function from \( \mathbf{x} \), the interface \( \Gamma \) is the \( r = 0 \) isosurface. Alternatively, using a phase field function \( c \), which is \( 1 \) in \( \Omega_1 \) and \( 0 \) in \( \Omega_2 \), we may define \( G(\mathbf{x}) = (c \in \Omega_1 \ | x) - \frac{1}{2} \). We follow the latter here and evolve the phase field function using an advective Cahn-Hilliard equation

\[
\frac{dc}{dt} + \nabla \cdot (c \mu c \nabla g) = 0 \tag{30}
\]

where \( M = \sqrt{1 + \nabla^2} \) is a mobility function, and \( g = e^{-|c-\frac{1}{2}|^2} \) is a double well potential. The function \( \mu \) is called the chemical potential and \( t \) is a small parameter related to the interface thickness. Note that the above equation system is fourth-order and non-linear, which requires specialized numerical methods to solve in an efficient manner. Note that for small \( t \), the following relation holds near \( \Gamma \):

\[
c(\mathbf{x}, t) \approx \frac{1}{2} \left[ 1 - \tanh \left( \frac{\| \nabla c \|}{\sqrt{2}} \right) \right] \tag{32}
\]

2.3. Regularized delta and characteristic functions

To be able to evaluate Eqs. (3), (25) and (26) numerically, regularizations of the surface delta function and characteristic function are needed. In the phase-field context, several definitions of the delta function are available from the literature. In this work, the approximation from [50],

\[
\delta_k(\nabla c) \approx \frac{\nabla^2 e^{-|\nabla c|^2}}{\epsilon} \tag{33}
\]

is used for the surface equation. For the surface tension term and the boundary condition in the bulk equation, the approximation

\[
\delta_k \approx \nabla |\mathbf{c}| \tag{34}
\]

is used. This is to avoid any scaling of the equations. Note that in the surface equation (25), the constants in Eq. (33) cancel out in the discretized equations. The regularized characteristic function, is simply taken as \([58]\)

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\chi \approx 1 - c \tag{35}
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In [59], it was shown that the regularized equations for the interfacial surfactant and the bulk surfactant converge to the sharp interface equations in the sharp interface limit.

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3. Numerical methods

This section briefly describes the numerical methods used to solve the above equations. The algorithm follows that developed in [67]. In particular, the equations are discretized using finite differences in space and a semi-implicit time discretization. A block-structured, adaptive grid is used to increase the resolution around the interface in an efficient manner. The non-linear equations at the implicit time level are solved using a non-linear Adaptive Full Approximation Scheme (AFAS) multigrid algorithm.

Special care has to be taken for the temporal discretization. The Cahn-Hilliard system is fourth order in space, and requires the use of an implicit method to avoid severe limitations in the time step. Here, we employ a combination of explicit Adams-Bashforth schemes for the convective terms and implicit Crank-Nicholson schemes for other terms.

First, the Cahn-Hilliard system is solved to find the phase-field function at the new time step. This is solved using

$$\frac{\partial c}{\partial t} = -\nabla \cdot \left( \frac{\nabla c}{\rho} \right) + \nabla \cdot \left( \nabla \phi \right)$$

The velocities and concentration at the half-step are found by extrapolation, \(u^{h+1/2}_{i,j} = \frac{u^{h+1}_{i,j} + u^{h}_{i,j}}{2} \) and \(c^{h+1/2}_{i,j} = \frac{c^{h+1}_{i,j} + c^{h}_{i,j}}{2} \). The velocities at the cell-edges are needed to construct the convective term. These are found by

$$
\begin{align*}
\upsilon_{x,i-1/2,j} & = \frac{-u^{h+1}_{i,j} + u^{h}_{i,j} + \frac{1}{2} \left( \nabla c^{h+1}_{i,j} - \nabla c^{h}_{i,j} \right)}{2 \\
\upsilon_{y,i,j-1/2} & = \frac{-u^{h+1}_{i,j} + u^{h}_{i,j} + \frac{1}{2} \left( \nabla c^{h+1}_{i,j} - \nabla c^{h}_{i,j} \right)}{2} \\
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where \(\Psi\) is the MAC projection found by solving

$$\nabla \cdot \upsilon = \nabla \cdot u^{h+1/2},$$

with \(\Psi \neq 0\) on \(\Omega\) (assumed to be along Cartesian directions). In the AFAS nonlinear multigrid method used to solve Eqs. (36)-(37), the non-linear term in the chemical potential potential, \(g(c^{h+1})\), is linearized in the smoother (local linearization) by

$$g(c^{h+1}) \approx g(c^{h}) + \frac{\partial g(c)}{\partial c} \mid_{c^{h}} \left( c^{h+1} - c^{h} \right),$$

where \(m\) is the V-cycle iteration index. See [67] for details.

