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Mechanisms of symmetric and asymmetric drainage of foam films

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MECHANISMS OF SYMMETRIC AND ASYMMETRIC DRAINAGE OF FOAM FILMS

by

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ABSTRACT

MECHANISMS OF SYMMETRIC AND ASYMMETRIC DRAINAGE OF FOAM FILMS

by

Jean-Luc Joye

The drainage of horizontal thin liquid films produced from aqueous solutions of ionic surfactants was studied experimentally, using videomicroscopy and interference techniques, for several surfactants in a wide range of concentrations. Two types of drainage were observed: asymmetric and symmetric. The film drainage was found to be much faster in the asymmetric case.

First, axisymmetric drainage was investigated. In this case, a numerical model was developed to simulate the entire drainage process, including the film formation.

The condition for the transition from a nearly "plane-parallel" film to a dimpled film in the absence of disjoining pressure was determined. The ratio of the minimum to maximum thickness in the film and a dimensionless rate of drainage was correlated with the ratio of the maximum possible curvature in the dimple to the curvature in the meniscus.

The presence of disjoining pressure makes a qualitative difference in film drainage. Low electrolyte concentrations in a film containing ionic surfactants produce a repulsive disjoining pressure that inhibits formation of the thin barrier ring and thus of the dimple itself. The film
drains rapidly to its equilibrium thickness. For high electrolyte concentrations, disjoining pressure is dominated by van der Waals attraction. As a result, a thin annular film forms that forces the dimple into a lens with a finite contact angle. These types of behaviors were observed experimentally.

Then, the mechanisms of asymmetric thin film drainage were investigated. A simple linear stability analysis and a two dimensional numerical model were developed and showed that asymmetric drainage is caused by a hydrodynamic instability that is produced by a surface-tension-driven flow and stabilized by surface viscosity, surface diffusivity and system length scale. A criterion for the onset of instability causing asymmetric drainage was determined. Experiments performed on aqueous solutions of SDS and SDS:1-dodecanol showed the strong dependence of the drainage type on the surface shear viscosity. Experimental results were found to be in good agreement with the stability predictions.
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NOMENCLATURE

Notation

\begin{align*}
a &= \text{dimensionless group} \\
A &= \text{Hamaker constant, J} \\
b &= \text{dimensionless group} \\
c &= \text{dimensionless group} \\
C &= \text{constant, N m}^{-1} \\
C_a &= \text{capillary number} \\
C_{el} &= \text{electrolyte concentration, mol/l} \\
CR &= \text{ratio of maximum possible curvature in the dimple to the curvature in the meniscus} \\
C_r &= \text{crispation number} \\
d &= \text{dimensionless group} \\
D_s &= \text{surface diffusivity, m}^2 \text{s}^{-1} \\
E_d &= \text{dimensionless elasticity} \\
g &= \text{acceleration due to gravity, m s}^{-2} \\
H &= \text{dimensionless half-thickness} \\
h &= \text{half-thickness of the film, m} \\
h_0 &= \text{half thickness at the film center, m} \\
h_{Br} &= \text{thickness given by the Bretherton theory, m} \\
h_i &= \text{half-thickness separating the two initial menisci, m} \\
h_{\text{min}} &= \text{half-thickness at the ring, m} \\
h_o &= \text{uniform half-thickness solution of the steady state solution, m} \\
h_R &= \text{half thickness at the film radius, m} \\
k &= \text{wave number, m}^{-1} \\
K &= \text{dimensionless k} \\
k_b &= \text{Boltzman constant, J/K} \\
M_a &= \text{Marangoni number} \\
n &= \text{number of counterions per cubic centimeter}
\end{align*}
$n_i$ = number of periodicity in initial perturbation
$N_1$ = dimensionless group
$N_2$ = dimensionless group
$N_3$ = dimensionless group
$N_4$ = dimensionless group
$N_5$ = dimensionless group
$p$ = bulk pressure, Pa
$P$ = dimensionless bulk pressure
$P_c$ = capillary pressure, Pa
$P_d$ = Pressure in the dimple, Pa
$P_g$ = gas pressure, Pa
$P_{Re}$ = pressure given by the Reynolds' theory, Pa
$Q$ = withdrawal rate, m$^3$/s
$R_f$ = film radius, m
$r$ = radial position, m
$R$ = dimensionless radial position
$R_a$ = approximate film radius, m
$R_c$ = radius of the capillary wall, m
$R_d$ = radius of curvature in the dimple, m
$R_s$ = radius of the initial hemispherical menisci, m
$s$ = slope at the capillary wall
$S_{d+sh}$ = dimensionless surface dilational+shear viscosity group
$S_{sh}$ = dimensionless surface shear viscosity group
$T$ = dimensionless time
$t$ = time, sec
$t_1$ = time of withdrawal, sec
$t_{min}$ = minimum time of withdrawal for film formation, sec
$T^*$ = temperature, K
$U$ = dimensionless x-component of surface velocity
$U_m$ = meniscus velocity during withdrawal, m/sec
$V$ = dimensionless y-component of surface velocity
$v$ = bulk velocity, m s$^{-1}$
$va$ = valence
\( V_c \) = volume per unit length under a spherical cap of radius \( R_d \) and height \( h_0 \)

\( V_{F-M} \) = rate of thinning given by Frankel-Mysels' theory, m/s

\( V_{Re} \) = rate of thinning given by Reynolds' theory, m/s

\( v_s \) = surface velocity, m s\(^{-1}\)

\( W \) = dimensionless concentration

**Greek Letters**

\( \alpha \) = concentration coefficient of interfacial tension, m\(^2\) s\(^{-2}\)

\( \beta \) = time growth constant, s\(^{-1}\)

\( \beta' \) = dimensionless time growth constant

\( \delta \) = thickness of the adsorbed monolayer, m

\( \varepsilon_d \) = dielectric constant of the solution

\( \phi \) = contact angle, \(^\circ\)

\( \Gamma \) = surfactant concentration at the surface, Kg m\(^{-2}\)

\( \Gamma_{eq} \) = equilibrium surfactant concentration at the surface and at rest, Kg m\(^{-2}\)

\( \kappa \) = inverse Debye length, m\(^{-1}\)

\( \mu \) = bulk viscosity, Kg m\(^{-1}\) s\(^{-1}\)

\( \mu_d \) = surface dilational viscosity, Kg s\(^{-1}\)

\( \mu_s \) = surface shear viscosity, Kg s\(^{-1}\)

\( \Pi \) = disjoining pressure, Pa

\( \Pi_w \) = disjoining pressure due to van der Waals forces, Pa

\( \Pi_e \) = disjoining pressure due to electrical double layer repulsion forces, Pa

\( \Pi_s \) = disjoining pressure due to short range repulsion forces, Pa

\( \Theta \) = dimensionless group

\( \theta \) = dimensionless group

\( \rho \) = density, Kg m\(^{-3}\)

\( \sigma \) = interfacial tension, N m\(^{-1}\)

\( \psi \) = electrical potential at the surface, mV
List of Superscripts
\( ss \) steady state solution

List of Subscripts
\( x \) vector component in x-direction
\( y \) vector component in y-direction

List of Accents
\( \bar{\cdot} \) average value
\( \sim \) perturbation around steady state solution
\( \wedge \) amplitude of perturbations
CHAPTER ONE
INTRODUCTION

Thin liquid films were probably first observed in the form of soap bubbles. The qualitative observations made by Newton (1) and Gibbs (2) revealed that the walls of the soap bubbles grow thinner in time and pass through thicknesses of the order of visible light wavelength. Then different colors appear due to the interference of light reflected from the front and back interfaces. When the thinning process is advanced, thin spots are formed and appear as black spots which are sometimes very unstable. The interest in thin liquid films has kept growing because of their importance to the understanding of dispersed fluid systems. As two drops or bubbles approach one another a film forms between them. The coalescence of the dispersion is directly related to the drainage time and the stability of these films.

An emulsion is defined as a liquid phase dispersed in another liquid phase. Emulsions are important in such diverse industrial operations as waste water treatment and liquid-liquid extraction (3).
A gas phase dispersed in a liquid is called a liquid foam. Foams have various scientific and technological applications (4). For example, because of their low density and their low thermal conductivity, foams have been useful in thermal insulation and fire fighting. Also foaming can be used to increase fractional conversion in gas-liquid reactions (Triandafilidi, 1958) (5).

Recently, in enhanced oil recovery, foam has been used as a mobility control agent. During gas injection recovery process large amounts of oil are bypassed. For example, in steam injection projects, steam channels or fingers through the formation because of its high mobility. In order to alleviate this problem a dilute aqueous surfactant solution is injected with steam. For suitable conditions thin liquid films are generated, retarding flow of steam through certain pathways and therefore reducing its mobility. In 1961, Fried (6) showed that the injection of aqueous surfactant solutions could reduce drastically gas mobility through porous media.

Hirasaki (7), Chambers and Radke (8) have recently reviewed current knowledge of basic mechanisms of foam flow. The mechanism of initial formation and subsequent drainage of thin liquid films leading to their breakage are major inputs to the population balance that predicts the average bubble size or foam texture, a key factor influencing the reduction in gas mobility. Another important parameter is the capillary pressure, i.e., the pressure difference which exists between liquid and gas during foam flow. It depends on, among other things, the surface tension of the liquid and on the relative amounts of liquid and gas present.
Khatib et. al. (9) measured capillary pressures in glass bead packs during steady foam flow. They found that drastic foam collapse was occurring at a specified capillary pressure, called "limiting capillary pressure", $P_{lc}$. In other words, the coalescence of flowing foam is large for capillary pressure above $P_{lc}$ and minimal below $P_{lc}$. Aronson et. al. (10) found that the limiting capillary pressure is strongly related to the critical capillary pressure above which a single static liquid film collapses. However Khatib et. al. (9) reported that limiting capillary pressures were also dependent on the gas flow rate and absolute permeability in addition to the critical capillary pressure of a single static liquid film. This last observation indicates that dynamic effects are also important in the stability of foam flowing through porous media.

In this thesis, the subject of interest is the drainage of thin films leading to their breakage and thus to the coalescence of dispersions. A thin liquid film consists of two surface layers bounding a liquid interior. The surface active material, present in the liquid phase, is preferentially adsorbed at the surface. A typical diagram of a liquid film is shown figure I-1. The thinning of the liquid film is governed by forces within the film which are discussed in the following section.
I-1 Forces in thin liquid films

I-1-a Capillary Pressure

The main driving force for film drainage is the capillary pressure. In the case of an axisymmetrical film, two regions can be observed (see Fig I-1). The first region is located near the center of the film where the curvature of the interface is small. Thus according to the Young-Laplace equation, the pressure in the first region is nearly equal to the pressure in the disperse phase. The second region, located at the periphery of the
film, is called the meniscus region or Plateau border. Here the shape of the interface is concave and, according to the Young-Laplace equation, the pressure in the meniscus region is then less than that in the disperse phase. The pressure difference between the center of the film and the meniscus causes the fluid to drain out of the film. The capillary pressure is defined as the pressure difference between the disperse phase and the liquid in the meniscus region. For a horizontal axisymmetrical planar film of radius $R_f$ formed in a capillary ring of internal radius $R_c$, neglecting gravity effects, Exerowa (11), expressed the capillary pressure $p_c$ as:

$$p_c = 2\sigma \frac{R_c}{R_c^2 - R^2}$$

(1-1)

where $\sigma$ is the interfacial tension. Note that for $R_f<<R_c$ one gets:

$$p_c = \frac{2\sigma}{R_c}$$

(1-2)

I-1-b Disjoining Pressure

Studies on film drainage indicate that when a film reaches a thickness of about 100 nm., other forces besides gravity and capillary forces influence its drainage. Such forces have a molecular origin and operate within the film. Their influence is expressed as a pressure, $\Pi$,
called by Derjaguin (12), disjoining pressure. By definition, $\Pi$ is
assumed positive when it resists film thinning. In an equilibrium, flat
film, the disjoining pressure $\Pi$ is equal to the capillary pressure.

There are two major components of the disjoining pressure. The
first component is the London-van der Waals attraction term which acts
to thin a symmetrical film. Using the theory of London (13), which gives
the interaction energy between two atoms, one can express the van der
Waals disjoining pressure $\Pi_w$ as a function of the film
thickness $2h$ (14) (15).

$$\Pi_w = -\frac{A}{6\pi(2h)^3} \quad (1-3)$$

$A$ is the Hamaker constant (16), which can be calculated or
determined experimentally. Sheludko found an average value for the
Hamaker constant of $6 \times 10^{-12}$ erg for non-aqueous films in air (17) (18)
and about $7.5 \times 10^{-13}$ erg for aqueous films (19). Lyklema and Mysels
(20), using equilibrium aqueous foam films, obtained a value of $6 \times 10^{-13}$
erg for the Hamaker constant.

In the case of an aqueous surfactant solution, the second
component of the disjoining pressure is the electrical double-layer
repulsion. The interfaces of films often bear a charge that results from
the adsorption of charged surfactant molecules on the surfaces. A
double-layer system is thus established in which the surface charge is
balanced by the net charge residing in a diffuse layer of counterions that
extend from the surface into the interior. For films thinner than about
100 nm, the electrostatic repulsion due to the diffuse layer of counterions
becomes significant. Verwey and Overbeek (21), Deryagin and Landau (22) gave a good approximation for the pressure $\Pi_e$ due to electrostatic repulsion:

$$\Pi_e = 64nkT_0 \Theta^2 \exp(-\kappa(2h - 2\delta))$$  \hspace{1cm} (1-4)

where $n =$ number of counterions per cubic centimeter in the bulk solution.

$\Theta = \tanh(ze\psi/4kT^*)$

$\kappa^{-1} = (8\pi\varepsilon_0 z^2 n/\varepsilon_0 kT^*)^{-1/2}$

$2h =$ thickness of the film

$\delta =$ thickness of the adsorbed monolayer

$z =$ valency

$e =$ electronic charge

$\varepsilon_d =$ dielectric constant for the solvent

$\psi =$ potential at the interface

$\kappa^{-1}$ is called the Debye-Hückel characteristic length.

With the combined effect of the capillary pressure and disjoining pressure, one finds that a film can reach an equilibrium thickness if electrical forces are strong enough to balance the combined effect of capillary pressure and the van der Waals forces (see section III-5-b).

Such films are called "common black films" (17) (23). In contrast, if electrical forces are weak, the equilibrium thickness of very thin liquid films called, "Newton black films" or "Perrin films", is determined by the
short range-repulsive disjoining pressure, which prevents further thinning (17) (23) (24). This short range-repulsive pressure is called the structural or hydration disjoining pressure. The Derjaguin, Landau, Verwey, Overbeek (DLVO) theory fails to explain the stability of "Newton black films". Kashiev (25) has shown that the theory of rupture by hole nucleation of a bilayer foam can predict the stability of "Newton black films".

Recently, in the case of an aqueous surfactant solution above the critical micelle concentration, it has been found that stepwise drainage, which involves two or more black films of different thicknesses, occurs. The reason for this phenomenon is that the micelles of ionic or nonionic surfactant in the aqueous solution acquire an ordered structure which provides an additional disjoining pressure term, due to the micellar interactions in the film solution (26, 27).

