DIRECT NUMERICAL SIMULATION OF MARANGONI FLOWS: DYNAMICAL REGIMES AND TRANSITIONS

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ABSTRACT

Zhang, Qian MSME, Purdue University, August 2019. Direct Numerical Simulation of Marangoni Flows: Dynamical Regimes and Transitions. Major Professor: Carlos M. Corvalan Associate Professor, Department of Food Science and Paul E. Sojka Professor, School of Mechanical Engineering.

Marangoni flows are free-surface flows driven by gradients of surface tension. Because surface tension depends on chemical composition, Marangoni flows may be generated by the uneven distribution of surface-active species at an interface. The primary goal of this thesis is to develop a rigorous computational framework for the simulation of the fluid dynamical and interfacial phenomena underlying the physics of Marangoni flows. The focus is on characterizing the different dynamical regimes generated by the presence of surface-active species (surfactants) at an interface. The computational framework was developed using direct numerical simulation, that is, by simultaneously solving the full system of partial differential equations governing the free-surface flow and the surfactant transport on a continually deforming interface. Results from the simulations enabled detailed examination of the interfacial mechanisms of surfactant transport and provided a comprehensive picture of the free-surface flow. Analysis of the results established limits of applicability of scaling solutions previously proposed in the literature, calculated the necessary corrections, and also lead to the discovery of previously unobserved scaling laws in viscous Marangoni flows. New findings from this research not only enhance the fundamental understanding of the physics of Marangoni flows, but also the ability to accurately predict the behaviour of Marangoni flows and the associated transport of surface-active species, which is critical to the understanding of important natural and biomedical processes, ranging from the surfactant-driven propulsion of insects and microorganisms to the spreading of drugs and natural surfactants (proteins) in the eye and lungs. Controlled Marangoni transport of chemical species is also relevant to a wide range of environmental and technological processes, with applications ranging from cleaning of oil spills to coating of microfluidic devices.

1. INTRODUCTION

1.1 Overview

Marangoni flows are flows driven by surface tension gradients. Since surface tension depends on chemical composition, Marangoni flows may be generated by gradients in chemical concentration at an interface (Figure 1.1).

This work discusses in detail results from a rigorous numerical model capable of accurately simulating Marangoni flows generated by gradients in concentration of surface-active species (surfactants) at an interface. By simultaneously solving the full system of governing equations, the multi-scale model enables both a detailed examination of the microscopic physical mechanisms of surfactant transport, and a comprehensive picture of the macroscopic free-surface flow. Particular attention is given to characterize how the Marangoni dynamics is influenced by the geometry of the system, the properties of the fluid, and the properties of the surfactant.

An enhanced understanding of the fundamental physics of Marangoni flows and the resulting transport of chemical species is relevant to important natural and biomedical processes, from the surfactant driven propulsion of microorganisms to the spreading of drugs in the eye and lungs. Controlled Marangoni transport of chemical species is also relevant to a wide range of environmental and technological processes, with applications ranging from cleaning of oil spills to interfacial transport in microfluidic devices. Moreover, precise understanding of the mechanisms of Marangoni transport of surfactants and chemical species at the microscale provides opportunity for tuning the interfacial surfactant coverage, and therefore the interfacial properties of films, droplets, and bubbles.



Fig. 1.1. Schematic of a surfactant drop spreading on a liquid film. A drop of insoluble surfactant on the surface of a liquid film generates an interfacial concentration profile γ . The concentration profile creates a difference in surface tension (Marangoni stress, red arrow) that pulls the surfactant forward, from the region of high surfactant concentration to the region of low concentration.

1.2 Research Objective and Thesis Outline

1.2.1 Research Objective

The overall goal of this thesis is to develop a rigorous computational framework to enhance the understanding of the fundamental flow physics of Marangoni flows, with focus on characterizing the different flow and spreading regimes of an insoluble surfactant on the surface of a liquid film (Figure 1.2).

By accurately solving the full system of governing equations, the computations determine the accuracy of limiting scaling solutions previously proposed in the literature for different Marangoni regimes, establish their limits of applicability, and calculate necessary corrections. Importantly, the rigorous computational framework develop in this thesis also leads to the discovery of previously unobserved features of Marangoni flows that suggest new avenues of research.

1.2.2 Thesis Outline

To support the research objectives, a realistic computational model is developed in Chapter 2 to characterize the effect of geometry and material properties on Marangoni flows generated by gradients of surfactant concentration. Chapter 2 describes how unnecessary simplifications on the description of the free-surface dynamics are avoided by solving the full Navier-Stokes system of governing equations that describes the flow dynamics. By solving the full Navier-Stokes system, the resulting model has no limitations to Euler or Stokes flow, and the full interaction between inertial, viscous and interfacial forces in the flow dynamics can, in principle, be explored.

In this realistic framework, the influence of interfacial forces is described using the Young-Laplace pressure jump coupling the normal interfacial stresses (capillary pressure) to the shape of the fluid interface. Critically, the interfacial stress condition is extended to account for tangential interfacial forces (Marangoni stresses) that couple the surface tension gradients at the interface with the bulk fluid flow. The coupling of



Fig. 1.2. Surfactant drop diluting and spreading on a continuously deforming liquid film. Direct numerical simulations enable accurate temporal and spatial characterization of the free-surface Marangoni problem, which involves strongly coupled fluid flow, interfacial surfactant transport (red drop), and large interfacial deformations in a liquid film (grey).

the bulk flow and the spreading of the chemical species at the interface is described by the full convection-diffusion equation governing the interfacial surfactant transport.

The free-surface model is solved using direct numerical simulation. The highfidelity direct numerical simulation scheme is based on the finite element method for discretization in space, and adaptive finite difference for discretization in time. Because of the presence of a free surface, the scheme uses an arbitrary Lagrangian-Eulerian method to trace the deforming fluid interface. The direct numerical simulation scheme is able to accurately characterize this challenging free-surface problem that involves strongly coupled and highly nonlinear equations governing fluid flow, interfacial mass transport, and large interfacial deformations.

The second part of Chapter 2 summarizes and discusses the model results for Marangoni flows in highly-viscous liquid films. The direct numerical simulations enable a detailed analysis of the microscopic physical mechanisms of surfactant transport, and a comprehensive picture of the macroscopic free-surface flow. Initially, both experiments and limiting theoretical predictions from the literature are benchmarked against the solutions of the full Navier-Stokes system. Then, scaling arguments are developed to identify different dynamical regimes and their transitions for a wide range of film thickness. Parametric studies demonstrate, apparently for the first time, that in highly-viscous films the surfactant spreads faster than expected from theoretical predictions, and the difference with the expected spreading speed increases rapidly as the film thickness increases.

Chapter 3 extends the results of Chapter 2 to arbitrary fluid viscosities. The chapter provides a thorough quantitative study of the influence of film thickness and the material properties of both fluid and surfactant on the Marangoni flow dynamics. By contrasting approximate similarity solutions proposed in the literature against the results from the numerical solution of the full governing equations, results establish their limits of applicability. During the process a number of limitations of the theoretical predictions are identified, and the necessary corrections are calculated. Moreover, computations enable the construction of master curves in function of film thickness,

fluid properties and surfactant properties to accurately determine the transitions between different Marangoni dynamical regimes.

Finally, Chapter 4 presents concluding remarks and suggestions for future work, highlighting the need of experimental work to test previously unobserved features uncovered by the simulations, and to extend the numerical study to characterize the effect of surfactant solubility on the different Marangoni regimes and their transitions.

1.3 Background

The motivation for this work is twofold: a fundamental fluid mechanics interest on free-surface flows driven by gradients of surface tension, and its practical implications for a large number of important natural and technological processes which are summarized below.

The presence of uneven surface tension at an interface often causes liquid to flow from regions of low surface tension to regions of high surface tension. This type of flows, driven by surface tension gradients, are called Marangoni flows, after the physicist Carlo Marangoni who studied this flow for his dissertation. In general, a surface tension gradient can be induced by either temperature difference [1] or uneven chemical compositions at a liquid interface. The focus of this work is on Marangoni flows generated by gradients in chemical composition. Marangoni flows, especially Marangoni flows modulated using surface-active species (surfactant) [2] [3] [4], have been extensively studied for several decades due to how common yet important the phenomenon is in nature and in medical, environmental and technological applications.

In nature, the movement of microorganisms, such as the expansion of bacterial colonies, frequently relies on Marangoni flows [5] [6]. Often, the spreading of bacterial colonies is not only result of the mobility of individual bacteria. Instead, bacteria produce surfactant molecules to locally reduce the surface tension of a biofilm and

thus generate a surface tension gradient. Consequently, a convective Marangoni flow is induced and colonies expand by convecting with the bulk flow of the biofilm.

The surfactant-induced Marangoni flow is an important phenomenon not only in nature, but also in many biomedical processes. One of the most important medical applications of Marangoni flows is in the treatment of respiratory distress syndrome (RDS), which is a common problem for premature babies [7] [8] [9] [10]. This syndrome occurs when the lungs cannot produce enough surfactant to keep the airways open, and therefore a common treatment is inhaling artificial surfactants. The inhaled surfactant attaches to the surface of the mucus layer in the lung airways, reducing the local surface tension and consequently generating a convective Marangoni flow. Understanding the Marangoni dynamics on the mucus layer is extremely important to the success of the treatment because increasing the amount of surfactant enhances its effectiveness but, at the same time, increases the risk of further blocking the airways by inducing interfacial disturbances on the mucus layer (Figure 1.2).

The surfactant-induced Marangoni flows is critical to coating technologies because surface tension plays a major role in lessening irregularities on the coating layer [11]. In general, uniform surface tension reduces surface irregularities and produces a consistent and level coating. However, capillarity can also create coating defects in the form of a thick coating layer, especially when the underlying substrate is highly curved [12]. To correct these coating defects and ensure a uniform film, surfactants are commonly used to induce Marangoni flows to reverse the net mass transfer away from the defects.

Another important application is related to ink-jet printing [13]. One of the major issues of ink-jet printing is that particles suspended in the ink often accumulate at the edge of the printed ink droplet forming a non-uniform impression on the substrate. The accumulation of the suspended particles is due to a Marangoni convective flow created by the uneven evaporation of the ink solvent. To solve this issue, solvent composition is changed to create surface tension gradients between the periphery and the interior of the droplet to counterbalances the flow that drives the accumulations of particles at the edge of the droplet [14].

Marangoni flows are also important for integrated circuit manufacture [15] [16]; where it is used as a method for drying silicon wafers. Silicon wafers are normally dried by centrifugation (spin drying); however, centrifugation can add contaminants to the substrate. Surfactant-induced Marangoni flow have been introduced as a cleaner way of drying [17]. In this method, a surfactant is applied to induce surface tension gradients on the wet surface and initiate a Marangoni convective flow. As a result of the Marangoni flow, the wetting film quickly drains into a rinse bath, resulting in a dry and uncontaminated silicon wafer.

Because of the important fundamental and practical implications of Maranogni flows, this work develops high-fidelity numberical simulations to enhance the understanding of the Marangoni flow physics, considering the full interaction between inertial, viscous and interfacial forces in the dynamics.

2. MARANGONI FLOW IN VISCOUS FILMS: IDENTIFYING REGIMES AND TRANSITIONS

In this chapter, high-fidelity simulations are used to gain new insight into the dynamics of viscous Marangoni flows induced by surfactant concentration gradients. Results from the simulations enable accurate characterization of different dynamical regimes and the transitions between these regimes, as well as uncover previously unobserved scalings for Marangoni flows in purely-viscous liquid films. In addition to the fundamental fluid mechanics interest, the new findings have implications for a range of important natural and biomedical processes in viscous films ranging from the surfactant driven propulsion of microorganisms to pulmonary drug delivery.

2.1 Introduction

Surfactant-driven Marangoni flows are flows induced by the uneven distribution of surface-active species (surfactants) at an interface [2] [3] [4]. In this chapter, direct numerical simulations are used to gain new insight into the dynamics of surfactantdriven Marangoni flows in highly-viscous liquid films.

Characterizing the different dynamics of Marangoni flows in viscous films is critical to understand, predict, and ultimately control important natural and technological processes including coating processes [11] [12], pulmonary drug delivery [7] [8] [9] [10], and surfactant-driven propulsion of microorganisms [5] [6]. Motivated by both practical applications and fundamental fluid mechanical interest, Marangoni flows in viscous liquid films have been studied theoretically and experimentally for several decades [2] [3] [4] [18].

Previous studies have identified two qualitatively different dynamical regimes for Marangoni flows in viscous films: a slower *thin-film* dynamical regime and a faster *deep-film* dynamical regime. In the thin-film regime, the dynamics of viscous Marangoni flow has been studied since the pioneering works by Levich [3] and Yih [4]; and mathematical analysis and modeling using lubrication approximations [19] [20], as well as experiments [21] [22] [23] showed that the characteristic length (radius) of a spreading drop of surfactant on a viscous film scales as $t^{1/4}$ with time.

Similarly, the dynamics of viscous Marangoni flows has been studied in the limit of deep films by Foda and Cox [24] and Hoult [25], and mathematical analysis using boundary-layer approximation [26] showed that the characteristic length of a spreading drop of surfactant scales as $t^{3/8}$ with time. Although much progress has been made in the understanding of viscous Marangoni hydrodynamics and associated surfactant transport over the last several decades, the spreading of surfactant in purely-viscous flow environments still poses unsolved questions that require predictive modeling under more realistic conditions.

Here, direct numerical simulation is used to advance the understanding of physical mechanisms behind Marangoni flows in highly-viscous liquid films. By simultaneously solving the full Navier-Stokes system and the convection-diffusion equation that governs the transport of surfactant, the rigorous numerical model enabled a detailed examination of the microscopic physical mechanisms of surfactant transport, and a comprehensive picture of the macroscopic free-surface flow induced by Marangoni stress in highly-viscous films.

Section 2.2 describes the model system under study, and presents the equations governing the fluid mechanics of Marangoni flows. Section 2.3 first validates the simulation results against experimental data and previous theoretical work for Marangoni flows in thin viscous films, and then extends the study to Marangoni flows in deep viscous films. By varying the film thickness over about three decades, the computations determine the accuracy of limiting scaling solutions previously proposed in the literature, establish their limits of applicability, and calculate necessary corrections for deep films. Moreover, results lead to the discovery of previously unobserved scaling laws describing the dynamics of Marangoni flows in deep and purely-viscous liquid films. Finally, Section 2.4 studies the early-time dynamics of Marangoni flows in viscous films. Results establish, apparently for the first time, the existence of a *waiting-time* regime — an early-time regime in which the interfacial shape becomes suddenly motionless, and remains quasi-static for some finite time before moving again, despite the presence of strong surfactant-induced stresses.