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\frac{(\vec{B}'(t)^{i+1} - \vec{B}'(t)^i)}{\Delta t} = -\nabla \cdot (\vec{\alpha}(\vec{B}') f^{i+1}) + \frac{1}{\Delta t} \left( \frac{1}{2} \left( (\vec{B}' f^{i+1}) + (\vec{B}' f^i) \right) \right) + \frac{1}{\Delta t} \left( \frac{1}{2} \left( (\vec{B}' f^{i+1}) + (\vec{B}' f^i) \right) \right)
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\[\frac{(\vec{y}'(t)^{i+1} - \vec{y}'(t)^i)}{\Delta t} = -\nabla \cdot (\vec{\alpha}(\vec{y}') f^{i+1}) + \frac{1}{\Delta t} \left( \frac{1}{2} \left( (\vec{y}' f^{i+1}) + (\vec{y}' f^i) \right) \right) - \frac{1}{\Delta t} \left( \frac{1}{2} \left( (\vec{y}' f^{i+1}) + (\vec{y}' f^i) \right) \right)
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c as a coupled system, where we use \( \gamma = 1 - e \). The source terms at the new time step lagged in the V-cycle of the multigrid algorithm \([59]\), i.e. \( B^{i+1} = B^{i+1} \) where \( m \) is the V-cycle iteration index. This did not degrade the multigrid performance, the residual is typically reduced by an order of magnitude for each iteration.

The Navier–Stokes equations are solved using a second-order projection method. The details can be found in \([70, 71, 44]\).

### 3.3. Mesh adaptivity

We use block-structured, adaptive mesh refinement to increase the resolution around the interface in an efficient manner. Near the interface, patches of overlapping, uniform, Cartesian grids are applied.

At every time step, we check grid cells for refinement using a simple unidirectional gradient test. Since it is essential for our problem to have a fine resolution in the diffuse interface region, this test marks grid cells where the finite difference of the phase-field function is large. In particular, we mark a cell for refinement if

\[
\sqrt{(u_{i+1,j} - u_{i,j})^2 + (u_{i+1,j} - u_{i,j})^2} > C_1,
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(43)

c as a coupled system, where we use \( \gamma = 1 - e \). The source terms at the new time step lagged in the V-cycle of the multigrid algorithm \([59]\), i.e. \( B^{i+1} = B^{i+1} \) where \( m \) is the V-cycle iteration index. This did not degrade the multigrid performance, the residual is typically reduced by an order of magnitude for each iteration.

The Navier–Stokes equations are solved using a second-order projection method. The details can be found in \([70, 71, 44]\).

#### 3.3.1. Mesh adaptivity

We use block-structured, adaptive mesh refinement to increase the resolution around the interface in an efficient manner. Near the interface, patches of overlapping, uniform, Cartesian grids are applied.

At every time step, we check grid cells for refinement using a simple unidirectional gradient test. Since it is essential for our problem to have a fine resolution in the diffuse interface region, this test marks grid cells where the finite difference of the phase-field function is large. In particular, we mark a cell for refinement if

\[
\sqrt{(u_{i+1,j} - u_{i,j})^2 + (u_{i+1,j} - u_{i,j})^2} > C_1,
\]

(44)
4. Code validation

In this section, three test cases are presented to validate the proposed numerical method. Because the bulk/surface coupling was thoroughly tested in [59], we will here focus on validating the flow solver and the coupling between the flow solver and the surfactant concentration.

In the numerical implementation, surface quantities are defined at grid points near the interface. To find values on the interface, we use a marching squares algorithm (see e.g. [73]) to generate a set of points on the 0.5 isocontour of the phase-field function. Bilinear interpolation is then used to interpolate the grid values of the surface concentration to these interface points.

4.1. Oscillations of a capillary wave

First a two-phase system without surfactants is considered to test the Navier–Stokes solver and the adaptive grid algorithm. The test problem is the damping of a sinusoidal, capillary wave. For the case of small amplitudes and matched viscosities, an analytical solution for the amplitude was found in [74].