**I-2 Kinetics of Thinning**

Numerous investigators have developed models describing the transport processes that take place during drainage of liquid from a film. The simplest approach is to apply the Reynolds (28) theory for the flow of a Newtonian fluid between two parallel plane discs forced towards one another. Enough surfactant is present that no tangential flow occurs at the film surface (rigid surface model). The flow is symmetrical with
respect to the two surfaces. The radius R_f of the flat portion is much greater than the film thickness 2h (R_f >> 2h, lubrication approximation). The fluid flow is then governed by the following equations:

\[ \frac{\partial p}{\partial r} = \mu \left( \frac{\partial^2 v_r}{\partial z^2} \right) \quad (1-5) \]

\[ \frac{\partial p}{\partial z} = 0 \quad (1-6) \]

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r v_r \right) + \frac{\partial v_z}{\partial z} = 0 \quad (1-7) \]

where p is the pressure in the flat portion of the film, v_r and v_z are fluid velocities along the coordinates r and z, \( \mu \) is the dynamic viscosity, \( \Pi \) the disjoining pressure. Solving the above system one gets the Reynolds velocity of thinning of the liquid film \( V_{RE} \)

\[ V_{RE} = - \left( \frac{\partial h}{\partial t} \right) \quad (1-8) \]

\[ V_{RE} = \frac{8h^3 \Delta p}{3\mu R_f^2} \quad (1-9) \]

\[ p_c = p_g - p_l, \Delta p = p_c - \Pi \quad (1-10) \]

where \( \Delta p \) is the pressure difference causing drainage, \( p_g \) the pressure in the disperse phase, \( p_l \) the pressure in the liquid and \( p_c \) is the capillary
pressure. The Reynolds theory has been used with various degrees of success by several authors (29) (30) (31). Wasan and Malhotra (32) extended the application of the Reynolds model by accounting for flow in the meniscus region as well as the effect of van der Waals forces. Mysels et. al (1959) (33) found that slow drainage occurs in liquid films with immobile surfaces and fast drainage occurs in those with mobile surfaces. This latter observation leads one to conclude that thin film drainage depends strongly upon the properties of the film surface. The surface properties include: surface tension, surface tension gradient, surface diffusion, surface composition, and surface rheological properties, such as surface shear and dilational viscosities.

In order to describe the film drainage with mobile surfaces two major boundary conditions at the film surface are needed. The first is the surfactant mass balance at the film surface (see ref (34)). As the liquid flows out of the film it carries away the surfactant adsorbed at the surface (convective flux), thus perturbing the equilibrium distribution. Additional fluxes such as surface diffusive flux, bulk fluxes from the film and the disperse phase are generated to restore the equilibrium distribution. The sum of all the fluxes constitutes the surfactant mass balance at the film surface. The second boundary condition is the tangential stress balance at the film surface. The difference in surfactant concentration along the surface results in different values of the surface tension along the surface, which produce a force opposite to the liquid flow. Also, during the thinning of the film, the surfactant monolayer adsorbed at the surface may be subject to dilating and shearing
deformations which produce surface stresses. The sum of the above surface stress, the tangential stress from the disperse phase, and the tangential stress from the liquid in the film constitutes the tangential stress balance at the surface. A complete formulation of the tangential stress balance can be found in reference (35) (see chapter V).

Other researchers, such as Barber and Hartland (36), Ivanov (34), Tambe and Sharma (37) developed hydrodynamic models describing film drainage based on the Reynolds model but accounting, in various degrees of detail, for some of the surface properties listed above.

Observations have shown that most foam or emulsion films are of non uniform thickness. The central part of the film is thicker than its periphery. Thus a "dimple" is formed, entrapped by a thinner "barrier ring." The first hydrodynamic theory for the profile and evolution of a dimple was developed by Frankel and Mysels (38), who presented expressions for the thickness at the center of the film and at the barrier ring. The calculated rate of thinning at the barrier ring was nearly equal to the one predicted by the Reynolds model, whereas the rate of thinning at the center of the film was much lower. The results were in reasonable agreement with subsequent experiments carried out by Platikanov (24).

Hartland (39) presented a solution for symmetrical film drainage. He assumed that the center of the film was a spherical cap and that the profile outside the film border was independent of time. Later, Hartland and Robinson (40) developed an improved solution, assuming that the film interface was parabolic. Jain and Ivanov (41) introduced a very simplified model where the "barrier ring" was considered to be a layer of
small but uniform thickness $h_b$ bounded by two thicker regions representing the dimple, which was assumed to be a spherical cap, and the outer meniscus.

Numerical solutions for the drainage of a dimpled film have been carried out by Lin and Slattery (42). The results are in good agreement with Platikanov's observations (43) when the effects of disjoining pressure are negligible. Chen and Slattery (44) (45) extended the model developed by Lin and Slattery (45) to account for the effect of disjoining pressure. These numerical solutions simulated only the drainage of a dimple already formed. Babak (46) developed a criterion for dimple formation in the case of two air bubbles or two liquid drops in a liquid medium brought together at a velocity $V$ by exerting a known pressure force on one of the fluid particles.

Thin film drainage is not limited to the case of axisymmetric flow. Experimental studies indicate that drainage is frequently asymmetric (33, 47). The reasons for this behavior are not well understood. However it is known that asymmetric drainage is associated with mobile films, greatly increases the rate of film drainage and can thus influence the rate of foam or emulsion coalescence.

Mysels et al (33) were the first to investigate in detail the different types of thin film drainage, concentrating on vertical films formed by withdrawal of glass frames from pools of surfactant solutions. They observed mobile films which drained in minutes and showed turbulent motions along the edges and rigid films which drained in hours and showed little or no motion. They proposed that the rapid drainage
and turbulence seen for the mobile films were the result of "marginal regeneration", a phenomenon in which thick film flowed into the Plateau borders near the legs of the frame at some elevations owing to the greater suction force exerted on thick films by the low pressure in the borders. Simultaneously, thin film was pulled out of the borders at other elevations to maintain constant surface area for the overall film. Prins and van Voorst Vader (48) and Lucassen (49) showed that marginal regeneration caused by this mechanism would be suppressed in systems having high surface dilational modulus. Hudales and Stein (50, 51) observed marginal regeneration in mobile, vertical films and made measurements of film thickness as a function of position and time. Baets and Stein (52) described experimental observations of a phenomenon similar to marginal regeneration that developed at the base of their vertical films. Based on these observations Stein (53, 54) proposed a modified mechanism for marginal regeneration which, in essence, attributed it to a hydrodynamic instability. However, no quantitative stability analysis was given.

In this thesis, Objectives are: to improve understanding of dimple formation and behavior during symmetric drainage: to determine the reasons causing asymmetric drainage and find a criterion that predicts the transition from symmetric to asymmetric drainage as a function of surfactant properties.

Following a description of the experimental technique for studying thin film drainage in chapter two, theoretical and experimental results on axisymmetric film drainage are given in chapter three. First, the
investigation is limited to the dimple formation and behavior during axisymmetrical film drainage which is a prerequisite in determining the transition to asymmetrical drainage. We develop a model to describe the entire process of dimple formation and drainage for the experimental technique used by Scheludko and Exerowa (15) to study thin liquid films. The drainage is assumed to be symmetric and the film interfaces to be immobile. In the absence of disjoining pressure, the transition from nearly "plane-parallel" to dimpled film as well as the drainage rate are correlated in terms of a single dimensionless parameter. The model also includes the effects of disjoining pressure. In this case, results are in qualitative agreement with experiments, for both low and high electrolyte contents in the film.

Then, the results of our experimental investigation on asymmetric film drainage are given in chapter IV. In chapter V, a simple analytical linear stability analysis and in chapter VI a two dimensional numerical model are developed to describe the mechanisms of surface instability causing asymmetric drainage. Asymmetric drainage in circular films and marginal regeneration and the behavior observed by Baets and Stein (52) in vertical films all stem from the hydrodynamic instability described by the linear stability analysis and the numerical simulator. The models predict that large surface shear and dilational viscosity, large surface diffusivity and small system length reduce or eliminate the surface instability. A criterion determining the transition from axisymmetric to asymmetric drainage is then deduced. Results are in good agreement with experiments.
CHAPTER TWO

EXPERIMENTAL PROCEDURE

Experiments on film drainage are conducted using a video microscopy system. Thin liquid film thicknesses are measured using the interference method, proposed by Derjaguin (55) and Scheludko and Exerowa (15). A specially designed glass cell is used to form thin liquid films and is shown figure II-1.

- Figure II-1: Diagram of the glass cell
It was given to us by A. D. Nikolov and consists of a horizontal glass ring, having a radius of 1.8 mm, fused to a capillary tube. The ring and part of the capillary tube, which is connected to a syringe pump though a rubber tube, are enclosed in a glass cell. In the case of liquid-gas systems, evaporation can affect very much the rate of the film drainage and must be avoided. It can be suppressed by pouring a small quantity of water into the bottom of the glass cell and by covering the cell. The surrounding atmosphere is then saturated in water. Liquid films are formed in the central portion of the ring by withdrawing an aqueous surfactant solution, placed earlier on the ring (figure II-2).

That procedure presents the following advantages:
- The same apparatus can be used, as well, to study liquid-liquid systems (oil-surfactant solution, for example), (56), just by pouring another liquid phase (oil) into the cell.
- Films of different sizes can be formed, depending on the amount of liquid withdrawn.
- The rate of withdrawal is controlled by the syringe pump and can be set at any desired value.

In order to collect information concerning film thickness and profile, the cell is placed on the microscope stage (Nikon Optiphot-Pol). Monochromatic light (wave length 546.1 nm) is directed downward toward the film. Light waves reflected from the top and the bottom surfaces of the film interfere. The interference patterns, resulting from the film drainage, are recorded on videotape. The schematic of the experimental set-up is shown figure II-3.
Figure II-2. Film, of radius $R_f$, formed in a capillary ring of radius $R_c$
Figure II-3. Experimental set-up diagram.
The magnification of the objective used is 20X. The use of a video scaler (IV-550) as well as a time generator (Cypter BTX) provides information on the film profile as a function of position and time.

The thickness of the film can be determined using the formula derived by Scheludko (17).

For thicknesses greater than 20nm:

\[
\sin^2 \left( \frac{2\pi n}{\lambda} (2h) \right) = \Delta \tag{2-1}
\]

with:

\[
\Delta = \frac{J - J_{\text{min}}}{J_{\text{max}} - J_{\text{min}}}
\]

\(\lambda\) is the wavelength of the monochromatic light, \(n\) the refractive index of the aqueous surfactant solution, \(h\) the half thickness of the film and \(J\) represents the light intensity.

The resulting image of the film shows, (in the case of axisymmetric drainage), concentric Newton rings of maximum and minimum intensity.

Maximum intensity fringes occur at \(2h = \lambda/4n, 3\lambda/4n, 5\lambda/4n, \ldots\), and minimum intensity fringes occur at \(2h = 0, \lambda/2n, \lambda/n, 3\lambda/2n, \ldots\).

A qualitative profile of the film can be obtained by determining the radial location of the minimum and maximum intensity fringes. Digital image processing can be used to determine the intensity ratio \(\Delta\) as a function of radial position and thus generate quite accurate film profiles.

Experiments were conducted on aqueous foam drainage with different surfactants. Deionized and distilled water was used to prepare
the surfactant solutions. Several surfactants exhibited asymmetric drainage at all times. However other surfactants, such as AOS 16-18, alpha olefin sulfonate with carbon chain length of 16-18 and some surfactant mixtures drained axisymmetrically for a range of concentrations. These results are discussed in subsequent chapters.
CHAPTER THREE

AXISYMMETRICAL FILM DRAINAGE WITH IMMOBILE INTERFACES

In this section, we assume that the film drainage is axisymmetrical with immobile interfaces. Our objective is to simulate the film formation and drainage according to the experimental procedure. As discussed in the previous section, an aqueous solution is placed inside the capillary ring. The thin liquid film is formed by withdrawing fluid at a certain rate, during a time $t_1$. Then the liquid withdrawal is stopped and the liquid film drains due to the capillary suction.

III-1 Statement of problem:

To keep the problem as simple as possible we made the following assumptions:
1.) The drainage is axisymmetric. The thickness of the film is considered to be $2h$
2.) The liquid is an incompressible Newtonian fluid with constant viscosity.
3.) The pressure $p_g$ in gas (or in the disperse phase) is independent of time and position.
4.) The effect of mass transfer on the velocity distribution is neglected.
5.) All inertial effects are neglected.
6.) The effect of gravity is neglected.
7.) There is enough surfactant present in the system so that the resulting interfacial tension gradients can maintain the tangential components of the velocity at the surface equal to zero. However, variations in surface tension in position and time are small enough so that the surface tension is considered constant in the normal stress boundary condition.
8.) The flow obeys the lubrication approximation.
9.) The governing equations derived from the lubrication approximation can be used in the meniscus region, because the flow causes negligible departure from the Young-Laplace equation.
10.) The interface forms a non-zero contact angle with the capillary wall. When the liquid wets the capillary wall, we assume the contact angle to be small but finite. The use of a non-zero contact angle avoids the numerical complications of an infinite slope at the capillary wall.
11.) In the initial state the liquid is bounded by a pair of static hemispherical menisci of radius of curvature $R_S$, separated by a distance $2h_i$ (see figure III-9).
III-2 Governing equations

In the lubrication approximation, the Navier-Stokes equation can be simplified to the following form:

\[ \frac{\partial p}{\partial r} = \mu \left( \frac{\partial^2 v_r}{\partial z^2} \right) \]  \hspace{1cm} (3-1)

\[ \frac{\partial p}{\partial z} = 0 \]  \hspace{1cm} (3-2)

and the mass conservation equation is:

\[ \frac{\partial h}{\partial t} = - \frac{1}{r} \frac{\partial}{\partial r} (r \ h \ \bar{v}_r) \]  \hspace{1cm} (3-3)

with \( \mu \) being the viscosity of the liquid, \( h \) the half thickness of the film, \( p \) the pressure in the film, \( v_r \) the radial velocity, \( \bar{v}_r \) the average value over the thickness, \( t \) the time.

From assumptions 1) and 7):

\[ v_r (h) = 0 \]  \hspace{1cm} (3-4)

\[ \frac{\partial v_r}{\partial z} = 0 \text{ at } z=0 \]  \hspace{1cm} (3-5)

Integrating twice equation (3-1) with respect to \( z \), knowing that \( p \) is only a function of \( r \), one finds that the velocity \( v_r \) can be written as:
\[ v_r = \left( \frac{z^2 - h^2}{2\mu} \right) \left( \frac{\partial p}{\partial r} \right) \]  \hspace{1cm} (3-6)

The average velocity can be obtained from equation (3-6):

\[ \overline{v_r} = - \left( \frac{h^2}{3\mu} \right) \left( \frac{\partial p}{\partial r} \right) \]  \hspace{1cm} (3-7)

Substituting equation (3-7) into equation (3-3), we obtain:

\[ \frac{\partial h}{\partial t} = \frac{1}{3\mu} \frac{1}{r} \left( \frac{\partial}{\partial r} \left( r h^3 \left( \frac{\partial p}{\partial r} \right) \right) \right) \]  \hspace{1cm} (3-8)

In view of assumption 4), we do not need to consider the transport of surfactant from the liquid phase onto the interface. Hence, we do not need to formulate the surfactant conservation equations for the liquid phase and surfactant mass balance at the interface.

Since we assumed immobile interfaces, the tangential stress boundary condition is not necessary. With assumption 6), the normal stress boundary condition at \( z=h \) reduces to

\[ p_g - p = \sigma \frac{1}{r} \frac{\partial}{\partial r} (r \sin \theta) + \Pi(2h) \]  \hspace{1cm} (3-9)
where \( \sin \theta = \frac{\frac{\partial h}{\partial r}}{\left(1 + \left(\frac{\partial h}{\partial r}\right)^2\right)^{\frac{1}{2}}} \)

and \( \sigma \) is the equilibrium interfacial tension between the liquid and the dispersed phase. \( \Pi \) is the disjoining pressure and is the sum of three different terms:

\[
\Pi = \Pi_w + \Pi_e + \Pi_s
\]  

(3-10)

\( \Pi_w \) is the van der Waals attraction term and is given by equation (1-3). \( \Pi_e \) is the pressure due to electrostatic repulsion and is given by equation (1-4). \( \Pi_s \) is the short-range repulsion term and can be expressed as:

\[
\Pi_s = C_1 \exp(-C_2(2h))
\]  

(3-11)

\( C_1 \) and \( C_2 \) are constants and are chosen such that the disjoining pressure curve has almost an infinite slope at a thickness \( 2h \) of 30 Å corresponding to the thickness of a Newton black film for a typical surfactant.

Due to the natural symmetry of the system, we have at \( r=0 \)
\[
\frac{\partial h}{\partial r} = 0 \quad (3-12)
\]

\[
\frac{\partial p}{\partial r} = 0 \quad (3-13)
\]

According to assumption 10.), the interface forms with the capillary wall a non-zero contact angle, independent of time:

\[
\frac{\partial h}{\partial r} = s = \text{constant} \quad \text{at } r = R_c \quad (3-14)
\]

s is chosen large enough so that the numerical solution is not sensitive to s. A typical value of s is 5.