2.2 System Description and Governing Equations

2.2.1 The Fluid Mechanics of Marangoni Flows

The free-surface dynamics of surfactant-induced Marangoni flows is studied here by following the spreading of a drop of insoluble surfactant on the surface of an incompressible liquid film of density ρ and viscosity μ .

At time $\hat{t} = 0$, the undisturbed film thickness is \hat{H}_0 , and the surfactant drop has an initial radius of \hat{R}_0 . The initial surface tension in the region covered by surfactant is $\hat{\sigma}_0$, which corresponds to a uniform initial concentration of surfactant $\hat{\gamma}_0$. Since the system is considered axisymmetric, it is described using a cylindrical coordinate system (\hat{r}, \hat{z}) as shown in Figure 2.1. The dimensional velocity components in \hat{r} and \hat{z} directions are \hat{v} and \hat{u} respectively. The height of the gas-liquid interface \hat{h} is a function of both time \hat{t} and radial distance \hat{r} .

The system and results are described in dimensionless forms in the thesis. The system is cast dimensionless using capillary velocity $\hat{\sigma}_0/\mu$ as characteristic velocity scale, and initial film thickness \hat{H}_0 as characteristic length scale. Accordingly, the characteristic time scale is $\tau = \hat{H}_0 \mu / \hat{\sigma}_0$. The dimensionless concentration of surfactant γ is measured in units of initial dimensional concentration $\hat{\gamma}_0$, and the corresponding dimensionless surface tension σ is measured in units of the initial surface tension $\hat{\sigma}_0$. The relationship between the dimensional variables and dimensionless variables are given as:

$$h = \frac{\hat{h}}{\hat{H}_0}, \quad r = \frac{\hat{r}}{\hat{H}_0}, \quad \sigma = \frac{\hat{\sigma}}{\hat{\sigma}_0}, \quad \gamma = \frac{\hat{\gamma}}{\hat{\gamma}_0}, \tag{2.1}$$



Fig. 2.1. Schematic of surfactant spreading on a liquid film. A drop of surfactant (red) on the surface of a clean liquid film (blue) generates Marangoni flow and interfacial deformation. The dimensionless radius of the spreading surfactant drop is $r_s(t)$, the initial drop radius is R_0 , and the local dimensionless height of the film is h(r,t). The Newtonian liquid has constant density ρ and viscosity μ . The local dimensionless surface tension is $\sigma(r,t)$ and corresponds to a local surfactant concentration $\gamma(r,t)$.

$$t = \frac{\hat{\sigma}_0}{\hat{H}_0 \mu} \hat{t}, \quad (v, u) = \frac{\mu}{\hat{\sigma}_0} (\hat{v}, \hat{u}), \quad p = \frac{H_0}{\hat{\sigma}_0} \hat{p}$$
(2.2)

where a hat (^) specify dimensional variables. The aspect ratio between initial film thickness and initial drop radius is defined as:

$$\varepsilon = \hat{H}_0 / \hat{R}_0 \tag{2.3}$$

thus, a large aspect ratio $\varepsilon \gg 1$ describes a film that is deep in relation to the surfactant drop, whereas $\varepsilon \ll 1$ describes a comparatively thin liquid film.

The evolution of the velocity field $\mathbf{v}(v, u)$ and pressure p in the liquid films is governed by the axisymmetric dimensionless continuity equation,

$$\nabla \cdot \mathbf{v} = 0, \tag{2.4}$$

and the conservation of momentum,

$$Re(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v}) = \nabla \cdot \mathbf{T}, \qquad (2.5)$$

where \mathbf{T} is the viscous stress tensor and is given by

$$\mathbf{T} = -p\mathbf{I} + (\nabla \mathbf{v} + \nabla \mathbf{v}^T).$$
(2.6)

Since the choice of characteristic length scale and characteristic velocity scale are \hat{H}_0 and $\hat{\sigma}_0/\mu$ respectively, the Reynolds number in Equation (2.5) is

$$Re = \frac{\rho \hat{\sigma_0} \hat{H}_0}{\mu^2},\tag{2.7}$$

which measures the relative significance of the inertial and viscous forces.

At the liquid film surface, the traction boundary condition is applied [27]

$$2\mathcal{H}\sigma\mathbf{n} + \nabla_s\sigma = \mathbf{n}\cdot\mathbf{T},\tag{2.8}$$

where **n** is the unit vector normal to the interface and $2\mathcal{H}$ is the mean interface curvature $2\mathcal{H} = -\nabla_s \cdot \mathbf{n}$. The traction boundary condition includes both normal capillary stresses $2\mathcal{H}\sigma\mathbf{n}$ and tangential (Marangoni) stresses $\nabla_s\sigma$ induced by surface tension gradient due to the presence of surfactant. At the liquid film surface z = h, kinematic boundary condition is also imposed assuring that there is no mass transfer across the gas-liquid interface

$$\mathbf{n} \cdot (\mathbf{v} - \mathbf{v}_s) = 0, \tag{2.9}$$

where $\mathbf{v}_s(r,t)$ is the velocity of the free surface.

At the lower solid boundary of the liquid film, z = 0, the no-slip and no-penetration boundary conditions are applied:

$$u(r,0) = 0, \quad v(r,0) = 0.$$
 (2.10)

Since the system is considered axisymmetric, at the centerline, r = 0, the symmetric boundary condition is applied:

$$v(0,z) = 0, \quad \frac{dv}{dr}(0,z) = 0.$$
 (2.11)

The simulations start with undisturbed liquid film with spatially uniform thickness and liquid is considered at rest. Thus, at t = 0, the initial conditions are:

$$u(r, z) = 0, \quad v(r, z) = 0, \quad h(r) = 1.$$
 (2.12)

2.2.2 Surfactant Transport and Marangoni Stress

The transport of surfactant on the surface of liquid films is described by the full convection-diffusion equation [28] [29] [30], and is solved simultaneously with the full Navier-Stokes system of equations,

$$\left(\frac{\partial\gamma}{\partial t}\right)_{s} + \gamma(\mathbf{v}_{s}\cdot\mathbf{n})(\nabla_{s}\cdot\mathbf{n}) + \nabla_{s}\cdot(\gamma\mathbf{v}_{s}\cdot\mathbf{t})\mathbf{t} - Pe^{-1}\nabla_{s}^{2}\gamma = 0, \qquad (2.13)$$

where **t** is the unit vector tangent to the interface and $\nabla_s = (\mathbf{I} - \mathbf{nn}) \cdot \nabla$ is the surface gradient operator. The second term of Equation (2.13) describes changes in surfactant concentration due to changes in local surface area, the third term is changes in surfactant concentration due to convection and the fourth term is changes

in surfactant concentration due to diffusion. In the diffusion term, the Peclet number is given as:

$$Pe = (\hat{H_0}^2/D)/\tau,$$
 (2.14)

where D is the diffusion coefficient and $\tau = \hat{H}_0 \mu / \hat{\sigma}_0$ is the viscous time scale. In the simulations presented in this thesis, the Peclet number is set to be $Pe = 10^6$ since the time scale for surfactant diffusion \hat{H}_0^2/D is typically much larger than the viscous time scale τ .

The surfactant transportation is strongly coupled with the free-surface hydrodynamics since both terms in the left side of Equation (2.8) depend on the surfactant concentration distribution $\gamma(r, t)$ through surface tension $\sigma(r, t)$. Here, a linear equation of state is used to represent the relationship between surfactant concentration γ and surface tension σ [31] [32] [33]:

$$\sigma = 1 - Ma(\gamma - 1), \qquad (2.15)$$

where Ma is the Marangoni number, which characterizes the surfactant strength. Larger Marangoni numbers create greater surface tension gradients and consequently higher Marangoni stress. The Marangoni number is given as:

$$Ma = \frac{d\hat{\sigma}}{d\hat{\gamma}}\frac{\hat{\gamma}_0}{\hat{\sigma}_0}.$$
(2.16)

As stated in the previous section, simulations start with an initially uniform liquid substrate of thickness h = 1. The center of the liquid film is covered by a surfactant drop with initial dimensionless radius of R_0 ,

$$\gamma(r,t=0) = \begin{cases} 1 & : r \le R_0, \\ 0 & : r > R_0. \end{cases}$$
(2.17)

2.2.3 Direct Numerical Simulation

This section presents the numerical methods used to solve the theoretical model in sections 2.2.1 and 2.2.2. The non-linear system of partial differential equations (Equations (2.4), (2.5), and (2.13)) describing the free-surface dynamics of Marangoni flows induced by surfactant is solved based on a finite element algorithm. The algorithm used in this Chapter is also applied to the simulations in Chapter 3.

The complexity of the numerical algorithm is considerable since the problem of surfactant-induced Marangoni flows is highly nonlinear and strongly coupled. The transport of surfactant is coupled with the bulk liquid flow. Indeed, the surfactant concentration over the liquid film surface, through the surface tension, determines the Marangoni stress. The Marangoni stress drives the Marangoni flow, which in turn determines the surfactant concentration distribution on the liquid interface. Thus leading to a strongly coupled moving boundary problem.

To solve for velocity field $\mathbf{v}(r, z, t)$, pressure field p(r, z, t), surfactant concentration $\gamma(r, t)$, and shape of the liquid interface h(r, t); the full Navier-Stokes system (Equations (2.4) and (2.5)) and full convection-diffusion equation (Equation (2.13)) are solved simultaneously using direct numerical simulation [34] and the algorithm described in detail in papers by Lu and Corvalan [35], Xue et al. [36] and Lu et al. [37].

This numerical algorithm uses a finite-element method with arbitrary Lagrangian-Eulerian method of spines [38] to parametrize the deforming liquid film surface and incorporates with the interfacial surfactant transport following the scheme described by Campana et al. [39]. The time derivatives are discretized using a second-order Adam-Bashforth predictor with a trapezoidal rule [40]. The time steps are adaptively chosen using first-order continuation [41]. As proposed by Kheshgi and Scriven [42], the first four transient solutions are smoothed using a backward difference method with constant time step. The set of coupled non-linear equations resulting from the spatial and temporal discretization is simultaneously solved using Newton's method with analytical Jacobian [38].

2.3 Regimes and Transitions in Highly-Viscous Marangoni Flows

The free-surface dynamics of Marangoni flows in a thin liquid film is different from that of a deep liquid film. Unimpeded by the presence of the solid lower boundary, a surfactant drop spreads faster on the surface of a deep film than on the surface of a thin film.

Remarkably, the surfactant spreading dynamics on a deep liquid film changes as time progresses. Indeed, the initially faster dynamics on a deep film eventually transition to the slower dynamics characteristic of a thin liquid film. The reason for this later-time transition can be understood by considering that, from the point of view of the flow dynamics, the liquid film behaves as either deep or thin in relation to the size of the surfactant drop. A liquid film that is initially considered deep in relation to the small initial size of the surfactant drop becomes dynamically thin as the size of the spreading surfactant drop increases on the surface of the liquid film. Here, high-fidelity simulations are used to characterize the faster dynamics of deep viscous films and identify the transition to the slower thin-film dynamics.

The dynamics of surfactant-induced Marangoni flows is first illustrated for a thin viscous film where theoretical scalings and experimental data from the literature are benchmarked against the solutions of the full Navier-Stokes system (Section 2.3.1). Next, the influence of the film thickness on the dynamics of Marangoni flows is examined and scaling arguments are developed to predict the characteristic time and length scales of a surfactant drop spreading on deep and highly-viscous liquid films (Section 2.3.2). By varying the film thickness over about three decades, the computations test the accuracy of the limiting scaling solutions previously proposed in the literature, establish their limits of applicability, and calculate necessary corrections for deep-film dynamics. Moreover, results lead to the discovery of previously unobserved scaling laws describing the dynamics of highly-viscous Marangoni flows in deep films. Finally, the crossover time and radius at which the Marangoni dynamics of a deep viscous film transition to the dynamics of a thin viscous film is fully characterized (Section 2.3.3).

2.3.1 Dynamics of Highly-Viscous Marangoni Flows in Thin Films

In this section, the free-surface dynamics of viscous Marangoni flows is illustrated for the case of thin films. Both limiting theoretical predictions by Jensen and Grotberg [43] and experiments by Dussaud et al. [22] are benchmarked against the solutions of the full Navier-Stokes system. Results show that for thin viscous films, both theory and experiments agree well with the solution of the full system of governing equations.

To gain preliminary insight into the physics of Marangoni flows, the dynamics of a surfactant drop spreading on a thin viscous film is briefly illustrated in Figures 2.2 to 2.4. When a drop of insoluble surfactant (red in Figure 2.2) is placed over the free surface of a liquid film (grey in Figure 2.2), a Marangoni convective flow is spontaneously developed. The uneven concentration of surfactant on the surface of the liquid film (Figure 2.2a) creates a surface tension gradient $\nabla_s \sigma$ (Marangoni stress, Equation (2.8)) that drives the liquid radially outward from the low surface tension region to the high surface tension region (Figure 2.2b). In a viscous film, the Marangoni flow is opposed by viscous stress, which creates an upward motion of the free surface, forming a liquid ridge near the leading edge of surfactant drop. At the same time, the central region of the film depresses due to mass conservation.

Figure 2.3 illustrates the temporal evolution of both the rising liquid ridge and the thinning central region. The figure shows the film thickness h at five different dimensionless times t for Marangoni flow in a purely-viscous liquid film (Re = 0). The liquid film is very thin compared to the initial size of the surfactant drop, with a small aspect ratio of $\varepsilon = 0.05$. Clearly, the liquid ridge — which at time t = 0 starts to form at the leading edge of the surfactant drop $R_0 = 1/\varepsilon = 20$ — rises to heights comparable to the film thickness and travels outwards for very long distances as time progresses. This behavior is highly relevant to applications involving coating films, particularly at the microscale [11] [12].

The direct numerical simulations enable a precise examination of the interfacial shapes — which have been observed in careful experiments using fluorescent visual-



Fig. 2.2. Surfactant drop spreading on a continuously deforming liquid film. A drop of surfactant (red) spreads over the surface of a thin and viscous liquid film (grey). The Reynolds number is Re = 0, Marangoni number is Ma = 1, and film thickness is $\varepsilon = 0.05$. The times are (a) t = 20 and (b) t = 1000.