The frequency of a wave with wavenumber \( k = 2\pi/\lambda \), where \( \lambda \) is the wave length, is given by

\[
\omega_0 = \frac{a k^3}{\rho \lambda + p_1}.
\]  

(45)

Assuming the amplitude is small, the analytical solution for the amplitude \( \alpha(t) \) is given in dimensional form by

\[
\alpha(t) = \frac{4(1 - 4b \lambda^2) \exp(\text{erfc}(\sqrt{b} \lambda t))}{8(1 - 4b \lambda^2) \exp(\text{erfc}(\sqrt{b} \lambda t)) + \omega_0^2}
\]

\[\sum_{i=1}^{4} \left( \frac{\mu_{ij} a_i - \mu_j}{\sqrt{4 - \mu_{ij}^2}} - a_i \right) \exp(\text{erfc}(\sqrt{b} \lambda t)) \text{erfc}(\sqrt{b} \lambda t)
\]  

(46)

where the \( \zeta_i \)’s are the four roots of the algebraic equation

\[
\zeta^4 - 4b(\lambda^2 - 1/2)^2 + 2(1 - 6b)\lambda^2 \zeta^4 + 4(1 - 12b)\lambda^2 \zeta^2 + (1 - 4b)\lambda^2 + \omega_0^2 = 0
\]

(47)

and \( Z_i = (z_i - z)(z_i + z)(z_i - z^2) \) with \( z_1, z_2, z_3, z_4 \) obtained by circular permutation of the indices. Further, \( \delta \) is given by

\[
h = \frac{\rho \delta b (\mu \rho + p_1)^3}{(\rho b \rho + p_1)^3}.
\]  

(48)

Here, we will consider a computational domain given by a unit square box, with an interface given by

\[
y = 0.5 - 0.01 \cos(2\pi x),
\]

(49)

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Here, we will consider a computational domain given by a unit square box, with an interface given by

\[
y = 0.5 - 0.01 \cos(2\pi x),
\]

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We choose dimensional variables $p_0 = p_i = 18.3$, $\mu_0 = \mu_i = 0.078$ and $\sigma = 1.0$, giving $nL_0 = 6.778$. Periodic boundary conditions are used in the horizontal direction, no-slip boundary conditions are imposed on the upper and lower boundaries, and an interface thickness parameter of $\varepsilon = 5 \times 10^{-3}$ is used along with a time step of $\Delta t = 5 \times 10^{-3}$. The initial condition is shown in Figure 3 (left). An adaptive grid with 16 × 16 grid points at the root level and three levels of mesh refinement are used ($h_{\text{min}} = 6.25 \times 10^{-2}$ and $h_{\text{max}} = 7.8125 \times 10^{-3}$). There are 8 × 10 grid points across the interface layer. Figure 3 (right) shows the evolution of the amplitude compared to the analytical solution. The numerical method is clearly capable of accurately simulating the oscillatory behavior.

4.2. Rising drop in a linear surfactant gradient

In [75], an approximation for the rise velocity of a viscous drop in a linear temperature gradient was found. This approximation is used here to test the implementation of the Marangoni stresses. Instead of a temperature gradient, the interfacial surfactant gradient was found. This approximation is used here to test the implementation of the Marangoni stresses. Instead of a temperature gradient, the interfacial surfactant concentration is assumed to vary linearly in the vertical direction.

In dimensional variables, consider an axisymmetric drop of radius $R$ in a channel of radius $5R$ and height $L = 15R$. Let the interfacial surface concentration be given by

$$f(\bar{r}) = \frac{\bar{z}}{\bar{L}},$$

and the relationship between surfactant and surface tension as

$$\sigma(z) = \sigma_i \left(1 - \frac{\sqrt{f(\bar{r})}}{\bar{r}}\right),$$

(51)

Figure 3: Capillary wave test case. An adaptive grid with root level $16 \times 16$ and three levels of refinement are used: $\varepsilon = 5 \times 10^{-3}$. Left: Computational domain with initial interface position and adaptive grid; Right: Amplitude of capillary wave, simulation versus linear theory.

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We choose dimensional parameters $\rho_0 = \rho = 0.2$, $m_0 = \mu = 0.1$, $R = 0.5$, $\sigma = 1.0$ and $\beta = 1.0$. According to Eq. (52), this should give a Reynolds number of $Re = 0.0889$, which is well within the creeping flow regime for which the equation is valid.