During the time of withdrawal \( t_1 \), the withdrawal rate Q is constant and is equal to the flux at the capillary wall. For \( 0 < t < t_1 \) we have:

\[
-\frac{2\pi R_c h^3}{3\mu} \left( \frac{\partial p}{\partial r} \right) = Q \quad \text{at } r = R_c \quad (3-15)
\]

When the withdrawal is stopped, a no flow boundary condition at the capillary wall is imposed. For \( t > t_1 \) we have:

\[
\frac{\partial p}{\partial r} = 0 \quad \text{at } r = R_c \quad (3-16)
\]

In order to integrate equations (3-8) and (3-9) an initial condition is needed. According to assumption 11.) and Figure II-2 the initial profile is given by:

\[
r^2 + (h - (R_s + h_i))^2 = (R_s)^2 \quad (3-17)
\]
$h_i$ is the initial half-thickness at the center. $R_s$ is the radius of the hemispherical menisci and is chosen so that the slope at the capillary wall corresponds to the slope in (3-14). It can be expressed as:

$$R_s = R_c \sqrt{\frac{1+s^2}{s^2}} \quad \text{(3-18)}$$

Equations (3-8) and (3-9) can be made dimensionless by using the following dimensionless quantities:

$$R = \frac{r}{R_c}, \quad H = \frac{h}{R_c}, \quad T = \frac{\sigma t}{3\mu R_c}, \quad P = (p-p_g) \frac{R_c}{\sigma}$$

Equations and boundary conditions become:

$$\frac{\partial H}{\partial T} = \frac{1}{R} \frac{\partial}{\partial R} \left( RH^3 \frac{\partial P}{\partial R} \right) \quad \text{(3-19)}$$

$$P = -\frac{1}{R} \frac{\partial}{\partial R} \left( R \sin \theta \right) + \Pi(2H) \quad \text{(3-20)}$$

with

$$\sin \theta = \frac{\frac{\partial H}{\partial R}}{\left(1 + \left(\frac{\partial H}{\partial R}\right)^2\right)^{1/2}}$$

$$\frac{\partial H}{\partial R} = 0 \quad \text{and} \quad \frac{\partial P}{\partial R} = 0 \quad \text{at} \quad R = 0 \quad \text{(3-21)}$$
\[ \frac{\partial H}{\partial R} = \text{constant} \quad \text{at} \quad R = 1 \quad (3-22) \]

\[ 0 < T < T_1 \quad \frac{\partial P}{\partial R} = -\frac{3\mu Q}{2\pi \sigma R_c^2} \quad \text{at} \quad R = 1 \quad (3-23) \]

\[ T > T_1 \quad \frac{\partial P}{\partial R} = 0 \quad \text{at} \quad R = 1 \quad (3-24) \]

with \[ T_1 = \frac{\sigma t_1}{3\mu R_c} \]

-Initial condition:

\[ R^2 + \left( H\left(\frac{R_s}{R_c} + \frac{h_i}{R_c}\right) \right)^2 = \left(\frac{R_s}{R_c}\right)^2 \quad (3-25) \]

### III-3 Numerical method

The set of partial differential equations for thin liquid film drainage derived in the previous section can be solved numerically by employing a finite difference method. The solutions to thin film drainage equations (thickness and pressure) are computed at discrete time intervals.

\[ T = T_0, T_1, \ldots, T_n, T_{n+1}, \ldots \]
where $T_0$ is the time when initial conditions are specified. The time increment of the time-step size is denoted $\Delta T$.

$$\Delta T = T_{n+1} - T_n$$

$\Delta T$ can be specified arbitrarily at each time step. In our case, we adopted an automatic time-step size selection such that the maximum relative change in the thickness per time step approximately equals a given value $\Delta H_{\text{max}}$.

The time derivative appears in the accumulation term of the conservation equation (3-8). The finite-difference expression of the time derivative can be approximated as:

$$\frac{\partial H}{\partial T} = \frac{H^{n+1} - H^n}{\Delta T} = \frac{\Delta H}{\Delta T}$$

(3-26)

The accuracy of the method depends on the time level at which the flux terms (right side of equation (3-8)) are evaluated. We use the so-called "semi-implicit" procedure, where the spatial differences for the flux terms are evaluated on the new time level, $T_{n+1}$, using unknown values of the independent variable $H$. In order to be solved the equations have to be linearized. Any non-linear function $F$ of the independent variable $H$ is approximated at the new time level using the following formula:

$$F(H^{n+1}) = F(H^n) + \frac{dF}{dH}(H^n) \Delta H$$

(3-27)
The formulation of the finite difference equations will neglect terms containing $(\Delta H)^2$.

Spatial derivatives appear in the conservation equations. In order to approximate these derivatives in a finite-difference form, a grid system in the $r$ direction with uneven grid spacing is used. The grid is uniform and fine in the film region, then ramped to a coarse uniform grid in the meniscus region. In the figure shown below, the grid points are denoted by a solid point in the center of each grid block.

![Grid schematic](image)

Figure III-1

From equation (18) the pressure at $r_i$ can be expressed as:

$$ p_i = -\frac{1}{R_i} \frac{R_{i+1/2} \sin \theta_{i+1/2} - R_{i-1/2} \sin \theta_{i-1/2}}{\Delta R_i} $$  \hspace{1cm} (3-28)

$$ \sin \theta_{i+1/2} = \frac{H_{i+1} - H_i}{\Delta R \left(1+\left(\frac{H_{i+1} - H_i}{\Delta R_{i+1/2}}\right)^2\right)^{1/2}} $$
The right side of the conservation equation at \( r_i \) can be expressed as

\[
\frac{1}{R} \frac{\partial}{\partial R} \left( R H^3 \frac{\partial P}{\partial R} \right) = \frac{1}{R_i} \left( \frac{R_{i+1/2} H_{i+1/2}}{\Delta R_{i+1/2}} \left( \frac{P_{i+1}-P_i}{\Delta R_{i+1/2}} \right) - \frac{R_{i-1/2} H_{i-1/2}}{\Delta R_{i-1/2}} \left( \frac{P_i-P_{i-1}}{\Delta R_{i-1/2}} \right) \right) \quad (3-29)
\]

The finite difference equation for the \( i^{th} \) grid block requires the value of \( h \) at the faces of the grid block, denoted by the indexes \( i+1/2, i-1/2 \). These values of \( h \) are calculated using "upstream" weighting. From the previous time steps, the direction of the flow is known by calculating the flow potential. When the flow occurs in the increasing direction of \( i \), we assume that:

\[
H_{i+1/2} = H_i
\]

When the flow occurs in the decreasing \( i \) direction then:

\[
H_{i-1/2} = H_{i+1}
\]

Using the above method, the governing equations (3-21) and (3-22) can be transformed into a system of linear equations, where the unknowns are the variables \( (\Delta H_i)_{1 \leq i \leq n} \). The equations are pentadiagonal with respect to each variable. The system is solved using an LU decomposition and then an upper and lower back substitution.
III-4 Convergence and validity of the numerical solution.

As mentioned in the previous section, an automatic time step selector is used in the numerical method. At each step, the time increment is selected such that the corresponding maximum relative change in thickness approximately equals a desired value $\Delta H_{\text{max}}$. The convergence of the solution was checked by varying space intervals and $\Delta H_{\text{max}}$. Figure III-2 shows the numerical solutions with decreasing $\Delta H_{\text{max}}$. Figure III-3 shows the numerical solution with increasing number of grid blocks. It can be seen that the method converges to a unique solution and good convergence can be achieved at a value of 0.05 for $\Delta H_{\text{max}}$ and a total number of grid block of 200.

In some cases, analytical solutions exist and can be used to check the validity of the numerical solutions. First, consider the case when the liquid inside the capillary ring is in hydrostatic equilibrium and the pressure in the gas phase is greater than the pressure in the liquid. The shape of the gas-liquid interface is then hemispherical. The analytical solution is given by the equation of a sphere. Employing a flat initial profile, a non-zero slope, $dh/dr$, at the capillary ring radius and a no-flow boundary condition at the capillary ring radius, the numerical solutions reach hydrostatic equilibrium. Figure III-4 shows the numerical solution compared to the analytical solution. It can be seen that the two solutions match.
Figure III-2. Convergence with increasing $\Delta H_{\text{max}}$. $R_c=1$ mm, $\sigma=72$ dyne/cm, 200 grid blocks, rate of withdrawal $Q = 5 \times 10^{-11}$ m$^3$/s, time of withdrawal 3 s, time 20 s, slope $s=5$. 
Figure III-3. Convergence with increasing number of grid blocs.

$R_c = 1 \text{ mm, } \sigma = 72 \text{ dyne/cm, } \Delta H_{\text{max}} = 0.05$, rate of withdrawal $Q = 5 \times 10^{-11}$ m$^3$/s, time of withdrawal 3 s, time 20 s, slope $s = 5$. 
Figure III-4. Static solution. Initial uniform 1/2 thickness = 3x10^{-4} m, 
R_c=1 mm, \sigma=72 \text{ dyne/cm}, \Delta H_{\text{max}} = 0.05, \text{ slope } s= 5.
Consider a circular axisymmetrical liquid film of radius \( R_f \). Initially, the film is of uniform thickness \( h_0 \). At time \( t=0 \), liquid is injected at the center of the film and withdrawn, at the same rate, at the periphery of the film (\( r=R_f \)). After a certain time, the film reaches a steady state, where the flow rate of liquid within the film is constant along the \( r \)-axis. The governing equations for the flow become:

\[
Q = -\frac{2\pi rh^3}{3\mu} \left( \frac{\partial p}{\partial r} \right) \\
p - p_g = -\sigma \frac{1}{r} \frac{\partial}{\partial r} (r \sin \theta) \quad \text{with} \quad \sin \theta = \frac{\frac{\partial h}{\partial r}}{\left(1 + \left(\frac{\partial h}{\partial r}\right)^2\right)^{1/2}}
\]

When the flow rate, \( Q \), is very small and the derivative of the film profile at the outlet of the film is zero, an analytical solution can be found by performing a perturbation analysis around the initial uniform thickness of the film. The thickness of the film and the pressure within the film are then given by:

\[
h = a + \frac{3\mu QR^2}{8\pi \sigma h_0^3} \left( \frac{r}{R_f} \right)^2 \left[ \log \frac{r}{R_f} - \frac{1}{2} \right] \\
p - p_g = -\frac{3\mu Q}{2\pi h_0^3} \left[ \log \frac{r}{R_f} + \frac{1}{2} \right]
\]

where \( a \) is a constant of integration, which is calculated from the numerical solution. Figures III-5 and III-6 show the numerical solution compared to the analytical solution. It can be seen that the two solutions match.
Figure III-5. Steady film pressure profile. Initial uniform 1/2 thickness = 10^{-5} m, R_c=1 mm, \sigma=72 \text{ dyne/cm}, \Delta H_{\text{max}} =0.05, \text{ flux } Q = 5\times10^{-14} \text{ m}^3/\text{s}. 
Figure III-6. Steady film profile. Initial uniform 1/2 thickness = $10^{-5}$ m, $R_c=1$ mm, $\sigma=72$ dyne/cm, $\Delta H_{max} = 0.05$, flux $Q=5\times10^{-14}$ m$^3$/s.
III-5 Results and discussion

The results are presented and discussed in two parts. The first part treats the hydrodynamics of thin film drainage and dimple formation in the absence of disjoining pressure. The second part shows the influence of disjoining pressure on drainage once the dimple has formed.

III-5-a Drainage without disjoining pressure

Figure III-7 shows the half-film thickness as a function of radial position and time for one set of conditions representative of those employed experimentally. Although the entire drainage process was simulated, film profiles are shown only for times after fluid withdrawal has been stopped. During the early stages of drainage, no dimple is formed. Then the half-thickness at the center, denoted by $h_0$, becomes larger than that at the barrier ring, denoted by $h_{min}$, and a dimple forms. As the dimple drains, the barrier ring reaches a final radial location $R_f$, which we define as the film radius (see figure III-8). The significance of $C_r$ on Figure III-8 will be discussed later.

III-5-a-1 Estimation of film radius

The film radius, $R_f$ as defined above, is obtained from the solution to the Young-Laplace equation subject to equation (3-14) and a zero contact angle with zero thickness at $R_f$, and to the constraint that meniscus
Figure III-7. Typical film profile as a function of time: $R_C = 1.8$ mm, $Q = 2.5 \times 10^{-11}$ m$^3$/s, $\sigma = 30$ dyne/cm, disjoining pressure not included. Points are predictions of the Frankel-Mysels theory. Time of withdrawal 4 sec.
Figure III-8. Thin film features.
volume is the difference between the initial volume and the volume of liquid withdrawn. However, the solution for the film radius can only be obtained numerically in this way.

Using the following scheme, we develop an approximate analytical solution that predicts the film radius for various conditions. Before withdrawal, the initial hemispherical menisci, of radius $R_s$, are separated from the mid-plane ($z=0$) by $h_i$, as shown in figure III-9. The curvature of the menisci is assumed to remain constant during withdrawal. If enough liquid is withdrawn the hemispherical menisci intersect the mid-plane and determine a film radius (see figure III-9). This approximate scheme yields a film radius $R_a$ given by:

$$R_a = \sqrt{R_s^2 - (R_s + h_i - \frac{Q t}{\pi R_s^2})^2}$$  (3-33)

$Q_t$ represents the volume of liquid withdrawn. For a given rate of withdrawal $Q$ the minimum time of withdrawal required to form a film is:

$$t_{\text{min}} = \frac{h_i \pi R_s^2}{Q}$$  (3-34)

$R_a$ gives only an approximate value of the film radius $R_f$. However, we have found that $R_a$ can be correlated with the film radius $R_f$ obtained from the numerical simulations for a wide range of parameters. Figure III-10 shows the plot of $R_f/R_s$ versus $R_a/R_s$. A good representation of this correlation is given by:

$$\frac{R_f}{R_s} = 0.72 \left(\frac{R_a}{R_s}\right)^{1.263}$$  (3-35)
Figure III-9. Scheme for approximate solution for the film radius.
Figure III-10. Film radius prediction. Ranges of variables investigated:

$10 \mu m \leq R_f \leq 300 \mu m$, $1 \text{mm} \leq R_c \leq 10 \text{ mm}$, $30 \text{ dyne/cm} \leq \sigma \leq 72 \text{ dyne/cm}$
Equations (III-26) and (III-28) allow the film radius to be estimated for various conditions without detailed simulations and numerical calculations.

**III-5-a-2 Estimation of film thickness during liquid withdrawal**

It is also useful to have an approximate value of film thickness immediately following liquid withdrawal. During withdrawal, one finds that the meniscus advances radially at a certain velocity $U_m$ and leaves a film of liquid behind (see figure III-11). If we approximate the radius of curvature of the meniscus as a constant equal to $R_s$, the initial radius of curvature, and the velocity $U_m$ as the derivative of $R_f$ with respect to the time of withdrawal, the problem becomes equivalent to a long bubble moving at the same velocity $U_m$ in a capillary tube of radius $R_s$. Bretherton (57) developed an approximate asymptotic solution for the thickness of the liquid film formed between the front and rear menisci of a long advancing bubble. The thickness given by the Bretherton theory corresponds to the half-thickness of the film in our case and can be expressed as:

$$h_{Br} = 0.46 R_s \left(\frac{3 \mu U_m}{\sigma}\right)^{2/3} \quad \text{with } U_m = \frac{dR_f}{dt} \quad (3-36)$$
Figure III-11. Film profile during withdrawal: $R_c = 1.8$ mm, $Q = 2 \times 10^{-11}$ m$^3$/s, $\sigma = 30$ dyne/cm.
The minimum half-thickness of the film during withdrawal and its radial position as predicted by our detailed simulations are compared in figure III-12 with those given by equation (3-36). For the latter case radial position $R_f$ and velocity $(dR_f/dt)$ are obtained using equation (3-33). The agreement is reasonable. The faster the rate of withdrawal, the thicker the film formed.