Fig. 2.3. Temporal evolution of liquid film surface. Shape of the liquid film surface h at dimensionless times $t \approx 0, 5 \times 10^1, 5 \times 10^2, 3 \times 10^3$ and 10^4 for a moderate (Ma = 1) surfactant drop spreading on a thin ($\varepsilon = 0.05$) and purely-viscous (Re = 0) liquid film. The liquid ridge formed by the upward motion of liquid film surface spreads radially outward as time progresses.

ization [23]. Moreover, they also enable detailed observation of the Marangoni flow field, and the surface tension gradients that drives the Marangoni flow — which are much more challenging to observe experimentally. This is exemplified in Figure 2.4, which shows the cross-sectional velocity field, the distribution of surfactant concentration γ , and the Marangoni stress $\nabla_s \sigma$ for the system shown in Figure 2.3 at time t = 500. The non-uniform distribution of surfactant concentration (Figure 2.4b) creates a large Marangoni stress $\nabla_s \sigma$ tangential to the interface (Figure 2.4c). The interfacial Marangoni stress drives the Marangoni flow as illustrated by the velocity field of Figure 2.4a. At this time step, the largest radial velocities (red in the Figure 2.4a) occur at approximately $r \approx 40$, where opposing viscous stresses create an upward motion that forms a liquid ridge downstream of the Marangoni stress.

Similarity and theoretical scaling

Here, the limiting theoretical predictions by Jensen and Grotberg [43] and experiments by Dussaud et al. [22] are benchmarked against the solutions of the full Navier-Stokes system.

According to a scaling theory developed by Jensen and Grotberg [43] using lubrication approximation with the extra assumptions of no capillary or gravitational forces, the shape of the interface h(r,t) in the vicinity of the liquid ridge for a thin $(\varepsilon \ll 1)$ and viscous $(Re \ll 1)$ liquid film is expected to follow a similarity solution

$$h = \left(\frac{r}{(16\varepsilon^{-2}Ma)^{1/4}t^{1/4}}\right)^2 \tag{2.18}$$

at later times.

In Figure 2.5, the temporal evolution of the interfacial shapes of the liquid film from the solution of the full Navier-Stokes system (black lines) is compared against the similarity shape of Equation (2.18) (red dashed line) for two orders of magnitude in time. To emulate the limiting conditions of the lubrication approximation, the computed shapes correspond to a thin film with small thickness $\varepsilon = 0.05$ in the Stokes regime Re = 0. Results show that the similarity solution cannot reproduce


Fig. 2.4. Cross-sectional velocity field, surfactant concentration distribution, and Marangoni stress for a surfactant drop spreading on a thin viscous film. Cross-sectional velocity field, surfactant concentration distribution, and Marangoni stress for the system shown in Figure 2.3 at time t = 500. (a) Cross-sectional velocity field and stream path, with red representing high radial velocity. (b) Dashed line represents initial surfactant concentration distribution. As time progresses, surfactant concentration approaches zero asymptotically (solid line). The leading edge of the surfactant drop r_s is marked by the red dot. (c) Non-uniform concentration distribution creates a large Marangoni stress $\nabla_s \sigma$ which drives the convective flow from low surface tension region to high surface tension region.

the early time evolution, but the similarity shapes agree well with the simulations at times larger than approximately $t \approx 5000$, when the height of the liquid ridge has reached approximately $h \approx 1.5$.

The convergence of the inner part of the ridge toward the similarity solution is further illustrated in Figure 2.6. This figure shows the interfacial shapes of a liquid film as a function of the similarity coordinate $\xi = r/(16\varepsilon^{-2}Mat)^{1/4}$, which combines both time and spatial coordinates. Results show that after $t \approx 5000$, the computed shapes agree well with the similarity solution in the range $-0.5 < \xi < 1$.

By considering the balance of viscous and Marangoni stresses, Jensen and Grotberg derived a theoretical equation that predicts the location of the spreading surfactant front r_s as a function of relative film thickness ε , Marangoni number Ma, and time t in the lubrication limit [43].

The Marangoni flow is driven by Marangoni stress $\nabla_s \sigma$, which can be approximated as

$$\nabla_s \sigma \approx d\sigma/dr \tag{2.19}$$

because in the lubrication approximation, the curvature of the liquid film is small. The surface tension σ is related to the local surfactant concentration γ through a linear equation of state $\sigma = 1 - Ma(\gamma - 1)$ (Equation (2.15)); therefore, the Marangoni stress can be further written as

$$\nabla_s \sigma \approx Mad\gamma/dr \tag{2.20}$$

where, following the analysis by Jensen [26], defining the total mass of surfactant as M, the concentration scales as $\gamma \sim M/r_s^2 \sim \pi \varepsilon^{-2} r_s^{-2}$, yielding

$$\nabla_s \sigma \sim Ma\pi \varepsilon^{-2} r_s^{-3}. \tag{2.21}$$

Over the film surface, the Marangoni stress is balanced by the viscous stress approximated as dV/dz, where V is the radial velocity scale given by the average velocity of the surfactant front $V \sim r_s/t$. Because the liquid film is thin the characteristic



Fig. 2.5. Temporal evolution of interfacial shapes of a liquid film. Temporal evolution of interfacial shapes for the system shown in Figure 2.2. The computed shapes (black lines) are compared with corresponding similarity shapes (red dashed lines) calculated from Equation (2.18). After $t \approx 5000$ the simulation results agree well with the similarity shapes.



Fig. 2.6. Interfacial shapes of a liquid film in similarity coordinates. As time t increases, shapes of the liquid film presented in Figure 2.5 approach the similarity solution defined in Equation (2.18) (red dashed line). Here interfacial shapes corresponds to times $t = 750, 2500, 5000, 1 \times 10^4$ and 2.5×10^4 .

length in the axial direction is the film thickness $\hat{z} = \hat{H}_0$, or z = 1 in dimensionless form. Rearranging the equations, the viscous stress can be estimated by

$$dV/dz \sim r_s/t. \tag{2.22}$$

Finally, using the stress balance over the liquid film surface

$$d\sigma/dr \sim dV/dz \tag{2.23}$$

yeilds the scaling for the radius of the surfactant front

$$r_s \sim (\pi \varepsilon^{-2} Mat)^{1/4}. \tag{2.24}$$

Jensen and Grotberg [43] combined the balance of viscous and Marangoni stresses (Equation (2.23)) with an extra assumption that the speed of the leading edge of the surfactant drop equals the velocity of the film at the leading edge. Through rigorous mathematical derivation using similarity analysis, they found the prefactor to Equation (2.24) as

$$r_s = (16Ma\varepsilon^{-2}t)^{1/4}.$$
 (2.25)

In Figure 2.7, the solutions of the full Navier-Stokes system are benchmarked against the theoretical Equation (2.25). This figure illustrates the temporal evolution of the surfactant front r_s for the spreading of a drop of moderate surfactant (Ma = 1) on the surface of two purely viscous (Re = 0) liquid films with different film thickness ($\varepsilon = 0.05$ and 0.1). For Marangoni flows in thin and purely viscous liquid films, the simulations (symbols) show good agreement with the theoretical Equation (2.25) (black lines).

Figure 2.8 illustrates the temporal evolution of the surfactant front r_s for the spreading of surfactant drops with three different Marangoni numbers Ma = 0.5, 1 and 2 on the surface of a purely-viscous (Re = 0) liquid film. The liquid film is very thin compared with the initial sizes of the surfactant drops ($\varepsilon = 0.05$). Results from the simulations (symbols) shows good agreement with the theoretical Equation (2.25) (black lines).



Fig. 2.7. Temporal evolution of the surfactant front for different film thicknesses. Location of the surfactant front r_s as a function of time t for Marangoni flows in thin films of thickness (a) $\varepsilon = 0.05$ and (b) $\varepsilon = 0.1$. Reynolds number and Marangoni number for both simulations are Re = 0 and Ma = 1. Simulation results (symbols) show good agreement with Equation (2.25) (black lines).



Fig. 2.8. Temporal evolution of the surfactant front for different Marangoni numbers. Location Ma = 2. Reynolds number and film thickness for all simulations are Re = 0 and $\varepsilon = 0.05$ respectively. of the surfactant front r_s as a function of time for Marangoni numbers (a) Ma = 0.5 (b) Ma = 1 and (c) Simulation results (symbols) show good agreement with Equation (2.25) (black lines).

According to Equation (2.25), the location of the surfactant front r_s follows a power law of $(16\varepsilon^{-2}Ma)^{1/4}t^{1/4}$. This power law is confirmed in Figure 2.9. The figure illustrates the evolution of the surfactant front r_s as a function of the scaling coordinate $(16\varepsilon^{-2}Ma)^{1/4}t^{1/4}$ for systems shown in Figures 2.7 and 2.8. Simulation results (symbols) show good agreement with Equation (2.25) (black line).

The location of surfactant front r_s plays a critical role in the analysis of the dynamics of Marangoni flows. However, due to both convection and diffusion, the initially sharp concentration front (Figure 2.4b, dashed line) spreads and approaches zero asymptotically at later times (Figure 2.4b, solid line). Therefore, the way in which r_s is calculated as time progresses requires clarification. Following the method proposed by Gaver and Grotberg [20], the radius of the spreading drop r_s is defined as the radius that contains exactly 99.5% of the total mass \hat{M} of the spreading surfactant (Figure 2.4b, red dot). Specifically, the location r_s at each instant \hat{t} is calculated by numerical solution of the integral equation

$$0.995\hat{M} = 2\pi \int_0^{\hat{r}_s} \hat{\gamma}(\hat{r}, \hat{t}) \hat{r} d\hat{r}, \qquad (2.26)$$

where $\hat{\gamma}(\hat{r}, \hat{t})$ is the instantaneous surfactant concentration over the surface of the liquid film. Because of mass conservation, the total mass of surfactant \hat{M} in Equation (2.26) remains constant and can thus be calculated as its value at time $\hat{t} = 0$

$$\hat{M} = 2\pi \hat{R_0}^2 \hat{\gamma_0} \tag{2.27}$$

where $\hat{\gamma}_0$ is the initial surfactant concentration and \hat{R}_0 is the initial radius of the area covered by surfactant. Finally, the surfactant front \hat{r}_s is made non-dimensional as $r_s = \hat{r}_s / \hat{H}_0$.

The solution of full Navier-Stokes system is finally compared against experimental results of surfactant spreading on thin films by Dussaud et al. [22]. Figure 2.10 compares simulation results (black line) with experiments identified as Experiment 3 (red circles) and Experiment 4 (blue squares) in Dussaud et al. [22]. The experiments were carried out using an aqueous mixture of 60% wt glycerol as liquid substrate.



Fig. 2.9. Evolution of the surfactant front as a function of scaling coordinates. Locations of the surfactant front r_s as a function of the scaling coordinate $(16Ma\varepsilon^{-2}t)^{1/4}$ for the simulations in Figures 2.7 and 2.8. Simulation results (symbols) show good agreement with Equation (2.25) (black line). Film thicknesses are $\varepsilon = 0.05$ (circle) and 0.1 (square), and Marangoni numbers are Ma = 0.5 (blue), 1 (red) and 2 (green).

The density and dynamic viscosity of the liquid substrate are $\rho = 1.15 \text{ g/cm}^3$ and $\mu = 0.107$ poise respectively. In the experiments, 0.5 μ l oleic acid was deposited on the liquid film of approximately 250 μ m in thickness. The initial radius of the area covered by oleic acid was $\hat{R}_0 \approx 0.2 \text{ cm}$, and the surface tension in the region covered by surfactant was around $\hat{\sigma}_0 \approx 40.2 \text{ dyn/cm}$. Converting all the dimensional parameters to dimensionless forms described in section 2.2 results in $Re \approx 100$, $Ma \approx 0.6$ and $\varepsilon \approx 0.125$. Clearly, the simulation results (black line) in Figure 2.10 agree very well with both the experimental data (symbols) and the theoretical scaling $t^{1/4}$ of Equation (2.25).

Together, the comparisons between simulation results, experiments, and theoretical works strengthen the confidence in the findings in this work.

2.3.2 Dynamics of Highly-Viscous Marangoni Flows in Deep Films

This section extends the study of Marangoni flows to deep viscous films. Results from the simulations enable accurate characterization of physical mechanisms governing the distinct early-time and late-time dynamics of Marangoni flows in deep viscous films. By varying the film thicknesses over about three decades, the computations test the accuracy of the limiting scaling solutions previously proposed in the literature, establish their limits of applicability, and calculate necessary corrections for deep films. Moreover, results lead to the discovery of previously unobserved scaling laws describing the dynamics of purely-viscous Marangoni flows in deep films.

Late-time dynamics in deep viscous films

Here, simulations of surfactant spreading on deep liquid films ($\varepsilon \gg 1$) are used to establish the appropriate late-time dynamics in the Stokes regime (Re = 0). The computations calculate necessary corrections to the scaling laws previously proposed in the literature.



Fig. 2.10. Comparison between experimental data and simulation results. Location of surfactant front r_s as a function of time t for Re = 100, Ma = 0.6 and $\varepsilon = 0.125$. Simulation results (black solid line) show good agreement with experimental data identified as Experiment 3 (red circles) and Experimentv4 (blue squares) in Dussaud et al. [22]. Both simulations and experiments show the scaling $r_s \sim t^{1/4}$ in the thin film limit.

To gain preliminary insight into the dynamics of surfactant-induced Marangoni flows in deep films, Figure 2.11 illustrates the spreading of a drop of moderate surfactant (Ma = 1) on the surface of four increasingly deeper films ($\varepsilon = 0.1, 1, 10$ and 100) in the Stokes limit (Re = 0). For the thin film (Figure 2.11a), the simulations (symbols) confirm that the surfactant front follows a power law $t^{1/4}$ with time (black line) as discussed in Section 2.3.1. The dynamics in the deeper liquid films, however, is different from the dynamics in the thinner films. At early times, the surfactant drop spreads faster on the surface of the deep films (Figures 2.11c and 2.11d) than on the surface of the thinner films (Figures 2.11a and 2.11b).