Because of the relatively large domain needed to keep the boundary conditions from interfering with the solution, this test case lends itself very well to an adaptive grid. Here, a root level grid spacing of $h_{max} = 5.64 / 7.8125 \times 10^{-3}$ is chosen with three levels of refinement $h_{max} = 5.712 \times 9.76 \times 10^{-3}$. The number of nodes is approximately 9000 throughout the simulation, compared to the 196608 nodes needed for a uniform grid.

An interface thickness parameter of $\epsilon = 6.0 \times 10^{-3}$ is used (6-10 grid points across the interface), and the time step is $\Delta t = 5.0 \times 10^{-3}$. The rise velocity is calculated by

$$V = \frac{\int \left( \nabla \cdot (\rho \mathbf{u} \, \mathbf{e}_z) \right) \, \mathbf{e}_z \, dV}{\int \rho \, dV},$$

where $\mathbf{e}_z$ is the unit vector in the z-direction. This integral was evaluated using the midpoint rule.

The velocity field around the drop at steady state is shown in Figure 4 (left). The figure is in good agreement with the corresponding Figure 10a in [15]. Figure 4 (right) shows the normalized rise velocity. After an initial acceleration phase, the velocity approaches the theoretical prediction asymptotically.

**Figure 4:** Velocity field at steady state shown every fourth grid point (left) and rise velocity versus time (right), compared to the theoretical result, for the linear surfactant gradient test case.

then an approximation for the terminal rise velocity is [75]

$$V_{T, \infty} = \frac{2(\sigma \mu \Delta \rho / (\rho \mu))}{(1 + \rho \mu / \rho_0)}$$

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Assuming the pressure in the surrounding fluid is zero, the pressure inside the drop is given by

\[ p(z) = \frac{2 \sigma}{\kappa} \left( \frac{1}{\lambda} - 1 \right) \]  

(54)

Figure 5 shows a closeup of pressure contours inside the drop (left), and the pressure along the vertical center line compared to the analytical result (right). Good agreement is observed.

### 4.3. Drop stretching in linear flow

In [7], an expression was presented for the deformation of a surfactant-covered drop in the creeping flow limit under the assumptions \( \text{Ca} \ll 1 \), \( \text{Pe} \ll 1 \), and \( \lambda \sim O(1) \). This can be written as

\[ D \cdot \frac{L - B}{L + B} \approx 3 \text{Ca} \cdot \frac{b_1}{L + b_2} \]  

(55)

where \( L \) and \( B \) denote the drop extension along the \( z \) and \( x \) axes, respectively, and the coefficient \( b_1 \) is given by

\[ b_1 = \frac{(80 + 95\kappa) + 48\text{Pe}}{40(1 + \lambda) - \exp(-\lambda)} \]  

(56)

Here, we simulate a 3D drop in a velocity field given by \( \mathbf{u} = (-z, \gamma, 2/z) \), with varying \( \text{Ca} \). The viscosity ratio is set to \( \lambda = 1 \) and the surfactant parameters are \( \text{Pe} = 0.1 \) and \( \beta = 0.5 \). Due to symmetry, we only simulate one octant of the drop, and the domain

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**Figure 5**: Pressure after one time step for a drop rising in a linear surfactant gradient. Left: Pressure contours (color online), Right: Pressure along vertical centerline compared to analytical result, Eq. (54).

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size is $4R \times 4R \times 4R$. We use an adaptive mesh with three levels of adaptivity, where the finest level has grid spacing $h = 1/64$. The interface thickness parameter is $\varepsilon = 0.025$.

Figure 6 shows the simulated results together with small deformation theory and results from [7]. We see that there is good agreement with the theory at low Ca and then the discrepancy gets larger at higher Ca. Our results are also in good agreement with the boundary-integral simulations of [7].

5. Influence of soluble surfactant on drop deformation and break up in shear flow

In this section, we consider the deformation of an initially circular drop placed in a shear flow. We begin by presenting 2D results. The (nondimensional) computational domain chosen for the simulations is a rectangular domain of size $12 \times 4$. The nondimensional velocity, $u = y$ is imposed on the upper and lower boundaries, and periodicity is assumed in the horizontal direction. In effect, we are simulating an infinite array of drops placed 8 units (in drop radii) apart. The root level grid spacing is $h_{\text{max}} = 1/16$, and three levels of refinement are used ($h_{\text{max}} = 1/128$), unless otherwise specified. The interface thickness parameter is $\varepsilon = 1/160$, and we choose a time step of $1 \times 10^{-3}$. There are approximately 8-10 grid points across the interface layer. We use $C_{\alpha} = 0.5$, $Re = 1.0$, viscosity ratio $\lambda = 1.0$, and $Pe = 10$ for all simulations unless otherwise noted.