III-5-a-3 Transition from nearly uniform to dimpled film

Once withdrawal of liquid is stopped, the film drains by capillary suction. In order to describe the transition from a nearly uniform or "plane-parallel" film to a dimpled film, a dimensionless parameter $C_R$ is introduced. $C_R$ represents the ratio of the maximum possible curvature in the dimple to the curvature in the meniscus. The former, which we designate $R_d$, is the radius of a section of a sphere tangent to the film surface at the center and intersecting the mid-plane at the film radius $R_f$ (see figure III-13). From geometry one finds that $R_d$ can be expressed as:

$$R_d = \frac{R_f^2}{2h_0} \left( 1 + \left( \frac{h_0}{R_f} \right)^2 \right) \approx \frac{R_f^2}{2h_0} \quad (3-37)$$

In a typical experiment the film radius in much smaller than that of the capillary ring. Therefore, the radius of curvature of the meniscus is approximately equal to $R_C$ and $C_R$ can be expressed as:
Figure III-12. Half-thickness prediction during withdrawal: $R_C = 1.8$ mm, $\sigma = 30$ dyne/cm
\[ C_R = \frac{1}{\frac{R_d}{R_c}} = \frac{2 h_0 R_c}{R_f^2} \quad (3-38) \]

Note that \( C_R \) is proportional to the half-thickness at the center, \( h_0 \), and therefore does not remain constant during drainage of the film.

Figure III-13. Radius of curvature in the dimple and the meniscus.
A physical interpretation can be made for the curvature ratio $CR$ as follows:

The maximum possible curvature in the dimple $1/R_d$ represents the driving force for the liquid to flow from the center to the periphery of the film. The curvature in the meniscus $1/R_c$ represents the driving force for the liquid to flow from the periphery of the film into the meniscus region. If $1/R_d$ is less than $1/R_c$, not enough liquid can be "pushed" out of the film to satisfy the amount of liquid "pulled" out by capillary suction. Therefore, the fluid at the periphery of the film gets depleted and a dimple forms. If $1/R_d$ is larger than $1/R_c$, liquid in the film can be provided at a high enough rate to satisfy the capillary suction and no dimple forms.

We found from our simulations that for values of $CR$ larger than about 0.7 no dimple is formed. The film is slightly concave and the transition from the film region to the Plateau border is gradual (see figure III-7). The departure from a plane-parallel film can be characterized by the ratio of half-thickness at the film radius $h_R$ to the half-thickness at the center $h_0$ (see figure III-8). The ratio $h_R/h_0$ is correlated to $CR$ in figure III-14 ($CR > 0.7$). It is greater than unity but does not exceed 1.2. Under these conditions the film is approximately plane-parallel. When $CR$ becomes less than 0.7, a dimple is formed. The half-thickness at the center, $h_0$, becomes larger than that at the barrier ring, $h_{min}$, and the dimple can be characterized by the ratio $h_{min}/h_0$ (see figure III-8). The latter is plotted as a function of $CR$ in figure III-14 ($CR < 0.7$).
Figure III-14. Transition from a plane-parallel film to a dimpled film. Values of variables are the same as those of figure III-10.

As one can observe, the dimple becomes more pronounced as $C_R$ decreases. The reason for the discontinuity between the two curves is that at $C_R = 0.7$, $h_{\text{min}}$ is equal to $h_0$ and is located at the center of the film. However, since the film is slightly concave, $h_R$ is larger than $h_{\text{min}}$ and $h_0$. 
III-5-a-4 Rate of thinning

The rates of thinning at the center of the film and at the barrier ring as predicted by the simulations were correlated with the curvature ratio $C_R$. Figure III-15 shows the results for the rates of thinning normalized by the Reynolds velocity $V_{Re}$ (28) for drainage between a pair of disks of radius $R$ separated by a liquid layer of thickness $2h$.

$$V_{Re} = \frac{8 h^3 p_c}{3 \mu R_f^2}$$

(3-39)

Figure III-16 shows the pressure profile during the film drainage as obtained by the numerical simulations for various $C_R$ and that given by the Reynolds theory $p_{Re}$ (28).

$$p_{Re} - p_g = p_c \left( 1 - 2 \left( \frac{1}{R_f} \right)^2 \right)$$

(3-40)

Figure III-15 shows that the rate of drainage is always less than the Reynolds' velocity of thinning. The reasons for this are:

1) The pressure drop from the center of the film to the Plateau border, as obtained from the simulations, is less than half of that predicted by the Reynolds' theory.
2) There is a significant pressure gradient beyond the nominal film radius for large $C_R$. Therefore the rate of thinning is significantly reduced due to the resistance to flow that extends into the Plateau border region. Wasan and Malhotra (32) recognized the influence of the flow in the
Plateau border on the rate of film thinning and developed an approximate theory.

3) When the dimple is formed, most of the resistance to flow is in the thin barrier ring.

![Diagram showing rate of thinning](image)

Figure III-15. Rate of thinning. Values of variables are the same as those of figure III-10.
Frankel and Mysels (38) developed quasi-steady state solutions for the thicknesses at the center and at the barrier ring, neglecting accumulation at the barrier ring (see appendix A). They found that thinning at the barrier ring can be described using Reynolds' formula. However thinning at the center is much slower than predicted by Reynolds' theory, the half-thickness $h_0$ at the center being given by the following equation:
\[ h_0 = \left( \frac{0.0096 R_f^6 \mu}{\sigma R_c t} \right)^{\frac{1}{4}} \]  \hspace{1cm} (3-41)

Equation (3-41) was obtained assuming that the initial thickness at \( t=0 \) is infinite. Differentiating equation (3-41), one obtains the rate of thinning at the center \( V_{F-M} \). When \( V_{F-M} \) is normalized by the Reynolds velocity \( V_{Re} \) and then expressed in terms of \( C_R \), one finds:

\[ \frac{V_{F-M}}{V_{Re}} = 1.22 \left( C_R \right)^2 \]  \hspace{1cm} (3-42)

The rate of thinning given by equation (3-42) is plotted on figure III-15. Figure III-7 compares our calculated film profiles with the thicknesses at the center and at the barrier ring predicted by the Frankel-Mysels theory. For \( C_R \) larger than 0.45, the Frankel-Mysels theory predicts higher rates of thinning and smaller thicknesses at the center of the film than the numerical simulations. For \( C_R \) less than 0.45, the rate of thinning at the center from our simulations is in agreement with \( V_{F-M} \) (see figure III-15). However the thickness at the center line, from our calculated film profiles, reaches that predicted by the Frankel-Mysels theory only for \( C_R \) less than 0.3 (see figure III-7). A similar observation can be made for the barrier ring, except that the rate of thinning and the thickness at the ring, from our simulations, reach those predicted by Reynolds' theory only if \( C_R \) is less than or equal to about 0.1. The reason for this is shown in figure III-16. One sees that for small \( C_R \) (\( \leq \)...
0.1) the pressure gradient at the location of the barrier ring is the same as that given by Reynolds' theory.

Platikanov (43) measured experimentally the thicknesses at the center and at the barrier ring during the drainage of a dimpled film and found reasonable agreement with the Frankel-Mysels' theory and therefore with our simulations as well. However, Platikanov did not report experimental data before and during the dimple formation.

III-5-b Influence of disjoining pressure on film drainage

The presence of disjoining pressure makes a qualitative difference in film drainage. Figure III-17 shows the half-thickness as a function of radial position and time in the absence of disjoining pressure for a liquid withdrawal rate four times that of figure III-7. The radius of the film formed is 140 μm, almost five times that of figure III-7. As one can see, the drainage of the dimple in figure III-17 ultimately becomes very slow due to the high resistance to flow in the thin barrier ring.

At low electrolyte concentration the repulsive electrostatic component of disjoining pressure is dominant and inhibits the formation of the barrier ring. A disjoining pressure isotherm for one such case is shown figure III-18. Figure III-19 shows film profiles obtained from the
Figure III-17. Film profile: $R_c = 1.8$ mm, $Q = 10^{-10}$ m$^3$/s, $\sigma = 30$ dyne/cm, disjoining pressure not included.
Figure III-18. Disjoining pressure isotherms. Low electrolyte concentration: $C_e = 6 \times 10^{-4}$ mol/l, Hamaker constant $7.5 \times 10^{-20}$ J, electrical potential 94 mV. High electrolyte concentration: $C_e = 2 \times 10^{-2}$ mol/l, Hamaker constant $7.5 \times 10^{-20}$ J, electrical potential 26 mV.
Figure III-19. Film profile: $R_C = 1.8$ mm, $Q = 10^{-10}$ m$^3$/s, $\sigma = 30$ dyne/cm, disjoining pressure included. Low electrolyte concentration: $C_{el} = 6 \times 10^{-4}$ mol/l.
simulations for this disjoining pressure isotherm and the same conditions of initial film formation as figure III-17. The drainage is faster than in the absence of disjoining pressure. During the later stages of the drainage, the repulsive disjoining pressure stops the thinning and the film rapidly reaches its equilibrium thickness. Similar behavior was simulated by Chen and Slattery (44), (45) and is in qualitative agreement with experimental observations of Platikanov (43). We also observed similar behavior for a film containing 0.02 wt % of AOS 16-18, as shown in figure III-20-a through III-20-f.

At high electrolyte concentration the disjoining pressure is dominated by van der Waals attraction forces, as shown figure III-18. The resulting film profiles as a function of time are shown Figure III-21. Early in the drainage process, the barrier ring thins very quickly due to the van der Waals attraction forces. When the short range repulsion forces become dominant, a very thin annular film forms that forces the dimple into a lens with a finite contact angle. The drainage of the lens is then very slow because of the high resistance to flow in the thin annular film. The contact angle can be calculated from the disjoining pressure isotherm using the Frumkin-Derjaguin theory (58):

\[
\cos \phi = 1 + \int_{0}^{\Pi_{eq}} \frac{h \, d\Pi}{\sigma}
\]

(3-43)

The disjoining pressure isotherm at high electrolyte concentration, shown figure III-18, gives a contact angle of 3.1°, according to formula (3-43).
Figure III-20. Drainage of AOS 16-18 (0.02w%). $R_f = 140 \mu m$, $R_c = 1.8 mm$ at $t = 19$ s, 25 s, 2 min, 3 min, 4 min 42 s, 10 min. The film drainage started at time code 0:00:05:00.
Figure III-21. Film profile: $R_c = 1.8$ mm, $Q = 10^{-10}$ m$^3$/s, $\sigma = 30$ dyne/cm, disjoining pressure included. High electrolyte concentration: $C_{el} = 2 \times 10^{-2}$ mol/l.
The contact angle of the lens shown figure III-21 has a value of 2.5°, which is acceptable agreement considering the limitations on numerical resolution at the contact line.

Figures III-22-a though III-22-f show the interference patterns at different times during drainage of a film formed for the same conditions as figure III-17. A 0.5 wt % solution of AOS 16-18 was used, which corresponds to an electrolyte concentration of 2 \(10^{-2}\) mol/l, including the sodium sulfate impurity. Note that the concentration of surfactant is above the critical micelle concentration. A lens with a small finite contact angle, separated from the meniscus by a uniform annular film, does form (see figure III-22-c). The measured contact angle is 0.3°. However subsequent drainage is complicated by stepwise thinning of the annular film, a phenomenon not included in the present model. Nucleation of a thinner spot of the annular film is shown in figure III-22-d and its growth in figure III-22-e. The final lens (figure III-22-f) is smaller and thicker than that of figure III-22-c with a larger contact angle, measured to be 2.5°. A more complex disjoining pressure isotherm accounting for micelle ordering in the film would be required to extend our model to describe the observed stepwise thinning behavior (26), (27).
Figure III-22. Drainage of AOS 16-18 (0.5w%). $R_f = 140 \mu m$, $R_C = 1.8 mm$ at $t = 10 s, 29 s, 1 \text{ min} 41 s, 2 \text{ min} 39 s, 2 \text{ min} 51 s, 3 \text{ min} 51 s$. The film drainage started at time code 0:00:34:00.
CHAPTER FOUR

ASYMMETRIC DRAINAGE
EXPERIMENTAL RESULTS

Experiments on drainage of horizontal, circular films were conducted using the interference method proposed by Derjaguin (55), Scheludko and Exerowa (19) described in chapter two.

Experiments were performed on aqueous foam film drainage with different surfactant systems, such as Sodium Dodecyl Sulfate (SDS, 98% pure from Aldrich Chemical Company), Sodium Dodecyl Benzene Sulfonate (SDBS from Sigma Chemical Company), Saponin (a protein from Sigma Chemical Company), Alpha Olefin Sulfonate (Enordet AOS from Shell Development Company) 14-16, 16-18, 18, 20-24, Internal Olefin Sulfonate (Enordet IOS from Shell Development Company) 15-17, Linear Toluene Sulfate (Enordet LTS from Shell Development Company) 18 and Chevron Chaser SD1000. Two different types of drainage were observed, symmetric and asymmetric. Numerical simulations of symmetric drainage were described in the previous chapter. During symmetric film drainage, the interference patterns, recorded on video tape, are symmetric during the entire film drainage. Figure III-20. shows a typical axisymmetrical foam film drainage. In contrast to this behavior, Figure IV-1 shows the drainage of a foam film containing 0.2 wt % of SDBS. Initially, the drainage is symmetric and a dimple forms (figure IV-1-a). However, half a second later,
interference patterns are no longer symmetric (figures IV-1-a-d) and asymmetric drainage takes place. As shown in figure IV-2, fluctuations in film thickness at the barrier ring cause thick parts of the film to flow more rapidly from the dimple into the meniscus region while thin parts get thinner and extend further into the film. The dimple is squeezed, deforms and eventually slips to one side (figure IV-1-c). Asymmetric drainage was found to be always much faster than axisymmetric drainage.

The results of our foam film drainage experiments on different ionic commercial surfactants are listed below in table IV-1.

<table>
<thead>
<tr>
<th>Aqueous surfactant solution (0.01 to 1.0 w%)</th>
<th>Drainage behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDBS</td>
<td>Asymmetric at all concentrations</td>
</tr>
<tr>
<td>Chevron SD1000</td>
<td>Asymmetric at all concentrations</td>
</tr>
<tr>
<td>AOS 14-16</td>
<td>Asymmetric at all concentrations</td>
</tr>
<tr>
<td>SDS</td>
<td>Asymmetric at all concentrations</td>
</tr>
<tr>
<td>IOS 15-17</td>
<td>Asymmetric at all concentrations</td>
</tr>
<tr>
<td>LTS 18</td>
<td>Asymmetric at all concentrations</td>
</tr>
<tr>
<td>IOS 15-17 : C_{12}H_{25}OH, 100:1</td>
<td>Asymmetric at all concentrations</td>
</tr>
<tr>
<td>SDS : C_{12}H_{25}OH, 100:1</td>
<td>Symmetric near the CMC</td>
</tr>
<tr>
<td>AOS 14-16 : C_{12}H_{25}OH, 100:1</td>
<td>Symmetric from 0.05 to 0.1%</td>
</tr>
<tr>
<td>AOS 16-18</td>
<td>Symmetric from 0.01% to 0.8%</td>
</tr>
<tr>
<td>Saponin</td>
<td>Symmetric</td>
</tr>
<tr>
<td>SDS : C_{12}H_{25}OH, 100:1 + NaCl 0.02M</td>
<td>Asymmetric at all concentrations</td>
</tr>
</tbody>
</table>

Table IV-1. Experimental studies of thin film drainage.
Figure IV-1. Drainage of SDBS (0.02 w%). $R_f=100\mu\text{m}$, $R_c=1.8\text{mm}$ at $t=2$ s, 2 & 1/2 s, 3 s, 4 s, 16s, 20s. Drainage Started at 00:15:00s.
Figure IV-2 Drainage of SDBS 0.2w%. R_f = 100 μm. Film drainage started at 00:15:00s. A typical case of asymmetric drainage.
Films of most surfactant solutions were found to drain asymmetrically and very fast; exceptions were Saponin (figure IV-3) and AOS 16-18 figure (IV-4). By adding a small quantity of cosurfactant, 1-dodecanol (98% pure from Aldrich Chemical Company), to solutions of SDS, drainage became symmetric and much slower (see figure IV-5). A ratio of 1 molecule of 1-dodecanol to 100 molecules of SDS was used. Previous work (59) showed that the addition of 1-dodecanol to aqueous solutions of SDS greatly increased the surface shear viscosity. Figure IV-6 shows the surface shear viscosity of aqueous solutions of SDS:1-dodecanol, 100:1 as a function of concentration in the same range as our experiments. At low surfactant concentration, where the surface concentrations of surfactant and alcohol were low, causing a low surface shear viscosity (see figure IV-6), we observed asymmetric drainage (figure IV-5). Near the CMC, where the surface concentration of surfactant and alcohol were high, causing a high surface shear viscosity, we observed symmetric drainage (figure IV-5). Well above the CMC, most of the alcohol was solubilized by the micelles in solution. As a result the surface concentration of alcohol was lowered causing a decrease in surface shear viscosity and a return to asymmetric drainage (figure IV-5).