In addition, results in Figures 2.11c and 2.11d show that the spreading dynamics on the deeper films ($\varepsilon \gg 1$) change as time progresses. The faster early-time dynamics eventually transitions to the slower dynamics, although the physical thickness of the film does not change. For example, consider the spreading surfactant drop in Figure 2.11c, which corresponds to a moderately deep film with a ratio of film thickness to initial surfactant drop radius $\varepsilon = 10$. The surfactant front (symbols) follows the faster early-time dynamics for about three decades in time $(10^{-1} < t < 10^2)$. But after a crossover at $t \approx 10^2$ (red dot), the deep film dynamics transitions to a dynamics similar to that of a thin film $(t^{1/4}, \text{ black line})$. The reason for this later-time transition can be understood by considering that the instantaneous ratio of film thickness to drop radius becomes progressively smaller as the size of the spreading surfactant drop increases on the surface of the liquid film.

Although both follow a power law $t^{1/4}$ with time, simulation results reveal a discrepancy between the late-time dynamics of deep viscous films and the dynamics of thin viscous films. This discrepancy will play a critical role in the characterization of the crossover between the early and late dynamics of deep viscous films as will be discussed in Section 2.3.3 (see red dots in Figures 2.11c and 2.11d). Here, this discrepancy is quantified by introducing a correction factor C_0 . Based on the lubrication



 $\varepsilon = 10$ and (d) $\varepsilon = 100$. Reynolds numbers and Marangoni numbers for the simulations are held constant as Re = 0 and Ma = 1. Dynamical transitions are marked by the red dots and the corresponding transition Fig. 2.11. Influence of film thickness on the dynamics of Marangoni flows in highly-viscous films. Surfactant front r_s as a function of time for Marangoni flows in films of thickness (a) $\varepsilon = 0.1$, (b) $\varepsilon = 1$, (c) radii are marked by the red dashed lines.

approximation, Equation (2.25) predicts that on a thin viscous film, the surfactant front follows a power-law that can be extended by including the correction factor as

$$r_s = C_0 (16Ma\varepsilon^{-2}t)^{1/4}.$$
 (2.28)

For thin viscous films, the correction factor C_0 was confirmed from results in Section 2.3.1 to be $C_0 \approx 1$ (Figure 2.9). For deep viscous films, however, the simulations show that $C_0 \neq 1$. The correction factor C_0 for deep viscous film is thus characterized by fitting a scaling line through the simulation results as shown in Figure 2.11 (black line). The characterized values of correction factor C_0 are summarized in Figure 2.12 for a wide range of film thicknesses ($0.05 < \varepsilon < 100$). Figure 2.12 clearly identifies two regions based on film thickness ε . For deep films, the correction factor is estimated to be approximately $C_0 \approx 0.64$ by taking the average of the values of C_0 in the region $\varepsilon \geq 1$.

The calculated value of correction factor C_0 for deep films is further verified in Figure 2.13. Here, the temporal evolution of the surfactant front r_s for Marangoni flows in purely viscous (Re = 0) liquid films with different film thicknesses $\varepsilon = 1$ (red squares), 10 (green squares) and 20 (blue squares) is shown. The Marangoni number for these simulations are Ma = 1 (hollowed symbols) and Ma = 2 (filled symbols). The simulation results (symbols) collapse onto a single master line under the scaling coordinate $(16\varepsilon^{-2}Ma)^{1/4}t^{1/4}$, which confirms the power law suggested by Equation (2.28). Equation (2.28) with the correction factor $C_0 = 0.64$ (black line) fits throughout the collapsed region of the simulation results (symbols), confirming the accuracy of the characterized value of C_0 .

Early-time dynamics in deep viscous films

Here, simulations of Marangoni flows in deep liquid films ($\varepsilon \gg 1$) are used to establish the appropriate early-time dynamics for the Stokes regime (Re = 0). Simulations are also contrasted against the scaling laws derived by Jensen [26] for the surfactant-induced Marangoni flows in deep viscous films. Results demonstrate — for



Fig. 2.12. Correction factor C_0 as a function of film thickness. The value of the correction coefficient C_0 for thin films is $C_0 \approx 1$, and for deep films is $C_0 \approx 0.64$.



Fig. 2.13. Evolution of the surfactant front as a function of scaling coordinate. Location of the surfactant front r_s as a function of scaling coordinate $(16\varepsilon^{-2}Ma)^{1/4}t^{1/4}$ for Marangoni flows in purelyviscous (Re = 0) liquid films of thicknesses $\varepsilon = 1$ (red squares), $\varepsilon = 10$ (green squares) and $\varepsilon = 20$ (blue squares). Marangoni numbers for the simulations are Ma = 1 (hollowed symbols) and Ma = 2 (filled symbols). Equation (2.28) with the correction factor $C_0 = 0.64$ (black line) fits well the simulation results (symbols).

the first time — that in the Stokes limit $Re \to 0$, the surfactant spreads faster than expected and the difference in the expected velocity increases as the film thickness ε increases (by a factor $\varepsilon^{1/4}$).

According to the scaling analysis developed by Jensen using a boundary-layer approach [26], the surfactant front r_s for a drop of surfactant spreading on the free surface of a deep viscous film follows the scaling

$$r_s \sim (\frac{\pi^2 M a^2}{\varepsilon^4 R e})^{1/8} t^{3/8},$$
 (2.29)

in the dimensionless terms of Section 2.2. The objective is to establish the appropriate dynamics for the Stokes limit $Re \rightarrow 0$. To this end, Figure 2.14 shows the temporal evolution of the surfactant front r_s for Marangoni flows in three different (deep) films with relative thickness $\varepsilon = 10, 20$, and 100 in the Stokes limit (Re = 0). Results from the direct numerical simulation for a moderate surfactant with Ma = 1 (symbols) confirm that the early-time dynamics follows a power law $t^{3/8}$ with time (black lines) as predicted by Equation (2.29). Therefore, the location of surfactant front r_s can be written as

$$r_s = K^* t^{3/8}, (2.30)$$

where K^* is the prefactor that depends on the film thickness ε and Marangoni number Ma.

Figure 2.15 shows the values of the prefactor K^* as a function of the film thickness ε calculated by fitting Equation (2.30) to the simulation results, as illustrated by the black lines in Figure 2.14. Results in Figure 2.15 demonstrate that the calculated prefactors (symbols) follow a power law $\varepsilon^{-3/4}$ with film thickness (black line). Consequently, the location of the surfactant front scales as

$$r_s \sim \varepsilon^{-3/4} t^{3/8}.$$
 (2.31)

This scaling is further confirmed in Figure 2.16. The figure shows the surfactant front radius r_s as a function of the scaling coordinate $\varepsilon^{-3/4}t^{3/8}$ for the systems shown in Figure 2.14. Simulation results collapse (symbols) onto one master line under the scaling coordinate, confirming $r_s \sim \varepsilon^{-3/4}$ suggested by Equation (2.31).



surfactant front r_s as a function of time t for deep films of thickness (a) $\varepsilon = 10$, (b) 0.1 and (c) 100. Reynolds Fig. 2.14. Temporal evolution of the surfactant front for different film thicknesses. Location of the number and Marangoni number for the simulations are Re = 0 and Ma = 1 respectively. Simulation results (symbols) confirm that the early-time dynamics follow a scaling $t^{3/8}$ with time (black line).



Fig. 2.15. Coefficient \mathbf{K}^* as a function of film thickness. The coefficient K^* (symbols) follows a scaling $K^* \sim \varepsilon^{-3/4}$ with film thickness (dashed line).



Fig. 2.16. Evolution of the surfactant front as a function of scaling coordinates. Location of the surfactant front r_s as a function of the scaling coordinate $\varepsilon^{-3/4}t^{3/8}$ for the systems shown in Figure 2.14. Here, film thicknesses for the simulations are $\varepsilon = 10$ (red), 20 (blue) and 100 (green). Simulation results (symbols) confirm the scaling of Equation (2.31) (black line).

Having established the influence of film thickness on the dynamics, the influence of surfactant properties can now be similarly studied. To establish the influence of Marangoni number on the Stokes dynamics, Figure 2.17 shows the temporal evolution of surfactant front r_s for the spreading of different surfactant drops with three different Marangoni numbers Ma = 0.5, 1 and 2 on a purely-viscous liquid film (Re = 0). Results from the simulations for a moderately deep film with $\varepsilon = 10$ (symbols) confirm the location of surfactant front r_s follows a power law of $t^{3/8}$ and also show the prefactor K^* in Equation (2.30) is a function of Marangoni number.

Figure 2.18 shows the values of the prefactor K^* as a function of the Marangoni number Ma calculated by fitting Equation (2.30) to the simulation results, as illustrated by the black lines in Figure 2.17. In Figure 2.18, results from the fitting demonstrate that the calculated prefactor K^* (symbols) follows a power law $Ma^{1/4}$ relationship with Marangoni number (black line). Therefore, the location of the surfactant front scales as

$$r_s \sim M a^{1/4} t^{3/8}.$$
 (2.32)

The scaling in Equation (2.32) is further tested in Figure 2.19. This figure shows the location of surfactant front r_s as a function of the scaling coordinate $Ma^{1/4}t^{3/8}$ for the systems shown in Figure 2.17. Simulation results collapse onto one master line under the scaling coordinate confirming $r_s \sim Ma^{1/4}$ suggested by Equation (2.32).

Having established the individual influence of both film thickness (Figure 2.14) and Marangoni number (Figure 2.17), their combined effect on the dynamics of Marangoni flows can now be summarized by combining the results in Equations (2.31) and (2.32) as:

$$r_s = K M a^{1/4} \varepsilon^{-3/4} t^{3/8} \tag{2.33}$$

The dynamics can be further characterized by quantifying the prefactor K in the power-law relationship of Equation (2.33).

To quantify K, Figure 2.20 shows the evolution of the surfactant front r_s for systems shown in Figures 2.14 (influence of ε) and 2.17 (influence of Ma) as a function of the combined scaling coordinate $Ma^{1/4}\varepsilon^{-3/4}t^{3/8}$. The results from Figure 2.20 are



of the surfactant front r_s as a function of time for Marangoni numbers (a) Ma = 0.5 (b) Ma = 1 and (c) Ma = 2. Reynolds number and film thickness for all simulations are Re = 0 and $\varepsilon = 10$ respectively. Simulation results (symbols) confirm the early-time scaling $r_s \sim t^{3/8}$ with time (black lines). Fig. 2.17. Temporal evolution of the surfactant front for different Marangoni numbers. Location



Fig. 2.18. Coefficient \mathbf{K}^* as a function of Marangoni number. The coefficient K^* (symbols) follows a scaling $K^* \sim Ma^{1/4}$ with Marangoni number (dashed line).



Fig. 2.19. Evolution of the surfactant front as a function of scaling coordinates. Location of the surfactant fronts r_s as a function of scaling coordinate $Ma^{1/4}t^{3/8}$ for the systems of Figure 2.17. Here, Marangoni numbers are Ma = 0.5 (red), 1 (blue) and 2 (green). Simulation results (symbols) confirm the scaling of Equation (2.32) (black line).

twofold. First, it further confirms the scalings in Equation (2.33) because the results collapse onto one master curve. Second, the prefactor can be quantified as $K \approx 1.4$ by fitting Equation (2.33) onto the collapsed results. Consequently, the full Marangoni dynamics can be finally established as

$$r_s = 1.4 M a^{1/4} \varepsilon^{-3/4} t^{3/8}, \tag{2.34}$$

In conclusion, simulations of Marangoni flows in deep liquid films were used to establish the appropriate early-time dynamics for the Stokes regime. The dynamics — summarized by Equation (2.34) — demonstrates that in the Stokes limit $Re \rightarrow 0$, the surfactant spreads faster than expected from the boundary layer approximation for deep viscous films of Equation (2.29), and the difference with the expected velocity increases as the film thickness ε increases by a factor $\varepsilon^{1/4}$.

2.3.3 Dynamical Transitions in Highly-Viscous Films

Here, the dynamics of surfactant-induced Marangoni flows in deep films characterized in the previous sections are used to identify the crossover where the Marangoni flow will transition from the faster early-time dynamics, in which the surfactant drop radius r_s spreads as $r_s \sim t^{3/8}$, to the slower late-time dynamic, in which the surfactant spreads as $r_s \sim t^{1/4}$.

Results in Section 2.3.2 show that the early-time dynamics of Marangoni flows in deep films follows a power-law (Equation (2.34))

$$r_s = 1.4 M a^{1/4} \varepsilon^{-3/4} t^{3/8}, \tag{2.35}$$

in the Stokes regime. On the other hand, results in Section 2.3.2 show that, at later times the dynamics transition to Equation (2.28)

$$r_s = C_0 (16 M a \varepsilon^{-2} t)^{1/4} \tag{2.36}$$

with a departure from unity in the correction factor, which was characterized as $C_0 \approx 0.64$.



Fig. 2.20. Evolution of the surfactant front as a function of scaling coordinate. Evolution of surfactant fronts r_s as a function of the scaling coordinate $Ma^{1/4}\varepsilon^{-3/4}t^{3/8}$ for the systems of Figures 2.14 and 2.17. Simulation results confirm the scaling of Equation (2.33) with a prefactor $K \approx 1.4$. Film thicknesses are $\varepsilon = 10$ (red), 20 (blue) and 100 (green), and Marangoni numbers Ma = 0.5 (triangle), 1 (square) and 2 (diamond).

Consequently, the crossover time t^* and corresponding crossover radius r^* where the Marangoni flow will transition from the early-time dynamics to the late-time dynamics can be readily identified as

$$t^* = 0.47\varepsilon^2, \quad r^* = 1.05Ma^{1/4},$$
(2.37)

by equating Equations (2.35) and (2.36). Interestingly, for a given film, the size of the surfactant drop at the crossover radius r^* is independent of the initial drop size $R_0 = 1/\varepsilon$; although the crossover occurs earlier if the initial drop size is larger.

In conclusion, the results in Section 2.3 are summarized and further verified in the phase diagram of Figure 2.21:

For deep films, the viscous Marangoni flow initially proceeds in the faster dynamics $t^{3/8}$ until the radius of the spreading surfactant drop becomes larger than approximately $r_s \approx Ma^{1/4}$. This crossover between the faster dynamics $t^{3/8}$ of Equation (2.34) (blue region) and the slower dynamics $t^{1/4}$ of Equation (2.28) with $C_0 = 0.64$ (yellow region) is illustrated by the black diagonal line, which represents Equation (2.37) in the phase diagram. The measured transition radius (see Figure 2.11, red dashed line) (symbols) show good agreement with Equation (2.37).