5.1. Insoluble surfactant

First, we compare the evolution of a clean drop with a drop covered with insoluble surfactant using $Bi = 0$. We take $\beta = 0.3$, $x = 0.5$ and the initial surfactant distribution to be uniform: $f_{x,y} = 1.0$.

5.2. Soluble surfactant

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A common problem with interface capturing methods is that they do not exactly conserve mass. In the above simulation, there is about a 0.3% loss of surfactant mass throughout the simulation. The mass is measured by evaluating $m_t = \int \rho d\Omega$ using the midpoint rule. In [29], a simple mass correction scheme was used where the surfactant is multiplied by a constant to preserve mass. This scheme could also be easily adapted to our approach. The mass loss for the phase-field concentration was only $5.6 \times 10^{-8}$% (measured by the total integral $\int \rho d\Omega$ using the midpoint rule).

Correspondingly, the drop thins, elongates and rotates. The capillary forces reach a maximum at the tips due to the high curvature. The presence of surfactant does not alter the capillary forces significantly, but does lower the forces near the tips (not shown). Due to symmetry, the Marangoni forces are zero at the drop tips. Near the tips, the Marangoni force has local maxima and minima. The maxima occur on the upper part of the drop interface near the right tip and on the lower part of the interface near the left tip. The minima occur on the lower region near the right tip and the upper region near the left tip. The velocity near the maxima is larger, which leads to increased surfactant convection and thereby larger surface tension gradients.

Figure 7 shows the morphology of a clean drop and an insoluble surfactant-covered drop at times 0, 4 and 8. As expected, the surfactant-covered drop exhibits a larger deformation and rotates faster due to the lower surface tension. Figure 8 shows the surface quantities surfactant concentration, surface tension, capillary force and Marangoni force as a function of arc length $s$ at times 0, 4 and 8. The point $s = 0$ corresponds to the point $y = 0$ on the right side of the drop and $s$ increases counterclockwise along the drop. The capillary forces are calculated as $-\nabla \sigma \cdot \mathbf{t}$, where $\mathbf{t}$ is the unit tangential vector. Surfactant is swept to the drop tips, which lowers the surface tension. This reduces the drop the resistance to stretching. Correspondingly, the drop thins, elongates and rotates. The capillary forces reach a maximum at the tips due to the high curvature. The presence of surfactant does not alter the capillary forces significantly, but does lower the forces near the tips (not shown). Due to symmetry, the Marangoni forces are zero at the drop tips. Near the tips, the Marangoni force has local maxima and minima. The maxima occur on the upper part of the drop interface near the right tip and on the lower part of the interface near the left tip. The minima occur on the lower region near the right tip and the upper region near the left tip. The velocity near the maxima is larger, which leads to increased surfactant convection and thereby larger surface tension gradients.

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5.2. Soluble surfactant

We next investigate the effect of surfactant solubility. We again take $\beta = 0.5$, $\gamma = 0.5$, and the initial surface surfactant distribution to be uniform. $f_0|_{\beta} = 1.0$. The adsorption number is $k = 1.0$ and the adsorption depth is $h = 0.5$. We take the drop to be in equilibrium with the bulk at the start of the simulation, i.e. $f|_{\beta,t=0} = 0$, which gives the initial bulk concentration $F_0|_{\beta} = 1.0$. We vary the Biot number and the bulk Peclet number.

5.2.1. Influence of Biot number

We first set the bulk Peclet number $Pe_0 = 1$, and vary the Biot number. The morphology of the drops for varying Biot numbers is shown in Figure 9. The inner (magenta) drop corresponds to $Bi = 0$ and the outer drop (black) corresponds to $Bi = \infty$, simulated by enforcing $f|_{\beta} = 1$ throughout the simulation. The drop deformation is an increasing function of $Bi$. The reason for this is that surfactant adsorption/desorption decreases the surface tension gradients and hence Marangoni forces. If the Biot number tends to infinity, the surface surfactant should be uniform and the Marangoni forces vanishes. This is further elucidated in Figure 10. The left column of Figure 10 shows the surfactant concentration, the surface tension, the capillary force and the Marangoni force at $t = 4$. We see that by increasing the Biot numbers, the surfactant concentration becomes more uniform. This leads to lower surface tension gradients and thereby lower Marangoni forces, which enables the drop to deform more. The capillary force is dominated by the curvature, and remains largely unaffected by the variation in surface tension.