Figure IV-7 shows the drainage time of SDS and SDS:1-dodecanol, 100:1 films as a function of surface shear viscosity. Drainage experiments were also performed on solutions of AOS 14-16 and AOS 14-16:1-dodecanol with a ratio of 100:1. As shown on figure IV-8, a similar drainage behavior was observed for AOS 14-16 as that of
Figure IV-3. Drainage time as a function of concentration of aqueous solution of Saponin. Film radius $R_f=70 \, \mu m$
Figure IV-4. Drainage time as a function of concentration of aqueous solution of AOS 16-18. Film Radius \( R_f = 140 \, \mu m \)
Figure IV-5. Drainage time as a function of concentration of aqueous solutions of SDS and SDS: C_{12}H_{25}OH, 100:1. Film radius R_f = 100 μm.
Figure IV-6. Surface viscosity as a function of concentration of aqueous solution of SDS : $\text{C}_{12}\text{H}_{25}\text{-OH}$, 100:1. Surface shear viscosity from Djabbarah (59).
Figure IV-7. Film drainage Time as a function of surface shear viscosity for solutions of SDS and SDS:C_{14}H_{25}-OH, 100:1. R_{f} = 100\mu m. Shear viscosity from Djabbarah (59)
Figure IV-8. Film drainage time as a function of concentration of aqueous solutions of AOS 14-16 and AOS 14-16:C_{12}H_{25}-OH, 100:1. Film radius $R_f = 100 \mu m$
SDS which indicates that the surface shear viscosity of AOS 14-16 increases with addition of 1-dodecanol. By adding a small quantity of NaCl (0.02M) to solutions of SDS:1-dodecanol, 100:1, film drainage became asymmetric. Djabbarah et al. (59) showed that the addition of NaCl in small quantities to solutions of SDS:1-dodecanol, 100:1, significantly reduced surface shear viscosity. The transition from asymmetric to symmetric drainage was found to be strongly dependent on the value of surface shear viscosity. Symmetric drainage was associated with rigid surfaces that permit little or no tangential flow, as indicated by high values of surface shear viscosity. Asymmetric drainage was associated with more mobile and deformable surfaces which have low surface shear viscosity. As discussed in the following chapter, other parameters such as surface dilational viscosity, surface diffusivity and system size are also important factors in determining the drainage type.
CHAPTER FIVE

LINEAR STABILITY ANALYSIS

Experimental results described in the previous chapter indicate that asymmetric drainage is the result of a hydrodynamic instability that takes place at the barrier ring of a draining thin liquid film. In this chapter, we develop a linear stability analysis of the barrier ring region that clarifies the mechanisms of instability and provides a stability criterion.

In the case of horizontal film drainage, we approximate the film region between dimple and meniscus (barrier ring) by a film initially of uniform half-thickness $h_0$ (see figures V-1-a and V-1-b). For simplicity we used Cartesian coordinates instead of cylindrical coordinates in this analysis to clarify the basic mechanism of instability as shown in figure V-1-b. This assumption is reasonable when the width in the direction of flow of the barrier ring is small compared to the circumference of the barrier ring. For a typical film radius $R_f$ of 100 μm, numerical solutions (see chapter III) show that the width of the barrier ring is around 25 μm and is much smaller than the circumference of the ring $2\pi R_f$ which is 628 μm. During film drainage most of the pressure gradient takes place in the barrier ring region. The pressure gradient, causing the underlying bulk liquid to flow from the dimple into the
meniscus, is assumed to be constant. We assume that the interface contains an insoluble monolayer of surfactant which, at rest, has a uniform surface concentration $\Gamma_{eq}$.

**V-1 Steady State Solution**

We consider the steady state solution with uniform thickness $h_o$ and immobile interface, $v_s^{ss} = 0$. The average x and y components of velocity of the underlying bulk liquid are given by:

\[
\bar{v}_x^{ss} = -\frac{h_o^2}{3\mu}\left(\frac{\partial p^{ss}}{\partial x}\right)
\]

and

\[
\bar{v}_y^{ss} = 0
\]

(5-1)

(5-2)

The underlying liquid generates a constant tangential stress at the interface that must be balanced by a constant surface tension gradient in order to have an immobile interface. Therefore we have:

\[
\left(\frac{\partial \sigma^{ss}}{\partial x}\right) = -\mu \left. \frac{\partial v_x^{ss}}{\partial z} \right|_{z=h_o} = h_o \left(\frac{\partial p^{ss}}{\partial x}\right)
\]

(5-3)

The surface tension $\sigma$ can be related to the surface concentration of surfactant $\Gamma$ by an equation of state:

\[
\sigma = -\alpha \Gamma + C \quad \text{where} \quad \alpha = -\left(\frac{\partial \sigma}{\partial \Gamma}\right)_{eq} \quad \text{and} \quad C \quad \text{a constant.}
\]
Figure V-1. Schematic view of perturbation in thickness, surface velocity and surface tension in unstable film.
Hence, equation (5-3) can be written as

\[
\left( \frac{\partial \Gamma^{ss}}{\partial x} \right) = -\frac{h_0}{\alpha} \left( \frac{\partial p^{ss}}{\partial x} \right)
\]  

(5-4)

The tangential stress induces a constant surfactant concentration gradient, given by equation (5-4), in the same direction as the underlying liquid flow.

We realize that the pressure gradient in the direction of flow generates a curvature gradient in this direction. The curvature effects are neglected in the above steady state solution and in the following linear stability analysis. It is assumed that the wave lengths associated with the perturbations introduced below are much smaller than the minimum radius of curvature in the plane of direction of flow before perturbation (xz plane of figure V-I-b). In chapter six, a numerical model which includes variation in thickness in the direction of flow is developed to simulate the instability causing asymmetric drainage. The results show that deviations from predictions of the linear stability are very small when this assumption is satisfied.

V-2 Stability Analysis

The stability of the steady state solution is investigated by considering a small spatial and temporal perturbation for each of the dependent variables around steady state:
\[ \tilde{h} = h - h_0 \]  
(5-5)

\[ \tilde{\Gamma} = \Gamma - \Gamma^{ss} \]  
(5-6)

\[ \tilde{v}_{sx} = v_{sx} - 0 \]  
(5-7)

\[ \tilde{v}_{sy} = v_{sy} - 0 \]  
(5-8)

\( \tilde{v}_{sx} \) and \( \tilde{v}_{sy} \) are respectively the x and y components of the surface velocity.

For simplicity, we assume that perturbations are independent of x. Consequently, no boundary conditions are specified in the direction of flow, and perturbations in this direction are not considered. Accordingly, the following analysis is limited to the case where the wave length of an unstable perturbation in the transverse direction is small compared to the minimum radius of curvature. In chapter six, the effects of finite width of the barrier ring and resulting changes of each dependent variable in the direction of flow are investigated.

Neglecting second order terms, the equations of change for the perturbations are linearized. In the lubrication approximation, the equations are as follows:

- Bulk liquid mass balance (34):

\[
\frac{\partial \tilde{h}}{\partial t} = -h_0 \frac{\partial}{\partial y} \left( \tilde{v}_{sy} \right) - \frac{\sigma h_0^3}{3 \mu} \left( \frac{\partial^4 \tilde{h}}{\partial y^4} \right)
\]  
(5-9)

- Surfactant mass balance (60):

We assume that the surfactant concentration gradient necessary to balance the shear stress at the surface is very small compared to the
initial uniform concentration of surfactant present at the surface ($\Gamma^{ss} = \Gamma_{eq}$). Calculations show that this is the case for situations of interest. The surfactant mass balance becomes:

$$\frac{\partial \tilde{\Gamma}}{\partial t} = - \left( \frac{\partial \Gamma^{ss}}{\partial x} \right) \tilde{v}_{sx} - \Gamma_{eq} \frac{\partial \tilde{v}_{sy}}{\partial y} + D_s \frac{\partial^2 \tilde{\Gamma}}{\partial y^2} \quad (5-10)$$

$D_s$ is the surface diffusivity

- Surface momentum equations (inertial effects are neglected) (61):

  - x-component

  $$\mu_s \frac{\partial^2 \tilde{v}_{sx}}{\partial y^2} = \tilde{h} \left( \frac{\partial \rho^{ss}}{\partial x} \right) \quad (5-11)$$

  - y-component

  $$-\alpha \frac{\partial \tilde{\Gamma}}{\partial y} + (\mu_d + \mu_s) \frac{\partial^2 \tilde{v}_{sy}}{\partial y^2} = -\sigma h_0 \left( \frac{\partial^3 \tilde{h}}{\partial y^3} \right) \quad (5-12)$$

where $\mu_d$ and $\mu_s$ are respectively the surface dilational and shear viscosities.

Let's consider the following perturbations:

$$\tilde{h} = \hat{h} \exp(\beta t + \imath k_y y) \quad (5-13)$$

$$\tilde{\Gamma} = \hat{\Gamma} \exp(\beta t + \imath k_y y) \quad (5-14)$$

$$\tilde{v}_{sx} = \hat{v}_{sx} \exp(\beta t + \imath k_y y) \quad (5-15)$$

$$\tilde{v}_{sy} = \hat{v}_{sy} \exp(\beta t + \imath k_y y) \quad (5-16)$$
where \( \hat{h}, \hat{\Gamma}, \hat{v}_{sx}, \hat{v}_{sy} \) are constants, \( k_y \) is the wave number in the \( y \)-direction and \( \beta \) is the growth factor. \( k_y \) is equal to \( (2\pi/\lambda_y) \) where \( \lambda_y \) is the wave length of the perturbations. Substitution of the above expressions for the perturbations \( \hat{h}, \hat{\Gamma}, \hat{v}_{sx}, \hat{v}_{sy} \) into the differential equations and definition of the following dimensionless variables:

\[
W = \frac{\Gamma \alpha}{3 \mu v_{sx}^s}, \quad H = \frac{h}{h_o}, \quad U = \frac{v_{sx}}{3 v_{sx}^s} S_{sh},
\]

\[
V = \frac{v_{sy}}{3 v_{sx}^s} S_{sh}, \quad \beta' = \beta \left( \frac{\mu_s}{3 \mu v_{sx}^s} \right), \quad K = h_o k_y
\]

yields the following set of equations:

\[
\beta' \hat{H} = -iK \hat{V} - \left( \frac{S_{sh}}{9 C_a} \right) K^4 \hat{H}
\]

\[
\beta' \hat{W} = -\hat{U} - iK \left( \frac{E_d}{3 C_a} \right) \hat{V} - \frac{K^2}{M_a} \hat{W}
\]

\[
K^2 \hat{U} = \hat{H}
\]

\[
-iK \hat{W} - \left( \frac{S_{d+sh}}{S_{sh}} \right) K^2 \hat{V} = i \frac{K^3}{3 C_a} \hat{H}
\]

In order to have a nontrivial solution for \( \hat{H}, \hat{W}, \hat{U}, \hat{V} \), the determinant of the above set of equations must be equal to zero. This yields a second degree polynomial in \( \beta' \) with real coefficients. \( \beta' \) was found to be real and its expression is given as follows:

\[
\beta' = -\left( a + c \right) + \sqrt{(a - c)^2 + 4bd} \over 2
\]

(5-21)
with
\[
a = \frac{S_{sh}K^2}{3S_{sh+d}C_a} \left(1 + \frac{S_{sh+d}}{3}K^2\right) \quad b = \frac{1}{K^2} + \frac{E_dS_{sh}}{9S_{sh+d}C_a^2} K^2
\]
\[
c = \frac{E_dS_{sh}}{3S_{sh+d}C_a} + \frac{K^2}{M_a} \quad d = \frac{S_{sh}}{S_{sh+d}}
\]

The sign of $\beta'$ is given by:
\[
\frac{K^6}{3M_aC_a} \left(1 + \frac{M_aS_{sh}E_d}{3C_a} + \frac{S_{d+sh}K^2}{3}\right) \begin{cases} 
> 1, \beta' < 0, \quad \text{stable system} \\
= 1, \beta' = 0, \quad \text{marginal stability (5-22)} \\
< 1, \beta' > 0, \quad \text{unstable system}
\end{cases}
\]

with
\[
C_a = \frac{\mu v^{ss}}{\sigma}, \quad E_d = \frac{\Gamma_{eq} \alpha}{\sigma}, \quad S_{sh} = \frac{\mu_s}{\mu h_0},
\]
\[
S_{d+sh} = \frac{(\mu_d + \mu_s)}{\mu h_0}, \quad M_a = \frac{\alpha \left(\frac{\partial \Gamma^{ss}}{\partial x}\right) h_0^3}{D_s \mu_s}
\]

If $\beta'$ is positive, small perturbations grow and the system is unstable. If $\beta'$ is negative, small perturbations are damped and the system is stable. $C_a$ is a capillary number, $M_a$ a surface Marangoni number, $E_d$ a dimensionless elasticity, $S_{sh}$ and $S_{d+sh}$ are dimensionless surface viscosity groups. Scriven and Sternling (62) defined a 'crispation number' in their analysis of Marangoni instability in a thin layer heated.
from below. A similar crisption number, $C_r$, can be defined for the present system and is expressed as follows:

$$C_r = \frac{3C_a}{M_a S_{sh}} = \left( \frac{\mu D_s}{h_o \sigma} \right)$$

Expression (5-22) becomes:

$$\frac{K^6}{3M_a C_a} \left( 1 + \frac{E_d}{3C_r} + \frac{S_{sh+d} K^2}{3} \right) \begin{cases} > 1, \beta' < 0, \text{ stable system} \\ = 1, \beta' = 0, \text{ marginal stability} \\ < 1, \beta' > 0, \text{ unstable system} \end{cases}$$

(5-23)

It is clear that large capillary, Marangoni and crisption numbers promote instability whereas large surface elasticity, large shear and dilational viscosity and large wave number promote stability.

Substitution of expressions for the dimensionless parameters $C_a$, $E_d$, $M_a$, $S_{d+sh}$, $S_{sh}$ and $K$ in expression (5-22) yields the following stability criterion:

$$\frac{\mu \sigma}{\left( -\frac{\partial \rho^{ss}}{\partial x} \right)^2} \left( D_s + \frac{h_o \Gamma_{eq \alpha}}{3 \mu} \right)^6 \left( \frac{2\pi}{\lambda_y} \right)^8 \begin{cases} > 1, \text{ stable} \\ = 1, \text{ marginal} \\ < 1, \text{ unstable} \end{cases}$$

(5-24)

We expressed average bulk velocity and surface concentration gradient as a function of the pressure gradient in this equation because
the latter can be approximated by the difference between the pressure in the meniscus and pressure in the dimple divided by the width of the barrier ring region. These quantities can be obtained from experiments on film drainage or numerical simulations.

Note that in the linear stability analysis described above, the decrease in thickness over time due to film drainage is neglected. As indicated by Frankel-Mysels (38), drainage at the barrier ring for the case of immobile interfaces can be described by Reynolds theory. In the case of a typical film drainage experiment (parameters are given in table V-1), decrease in thickness due to film drainage at the barrier ring can be estimated using Reynolds formula and a ten percent decrease takes around two seconds at a thickness of 200 nm. Table V-1 shows the reciprocal of $\beta$ at different SDS and SDS:1-dodecanol concentrations for the same conditions. For pure SDS (low surface shear viscosity) $\beta^{-1}$, the characteristic time for instability to develop, is much smaller than the time it takes for the film to thin by ten percent. Therefore, the assumption of neglecting change in thickness due to film drainage is valid at least for low surface shear viscosity.