For thin films, the Marangoni flow always proceeds in the slower dynamics $t^{1/4}$. Indeed, if the predicted crossover radius $r^* = 1.05 M a^{1/4}$ is smaller than the initial drop radius $R_0 = 1/\varepsilon$, the initial faster dynamics $t^{3/8}$ no longer exists, and the Marangoni flow proceeds in the slower dynamics $t^{1/4}$ from the beginning. The crossover to the thin-film dynamics of Equation (2.28) with $C_0 = 1$ (red region) is illustrated by the vertical dashed line $\varepsilon M a^{1/4} = 1$, which represents the boundary $r^* \approx R_0$ in the phase diagram.

This section presented a numerical analysis on the Marangoni flow dynamics in the Stokes limit. After comparing the solutions of full Navier-Stokes system with limiting theoretical predictions and experimental data in thin films, computations were used to study the Marangoni flow dynamics in deep films. Simulations tested the accuracy of limiting scaling solutions previously proposed in the literature, and



Fig. 2.21. **Phase diagram.** For deep films ($\varepsilon > 1$), the Marangoni flow initially proceeds in the $t^{3/8}$ dynamics (blue region) and eventually transition to the slower $t^{1/4}$ dynamics (yellow region). For thin films ($\varepsilon < 1$) the flow proceeds in the $t^{1/4}$ dynamics since the beginning (red region). The calculated crossover radii (symbols) show good agreement with the theoretical Equation (2.37) (black diagonal line). Reynolds numbers is Re = 0, and Marangoni numbers are Ma = 0.5(green), 1 (blue) and 2 (orange).

calculated necessary correction factors. Simulation results eventually lead to scaling laws describing the dynamics of purely-viscous Marangoni flows in deep films, and to equations characterizing the crossover from deep-film dynamics to thin-film dynamics in the Stokes limit.

2.4 Stationary Liquid Ridge

When a drop of surfactant is placed over the free surface of a liquid film, a Marangoni convective flow is spontaneously developed. The Marangoni flow not only drives the horizontal spreading of the surfactant but also drives a vertical upward motion of the free surface. The upward motion of the free-surface forms a liquid ridge, which is initially formed at the leading edge of the surfactant drop.

Understanding the evolution of the liquid ridge on the free surface is relevant to the prediction and control of interfacial defects, and therefore critical to industrial processes such as coating, drying, and painting; particularly at the microscale. Here, the simulation results of the full Navier-Stokes system of equations are used to characterize the motion of the liquid ridge at early times.

Results demonstrate — apparently for the first time — that the liquid ridge exhibits a "waiting-time" behavior: The ridge, which initially travels in the outward radial direction at a velocity much larger than the velocity of the surfactant front, essentially stops moving after a finite time. The ridge then remains quasi-static (the *waiting-time* period), forming a stationary circular ring with near constant size.

In this section, the establishment of the stationary ridge is first illustrated on a viscous film and simple scaling arguments are developed to predict the characteristic time and length scales of the stationary ridge (Section 2.4.1). Then, the influence of the film thickness and viscosity (Reynolds number) is examined, and the predicted lengths and time scales of the stationary ridge are compared to the solution of the full Navier-Stokes system (Section 2.4.2).

2.4.1 Development of a Stationary Liquid Ridge

Here, numerical experiments were developed to characterize the "waiting-time" behavior. The focus is on estimating the time scale T to establish the stationary ridge as well as the length scale R of the quasi-static ring.

To this end, Figure 2.22 illustrates both the spreading of a moderate surfactant (Ma = 1, red disk) and the evolution of the liquid ridge (black dashed line) on a highly viscous film. The location of the liquid ridge r_m , is measured at the highest point of the ridge. The relative thickness of the film is $\varepsilon = 1$, and the Reynolds number is $Re = 10^{-2}$. As shown in Figure 2.22a, the liquid ridge (dashed line) initially develops at the edge of the surfactant droplet (red disk). The ridge then propagates radially outwards from time $t \approx 0$ to $t \approx 10^{-2}$ while the surfactant drop remains stationary at $r_s = 1$ (Figures 2.22a to 2.22c). Unexpectedly, the liquid ridge essentially stops propagating in the radial direction after a finite time $t \approx 10^{-2}$ (Figures 2.22c) and forms a stationary circular ring with near constant size $r_m \approx 2.3$ while the surfactant drop still remains stationary at $r_s \approx 1$ (Figures 2.22c to 2.22f). The figure also makes clear that the stationary ridge develops rapidly. Compared to the surfactant spreading timescale. Similar results have been observed experimentally by Kim et al. [44] for the spreading of soluble drops, although the flow physics is different.

Time scale to establish the stationary ridge

The Marangoni convective flow at the surfactant leading edge $(r = r_s)$ originates a boundary layer that grows in the downward vertical direction. The thickness of this boundary layer can be estimated from a balance of radial momentum as $\hat{\delta} \approx (\mu \hat{t}/\rho)^{1/2}$ [45] or, in dimensionless terms, as

$$\delta \approx (t/Re)^{1/2}.$$
(2.38)



Fig. 2.22. Location of surfactant front and liquid ridge at early times on a highly viscous film. Location of the liquid ridge r_m (dashed line) and the surfactant front r_s (red disk) at times $t \approx 0, 10^{-3}, 10^{-2}, 3 \times 10^{-2}, 10^{-1}$ and 5×10^{-1} . A quasi-static ridge of radius $r_m \approx 2.34$ is formed at $t \approx 10^{-2}$. The liquid film thickness is $\varepsilon = 1$, the Reynolds number $Re = 10^{-2}$, and the Marangoni number Ma = 1.

To estimate the time scale T to establish the stationary liquid ridge, it is assumed that when the boundary layer δ reaches the lower solid boundary of the liquid layer, the ridge velocity reduces significantly, and the liquid ridge essentially stops propagating on the liquid surface. From Equation (2.38) and the assumption that the liquid ridge stops propagating when the dimensionless boundary layer reaches lower boundary $\hat{\delta} \approx \hat{H}_0$ (or $\delta \approx 1$ in dimensionless terms), results that the required time scale T to establish the stationary ridge is approximately

$$T \approx Re,$$
 (2.39)

which agrees well with the results in Figure 2.23 (red circles).

Figure 2.23 shows the early-time evolution of both the radius of the liquid ridge r_m (red circles) and the location of the surfactant front r_s (red squares) for the system shown in Figure 2.22. This figure shows that the liquid ridge initially develops at the leading edge of the surfactant drop ($t < 10^{-4}$) but then the ridge propagates at a significantly larger speed than the surfactant front ($10^{-4} < t < 10^{-2}$). The liquid ridge stops propagating radially outwards after time $t \approx 10^{-2}$, which shows good agreement with the estimation from Equation (2.39) since the Reynolds number of the liquid film is $Re = 10^{-2}$.

For times $t \ge 10^{-2}$ (Figure 2.23), the ridge forms a stationary ring with a near constant size $r_m \approx 2.34$, or approximately twice the radius of the original surfactant drop. The "waiting-time" behavior of the ridge extends up to a time $t \approx 1$. For times $t \ge 1$, the radius of the liquid ridge increases at the same rate $t^{1/4}$ as the radius of the surfactant front.

Length scale of the stationary ridge

Taking x = 0 to be the location of the surfactant front at t = 0, the liquid ridge propagates a growing distance $x(t) = r_m(t) - R_0$ with time, where R_0 is the initial radius of the surfactant drop. In this translated radial coordinate, a stationary ridge



Fig. 2.23. Temporal evolution of the locations of the liquid ridge and surfactant front. Locations of the liquid ridge r_m (circle) and surfactant front r_s (squares) as a function of time t for the system of Figure 2.22. The liquid ridge forms a stationary ring at $r_m \approx 2.34$ after $t \approx 10^{-2}$ in good agreement with Equation (2.39). The radius of the liquid ridge r_m (black line) and the surfactant front r_s (black dashed line) for Re = 0 are shown for comparison.

of characteristic size R is established at a radial distance $x(T) = R - R_0$ from the surfactant front.

Figure 2.24 shows the temporal evolution of the distance $x = r_m - R_0$ between the liquid ridge and the location of the surfactant front. Results show that the distance x(red circle) follows a power-law behavior with time $x \sim t^{1/2}$ (dashed line). Using this result and Equation (2.39) results in $x(t)/x(T) \sim (t/Re)^{1/2}$, so that the liquid ridge propagates proportionally to the growth of the boundary layer. The resulting velocity is thus $u_m \sim (Ret)^{-1/2}$. Taking the characteristic velocity scale as $U \equiv u_m(T)$, results

$$U \sim \frac{1}{Re}.\tag{2.40}$$

The time and velocity scales are corroborated by the size of the stationary ridge observed from the simulations. Indeed, from Equations (2.39) and (2.40) the length scale of distance $x(T) = R - R_0$ results

$$x(T) \approx UT = O(1), \tag{2.41}$$

which agrees well with the results in Figure 2.23.

2.4.2 Influence of Film Viscosity, Thickness and Surfactant Strength on the Stationary Ridge

The time scale T and length scale x(T) to establish the stationary ridge has been discussed in the previous section. However, how liquid viscosity, film thickness, and surfactant strength affect the findings remains unclear.

Influence of the Reynolds number

Figure 2.25 illustrates the influence of the Reynolds number on the early-time evolution of both the location of the liquid ridge r_m (solid lines) and the location of the surfactant front r_s (dashed line) for the conditions of Figure 2.22. The figure shows as Re increases, the stationary ridge is formed at a later time. For example,



Fig. 2.24. Temporal evolution of the distance $\mathbf{x}(\mathbf{t})$. Evolution of the distance $x(t) \equiv r_m(t) - R_0$ as a function of time t for the system shown in Figure 2.22. The distance x(t) from the original drop size to the instantaneous liquid ridge grows as $t^{1/2}$ (dashed line).

the liquid ridge with Reynolds number $Re = 10^{-3}$ (blue line) stops propagating and becomes motionless at approximately $t \approx 10^{-3}$ while the liquid ridge with Reynolds number $Re = 10^{-2}$ (green line) reaches the constant radius R at a later time, around $t \approx 10^{-2}$, which confirms Equation (2.39). It is also shown in the figure that the constant radius R does not change with Reynolds number, which agrees well with Equation (2.41). The surfactant fronts r_s on the other hand are not affected by the viscosity of the liquid film as shown in Figure 2.25.

Influence of the film thickness

Apart from the liquid viscosity, film thickness also plays an important role in the formation of the stationary liquid ridge. In this section, simulation results with a wide range of aspect ratios $0.05 \le \varepsilon \le 10$ are analyzed and discussed in order to understand how film thickness affects the stationary ridge.

The simulation results are summarized in Figures 2.25 to 2.27. Figure 2.26 illustrates the early-time evolution of the locations of the liquid ridge r_m (solid lines) and surfactant front r_s (dashed lines) for Marangoni flows in a viscous liquid film with film thicknesses of $\varepsilon = 0.05$. In this figure, the stationary ridge is approached at around $T \approx Re$. Using the simulation results with Reynolds number of $Re = 10^{-3}$ (blue line) as an example, the stationary ridge $R \approx 21$ is reached at around $T \approx 10^{-3}$, which shows good agreement with Equation (2.39). Figure 2.27 illustrates the early-time evolution of the liquid ridge r_m (solid lines) and surfactant front r_s (dashed lines) for Marangoni flows in a viscous liquid film with film thicknesses of $\varepsilon = 10$. Results in this figure also shows the the stationary ridge is approached at around $T \approx Re$, further confirming Equation (2.39).

Comparing the simulation results for Marangoni flows in a thin film with $\varepsilon = 0.05$ (Figure 2.26), a film with intermediate thickness $\varepsilon = 1$ (Figure 2.25), and a deep film with $\varepsilon = 10$ (Figure 2.27) shows a slight increase in the length scale x(T) as the film thickness increases. As shown in Figure 2.26, for Marangoni flows in a thin liquid


Fig. 2.25. Influence of Reynolds number on the evolution of the liquid ridge r_m in a liquid film of thickness $\varepsilon = 1$. The radius of the stationary ridge is $R = R_0 + O(1)$, and the time scale to establish the stationary ridge is $T \approx Re$. The Reynolds numbers are Re = 0 (black line), 10^{-3} (blue line), 10^{-2} (green line), 10^{-1} (red line) and 1 (orange line), and the Marangoni number is Ma = 1. The surfactant front r_s for Re = 0 (black dashed line) is also shown for reference.

film with thickness of $\varepsilon = 0.05$, the length scale distance is $x(T) \approx 1.0$. The length scale increases to $x(T) \approx 1.8$ when the liquid film thickness is $\varepsilon = 10$ as shown in Figure 2.27. However, the characteristic length scale x(T) only increases slightly for an increase of over two orders of magnitude in film thickness, and still results in a value that is O(1), showing good agreement with Equation (2.41).

Influence of surfactant strength

Here, simulations for a wide range of Marangoni numbers $(0.1 \le Ma \le 10)$ were performed to understand the influence of Maranogni number on the characteristic time and length scales of the stationary ridge.

Figure 2.28 illustrates the evolution of the liquid ridge r_m (solid lines) and surfactant front r_s (dashed lines) for three different Marangoni numbers in a liquid film of thickness $\varepsilon = 1$, and Reynolds number $Re = 10^{-2}$. As shown in Figure 2.28, the early-time ($t < 10^{-2}$) evolution of the liquid ridge r_m is similar for the three cases. The liquid ridge for Ma = 10 (green), Ma = 1 (blue) and Ma = 0.1 (red) reaches a radius $R \approx 2.34$ at similar time $T \approx 10^{-2} = Re$, as estimated by Equations (2.39) and (2.41).

Although the surfactant strength has little influence on the formation of the stationary ridge, it significantly affects the duration of the stationary ridge (waiting time). As shown in Figure 2.28, the ridge immediately starts to propagate again at $t \approx 10^{-2}$ for the simulation with Ma = 10 (green) but lasts until $t \approx 1$ for the liquid ridge with Ma = 10, a significantly longer time. Incidentally, the figure also shows that the surfactant strength has also a significant influence on the surfactant front r_s : whereas the surfactant starts spreading at $t \approx 10^{-2}$ for the surfactant with Ma = 10, it remains almost stationary until $t \approx 1$ for the surfactant with Ma = 0.1.