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Figure 9: Comparison of drop shapes for various Biot numbers. The times shown are $t = 0.4, 8$. Magenta: $Bi = 0$ (insoluble), blue: $Bi = 0.1$, red: $Bi = 1$, green: $Bi = 10$, and black: uniform ($Bi = \infty$). The inset shows a close-up of the drop tip for $t = 8$. Color online.

Figure 10: Influence of the Biot number on a drop in shear flow at $t = 4$. Left column shows from top to bottom: surfactant concentration, surface tension, capillary force and Marangoni force. The right column shows the bulk surfactant concentration, from top to bottom: $Bi = 0.1, Bi = 1$ and $Bi = 10$. Color online.
The right column of Figure 10 shows the bulk concentration at $t = 4$. It is evident that a larger Biot number leads to a faster depletion of bulk surfactant due to the higher adsorption at the interface. At the drop tips, there is desorption of surfactant off the interface leading to increased surfactant concentration in the bulk. Also note that the change in dynamics from $\text{Bi} = 1$ to $\text{Bi} = 10$ is not as significant as the change from $\text{Bi} = 0.1$ to $\text{Bi} = 1$. This is because the bulk diffusion is not large enough to maintain a high adsorption/desorption rate. The process has become diffusion-limited.

5.2.2. Influence of Peclet number

Next, we examine the effect of the bulk Peclet number $\text{Pe}_b$. The Biot number is $\text{Bi}=1$. Figure 11 shows the morphology of the drops for varying Peclet numbers. The deformation is larger for smaller Peclet numbers since stronger diffusion in the bulk enables the redistribution of bulk surfactant to maintain a more uniform bulk distribution. This in turn supports a larger rate of surfactant adsorption along the drop sides that keeps the surface surfactant concentration more uniform and thus decreases the Marangoni force.

The left column of Figure 12 shows the surfactant concentration, the surface tension, the capillary force and the Marangoni force at $t = 4$. Again, we see that the surface surfactant concentration becomes more uniform due to the mass transfer process when the Peclet number is smaller, thereby decreasing the Marangoni forces. However, the effect is most pronounced away from the drop tips. At the drop tips, the surfactant concentration (surface tension and Capillary force) are somewhat insensitive to $\text{Pe}_b$ because convection is relatively more important here than on the sides. In particular, at the sides surfactant is adsorbed to the interface, then swept by convection towards the tips, leaving room for more adsorption along the sides. This depletes the bulk concentration near the sides but at the tips, there is increased bulk concentration above $F_{\text{sc}} = 1$ because surfactant desorbs to the bulk. A small Peclet number is needed to redistribute bulk surfactant to maintain a more uniform bulk distribution and thus a large Biot number leads to a faster depletion of bulk surfactant due to the higher adsorption at the interface. At the drop tips, there is desorption of surfactant off the interface leading to increased surfactant concentration in the bulk. Also note that the change in dynamics from $\text{Bi} = 1$ to $\text{Bi} = 10$ is not as significant as the change from $\text{Bi} = 0.1$ to $\text{Bi} = 1$. This is because the bulk diffusion is not large enough to maintain a high adsorption/desorption rate. The process has become diffusion-limited.

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Figure 12: Influence of bulk Peclet number on drop in shear flow at $t = 4$. Left column shows from top to bottom: Surfactant concentration, surface tension, capillary force and Marangoni force. The right column shows the bulk surfactant concentration, from top to bottom: $Pe_F = 0.1$, $Pe_F = 1$ and $Pe_F = 10$. Color online.
high adsorption rate along the drop sides. In fact, when the Pelet number is small, the adsorption rate is not large enough to adsorb all the available bulk surfactant. Thus the differences between the results from $\text{Pe}_{2} = 0.1$ to $\text{Pe}_{2} = 1$ are less pronounced than the differences from $\text{Pe}_{2} = 1$ to $\text{Pe}_{2} = 10$. This is because the process becomes adsorption-limited for small Pelet numbers.