**V-3 Discussion**

The linear stability analysis shows that the mechanism of asymmetric drainage is a surface-tension-driven instability that is stabilized by surface viscosity, surface diffusivity, surface elasticity and system length scale. Consider a periodic perturbation in thickness as shown in figure V-1. In the thick parts of the film, the shear stress at
the surface due to the flow of the underlying liquid is larger than the initial surface tension gradient. Hence, surface flow is established in the same direction as the flow of the underlying liquid (from the dimple to the meniscus) that results in a decrease in surfactant concentration and an increase in surface tension in the film. In the thin parts of the film the shear stress at the surface is lower than the initial surface tension gradient causing surface flow in the reverse direction (from the meniscus to the dimple). The surfactant concentration increases and the surface tension decreases in the film. Therefore, in the direction perpendicular to the initial flow, surface tension gradients cause the surface and underlying fluid to flow from thin to thick parts of the film. As a result, perturbations grow and the system is unstable. For sufficiently small wavelengths, capillary flows (curvature driven), which promote lateral flow in the direction opposite to the surface-tension-driven flow, can prevent the instability from occurring. Surface diffusivity decreases surface tension gradients and therefore damps the effect of surface tension driven flow. Surface shear viscosity and dilational viscosity are also stabilizing factors due to their energy dissipating effect. In the stability criterion (5-24), one can see that every term is multiplied by surface shear viscosity, $\mu_s$. This property is therefore a key factor in determining the transition from symmetric drainage to asymmetric drainage as indicated by our experimental results.

Experiments on the radial film drainage of pure SDS and SDS:1-dodecanol can be compared with our linear stability analysis by taking
the wave length \( \lambda_y \) of the perturbation equal to \( 2\pi R_f \), the circumference of the film and using Djabbarah's data (63) on surface dilational and shear viscosity and elasticity for SDS and SDS:1-dodecanol systems. This value of \( \lambda_y \) represents the longest possible wave length and hence the least stable perturbation which can develop. Comparisons of the linear stability predictions with our experimental results are listed in Table V-1. As one can see, asymmetric drainage is seen whenever the left side of criterion (5-24) is less than one, in agreement with the theory. Table V-1 also shows the essential role of surface shear viscosity on the instability causing asymmetric drainage. Values of surface diffusivity are difficult to obtain experimentally. For surfactant systems, such as SDS, surface diffusivity ranges typically from \( 10^{-5} \) to \( 10^{-7} \) cm\(^2\) s\(^{-1}\)(34). Using such values of surface diffusivity and known values for the other parameters for SDS and SDS:1-dodecanol (61), we found that, in criterion (5-24), terms multiplied by \( D_s \) (terms 1 and 3) are small compared to the central term (term 2), which is:

\[
\frac{\mu_s \sigma h_0 \Gamma_{eq} \alpha}{3\mu \left(-\frac{\partial p^{ss}}{\partial x}\right)^2 \left( \frac{2\pi}{\lambda_y}\right)^6}
\]

(5-25)

Therefore effects of surface diffusivity and surface dilational viscosity are small compared to that of thickness, pressure gradient, surface shear viscosity and especially the system size which appears in expression (5-25) to the six power. One should note that the effect of
disjoining pressure is neglected, thus thicknesses smaller than 100nm are not considered.

The linear stability analysis can also be applied to marginal regeneration observed in the drainage of vertical films formed by withdrawal of glass frames. Two sites for marginal regeneration were observed (54). The first one is located at the vertical film/Plateau border boundaries where liquid flows horizontally from the film into the border due to a pressure difference. In this case, the linear stability analysis applies and provides a quantitative description of the mechanism described above, which is basically that proposed by Stein (53,54). It should be noticed that once this mechanism generates thick and thin regions, gravity may influence their motions within the film. But the instability is responsible for initial occurrence of significant variations in local thickness.

The second site for marginal regeneration is located at the film/bulk liquid transition (52,54), where drainage is vertical and governed by gravity and the capillary suction in the transition region. Our stability analysis can also be applied to this situation by adding \( \rho g \) to \( -\frac{\partial p^{ss}}{\partial x} \) where \( \rho \) is the density of the bulk liquid and \( g \) the acceleration due to gravity. Stein (53,54) also observed that marginal regeneration never occurs at the film/Plateau border located at top of the glass frame. A possible explanation of this observation is that gravity and capillary suction act in opposite directions, thereby reducing liquid flow in the film and shear stress at the surface.
<table>
<thead>
<tr>
<th>conc. Kgm⁻³</th>
<th>( \mu_s ) Kg s⁻¹</th>
<th>(( \mu_d^+\mu_s )) Kg s⁻¹</th>
<th>( \Gamma_{eq} \alpha ) N m⁻¹</th>
<th>Left side of criterion (5-24)</th>
<th>Experimental drainage Observation</th>
<th>1/( \beta ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>3x10⁻⁸</td>
<td>10⁻⁴</td>
<td>5x10⁻³</td>
<td>5x10⁻⁶</td>
<td>asymmetric</td>
<td>1.7x10⁻²</td>
</tr>
<tr>
<td>0.6</td>
<td>5x10⁻⁸</td>
<td>1.6x10⁻³</td>
<td>0.011</td>
<td>3x10⁻⁴</td>
<td>asymmetric</td>
<td>0.1</td>
</tr>
<tr>
<td>1.2</td>
<td>10⁻⁷</td>
<td>2x10⁻³</td>
<td>0.024</td>
<td>1.6x10⁻³</td>
<td>asymmetric</td>
<td>0.25</td>
</tr>
<tr>
<td>3.5</td>
<td>10⁻⁸</td>
<td>1.6x10⁻³</td>
<td>0.014</td>
<td>7.6x10⁻⁵</td>
<td>asymmetric</td>
<td>4x10⁻²</td>
</tr>
<tr>
<td>SDS:1-dodecanol, 100:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>10⁻⁵</td>
<td>2x10⁻⁴</td>
<td>0.01</td>
<td>0.887</td>
<td>asymmetric</td>
<td>7</td>
</tr>
<tr>
<td>0.6</td>
<td>1.5x10⁻⁴</td>
<td>1.5x10⁻²</td>
<td>0.016</td>
<td>31</td>
<td>symmetric</td>
<td>( \beta &lt; 0 )</td>
</tr>
<tr>
<td>1.2</td>
<td>2.1x10⁻⁴</td>
<td>4 10⁻²</td>
<td>0.021</td>
<td>75</td>
<td>symmetric</td>
<td>( \beta &lt; 0 )</td>
</tr>
<tr>
<td>3.5</td>
<td>10⁻⁶</td>
<td>2.5x10⁻²</td>
<td>5 10⁻³</td>
<td>0.05</td>
<td>asymmetric</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table V-1. Comparison of experimental results for SDS and SDS:1-dodecanol, 100:1 with linear stability analysis. \( \sigma = 3.3x10⁻² \) Nm⁻¹, \( P_c = 35 \) Pa, \( P_d = 0 \), \( D_s = 5x10⁻⁹ \) m²s⁻¹, \( R_f = 100 \) µm, \( \lambda_y = 2\pi R_f \), \( h_o = 100 \) nm, \( \mu = 10⁻³ \) Kg m⁻¹s⁻¹. If left side of criterion (5-24) is less than one instability occurs, if greater than one the system is stable. Data obtained from Djabbarah (59,63)
CHAPTER SIX

NUMERICAL MODEL

In this chapter, we develop a two dimensional model to simulate a section of a film in the transition or barrier ring region between the dimple and the meniscus where the thickness goes through a minimum, as shown in figure VI-1. Assumptions are similar to those of the linear stability analysis except that variations in the x-direction are permitted and symmetry boundary conditions are used in the y-direction. First, a steady state solution, with nonuniform film thickness in the x-direction, is found for a specified flux or pressure drop between the dimple and the meniscus. Then, the stability of the system is examined by imposing an initial perturbation in thickness around the steady state solution in the direction transverse to the liquid flow.

VI-1 Statement of Problem

In order to keep the problem as simple as possible we make the following assumptions:

1.) The problem is solved in Cartesian coordinates. \( L_x \) and \( L_y \) are the length of the system respectively in \( x \) and \( y \) directions
VI-1-a. Physical system

VI-1-b. Modeled domain.  Simulated region

Figure VI-1. Simulation of a section of film
2.) The drainage is symmetric in the vertical (thickness) direction. The thickness of the film is considered to be 2h.
3.) The bulk liquid is an incompressible Newtonian fluid with constant viscosity.
4.) The pressure \( p_g \) in the gas or in the disperse phase is independent of time and position.
5.) Mass transfer of surfactant from the underlying bulk liquid is neglected.
6.) All inertial effects are neglected.
7.) Disjoining pressure effects are neglected.
8.) The flow obeys the lubrication approximation.
9.) The flux of surfactant at the surface across the boundaries is zero.
10.) At rest, the surface is assumed to have a uniform surfactant concentration \( \Gamma_{eq} \).
11.) Variations in surface tension in position and time are small enough so that surface tension is considered constant in the normal stress boundary condition.
12.) Symmetry boundary conditions are assumed in the \( y \)-direction (direction perpendicular to the flow of the underlying liquid).
13.) Surface flow normal to the boundaries (i.e., surface flow across the boundaries) is not permitted. However, tangential surface flow along the boundaries is allowed.
14.) At the inlet boundary, \( x=0 \), a flux or pressure boundary condition is used as well as a specified slope. At the outlet boundary, \( x=L_x \), we
impose a pressure equal to the pressure in the meniscus with a finite slope.

15.) In order to find the steady state solution of the system, the one dimensional simulator was used with the following initial condition:

- Uniform surfactant concentration equal to $\Gamma_{eq}$
- Zero surface velocity
- Uniform flat film of radius, $R_f$, connected to a static meniscus.

16.) The stability of the system is examined by imposing an initial perturbation in thickness in the $y$-direction around the steady state solution. In this case, the two dimensional simulator was used.

**VI-2 Governing Equations**

In the lubrication approximation the mass conservation equation in the bulk liquid can be expressed as (34):

$$\frac{\partial h}{\partial t} = -\frac{\partial}{\partial x}(h \nu_x) - \frac{\partial}{\partial y}(h \nu_y)$$  \hspace{1cm} (6-1)

with

$$\nu_x = \nu_{sx} - \frac{h^2}{3\mu} \left( \frac{\partial p}{\partial x} \right) \quad \text{and} \quad \nu_y = \nu_{sy} - \frac{h^2}{3\mu} \left( \frac{\partial p}{\partial y} \right)$$

with $\mu$ being the viscosity of the bulk liquid, $h$ the half thickness, $p$ the pressures in the liquid film, $\nu_{sx}$ and $\nu_x$ are respectively the surface
velocity and average value of bulk velocity in the x-direction, \( v_{sx} \) and \( v_{sy} \) those in the y-direction.

Substituting expressions for \( \bar{v}_x \) and \( \bar{v}_y \) into equation (6-1), we obtain:

\[
\frac{\partial h}{\partial t} = -\left( \frac{\partial}{\partial x} (h v_{sx}) + \frac{\partial}{\partial y} (h v_{sy}) \right) + \frac{1}{3\mu} \left( \frac{\partial}{\partial x} (h^3 \frac{\partial p}{\partial x}) + \frac{\partial}{\partial y} (h^3 \frac{\partial p}{\partial y}) \right) \tag{6-2}
\]

In view of assumption 10.), the normal stress boundary condition at \( z=h \) reduces to

\[
p_g - p = \sigma \left( \frac{\partial}{\partial x} \left( \frac{\partial h}{\partial x} \left( \frac{\partial h}{\partial x} \right)^2 + \left( \frac{\partial h}{\partial y} \right)^2 \right)^{1/2} \right) + \frac{\partial}{\partial y} \left( \frac{\partial h}{\partial y} \left( \frac{\partial h}{\partial x} \right)^2 + \left( \frac{\partial h}{\partial y} \right)^2 \right)^{1/2} \right) \tag{6-3}
\]

where \( \sigma \) is the equilibrium surface tension.

According to assumption 5.), transport of surfactant from the bulk liquid phase onto the interface is neglected. We consider the total surface concentration of surfactant to be the sum of initial surface concentration \( \Gamma_{eq} \) and local change \( \Gamma \). The surfactant conservation equation at the surface becomes (60):

\[
\frac{\partial \Gamma}{\partial t} = -\Gamma_{eq} \left( \frac{\partial v_{sx}}{\partial x} + \frac{\partial v_{sy}}{\partial y} \right) - \frac{\partial}{\partial x} (\Gamma v_{sx}) - \frac{\partial}{\partial y} (\Gamma v_{sy}) + D_s \left( \frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial^2 \Gamma}{\partial y^2} \right) \tag{6-4}
\]
$D_s$ is the surface diffusivity.

Neglecting inertial effects, the surface momentum balance follows (61):

- x-component

$$-\alpha \frac{\partial \Gamma}{\partial x} + (\mu_d + \mu_s) \frac{\partial^2 v_{sx}}{\partial x^2} + \mu_s \frac{\partial^2 v_{sx}}{\partial y^2} + \mu_d \frac{\partial^2 v_{sy}}{\partial x \partial y} - h \frac{\partial p}{\partial x} = 0 \quad (6-5)$$

- y-component

$$-\alpha \frac{\partial \Gamma}{\partial y} + (\mu_d + \mu_s) \frac{\partial^2 v_{sy}}{\partial y^2} + \mu_s \frac{\partial^2 v_{sy}}{\partial x^2} + \mu_d \frac{\partial^2 v_{sx}}{\partial x \partial y} - h \frac{\partial p}{\partial y} = 0 \quad (6-6)$$

where $\alpha = \left( \frac{\partial \sigma}{\partial \Gamma} \right)_{eq}$, $\mu_s$ and $\mu_d$ are respectively surface shear and dilational viscosity.

Boundary condition are shown on figure VI-2. The system is assumed to be symmetric at the transverse boundaries in the y-direction. Thus we have:

- at $y = 0$ and $y = L_y$

  for all $x \in [0, L_x]$ we have

$$\begin{cases} 
\frac{\partial p}{\partial y} = 0 \\
\frac{\partial h}{\partial y} = 0 \\
\frac{\partial \Gamma}{\partial y} = 0 
\end{cases} \quad (6-7)$$
\( p = p_{\text{out}}, \frac{\partial h}{\partial x} = s_{\text{out}}, v_{sx} = 0, \frac{\partial v_{sy}}{\partial x} = 0, \frac{\partial r}{\partial x} = 0 \)

**Meniscus**

\( \frac{\partial p}{\partial y} = 0 \)

\( \frac{\partial h}{\partial y} = 0 \)

\( v_{sy} = 0 \)

\( \frac{\partial v_{sx}}{\partial y} = 0 \)

\( \frac{\partial r}{\partial y} = 0 \)

**Dimple**

\( p = p_{\text{inlet}}, \frac{\partial h}{\partial x} = s_{\text{inlet}}, v_{sx} = 0, \frac{\partial v_{sy}}{\partial x} = 0, \frac{\partial r}{\partial x} = 0 \)

Figure VI-2. Boundary conditions
From assumption 13.):

\[
\begin{align*}
- \text{ at } \begin{cases}
    x = 0 \text{ and } x = L_x \\
    \forall y \in [0, L_y]
    \end{cases}
\text{ we have } & \begin{cases}
    v_{sx} = 0 \\
    \frac{\partial v_{sy}}{\partial x} = 0
    \end{cases} \\
\text{ (6-8)}
\end{align*}
\]

\[
\begin{align*}
- \text{ at } \begin{cases}
    y = 0 \text{ and } y = L_y \\
    \forall x \in [0, L_x]
    \end{cases}
\text{ we have } & \begin{cases}
    v_{sy} = 0 \\
    \frac{\partial v_{sx}}{\partial y} = 0
    \end{cases} \\
\text{ (6-9)}
\end{align*}
\]

Constant pressure, \( p_{\text{inlet}} \) or flux, \( Q \), and finite slope, \( s_{\text{inlet}} \) are imposed at the inlet boundary.

\[
\begin{align*}
- \text{ at } \begin{cases}
    x = 0 \\
    \forall y \in [0, L_y]
    \end{cases}
\text{ we have } & \begin{cases}
    p = p_{\text{inlet}} \text{ or } -\frac{L_y h^3}{3\mu} \frac{\partial p}{\partial x} = Q \\
    \frac{\partial h}{\partial x} = s_{\text{inlet}}
    \end{cases} \\
\text{ (6-10)}
\end{align*}
\]

At the outlet boundary, we impose a constant pressure, \( p_{\text{out}} \), equal to that in the meniscus region with a finite slope \( s_{\text{out}} \).