This section focused on establishing the existance of a *waiting-waiting* regime an early-time regime in which the interfacial shape becomes suddenly motionless, and remains quasi-static for some finite time. By varying Reynolds number over four



Fig. 2.26. Influence of Reynolds number on the evolution of the liquid ridge r_m in a liquid film of thickness $\varepsilon = 0.05$. The radius of the stationary ridge is $R = R_0 + O(1)$, and the time scale to establish the stationary ridge is $T \approx Re$. The Reynolds numbers are Re = 0 (black line), 10^{-3} (blue line), 10^{-2} (green line), 10^{-1} (red line) and 1 (orange line), and the Marangoni number is Ma = 1. The surfactant front r_s for Re = 0 (black dashed line) is also shown for reference.



Fig. 2.27. Influence of Reynolds number on the evolution of the liquid ridge r_m in a liquid film of thickness $\varepsilon = 10$. The radius of the stationary ridge is $R = R_0 + O(1)$, and the time scale to establish the stationary ridge is $T \approx Re$. The Reynolds numbers are Re = 0 (black line), 10^{-3} (blue line), 10^{-2} (green line), 10^{-1} (red line) and 1 (orange line), and the Marangoni number is Ma = 1. The surfactant front r_s for Re = 0 (black dashed line) is also shown for reference.



Fig. 2.28. Influence of Marangoni number on the evolution of the liquid ridge . Temporal evolution of the location of the liquid ridge r_m (solid lines) and surfactant front r_s (dashed lines) in a viscous film ($Re = 10^{-2}$) of thickness $\varepsilon = 1$. The length scale x(T) and the time scale T are essentially independent of Ma. The Marangoni numbers for the simulations are Ma = 0.1 (red line), 1 (blue line), and 10 (green line).

decades, simulation results enabled the characterizations the length and time scales of the static liquid ridge.

2.5 Conclusion

In this chapter, a direct numerical simulation scheme was developed and used to gain new insight into the dynamics of viscous Marangoni flows. Results from the simulations enabled accurate characterization of different dynamical regimes and their transitions, and uncovered previously unobserved features for Marangoni flows driven by surfactant gradients in highly-viscous fluids.

Simulation results were first validated against both experiments and previous theoretical works in thin films, and then used to analyze the Marangoni dynamics in deep viscous films. By studying a wide range of film thicknesses, the computations tested the accuracy of limiting scaling solutions previously proposed in the literature, and established their limits of applicability. Moreover, necessary correction factors were identified and calculated by contrasting the approximate theoretical solutions against the solutions of the full Navier-Stokes system.

In addition, results lead to the discovery of previously unobserved scaling laws describing the dynamics of purely-viscous Marangoni flows in deep films. Results demonstrate — apparently for the first time — that approaching the Stokes limit $Re \rightarrow 0$, the surfactant spreads faster than previously expected, and the difference with the expected velocity was calculated as a power-law of the film thickness.

Finally, simulations were used to gain new insight into the early-time Marangoni dynamics. Results established, apparently for the first time, the existence of a *waiting-time* regime — a regime in which the interfacial shape becomes suddenly motionless, and remains quasi-static for some finite time despite the presence of strong surface tension gradients.

In addition to the fundamental fluid mechanics interest, the new findings may have important implications for natural and biomedical processes developing in highly viscous environments, including viscous coating, surfactant driven propulsion of microorganisms on biofilms, and the spreading of surface active pulmonary drugs on the lung lining fluid.

3. MARANGONI FLOW IN INERTIAL FILMS: IDENTIFYING REGIMES AND TRANSITIONS

In this chapter, high-fidelity simulations are used to gain new insight into the dynamics of Marangoni flows induced by surfactant concentration gradients. The chapter extends the results of Chapter 2 to arbitrary liquid viscosities. Results enable a thorough quantitative study of the influence of film thickness and material properties on the Marangoni dynamics. The computations test the accuracy of limiting scaling solutions previously proposed in the literature, establish their limits of applicability, and calculate necessary corrections. Moreover, computations enable the construction of master curves in function of measurable physical properties to characterize the transitions between different dynamical regimes. In addition to the fundamental fluid mechanics interest, the new findings have implications for a range of natural and technological processes, ranging from oil pollution remediation to the production of finely tuned emulsions in microfluidic devices.

3.1 Introduction

The dynamics of Marangoni flows generated by gradients of chemical concentration plays a central role in many technological and biomedical processes, ranging from silicon wafer drying during the production of microchips [15] [16] [17] to the spreading of drugs and natural surfactants in the eye and lung [7] [8] [9] [10]. Moreover, Marangoni transport of surface active agents provide opportunities for controlling surfactant coverage — and therefore interfacial properties — of films, bubbles, and droplets with a wide range of applications from film coating [11] [12] to the production of carefully tuned foams and emulsions in microfluidic devices [46] [47]. Previous theoretical works have shown that Marangoni flows driven by surfactant concentration gradients in a liquid film may exhibit two dynamical regimes: an inertial regime that either dominates at early times or does not occur, and a viscous regime that dominates at later times. In general, these regimes have been studied using limiting flow approximations in which either viscous or inertial forces dominate the dynamics. The viscous regime has been largely studied using lubrication approximation [19] [20] [43], while the inertial regime has been studied using boundary layer approximations [26], or high Reynolds number asymptotic approximations [48].

Here, direct numerical simulations are used to gain detailed insight into the dynamics of Marangoni flows in liquid films with arbitrary liquid viscosities. The direct numerical simulations solve the full Navier-Stokes and convection-diffusion system of governing equations, allowing the examination of the competition between all the different forces involved. By following surfactant-induced Marangoni flows for more than five decades in time, and about six decades in Reynolds number, results from the simulations enable a thorough quantitative study of the influence of film thickness, and liquid and surfactant properties on the Marangoni flow dynamics.

First, section 3.3 analyzes the free-surface dynamics of Marangoni flows in thin inertial films. By contrasting the limiting theoretical predictions proposed in the literature against the solutions of full Navier-Stokes system, results establish their limits of applicability. By varying Reynolds number over six decades, simulations enables the calculation of the necessary correction factors. Then, section 3.4 extends the study to Marangoni flows in deep and inertial liquid films. Results lead to the construction of master curves that accurately characterize the transitions between different dynamical regimes.

3.2 System Description

This section summarizes the problem description and governing equations, which were described in more detail in Chapter 2 (section 2.2). The free-surface dynamics of surfactant-induced Marangoni flows is studied here by following the spreading of a drop of insoluble surfactant on the surface of an incompressible liquid film of density ρ and viscosity μ .

At time $\hat{t} = 0$, simulations start with an undisturbed, spatially-uniform liquid film of thickness \hat{H}_0 with the center region covered by a surfactant drop. The surfactant drop has a initial radius of \hat{R}_0 . The initial surface tension in the region covered by surfactant is $\hat{\sigma}_0$, which corresponds to a uniform initial concentration of surfactant $\hat{\gamma}_0$. The system is considered axisymmetric and thus is described using a cylindrical coordinate system (\hat{r}, \hat{z}) as shown in Figure 3.1. The velocity components in r and z directions are \hat{v} and \hat{u} respectively. The height of the gas-liquid interface \hat{h} is a function of both time \hat{t} and radial distance \hat{r} .

In this thesis, the system and results are described in dimensionless numbers. The choice of characteristic velocity scale and characteristic length scales are capillary velocity $\hat{\sigma_0}/\mu$ and initial film thickness $\hat{H_0}$ respectively. Accordingly, the characteristic time scale is $\tau = \hat{H_0}\mu/\hat{\sigma_0}$. The surfactant concentration γ and corresponding surface tension σ are measured in units of initial dimensional concentration $\hat{\gamma_0}$ and initial dimensional surface tension $\hat{\sigma_0}$ respectively. Therefore, the relationships between the dimensional variables and dimensionless variables are given as:

$$h = \frac{\hat{h}}{\hat{H}_0}, \quad r = \frac{\hat{r}}{\hat{H}_0}, \quad \sigma = \frac{\hat{\sigma}}{\hat{\sigma}_0}, \quad \gamma = \frac{\hat{\gamma}}{\hat{\gamma}_0}, \tag{3.1}$$

$$t = \frac{\hat{\sigma_0}}{\hat{H_0}\mu}\hat{t}, \quad (v,u) = \frac{\mu}{\hat{\sigma_0}}(\hat{v},\hat{u}), \quad p = \frac{\hat{H_0}}{\hat{\sigma_0}}\hat{p}$$
(3.2)

where (^) represents dimensional numbers. The aspect ratio between initial film thickness and initial drop radius is defined as:

$$\varepsilon = \hat{H}_0 / \hat{R}_0 \tag{3.3}$$

thus, a large aspect ratio $\varepsilon \gg 1$ describes a film that is deep in relation to the surfactant drop, whereas $\varepsilon \ll 1$ describes a comparatively thin liquid film.



Fig. 3.1. Schematic of surfactant spreading on a liquid film. A drop of surfactant (red) on the surface of a clean liquid film (blue) generates Marangoni flow and interfacial deformation. The dimensionless radius of the spreading surfactant drop is $r_s(t)$, the initial drop radius is R_0 , and the local dimensionless height of the film is h(r,t). The Newtonian liquid has constant density ρ and viscosity μ . The local dimensionless surface tension is $\sigma(r,t)$ and corresponds to a local surfactant concentration $\gamma(r,t)$.

The evolution of the velocity field $\mathbf{v}(v, u)$ and pressure p in the liquid films is calculated by solving the full Navier-Stokes system:

$$\nabla \cdot \mathbf{v} = 0, \tag{3.4}$$

$$Re(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v}) = \nabla \cdot \mathbf{T}.$$
(3.5)

where **T** is the viscous stress tensor (see Equation (2.6)) and Re is the Reynolds number. Since the chosen length scale is \hat{H}_0 and velocity scale is $\hat{\sigma}_0/\mu$, Reynolds number can be written as

$$Re = \frac{\rho \hat{\sigma_0} H_0}{\mu^2},\tag{3.6}$$

which measures the relative significance of the inertial and viscous forces.

The transport of surfactant at the free surface is described by the full convectiondiffusion equation [28] [29] [30], and is solved simultaneously with the full Navier-Stokes system of equations,

$$\left(\frac{\partial\gamma}{\partial t}\right)_s + \gamma(\mathbf{v}_s \cdot \mathbf{n})(\nabla_s \cdot \mathbf{n}) + \nabla_s \cdot (\gamma \mathbf{v}_s \cdot \mathbf{t})\mathbf{t} - Pe^{-1}\nabla_s^2\gamma = 0, \qquad (3.7)$$

The relationship between surfactant concentration and surface tension is described using a linear equation of state [31] [32] [33]

$$\sigma = 1 - Ma(\gamma - 1), \tag{3.8}$$

where Ma is the Marangoni number which characterizes the surfactant strength. A larger Marangoni number creates a greater surface tension gradient and consequently, generates a higher Marangoni stress which drives the Marangoni flow. The Marangoni number is given as:

$$Ma = \frac{d\hat{\sigma}}{d\hat{\gamma}}\frac{\hat{\gamma}_0}{\hat{\sigma}_0}.$$
(3.9)

The governing equations, boundary conditions, and initial conditions for simulations in this chapter are the same as the ones used in Chapter 2 and are discussed in detail in Section 2.2.

3.3 Transitions in the Dynamics of Low-Viscosity Marangoni Flows in Thin Films

The free-surface dynamics of Marangoni flows in thin low-viscosity films are different from that in thin viscous films. The surfactant spreads faster on the surface of an inertial liquid film than on the surface of a viscous film. However, the spreading dynamics in the inertial film change as time progresses, and eventually transition to the slower dynamic characteristic of Marangoni flows in viscous films.

Characterizing the late inertial-to-viscous transition in low-viscosity films is important to predict and ultimately control surfactant coverage. Therefore, it is critical to many natural and biomedical processes, ranging from silicon wafer drying to the production of controled emulsions in microfluidic devices. In this section, solutions of the full Navier-Stokes system are compared against limiting theoretical predictions proposed in the literature to establish limits of applicability and calculate necessary corrections. Finally, results lead to the construction of a master curve that accurately characterize the late inertial-to-viscous transition in thin low-viscosity films.

In this section, Marangoni flows in thin films with different liquid viscosity will be discussed first (Section 3.3.1). Next, the influence of surfactant property on the Marangoni flow dynamics is discussed (Section 3.3.2). The results from the full Navier-Stokes system are compared with limiting theoretical predictions proposed in literature, establish the limits of applicability, and calculate the necessary correction factor. Simulations also enable the accurate characterization of the crossover from the faster inertial dynamics to the slower viscous dynamics (Section 3.3.3).

3.3.1 Influence of Reynolds Number on the Dynamics of Marangoni Flows in Thin Low-Viscosity Films

To gain insight into the influence of inertia on the dynamics of thin films, Figure 3.2 shows the spreading of a drop of surfactant on the surface of three liquid films spanning about four decades in Reynolds numbers. The figure shows the temporal

evolution of the surfactant front r_s for three different Reynolds numbers Re = 0, 10, and 1000 on a thin liquid film with small relative thickness $\varepsilon = 0.05$. For the purely viscous film (Figure 3.2a) and for the moderately inertial film (Figure 3.2b), the simulations (symbols) confirm that the surfactant front follows a power law $t^{1/4}$ with time (black lines), as expected for thin films. Indeed, as predicted by Jensen and Grotberg [43] and discussed in detail in Section 2.3.1 (Equation (2.25)), the scaling $r_s \sim t^{1/4}$ is associated to a thin film regime in which the viscous length scale l_{μ} is much larger than the film thickness ($l_{\mu} \gg 1$), and therefore the dominant (i.e., smaller) length scale is the film thickness.

The dynamics in the film of Figure 3.2c, however, is different from the dynamics in the previous films. When the Reynolds number of the liquid film is Re = 1000, the surfactant drop spreads faster at earlier times $(10^2 < t < 10^3)$ and then transitions to the slower dynamic $t^{1/4}$ at later times $(t > 10^3)$. This transition is marked by a red dot in Figure 3.2c, and the transition time is marked by the red dashed line.

The faster early-time dynamics can be more clearly identified by increasing the Reynolds number, as shown in Figure 3.3. The figure shows the evolution of the surfactant front r_s under the same conditions as the films of Figure 3.2, but for a lower viscosity liquid with Re = 5000. Results from the simulations (symbols) show that the early-time dynamics follow a scaling $r_s \sim t^{3/8}$ with time (dashed line). Together, the results in Figures 3.2 and 3.3 demonstrate that Marangoni flows in thin films ($\varepsilon \ll 1$) can transition to the inertial regime provided that the Reynolds number is sufficiently large.