This is further illustrated in Figure 14, which shows the source term $f$ for the three Pelet numbers. Away from the drop tips, $j$ is positive, which means that surfactant is transported from the bulk into the interface. At the tips, the transportation is reversed due to the accumulation of surfactant here. For a high Pelet number, the mass transfer is lower, because the bulk diffusion is not large enough to transport desorbed surfactant away from the interface or to replenish surfactant adsorbed to the interface. This effect is even more pronounced when the Pelet number is significantly increased to $\text{Pe}_{2} = 1000$ as seen in Figure 13. At this large Pelet number, a narrow boundary layer of depleted bulk surfactant is observed along the drop sides while the bulk concentration is significantly increased near the drop tips. In order to simulate this case, another level of refinement is required such that $h_{\text{max}} = 1/256$ and in addition the mesh is refined where the undiected gradient of $F$ is sufficiently large; the finest mesh covers the surfactant boundary layer. The thickness of the surfactant boundary layer along the drop sides is approximately 0.14 while at the drop tips the boundary layer thickness is approximately 0.09. For reference, the thickness, $O(e)$, of the diffuse interface describing the drop boundary is approximately 0.06.

5.2.3. Convergence study

A convergence study was carried out for the fluid velocity, the interface surfactant and the bulk surfactant for the case where $\text{Pe}_{2} = 1$ and $\text{Bi} = 1$. Since the analytical solution is not available, we use the solution for a fine mesh as a reference solution and measure the deviation from this solution in the $L_1$ norm. The $L_1$ norm is calculated as

$$ \sum | f_i - f_{i}^{\text{ref}} | $$

and the rate of convergence as

$$ \frac{\ln | f_i - f_{i}^{\text{ref}} |}{\ln 2} $$

for small Peclet numbers.

The results are summarized in Table 1. The rate of convergence is around two for the velocities and one for the surfactant concentrations. The result for the surfactant concentrations are in line with what was found in [59].

5.3. Three-dimensional results

Finally, we present some results from three-dimensional simulations. In particular, we investigate drop break up in a shear flow. The grid spacing at the root level is $h_{\text{max}} = 1/4$.

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Figure 13: Influence of large bulk Peclet number $\text{Pe}_F = 1000$ on a drop in shear flow at $t = 4$. Top: Bulk surfactant distribution, Bottom: Adaptive mesh. Four levels of refinement are used (black: level 0, blue: level 1, green: level 2, red: level 3, yellow: level 4). Color online.

Figure 14: Comparison of the source term $j$ along the interface for different Peclet numbers.

Figure 13: Influence of large bulk Peclet number $\text{Pe}_F = 1000$ on a drop in shear flow at $t = 4$. Top: Bulk surfactant distribution, Bottom: Adaptive mesh. Four levels of refinement are used (black: level 0, blue: level 1, green: level 2, red: level 3, yellow: level 4). Color online.

Figure 14: Comparison of the source term $j$ along the interface for different Peclet numbers.
three levels of refinement are used such that $\eta_{\text{ref}} = 1/32$. To elucidate the effects of the interface thickness parameter $\varepsilon$, we simulated two different cases: $\varepsilon = 1/30$ and $1/40$. There are approximately 5.6 grid points across the interface for smaller $\varepsilon$. These simulations took approximately 3 days to complete on one core of an Intel i7 processor.

We take $Ca = 0.42$ and $Re = 0.4$, which while smaller than used in 2D are still above the critical threshold for the existence of steady state solutions. This allows us to run the simulation until the drop breaks up to demonstrate the ability of our method to handle topological changes. A similar simulation was presented in [62], although their simulation used $Re = 0$. For the surfactant case, we assume a dilute concentration of $\chi = 0.1$ and a relatively strong coupling between surfactant and surface tension with $\beta = 0.2$. For the parameters associated with solubility, we again choose initial conditions at equilibrium, $k = 1/9$ and $h = 0.9$. The bulk Peclet number is set to $Pe = 10$.

The results for a clean drop and a drop covered by an insoluble surfactant are shown in Figure 15 (left and right columns respectively). After an initial regime of stretching, necks form near the two drop tips. These become thinner until the drop breaks up. In each case, two tiny satellite drops can be observed after the necks pinch off. In the surfactant case, the satellite drops are very small and are covered with nearly uniform surfactant. We see that the surfactant-covered drop breaks up at an earlier time. There are two principal reasons for this behavior. First, the non-uniform distribution of surfactant leads to larger deformation, as shown in the previous sections, which thins the drop more than the clean case. Second, in the necks, the surfactant concentration is low, which gives a larger surface tension (similar to the surface tension of a clean drop). Since the necks are thinner in the surfactant-laden drop this leads to faster breakup.

In Figure 16, the break-up of a clean drop is shown for a larger value of interface thickness $\varepsilon = 1/40$ compared to $\varepsilon = 1/30$ in Figure 15). For the larger value of $\varepsilon$, the drops break up at an earlier time and satellites are not observed. A similar behavior is shown in Figure 17 for $\varepsilon = 1/64$.