\[
\begin{align*}
- \text{ at } \begin{cases}
    x = L_x \\
    \forall y \in [0, L_y]
    \end{cases}
\text{ we have } & \begin{cases}
    p = p_{\text{out}} \\
    \frac{\partial h}{\partial x} = s_{\text{out}}
    \end{cases} \\
\text{ (6-11)}
\end{align*}
\]

Since the surface flow normal to the boundaries is zero and in view of assumption 9.), we have:
at \( x = 0 \text{ and } L_x \) we have \( \frac{\partial \Gamma}{\partial x} = 0 \) (6-12)

In order to integrate equations (6-2), (6-3), (6-4), (6-5) and (6-6), an initial condition is needed. Two initial conditions are used. The first one is used to find a steady state solution to the one dimensional system and follows as:

- Uniform surfactant concentration:

\[ \Gamma = 0 \] (6-13)

- Zero surface velocity:

\[ v_s = 0 \quad (x \text{ and } y \text{ components}) \] (6-14)

- Uniform film thickness from \( x=0 \) to the location of the barrier ring \( R_f \):

\[ h = h_i \quad 0 \leq x \leq R_f \] (6-15)

- Static menisci having a slope equal to zero at \( R_f \) and \( s_{\text{out}} \) at \( L_x \):

\[ h = h_i + \left( R_s - \sqrt{R_s - (x - R_f)^2} \right) \quad R_f \leq x \leq L_x \] (6-16)
with
\[ R_s = \frac{\sqrt{1 + s_{out}^2}}{s_{out}} (L_x - R_f) \]
\[ p_c = -\frac{\sigma}{R_s} \]

The second initial condition is used to determine the stability of the two-dimensional system by imposing an initial perturbation in thickness in the y-direction around the steady state solution.

\[
\begin{cases}
  h = h^{ss} + a \cos \left( \frac{n_i \pi y}{L_y} \right), & n_i = 1, 2, 3, \ldots \\
  \Gamma = \Gamma^{ss} \\
  v_{sx} = v_{sx}^{ss} \\
  v_{sy} = v_{sy}^{ss} = 0
\end{cases}
\]  \hspace{1cm} (6-17)

Equations (6-2), (6-3), (6-4), (6-5) and (6-6) can be made dimensionless by using the following dimensionless quantities:

\[
X = \frac{x}{L_x}, \quad Y = \frac{y}{L_y}, \quad H = \frac{h}{h_o}, \quad U = \frac{v_{sx}}{V_o}, \quad V = \frac{v_{sy}}{V_o},
\]

\[
p = \frac{p - p_g}{p_o}, \quad T = \frac{t}{t_o}, \quad W = \frac{\Gamma}{\Gamma_o}
\]

with
\[
h_o = \left( \frac{3 \mu L_x^2}{\sigma \left( \frac{Q}{L_y} \right)} \right)^{1/3}, \quad p_o = \frac{\sigma}{L_x}, \quad t_o = \frac{\mu_d + \mu_s}{h_o p_o}
\]
\[ V_0 = \frac{L_x}{\mu_d + \mu_s} \]
\[ \Gamma_0 = \frac{h_0 P_0}{\alpha} \]

Governing equations become:

\[ \frac{\partial H}{\partial T} = -\left( \frac{\partial}{\partial X} (H U) + \frac{\partial}{\partial Y} (H V) \right) + N_1 \left( \frac{\partial}{\partial X} (H^3 \frac{\partial P}{\partial X}) + \frac{\partial}{\partial Y} (H^3 \frac{\partial P}{\partial Y}) \right) \] (6-18)

with

\[ P = -\left( \frac{\partial}{\partial X} \left( \frac{\varepsilon \frac{\partial H}{\partial X}}{1 + \left( \frac{\varepsilon \frac{\partial H}{\partial X}}{\varepsilon \frac{\partial H}{\partial Y}} \right)^2} \right) \right) + \frac{\partial}{\partial Y} \left( \frac{\varepsilon \frac{\partial H}{\partial Y}}{1 + \left( \frac{\varepsilon \frac{\partial H}{\partial X}}{\varepsilon \frac{\partial H}{\partial Y}} \right)^2} \right) \] (6-19)

\[ \frac{\partial W}{\partial T} = -N_2 \left( \frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} \right) - \frac{\partial}{\partial X} (W U) - \frac{\partial}{\partial Y} (W V) + N_3 \left( \frac{\partial^2 W}{\partial X^2} + \frac{\partial^2 W}{\partial Y^2} \right) \] (6-20)

\[ -\frac{\partial W}{\partial X} + \frac{\partial^2 U}{\partial X^2} + N_4 \frac{\partial^2 U}{\partial Y^2} + N_5 \frac{\partial^2 V}{\partial X \partial Y} - H \frac{\partial P}{\partial X} = 0 \] (6-21)

\[ -\frac{\partial W}{\partial Y} + \frac{\partial^2 V}{\partial Y^2} + N_4 \frac{\partial^2 V}{\partial X^2} + N_5 \frac{\partial^2 U}{\partial X \partial Y} - H \frac{\partial P}{\partial Y} = 0 \] (6-22)

where
\[
\begin{align*}
\varepsilon &= \frac{h_0}{L_x}, \quad N_1 = \frac{h_0 (\mu_d + \mu_s)}{3\mu L_x^2}, \quad N_2 = \frac{\Gamma_{eq} \alpha}{h_0 p_0}, \\
N_3 &= \frac{D_s (\mu_d + \mu_s)}{h_0 p_0 L_x^2}, \quad N_4 = \frac{\mu_s}{(\mu_d + \mu_s)}, \quad N_5 = \frac{\mu_d}{(\mu_d + \mu_s)}
\end{align*}
\]

Boundary conditions become:

\begin{align*}
\left\{ \begin{array}{l}
Y = 0 \text{ and } Y = \frac{L_y}{L_x} \\
\forall X \in [0,1]
\end{array} \right.
& \quad \left\{ \begin{array}{l}
\frac{\partial P}{\partial Y} = 0 \\
\frac{\partial H}{\partial Y} = 0 \\
\frac{\partial W}{\partial Y} = 0
\end{array} \right. \\
(6-23)
\end{align*}

\begin{align*}
\left\{ \begin{array}{l}
X = 0 \text{ and } X = 1 \\
\forall Y \in \left[0, \frac{L_y}{L_x}\right]
\end{array} \right.
& \quad \left\{ \begin{array}{l}
U = 0 \\
\frac{\partial V}{\partial X} = 0
\end{array} \right.
(6-24)
\end{align*}

\begin{align*}
\left\{ \begin{array}{l}
Y = 0 \text{ and } Y = \frac{L_y}{L_x} \\
\forall X \in [0,1]
\end{array} \right.
& \quad \left\{ \begin{array}{l}
V = 0 \\
\frac{\partial U}{\partial Y} = 0
\end{array} \right. \\
(6-25)
\end{align*}

\begin{align*}
\left\{ \begin{array}{l}
X = 0 \\
\forall Y \in \left[0, \frac{L_y}{L_x}\right]
\end{array} \right.
& \quad \left\{ \begin{array}{l}
P = \frac{p_{inlet}}{p_0} \text{ or } H^3 \frac{\partial P}{\partial X} = -1 \\
\frac{\partial H}{\partial X} = \frac{s_{inlet}}{\varepsilon} \\
\frac{\partial W}{\partial X} = 0
\end{array} \right.
(6-26)
\end{align*}
- at \( \forall Y \in \left[0, \frac{L_y}{L_x}\right] \) we have

\[
\begin{align*}
X &= 1 \\
p &= \frac{P_{out}}{P_o} \\
\frac{\partial H}{\partial X} &= \frac{s_{out}}{\varepsilon} \\
\frac{\partial W}{\partial X} &= 0
\end{align*}
\]

(6-27)

Initial condition 1 for the one dimensional problem:

\[
\forall Y \in \left[0, \frac{L_y}{L_x}\right]
\begin{align*}
H &= \frac{h_i}{h_0} & 0 \leq X \leq \frac{R_f}{L_x} \\
&= \frac{h_i + \left( R_s - \sqrt{R_s^2 - (L_x X - R_f)^2} \right)}{h_0} & \frac{R_f}{L_x} \leq X \leq 1 \\
W &= 0 & 0 \leq X \leq 1 \\
U &= 0 & 0 \leq X \leq 1
\end{align*}
\]

Initial condition 2 for the two dimensional problem:

\[
\begin{align*}
H &= H^{SS} + A_p \cos \left( n_i \pi Y \left( \frac{L_x}{L_y} \right) \right) \\
W &= W^{SS} \\
U &= U^{SS} \\
V &= V^{SS} = 0
\end{align*}
\]

The two dimensional model derived above is used to simulate an entire rectangular film section and can be used to find a solution for the steady state problem provided the system is stable. However, the
solution for the steady state problem is independent of y. Therefore, a simpler one dimensional model is used to solve the steady state problem. Using the dimensionless variables defined above, the problem has the following form:

- Mass conservation equation in bulk liquid:

\[
\frac{\partial H}{\partial t} = - \frac{\partial}{\partial X} (HU) + N_1 \left( \frac{\partial}{\partial X} (H^3 \frac{\partial P}{\partial X}) \right) \tag{6-28}
\]

with

\[
P = - \frac{\partial}{\partial X} \left( \frac{\varepsilon \frac{\partial H}{\partial X}}{\left( 1 + \left( \varepsilon \frac{\partial H}{\partial X} \right)^2 \right)^{\frac{1}{2}}} \right) \tag{6-29}
\]

- Surfactant mass balance:

\[
\frac{\partial W}{\partial t} = -N_2 \left( \frac{\partial U}{\partial X} \right) - \frac{\partial}{\partial X} (WU) + N_3 \left( \frac{\partial^2 W}{\partial X^2} \right) \tag{6-30}
\]

- x-component of surface momentum balance:

\[
- \frac{\partial W}{\partial X} + \frac{\partial^2 U}{\partial X^2} - H \frac{\partial P}{\partial X} = 0 \tag{6-31}
\]
- Boundary conditions:

\[
\begin{align*}
-\text{at } X=0 \text{ we have} & \quad \begin{cases} 
P = \frac{P_{\text{inlet}}}{p_o} \\
\frac{\partial H}{\partial X} = \frac{s_{\text{inlet}}}{\varepsilon} \\
\frac{\partial W}{\partial X} = 0 \\
U = 0
\end{cases} \\
\text{(6-32)}
\end{align*}
\]

\[
\begin{align*}
-\text{at } X=1 \text{ we have} & \quad \begin{cases} 
P = \frac{P_{\text{out}}}{p_o} \\
\frac{\partial H}{\partial X} = \frac{s_{\text{out}}}{\varepsilon} \\
\frac{\partial W}{\partial X} = 0 \\
U = 0
\end{cases} \\
\text{(6-33)}
\end{align*}
\]

- Initial condition 1:

\[
\begin{align*}
H = \frac{h_i}{h_o} & \quad 0 \leq X \leq \frac{R_f}{L_x} \\
H = \frac{h_i + \left( R_s - \sqrt{R_s^2 - (L_x X - R_f)^2} \right)}{h_o} & \quad \frac{R_f}{L_x} \leq X \leq 1 \\
W = 0 & \quad 0 \leq X \leq 1 \\
U = V = 0 & \quad 0 \leq X \leq 1
\end{align*}
\]

**VI-3 Solution techniques**

The partial differential equations described in the previous section are of two kinds. The mass conservation equation in the bulk liquid
(thickness equation) and surfactant mass balance at the surface are parabolic equations. The X and Y components of the surface momentum balance are elliptic equations. The sets of partial differential equations are solved by using a semi-implicit (linear approximations of non linearities at the new time level, see section III-3) finite difference approximation. Up-stream weighting is used for the mobilities in the mass conservation equation (thickness, \( H \), cube of thickness, \( H^3 \)) and in the surfactant mass balance (concentration \( W \)).

For simplicity, thickness equation is formulated in residual form for only the change in thickness with time (semi-implicit in thickness and explicit in surface velocity). Surfactant conservation and surface momentum equations are solved simultaneously and formulated in residual form for the changes in concentration and surface velocity (semi-implicit in concentration and surface velocity and explicit in thickness). Thickness and surface equations are then coupled using a predictor-corrector method.

**VI-4 Matrix equations and solution methods**

Using the above method, governing equations can be transformed into systems of linear equations.

-One dimensional problem.

Thickness equation (6-28) yields a linear pentadiagonal system where unknowns are change in thickness for the new time level at each
grid block location, \((\Delta H_i)_{1\leq i \leq nx}\). Surfactant mass balance at the surface (6-29) and surface momentum balance (6-30) are solved simultaneously and yield a block 2x2 tridiagonal system. Unknowns are change in concentration and surface velocity for the new time level and have the following order:

\[
(\Delta W_1, \Delta U_1, \ldots, \Delta W_i, \Delta U_i, \ldots, \Delta W_{nx}, \Delta U_{nx})
\]

Both systems are solved using a L-U decomposition and then an upper and lower back substitution. An automatic time-step size selection is used such that the maximum relative change per time step in each dependent variable (\(\Delta H\), \(\Delta W\), \(\Delta U\)) approximately equals its respective maximum value (\(\Delta H_{\text{max}}\), \(\Delta W_{\text{max}}\), \(\Delta U_{\text{max}}\))

Two dimensional problem.

Thickness equation (6-18) is expressed in finite-difference form and yields a 13 point stencil, as shown in figure VI-3. Equation (6-18) can be transformed into a system of linear equations:

\[
A_h \Delta H = B_h \quad \text{where} \quad \Delta H^T = \left(\left(\Delta H_{i,j}\right)_{1 \leq i \leq nx} \left(\Delta H_{i,j}\right)_{1 \leq j \leq ny}\right)
\]

\(\Delta H\) is a \((nx \times ny)\) vector containing the change in thickness for the new time step. \(A_h\) is a \((nx \times ny)^2\) non symmetric sparse matrix. Elements of \(A_h\) are shown in figure VI-7. \(B_h\) is a \((nx \times ny)\) vector.
Figure VI-3. Stencil for thickness equation (6-18)

Figure VI-4. Stencil for surfactant mass balance equation (6-20)
Stencils for each surface equation (6-20), (6,21), (6,22) are shown respectively in figure (VI-4), (VI-5), (VI-6). Surfactant mass balance (6-20) and the X and Y components of surface momentum balance are solved simultaneously and are transformed into the following linear system:

$$A_s \Delta S = B_s \quad \text{where} \quad \Delta S^T = \left( \left( \Delta W_{i,j}, \Delta U_{i,j}, \Delta V_{i,j} \right)_{1 \leq i \leq nx} \right)_{1 \leq j \leq ny}$$

$\Delta S$ is a $(3 \times nx \times ny)$ vector containing the change for the new time step of concentration, $W$ and surface velocity, $U$ and $V$. $A_s$ is a $(3 \times nx \times ny)^2$ sparse matrix. Elements of $A_s$ are shown in figure VI-8. $B_s$ is a $(3 \times nx \times ny)$ vector.

A package for solving large sparse linear system, $A u = B$ is used. It is called NSPCG (Nonsymmetric Preconditioned Conjugate Gradient) and was developed by the Center for Numerical Analysis at the University of Texas at Austin. NSPCG provides a variety of different nonsymmetric preconditioned conjugate gradient methods. In simple terms, procedures, such as conjugate gradient, are minimization iterative methods that require little storage space, almost always guarantee convergence to a solution and usually are fast. Minimization methods are often called accelerators and are used in conjunction with preconditioning methods. That is, a new matrix $A'$ is created that resembles $A$ but is easily invertible. The new system $(A'^{-1} A) u = A' B$ is much better conditioned than the original system and provides faster convergence to the same solution.
Figure VI-5. Stencil for X-component of surface momentum equation (6-21)

Figure VI-6. Stencil for Y-component of surface momentum equation (6-22)
Figure VI-7. Locations of matrix elements for the linear system solving the thickness equation.
Figure VI-9. Locations of matrix elements for the linear system solving surfactant mass balance and surface momentum balance equations.
We found that biconjugate conjugate gradient square (64) as an accelerator in conjunction with modified incomplete L-U decomposition (Choleski) (65) as a preconditioner provided the most efficient results.