Indeed, as predicted by Jensen [26], the scaling $r_s \sim t^{3/8}$ corresponds to the inertial regime in which the viscous length scale l_{μ} is small in relation to the film thickness $(l_{\mu} \ll 1)$, and therefore the appropriate vertical length scale is the thickness of the boundary layer below the spreading surfactant drop. The $t^{3/8}$ scaling was characterized by Jensen considering the balance of viscous and Marangoni stresses



front follows a scaling $t^{1/4}$ with time, whereas for the inertial film the surfactant front initially follows a faster dynamics and later transition to the $t^{1/4}$ dynamics. The transition is marked by the red dot and the Re = 10 and (c) Re = 1000. For the purely-viscous film and the moderately inertial film the surfactant corresponding transition time is marked by the red dashed line. Here, the Marangoni number is Ma = 1 and Fig. 3.2. Influence of Reynolds number on the dynamics of Marangoni flows in thin films. Surfactant front r_s (symbols) as a function of time in liquid films with Reynolds number (a) Re = 0, (b) the film thickness $\varepsilon = 0.05$.

[26]. The Marangoni convective flow is driven by Marangoni stress $\nabla_s \sigma$, which can be approximated as

$$\nabla_s \sigma \approx d\sigma/dr \tag{3.10}$$

since the curvature of the liquid film is small. The surface tension σ of the liquid film is related to the concentration of the surfactant through a linear equation of state (Equation (3.8)); therefore, the Marangoni stress can be further written as

$$\nabla_s \sigma \approx Mad\gamma/dr \tag{3.11}$$

with γ being the concentration of the surfactant which, following the scaling analysis by Jensen [26], scales as $\gamma \sim M/r_s^2 \sim \pi \varepsilon^{-2} r_s^{-2}$ in dimensionless form. This yields a Marangoni stress that scales as

$$\nabla_s \sigma \sim Ma\pi \varepsilon^{-2} r_s^{-3}. \tag{3.12}$$

The Marangoni stress is balanced by viscous stress, which can be approximated as dV/dz in dimensionless form, where V is the fluid radial velocity scale, which is approximated by the average velocity of the surfactant front $V \approx r_s/t$. Since in highly inertial films the viscous length scale is smaller than the film thickness, the dominant vertical length scale is the boundary layer thickness $\hat{z} \sim (\mu \hat{t}/\rho)^{1/2}$, or $z \sim (t/Re)^{1/2}$ in dimensionless term. This yields a viscous stress

$$dV/dz \sim r_s R e^{1/2} t^{-3/2}.$$
(3.13)

Finally, including Equations (3.10) to (3.13) in the interfacial stress balance approximated as

$$d\sigma/dr \approx dV/dz$$
 (3.14)

yields a scaling for the surfactant front

$$r_s \sim \left(\frac{\pi^2 M a^2}{\varepsilon^4 R e}\right)^{1/8} t^{3/8}.$$
 (3.15)

The existence of an initial inertial regime in the dynamics of thin films with sufficiently large Reynolds numbers can be further verified by comparing the scaling



Fig. 3.3. Temporal evolution of the surfactant front in thin low-viscosity films. Temporal evolution of the surfactant front r_s in a thin ($\varepsilon = 0.05$) low viscosity (Re = 5000) film with Marangoni number Ma = 1. The surfactant front (symbols) follows a scaling $t^{3/8}$ with time (dashed line).

of Equation (3.15) to the solutions of the full Naviers-Stokes system. According to Equation (3.15), the surfactant front r_s should follow a power law $r_s \sim Re^{-1/8}$ with Reynolds number. This scaling is tested in Figure 3.4. The figure shows the evolution of the surfactant front r_s as a function of scaling coordinate $Re^{-1/8}t^{3/8}$ for a thin film ($\varepsilon = 0.05$) with three different Reynolds numbers Re = 500, 1000, and 5000. After an initial transient, the simulation results (symbols) collapse onto one master curve (black line), confirming the scaling with the Reynolds number $r_s \sim Re^{-1/8}$ in Equation (3.15).

3.3.2 Influence of Marangoni Number on the Dynamics of Marangoni Flows in Thin Low-Viscosity Films

To gain insight into the influence of the Marangoni number on the Marangoni dynamics in thin low-viscosity films, Figures 3.5 and 3.6 show the spreading of three increasingly stronger surfactants on the surface of a thin film with a small relative thickness $\varepsilon = 0.05$. Figure 3.5 shows the temporal evolution of the surfactant front r_s for three different Marangoni numbers Ma = 1, 2 and 3 on a low-viscosity (Re =1000) thin liquid film. For the three Marangoni numbers, the simulations (symbols) show little difference (although the spreading starts slightly earlier as the surfactant strength increases), and confirm that the surfactant front follows a power law $t^{3/8}$ with time (black lines).

According to Equation (3.15), the surfactant front r_s should follow a power law $r_s \sim Ma^{1/4}$ with Marangoni number. This scaling is tested in Figure 3.6. The figure shows the evolution of the surfactant front r_s as a function of scaling coordinate $Ma^{1/4}t^{3/8}$ for the three systems shown in Figure 3.5. After the initial transient period, the simulations (symbols) collapse onto one master curve (black line), confirming the scaling with Marangoni number $r_s \sim Ma^{1/4}$ in Equation (3.15).



Fig. 3.4. Evolution of the surfactant front as a function of scaling coordinates. Location of the surfactant fronts r_s as a function of the coordinate $(Re^{-1/8}t^{3/8})$ in thin liquid films with Reynolds numbers Re = 500 (green), 1000 (blue) and 5000 (red). Simulation results (symbols) confirm the scaling $r_s \sim Re^{-1/8}$ in Equation (3.15). Here, the Marangoni number Ma = 1 and film thickness $\varepsilon = 0.05$.



Surfactant front r_s as a function of time for Marangoni numbers (a) Ma = 1, (b) Ma = 2 and (c) Ma = 3. Simulation results (symbols) confirms that the early-time dynamics follows a scaling $t^{3/8}$ with time (black Fig. 3.5. Influence of Marangoni number on the dynamics of Marangoni flows in thin films. line). Here, Reynolds number Re = 1000 and film thickness $\varepsilon = 0.05$.



Fig. 3.6. Evolution of the surfactant front as a function of scaling coordinate. Location of the surfactant fronts r_s as a function of the coordinate $(Ma^{1/4}t^{3/8})$ for the systems shown in Figure 3.5. The Marangoni numbers are Ma = 1 (green), 2 (blue) and 3 (red). Simulation results (symbols) confirm the scaling $r_s \sim Ma^{1/4}$ in Equation (3.15).

3.3.3 Inertial to Viscous Transition in Thin Low-Viscosity Films

Here, the dynamics of Marangoni flows in thin and inertial films characterized in the previous sections are used to identify the crossover where the Marangoni dynamics transitions from the early-time *inertial dominated dynamics* $r_s \sim t^{3/8}$ to the late-time viscous dominated dynamics $r_s \sim t^{1/4}$.

The existence of a transition from the early-time inertial regime to the late-time viscous regime (see Figure 3.2c) is not evident, but can be rationalized by defining an instantaneous Reynolds number

$$Re^* \equiv \frac{\rho \hat{U} \hat{L}}{\mu} = ReUL. \tag{3.16}$$

which characterizes the relative importance of inertial and viscous forces as the surfactant drop spreads on the surface of the liquid film. As the drop spreads, the appropriate length scale L corresponds to the growing drop radius, and the appropriate velocity scale corresponds to the spreading velocity.

In the inertial regime, the characteristic length L scales as $L = r_s \sim t^{3/8}$, and the characteristic velocity scales as $U = dr_s/dt \sim t^{-5/8}$. According to Equation (3.16), in the inertial regime, the instantaneous Reynolds number should scale with time as

$$Re^* \sim t^{-1/4}$$
. (3.17)

Therefore, as time $t \to \infty$, the instantaneous $Re^* \to 0$, confirming that the inertial Marangoni dynamics cannot remain in the inertial regime as time progresses. Consequently, as the surfactant drop spreads, viscous forces should eventually become sufficiently strong to impact the evolution of the liquid film, and a potential transition of the Marangoni dynamics from the inertial regime to a viscous regime has to be considered (see Figure 3.2c).

As discussed in Section 2.3.1, the viscous regime in thin films has been previously characterized by Jensen and Grotberg [43] using the lubrication approximation as

$$r_s = (16Ma\varepsilon^{-2}t)^{1/4}. (3.18)$$

Similarly, the boundary layer approximation of Equation (3.15) predicts that the inertial regime in thin films follows a power-law scaling that can be extended by including a correction factor as

$$r_s = D_0 \left(\frac{\pi^2 M a^2}{\varepsilon^4 R e}\right)^{1/8} t^{3/8}.$$
 (3.19)

The direct numerical simulations show, however, that the correction factor $D_0 \neq 1$ and has to be calculated.

The value of D_0 is calculated by fitting a scaling line throughout the simulation results, as shown in Figure 3.5 (black lines). Figure 3.7 summarizes the calculated values of the correction factor D_0 for Marangoni flows in thin liquid films ($\varepsilon = 0.05$ and $\varepsilon = 0.1$); by taking the average value, the correction factor for thin films is approximated by $D_0 \approx 1.41$.

The estimated value of D_0 is tested further in Figure 3.8. The figure illustrates the evolution of the surfactant front r_s as a function of scaling coordinate $Bt^{3/8}$, where $B = (\pi^2 M a^2 \varepsilon^{-4} R e^{-1})^{1/8}$ in thin films ($\varepsilon = 0.05$ and 0.1) with a wide range of (large) Reynolds numbers Re = 500, 800, 1000, and 5000. The results from Figure 3.8 are twofold. First, it further confirms the scalings in Equation (3.19) since the simulation results collapse onto one master curve. Second, it confirms the accuracy of the calculated value of D_0 since the Equation (3.19) with $D_0 = 1.41$ fits well throughout the collapsed results (black line).

Having characterized the value of the correction factor D_0 , the crossover time t_c and crossover radius r_c for the inertial-to-viscous dynamical transition for Marangoni flows in thin liquid films ($\varepsilon < 1$) can be readily calculated as

$$t_c = 1.66Re,$$
 (3.20)

$$r_c = 2.27 (MaRe\varepsilon^{-2})^{1/4}, (3.21)$$

by equating Equations (3.18) and (3.19).

Finally, one important consequence of the newly calculated t_c and r_c is that the full Marangoni dynamics for thin low-viscosity films can be re-scaled onto a master



Fig. 3.7. Correction factor D_0 as a function of Reynolds number. The average correction factor for thin, low viscosity films is $D_0 \approx 1.41$. Here, film thicknesses are $\varepsilon = 0.05$ (red) and 0.1 (blue), and the Marangoni numbers are Ma = 1 (square), 2 (circle), and 3 (triangle).



Fig. 3.8. Evolution of the surfactant front as a function of scaling coordinates. Location of the surfactant front r_s as a function of the scaling coordinate $Bt^{3/8}$, where $B = (\pi^2 M a^2 \varepsilon^{-4} R e^{-1})^{1/8}$, in thin films with Reynolds numbers Re = 500 (red), 800 (green), 1000 (blue), and 5000 (grey). Simulation results (symbols) show good agreement with Equation (3.19) using a correction factor $D_0 = 1.41$ (black line). Here, the film thickness is $\varepsilon = 0.05$ (circle) and 0.1 (square), and the Marangoni number is Ma = 1 (hollow symbols) and 2 (solid symbols).

curve. In Figure 3.9, data from a large number of simulations are collapsed on a master curve by simply rescaling the drop radius and time by the crossover values r_c and t_c respectively. Importantly, the temporal evolution of the spreading dynamics for thin low-viscosity films (collapsed symbols) are well described by

$$r/r_c = (t/t_c)^{3/8}, \quad t/t_c < 1,$$
(3.22)

$$r/r_c = (t/t_c)^{1/4}, \quad t/t_c > 1,$$
(3.23)

(dashed lines in Figure 3.9) as a function of film thickness, Reynolds number and Marangoni number using the crossover values calculated from Equations (3.20) and (3.21).

This section presented a numerical analysis of effects of liquid viscosity on the Marangoni dynamics in thin films. Results from the simulations were compared with limiting theoretical scalings proposed in literature to calculate the necessary correction factor. Results from the simulations enabled accurate characterization of the crossover from inertial dynamics to viscous dynamics in the limit of thin films.

3.4 Transitions in the Dynamics of Inertial Marangoni Flows in Deep Films

As in the thin low-viscosity films discussed in the previous section, the dynamics of surfactant spreading in deep films also transition from an inertia-dominated dynamics to a viscous-dominated dynamics as time progresses. Characterizing the inertialto-viscous dynamical transition in deep low-viscosity films is relevant to important technological processes, ranging from oil pollution remediation to the production of finely tuned emulsions in microfluidic devices. In this section, solutions of the full Navier-Stokes system are compared against limiting theoretical predictions proposed in the literature to establish limits of applicability and calculate necessary corrections. Finally, results lead to the construction of a master curve that accurately characterize the late inertial-to-viscous transition in deep low-viscosity films.



Fig. 3.9. Evolution of the surfactant front in reduced coordinates. Evolution of the surfactant front r_s/r_c as a function of t/t_c for the systems of Figure 3.8. Simulation results (symbols) collapse on the master curve $r/r_c = (t/t_c)^{3/8}$ (solid line) and $r/r_c = (t/t_c)^{1/4}$ (dashed line). Here, the film thickness is $\varepsilon = 0.05$ (circle) and 0.1 (square); the Reynolds number Re = 500 (red), 800 (green), 1000 (blue) and 5000 (grey); and Marangoni number Ma = 1 (hollow symbols) and 2 (solid symbols).

3.4.1 Influence of Reynolds Number on the Dynamics of Marangoni Flows in Deep Low-Viscosity Films

To gain insight into the influence of inertia on the free-surface dynamics for Marangoni flows in deep films, Figure 3.10 illustrates the temporal evolution of the surfactant front r_s for three different Reynolds number Re = 0, 10, and 1000 on a deep liquid film with large relative thickness $\varepsilon = 10$. Interestingly, for all three cases, results (symbols) show that the surfactant drops spread at a fast initial rate $t^{3/8}$ and then transition (red dots) to the slower $t^{1/4}$ dynamics (black lines) characteristic of thin viscous films.