### Table 1: Error in $L_2$ norm and convergence rate for the fluid velocities and the surfactant concentrations.

<table>
<thead>
<tr>
<th>Grid ($\eta_{\text{ref}}$)</th>
<th>$L_2$ norm of fluid velocities (×10^3)</th>
<th>$L_2$ norm of surfactant (×10^3)</th>
<th>Rate</th>
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<td>8.49</td>
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<tr>
<td>1/128</td>
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<td>2.95</td>
</tr>
<tr>
<td>$[\ell - \epsilon f_{\text{ref}}]$</td>
<td>Rate $[\ell - \epsilon f_{\text{ref}}]$</td>
<td>Rate</td>
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</tr>
<tr>
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<td>5.96</td>
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<tr>
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<td>2.23</td>
<td>0.39</td>
<td>0.71</td>
</tr>
<tr>
<td>1/64</td>
<td>1.58</td>
<td>0.50</td>
<td>0.92</td>
</tr>
<tr>
<td>1/128</td>
<td>0.688</td>
<td>1.20</td>
<td>1.20</td>
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</tbody>
</table>

### Table 2: Error in $L_2$ norm and convergence rate for the fluid velocities and the surfactant concentrations.

<table>
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<tr>
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<td>1/128</td>
<td>0.688</td>
<td>1.20</td>
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Figure 15: Three-dimensional simulation of a drop in shear flow with interface thickness $\varepsilon = 1/80$. The left column shows a drop with no surfactant. The right column shows a drop with insoluble surfactant. The times shown are from top to bottom: 10, 25, 34, and 35.16.

Figure 16: Drop evolution in shear flow without surfactant at times $t = 25$ (left) and 35.16 (right) with $\varepsilon = 1/40$. All other parameters are the same as in Figure 15.
observed in the presence of surfactant.

The results for soluble surfactant are shown in Figure 17, using $e = 1/30$. The right column, which shows a slice of the bulk concentration, indicates that surfactant is adsorbed to the surface at the middle of the drop, and desorbed at the tips. This leads to a more uniformly distributed surfactant concentration. Comparing Figure 17 with Figure 15 we can see the soluble-surfactant-covered drop breaks up at a later time than the clean drop. The principle reason is the adsorption and desorption of surfactant. Since adsorption occurs over a larger surface area than desorption, which just occurs at the drop tips, the interfacial surfactant concentration becomes larger across the entire drop. This means that the deformation becomes larger and that there is significant concentration of surfactant near the drop necks. This slows the thinning of the necks since the surface tension is smaller. Thus, the drop breaks up at a later time than for the clean drop. This shows that the influence of solubility can have an important influence on drop dynamics.

6. Conclusions and future work

A diffuse-interface method to simulate two-phase flows with soluble surfactants was presented. The method handles advection, diffusion and adsorption/desorption of surfactant, and is easy to implement using standard numerical techniques. As an example of the applicability of the method, results were presented on the influence of surfactant on a drop in shear flow. It was shown that solubility could have a considerable influence on the flow dynamics. Simulations in 3D were also performed, which showed that the influence of soluble surfactants is important for the breakup behavior of the drop.

Although not presented here, asymptotic and numerical evidence suggests that the convergence to the sharp interface system is first order in the interface thickness parameter $\epsilon$ \cite{26}. It may be possible to gain second order accuracy in $\epsilon$ by explicitly removing the corresponding term in the asymptotic expansion as can be done in the context of solidification to enable simulations with arbitrary kinetic coefficients \cite{76, 77}. Also, more consistent projection methods for collocated grids were recently presented \cite{78}. These two improvements to the proposed method should be explored. In addition, as we have seen, when the bulk Peclet number is large, thin boundary layers develop near the deforming drop. Adaptive meshes can enable accurate simulations for a range of Peclet numbers but in some applications, the bulk Peclet number can reach $10^3$ (e.g., \cite{79}) at which point it is infeasible to use adaptive meshes. Instead, following the approach recently developed by Booey and Siegel \cite{80}, a singular perturbation analysis should be incorporated in the numerical algorithm.

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Figure 17: Three-dimensional simulation of a drop in shear flow with soluble surfactant, $\varepsilon = 1/80$. The left column shows the drop shape with the surface colored according to the interface surfactant concentration. The right column shows a slice of the bulk surfactant concentration along the x-axis. The times shown are from top to bottom: 10, 25, 34 and 35.16.