However, the transition in the film of Figure 3.10c is slightly different from the dynamics in the two previous films. Indeed, when the Reynolds number is Re = 1000, the dynamical transition occurs at approximately $t \approx 200$ (Figure 3.10c, red dashed line) but the dynamical transitions occur at approximately $t \approx 50$ (Figure 3.10a and Figure 3.10b, red dashed lines) for the films with Re = 0 and Re = 10. Whether the late transition in the film of Figure 3.10c is a result of deep-to-thin dynamical transition as discussed in Section 2.3 or inertial-to-viscous dynamic transition discussed in Section 3.3 is unclear.

This issue can be addresses by examining the influence of Reynolds number. The early time power law $t^{3/8}$ characteristic of a deep-film dynamic is not a function of Reynolds number (see Section 2.3.2, Equation (2.34)), but the power law $t^{3/8}$ characteristic of a inertial dynamic does depend on the Reynolds number (see Equation (3.15)). According to Equation (3.15), the surfactant front r_s should follow a scaling $r_s \sim Re^{-1/8}$ with Reynolds number. This scaling is tested in Figure 3.11. The figure illustrates the evolution of surfactant front r_s as a function of scaling coordinate $Re^{-1/8}t^{3/8}$ for a thin film ($\varepsilon = 0.05$) with three large Reynolds numbers Re = 500, 1000, and 2000. The simulation results collapse onto one curve (symbols), confirming the scaling $r_s \sim Re^{-1/8}$ with Reynolds number (solid line). This results suggest that the dynamical transition shown in Figure 3.10c is an inertial-to-viscous transition.



Evolution of the surfactant front r_s (symbols) as a function of time in liquid films with Reynolds number (a) Re = 0, (b) Re = 10 and (c) Re = 1000. For the three Reynolds numbers the surfactant front initially dots and the corresponding transition time is marked by the red dashed line. Here, the Marangoni number Fig. 3.10. Influence of Reynolds number on the dynamics of Marangoni flows in deep films. follows a faster dynamics and later transition to a slower $t^{1/4}$ dynamics. The transition is marked by the red is Ma = 1 and the film thickness $\varepsilon = 10$.



Fig. 3.11. Evolution of the surfactant front as a function of scaling coordinates. Location of the surfactant fronts r_s as a function of the coordinate $Re^{-1/8}t^{3/8}$ in a deep liquid films with Reynolds numbers Re = 500 (red), 1000 (blue) and 2000 (green). Simulation results (symbols) confirm the scaling $r_s \sim Re^{-1/8}$ in Equation (3.15). Here, the Marangoni numbers Ma = 1 and thickness $\varepsilon = 10$.

3.4.2 Influence of Marangoni number on the Dynamics of Marangoni Flows in Deep Low-Viscosity Films

To gain insight into the influence of the Marangoni number on the Marangoni dynamics in deep low-viscosity films, the spreading of three increasingly stronger surfactants on the surface of a deep film with large relative thickness $\varepsilon = 10$ is illustrated in Figures 3.12 and 3.13.

Figures 3.12 illustrate the temporal evolution of surfactant front r_s for three different Marangoni number Ma = 1, 5, and 10 on a deep liquid films with low viscosity (Re = 1000). Comparing simulation results (symbols) with the $t^{3/8}$ scaling (black lines), the simulations confirm that the surfactant front follows a power law $t^{3/8}$ with time. Results also show the spreading starts slightly earlier as the surfactant strength increases.

According to Equation (3.15), the surfactant front r_s should follow a power law $r_s \sim Ma^{1/4}$ with the Marangoni number. This scaling is tested in Figure 3.13. The figure illustrates the evolution of surfactant front r_s as a function of scaling coordinate $Ma^{1/4}t^{3/8}$ for the systems shown in Figure 3.12. After the initial transient, the simulation results (symbols) collapse onto one single curve confirming the scaling $Ma^{1/4}$ with the Marangoni number (black line).

3.4.3 Inertial to Viscous Transition in Deep Low-Viscosity Films

Here, the free-surface dynamics of Marangoni flows in deep and inertial films characterized in the previous sections are used to identify the crossover where the Marangoni flow dynamics transitions from the faster inertial dynamics — in which the surfactant front r_s follows a power law of $t^{3/8}$ — to the slower viscous dynamics — in which the surfactant front r_s follows a power law of $t^{1/4}$ — as shown in the preliminary results of Figure 3.10c.



Surfactant front r_s as a function of time for Marangoni numbers (a) Ma = 1, (b) Ma = 2 and (c) Ma = 3. Simulation results (symbols) confirm that the early-time dynamics follows a scaling $t^{3/8}$ with time (black Fig. 3.12. Influence of Marangoni number on the dynamics of Marangoni flows in deep films. line). Here, the Reynolds number Re = 1000 and film thickness $\varepsilon = 10$.



Fig. 3.13. Evolution of the surfactant front as a function of scaling coordinates. Location of the surfactant fronts r_s as a function of the coordinate $(Ma^{1/4}t^{3/8})$ for the systems shown in Figure 3.12. The Marangoni numbers are Ma = 1 (green), 5 (blue) and 10 (red). Simulation results (symbols) confirm the scaling $r_s \sim Ma^{1/4}$ in Equation (3.15).

As discussed in detail in Section 2.3.2, the viscous regime in deep films can be characterized as

$$r_s = C_0 (16Ma\varepsilon^{-2}t)^{1/4}, ag{3.24}$$

where $C_0 = 0.64$. Similarly, the boundary layer approximation of Equation (3.15) predicts that the inertial regime in deep films follows a power-law scaling that can be extended by including a correction factor as

$$r_s = D_0 \left(\frac{\pi^2 M a^2}{\varepsilon^4 R e}\right)^{1/8} t^{3/8}.$$
 (3.25)

However, the direct numerical simulations show that the correction factor $D_0 \neq 1$ and has to be calculated.

The value of D_0 is calculated by fitting scaling lines through the simulation results as shown in Figure 3.12 (black lines). Figure 3.14 summarizes the calculated values of D_0 , and clearly identifies two regions based on film thickness ε . The correction factor for thin low-viscosity films is $D_0 \approx 1.41$, as previously discussed in section 3.3.3. On the other extreme, by taking the average value in the deep region $\varepsilon \geq 10$, the correction factor for deep low-viscosity films is estimated as $D_0 \approx 1.12$.

The estimated value value of D_0 is tested further in Figure 3.15. The figure illustrates the surfactant front r_s as a function of the scaling coordinate $Bt^{3/8}$, where $B = (\pi^2 Ma^2 \varepsilon^{-4} Re^{-1})^{1/8}$, for deep films ($\varepsilon = 10, 20$ and 100) with a wide range of (large) Reynolds number Re = 200, 500, 1000, 2000 and 10000. The results from Figure 3.15 are twofold. First, it further confirms the scalings in Equation (3.25) since the results collapse onto one single curve. Second, it confirms the accuracy of the calculated value of D_0 since Equation (3.25) with $D_0 = 1.12$ fits well throughout the collapsed region of the simulation results (black line).

Having characterized the correction factor D_0 for deep films, the crossover time t_c and radius r_c for the inertial-to-viscous transition for Marangoni flows in deep liquid films ($\varepsilon \geq 10$) can be readily calculated by equating Equations (3.24) and (3.25) as

$$t_c = 0.29 Re,$$
 (3.26)



Fig. 3.14. Correction factor D_0 as a function of Reynolds number. The average correction factor for deep low-viscosity films is $D_0 \approx 1.12$. Here, Reynolds numbers are Re = 200 (gray), 500 (green), 800 (blue), 1000 (red), 5000 (cyan), and 10000 (black), and the Marangoni numbers are Ma = 1 (circle), 2 (square), 3 (triangle), 5 (diamond), and 10 (down triangle).



Fig. 3.15. Evolution of the surfactant front as a function of scaling coordinates. Location of the surfactant front r_s as a function of scaling coordinate $Bt^{3/8}$, where $B = (\pi^2 M a^2 \varepsilon^{-4} R e^{-1})^{1/8}$, in deep films with Reynolds numbers Re = 200 (gray), 500 (blue), 1000 (red), 2000 (green), and 10000 (orange). Simulation results (symbols) show good agreement with Equation (3.19) using a correction factor $D_0 = 1.12$ (black line). Here, the film thicknesses are $\varepsilon = 10$ (circle), 20 (square) and 100 (triangle); and Marangoni numbers are Ma = 1 (hollow symbols) and 2 (solid symbols).
$$r_c = 0.94 (MaRe\varepsilon^{-2})^{1/4}.$$
 (3.27)

Finally, one important consequence of the calculated t_c and r_c is that the full Marangoni dynamics for deep and inertial films can be re-scaled onto a master curve. In Figure 3.16, data from a large number of simulations are collapsed on a master curve by rescaling the drop radius and time by the crossover values r_c and t_c respectively. Importantly, the evolution of the spreading dynamics for deep low-viscosity films (collapsed symbols) are well described by

$$r/r_c = (t/t_c)^{3/8}, \quad t/t_c < 1,$$
(3.28)

$$r/r_c = (t/t_c)^{1/4}, \quad t/t_c > 1,$$
(3.29)

(dashed lines in Figure 3.16) as a function of film thickness, Reynolds number and Marangoni number using the crossover values from Equations 3.26 and 3.27.

3.5 Conclusion

In this chapter, a realistic computational model was used to gain insight into the dynamics of Marangoni flows induced by surfactant concentration gradients on liquid films. The chapter extends the highly viscous results of Chapter 2 to low liquid viscosities. Results from the simulation enabled a quantitative study of the influences of film thickness, liquid viscosity, and surfactant strength on the Marangoni dynamics. By varying the Reynolds number over about six decades, and the film thickness for about three decades, the simulations established limits of applicability of theoretical solutions proposed in the literature, and identified necessary corrections. Results lead to the accurate characterization of an inertial-to-viscous crossover in the dynamics of Maranagoni flows in low-viscosity films, and enabled the construction of master curves in function of film thickness, Marangoni number and Reynolds number to represent the full Marangoni dynamics including both viscous and inertial regimes.

In addition to the fundamental fluid mechanics interest, the new findings may have important implications for Marangoni driven processes developing in low-viscosity en-



Fig. 3.16. Evolution of surfactant front in reduced coordinates. Evolution of the surfactant front r_s/r_c as a function of t/t_c for the systems shown in Figure 3.15. Simulation results (symbols) collapse on the master curves $r/r_c = (t/t_c)^{3/8}$ (solid line) and $r/r_c = (t/t_c)^{1/4}$ (dashed line). Here, the film thickness is $\varepsilon = 10$ (circle), 20 (square), and 100 (triangle); the Reynolds number Re = 200 (gray), 500 (blue), 1000 (red), 2000 (green), and 10000 (orange); and Marangoni number Ma = 1 (hollow symbols) and 10 (solid symbols).

vironments, such as silicon wafer drying, oil pollution remediation, and the production of controlled emulsions in microfluidic devices.

4. SUMMARY AND OUTLOOK

In this work, a rigurous computational model was developed to study the free-surface dynamics of Marangoni flows driven by surfactant-concentration gradients. The freesurface model was solved using direct numerical simulation. By simultaneously solving the full Navier-Stokes equations that govern the free-surface hydrodynamics and the full convection-diffusion equation that governs the interfacial transport of surfactant, the direct numerical simulations enabled a better understanding of the fundamental flow physics of Marangoni flows.

The first part of the thesis focused on characterizing Marangoni dynamical regimes in viscous films. The direct numerical simulations enabled a detailed analysis of the microscopic physical mechanisms of surfactant transport, and a comprehensive picture of the macroscopic free-surface flow. After benchmarking the simulation results against experiments and limiting theoretical predictions, the computations were used to study the influence of film thickness on viscous Marangoni flows. By varying film thickness over several decades, the simulations tested the accuracy of scaling solutions previously proposed in the literature, and established their limits of applicability. Necessary corrections were also identified and calculated by comparing the results of the full Navier-Stokes system against the theoretical scalings. Results uncovered previously unobserved scaling laws describing the dynamics of purely-viscous Marangoni flows in deep films. It was found that when approaching the Stokes limit $Re \rightarrow 0$, the surfactant spreads faster than expected from previous works, and the difference with the expected velocity was calculated as a power-law of the film thickness.

The early time dynamics of Marangoni flows in highly-viscous liquid films were also studied using direct numerical simulations. Results established the existence of a *waiting-time* regime during surfactant spreading — an early-time regime in which the interfacial shape becomes suddenly motionless and remains quasi-static for some finite time despite the presence of strong surface tension gradients. Results from the simulations enabled the characterization of both the time and the length scales for the establishment of the stationary regime.

The second part of the thesis extended the study of viscous Marangoni flows to arbitrary fluid viscosities. Results from the simulation enabled a thorough quantitative understanding of the influence of film thickness, liquid viscosity, and surfactant strength on the Marangoni dynamics. By accurately solving the full system of governing equations for a wider range of geometries and material properties, the computations determined the accuracy of limiting scaling solutions previously proposed in the literature for different Marangoni regimes, established their limits of applicability, and computed necessary corrections. Computations also lead to the accurate characterization of the crossover between inertial and viscous regimes in the dynamics of surfactant driven Marangoni flows, enabling the construction of a master curve in function of film thickness, fluid properties and surfactant properties to accurately represent the different Marangoni regimes and their transitions.

In addition to the fundamental fluid mechanics interest, the enhanced understanding of the flow physics of Marangoni flows and the associated transport of chemical species resulting from this research is relevant to important natural and biomedical processes, from the surfactant driven propulsion of microorganisms to the spreading of drugs in the eye and lungs. Controlled Marangoni transport of chemical species is also relevant to a wide range of environmental and technological processes, with applications ranging from coating to cleaning of oil spills, and from drying of silicon wafers to interfacial transport in microfluidic devices. Moreover, precise understanding of the mechanisms of Marangoni transport of surfactants and chemical species at the microscale provides opportunity for tuning the interfacial surfactant coverage, and therefore the interfacial properties, of films, droplets, and bubbles in food, chemical and pharmaceutical industries.

The focus of this work was on computational modeling to characterize the different flow and spreading regimes of an insoluble surfactant on the surface of a Newtonian liquid film. This focus highlights the need for further experimental work to corroborate previously unobserved features uncovered by the simulations, and to extend the numerical study to characterize both the effect of surfactant solubility and non-Newtonian viscoelastic effects on the different Marangoni regimes and their transitions. REFERENCES

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