When the simulated domain includes a large portion of the meniscus region, we encountered the following numerical problem. For fine grid system ( > nx=100 x ny=40), negative pivots were found during the preconditioning of the matrix A_h that solves for the thickness equation, meaning the matrix A_h is close to being singular. The reason for this is that well into the meniscus region (far away from the minimum thickness), changes in thickness as a function of x are extremely important while the pressure gradient in the x-direction is almost negligible. Because the coefficients of the matrix A_h are proportional to h³, the contrast between the largest and smallest coefficient is too large, rendering the system of equations numerically hard to solve. By reducing the portion of the meniscus region in the simulated domain negative pivots were not encountered.

VI-5 Convergence of the numerical solution

The convergence of the solution was checked by varying space intervals (ΔX and ΔY) and time intervals (maximum change for each dependent variable per time step). To establish the order of convergence with ΔT, very small ΔX and ΔY are used and kept constant. For simplicity we take ΔH_{max}, ΔW_{max}, ΔU_{max}, ΔV_{max} to be
Figure VI-9. Convergence with $\Delta_{\text{max}}$. $n_x = 100$ and $n_y = 40$
Figure VI-10. Convergence with $\Delta X$. $\Delta_{\text{max}}=0.05$ and $n_y=40$
Figure VI-11. Convergence with $\Delta Y$. $\Delta_{\text{max}} = 0.05$ and $n_x = 100$
equal to $\Delta_{\text{max}}$. A reference solution is chosen for a very small $\Delta_{\text{max}}$ ($=10^{-4}$), at a given time during film drainage.

The relative difference from the reference solution, or error, in thickness, concentration and surface velocity are plotted as a function of $\Delta_{\text{max}}$ (i.e., $\Delta T$). Figure VI-9 shows that each plot of error is a straight line of slope approximately one. Thus, the rate of convergence of the numerical solution with $\Delta T$ is unity. Having established the convergence with $\Delta T$, $\Delta_{\text{max}}$ is kept constant (0.05) for the convergence with grid size. Similar to figure VI-9, figure VI-10 and figure VI-11 show that each plot of error is a straight line of slope approximately one and thus establish a first order convergence in grid size. Reference solutions in figures VI-10 and VI-11 were given for $\Delta x = 10^{-4}$ and $\Delta y = 10^{-2}$.

**VI-6 Comparison between linear stability analysis of a flat interface and numerical simulations**

We first consider the stability of a flat film to demonstrate that there is no instability without variation in film thickness. Let us consider a portion of a film of length $L_x$, width $L_y$ and uniform thickness $h_0$. For simplicity, we consider the case were $L_x = L_y$. As in chapter VI, we assume that the interface contains an insoluble monolayer of surfactant which, at rest, has a uniform concentration $\Gamma_{\text{eq}}$. During film drainage, the underlying liquid is subject to a constant pressure gradient in the $x$-direction.
The steady state solution is the same as that of chapter V: uniform thickness \( h_0 \), zero surface velocity, and constant surface tension gradient to balance the constant induced shear stress at the surface. The stability of the system is investigated by considering small perturbations in concentration and surface velocity around the steady state solution. Perturbations in thickness are not considered because the interface is assumed to remain flat. The linear stability analysis is detailed in appendix B, and shows that the system is always stable. For \( k_x = 0 \), the dimensionless growth factor of the perturbations \( \beta' \) is real and is expressed as:

\[
\beta' = -\left( \frac{\Gamma_{e\alpha}}{h_0 L_x \left( -\frac{\partial p^{ss}}{\partial x} \right)} \right) - \left( \frac{D_s (\mu + \mu_s)}{h_0 \left( -\frac{\partial p^{ss}}{\partial x} \right) L_x^3} \right) K_y^2
\]  

(6-34)

The growth factor is always negative, i.e. the system is always stable.

The numerical simulator is modified to solve for equations (6-20), (6-21), (6-22). Thickness equation is disregarded because changes in thickness are not considered. Boundary conditions are kept the same. Initial condition is a perturbation around the steady state solution and is the following:

\[
\begin{align*}
W &= W^{ss} + A_p \cos \left( 2\pi Y \left( \frac{L_x}{L_y} \right) \right) \\
U &= V = 0
\end{align*}
\]
Since \( L_x = L_y \) and the wave length of the initial perturbation is \( L_y \), the dimensionless wave number \( K_y \) in expression (6-34) becomes unity. Therefore, the dimensionless growth factor \( \beta' \) becomes:

\[
\beta' = -\left( \frac{\Gamma_{eq} \alpha}{h_0 L_x \left( -\frac{\partial p^{ss}}{\partial x} \right)} \right) - \left( \frac{D_s \left( \mu_d + \mu_s \right)}{h_0 \left( -\frac{\partial p^{ss}}{\partial x} \right) L_x^3} \right) \tag{6-35}
\]

Numerical results confirm the linear stability predictions and show that the system considered in this section is always stable. Departure from steady state for each dependent variable as a function of dimensionless time is shown on a semi-log plot in figure VI-12. As shown in figure VI-12, each dimensionless variable, \( W \), \( U \) and \( V \) have the same decay rate of 160, almost equal to the one predicted by the linear stability analysis of 166 (calculated using equation (6-35) for the case of figure VI-12).

**VI-7 Simulation of the instability causing asymmetric drainage**

In this section, the two dimensional numerical model is used to determine the stability of a section of a draining film in the transition region between the dimple and the meniscus (see figure VI-1). First, a steady state solution, with non uniform film thickness in the \( x \)-direction, is found for a specified flux or pressure drop between the dimple and
Figure VI-12. Decay of dependent variables for a flat interface.

\( \Gamma_{eq} = 5 \times 10^{-5} \text{ Kg m}^{-2} \), \( \Gamma_{eq} \alpha = 0.01 \text{ N m}^{-1} \), \( L_x = L_y = 1 \text{ mm} \), \( \mu_s = \mu_d = 10^{-6} \text{ Kg s}^{-1} \), \( h_0 = 200 \text{ nm} \), \( dp/dx = 3 \times 10^5 \text{ Pa m}^{-1} \). \( nx = ny = 100 \). \( \Lambda_p = 10^{-5} \).

The dimensionless time constant \( \beta' = -166 \).
the meniscus. Then, the stability of the system is examined by imposing an initial perturbation in thickness around the steady state solution in the direction transverse to the liquid flow.

**VI-7-a Steady state solution**

Since the steady state solution has no dependence on $y$, the one dimensional simulator was used in conjunction with initial condition 1 to determine the steady state solution. Figure VI-13 shows typical film thickness, surfactant concentration and surface velocity profiles when steady state is reached. Zero slope at the inlet and a flow rate per unit length in the $y$-direction were specified. As one can see surface velocity and surfactant concentration gradients are significant only in the barrier ring region where pressure gradients are the largest.

**VI-7-b Stability**

Stability of a draining film section of length $L_x$ and width $L_y$ is determined by imposing a small perturbation in thickness around the steady state solution (see initial condition 2). The two dimensional simulator was used in conjunction with initial condition 2.

For suitable conditions, we found that there is a critical width $L_{yc}$ above which perturbations around the steady state solution grow in time. In this case, instability develops. If $L_y$ is less than $L_{yc}$,
Figure VI-13. Steady state solution. $\Gamma_{eq} = 5 \times 10^{-5}$ Kg m$^{-2}$, $\Gamma_{eq} \alpha = 0.01$ N m$^{-1}$, $L_x=0.5$ mm, $R_f=0.25$ mm, $P_{inlet}=1$ Pa, $P_c=50$ Pa, $s_{inlet}=0$, $s_{out}=1$, $\sigma = 0.03$ N m$^{-1}$, $\mu_s = \mu_d = 10^{-6}$ Kg s$^{-1}$, $Q/L_y = 10^{-12}$ m$^2$ s$^{-1}$, $n_x=100$. 
perturbations from the steady state solution decay in time, and the system is stable.

Figures VI-14., VI-15 and VI-16 illustrate an unstable case. Parameters are approximately those of pure SDS, i.e. low surface viscosity, $\mu_s = \mu_d = 10^{-6}$ Kg s$^{-1}$, $\Gamma_{eq} = 0.01$ N m$^{-1}$, $\sigma = 0.03$ N m$^{-1}$. The steady state solution for this case is shown in figure VI-13. The width $L_y$ of 150 $\mu$m is greater than $L_{yc}$ of 110 $\mu$m. Figure VI-14, VI-15, VI-16 show respectively the relative change in thickness and concentration from the steady state solution and a plot of surface velocity at a given time during instability. As one can see, all changes in each dependent variable are located right at the barrier ring or minimum thickness. A circulation cell develops in the barrier ring region causing thick parts of the film to thicken and the surface to flow outward toward the meniscus, while thin parts of the film get thinner with the surface flowing inward towards the dimple. Figure VI-15 shows that surface tension gradients in the direction perpendicular to the initial steady flow cause the surface and the underlying liquid to flow from thin to thick parts of the film. As a result, perturbations grow and the system is unstable.

Figure VI-17 illustrates the growth of each dependent variable during instability and shows that, after a short initial transient, growth is exponential, as predicted by the linear stability analysis. When the width $L_y$ of the system is decreased to 50 $\mu$m ($L_y < L_{yc}$), perturbations from the steady state solution decay in time as shown in figure VI-18 and the system is stable.
Figure VI-14. Relative change in thickness from steady state solution during instability (same parameters as figure VI-13). $L_y = 150 \mu m$, $L_{yc} = 110 \mu m$. Amplitude of maximum initial perturbations $10^{-3}$. Time 10 s.
Figure VI-15. Relative change in surface concentration and surface tension from steady state solution during instability. Same case as figure VI-14
Figure VI-16. Surface velocity plot during instability. Same case as figure VI-14
Figure VI-17. Maximum change for each dependent variable over the whole domain during the unstable case, $L_\gamma = 150 \, \mu m$
Figure VI-18. Maximum change for each dependent variable over the whole domain during the stable case, $L_y = 50 \ \mu m$
As indicated by the linear stability analysis, interfacial shear stress and capillary flows (curvature driven) which promote flow in the direction opposite to the surface-tension-driven flow, are more important for small system length and can prevent the instability from occurring. The numerical simulations give the same basic flow pattern as in the linear stability analysis, i.e. thicker regions flow toward the meniscus and thinner regions flow toward the dimple.

For transversal length, $L_y$, larger than the critical length $L_{yc}$, one or multiple circulation cells were observed during instability. We define $n$ as the integer ratio of $L_y$ by $L_{yc}$. The number of cells obtained depends on the number of waves, $n_i$, imposed in the initial condition (see equation 6-17). When $n_i$ is less than or equal to $n$, the number of cells obtained is $n_i$ and the system is unstable. When $n_i$ is greater than $n$, the number of cells observed initially is $n_i$ and then decreases to an acceptable value less than $n$. The perturbations in thickness grow and the system is unstable.

In our experiments, we found that asymmetric drainage is much faster than symmetric drainage. Therefore the flow rate of liquid flowing through the barrier ring during asymmetric drainage must be greater than during symmetric drainage. The numerical simulations show the same trend. Average flow rates over $y$ per unit length, $L_y$, of the underlying bulk liquid at the barrier ring calculated from the simulations are shown in figure VI-19. During instability, the flow rate increases exponentially from its initial steady state value, causing faster
Figure VI-19. Flow rate of the underlying bulk liquid during instability.

Same parameters as of figure VI-13
film drainage. For stable systems, flow rate remains constant and equal to its initial steady state value.

VI-7-c Validity of the linear stability analysis

The validity of the stability analysis is examined by comparing the critical length, $L_{yc}$ given by the numerical simulations and marginal wave length, $\lambda_{yc}$, obtained from the stability criterion (5-24). Since we used a symmetry condition at the transverse boundary in our simulations, $L_{yc}$ corresponds to half the marginal wave length, $1/2 \lambda_{yc}$, of the linear stability analysis. $h_0$ and pressure gradient necessary for the linear stability analysis were obtained from the steady state solution at the minimum thickness location.

A wide range of values was investigated for parameters such as flow rate of the underlying liquid, injection and capillary pressure, system length in the x-direction. The surface diffusion coefficient was varied from $10^{-8}$ cm$^2$/sec to $10^{-4}$ cm$^2$/sec, a wider range than that given in chapter five. Surface shear and dilational viscosity were varied form $10^{-7}$ Kg/sec to $10^{-3}$ Kg/sec (see table VI-1). As indicated by experimental data for SDS system (63), surface tension and the surface Gibbs elasticity, ($\Gamma_{eq\alpha}$), were kept constant respectively equal to 0.03 N/m and 0.01 N/m.

The results of the simulations are in good agreement with the linear stability analysis developed in chapter five. For every case shown in table VI-1, surface diffusion was varied in the range given
above and the surface dilational viscosity was varied up to 100 times more than the surface shear viscosity. As discussed in section three of chapter five, numerical simulations confirmed that surface diffusion and surface dilational viscosity have a very small influence compared to those of thickness, pressure gradient, surface shear viscosity and system length scale.

However, departures from the linear stability analysis are observed when the half critical wave length is comparable to either the longitudinal dimension of the barrier ring or the total longitudinal length of the system, $L_x$. The longitudinal dimension of the barrier ring is represented by the minimum radius of curvature of the barrier ring region which can be obtained from the steady state solution. The linear stability analysis assumes that the thickness and the perturbations do not change in the x-direction.

The influence of $L_x$ was investigated by considering a case, such as the one of figure VI-13, where the critical half wave length is much smaller than the minimum radius of curvature of the barrier ring. $L_x$ was decreased so that the minimum thickness remains at the center of $L_x$. Both pressure and slope at $x=0$ and $x=L_x$ were chosen so that the steady state solution remains identical to that of figure VI-13. Figure VI-20 shows the influence of $L_x$ on the numerical results. Clearly, if $L_x$ is comparable to half critical wave length ($1/2 \, \lambda_{yc}$), the circulation cell causing instability, is stabilized by the proximity of the boundary conditions at $x=0$ and $x=L_x$. If $L_x$ is less than $1/2 \, \lambda_{yc}$, no instability is observed.
Figure VI-20. Influence of $L_x$. Same parameters as of figure VI-13

$(1/2 \lambda_{yc}) = 1/2$ critical wave length from linear stability analysis
$L_{yc} = $ critical length from numerical simulation
$L_x = $ length in x-direction
Then, influence of the longitudinal dimension (width) of the barrier ring was investigated. For all cases considered, \( L_x \) was chosen to be large enough so that the numerical results were not influenced by the proximity of the boundary conditions. The ratio of critical half wave length, \( 1/2 \lambda_{yc} \), from the stability analysis to the critical length, \( L_{yc} \), from the numerical simulations is plotted as a function of ratio of critical half wave length, \( 1/2 \lambda_{yc} \), from the stability analysis to the radius of curvature of the barrier ring region in figure VI-21. Table VI-1 illustrates the cases plotted in figure VI-21 and shows that the radius of curvature at the barrier ring is a decreasing function of the absolute value of the pressure gradient at the minimum thickness. As one can see good agreement between numerical simulations and linear stability analysis is obtained when \( 1/2 \lambda_{yc} \) is small compared to the longitudinal dimension of the barrier ring region. When the dimension of the barrier ring is comparable to \( 1/2 \lambda_{yc} \), the circulation cell cannot remain within the barrier ring and is stabilized by the thicker regions of the meniscus and dimple where pressure gradients are almost non existent.

By adding gravity, the numerical simulations could also be applied to study the development of marginal regeneration observed in the drainage of vertical films formed by withdrawal of glass frames.
Figure VI-21. Comparaison between stability analysis and simulations.  
\( \sigma \) and \( (\alpha, \Gamma_q) \) are the same as figure VI-13.

\( (1/2 \lambda_{yc}) = \)1/2 critical wave length from linear stability analysis 
\( L_{yc} = \) critical length from numerical simulation 
\( L_x = \) length in \( x \)-direction 
\( R_{curv} = \) radius of curvature at the barrier ring
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Table VI-1. Simulation cases plotted in figure VI-21, showing the influence of the radius of curvature at the barrier region on \(L_{yc}\) (simulations) compared to \(1/2 \lambda_{yc}\) (stability analysis). \(D_s = 10^{-5} \text{ cm}^2 \text{ s}^{-2}\), \(\mu = 10^{-3} \text{ Kg m}^{-1} \text{ s}^{-2}\), \(\Gamma_{eq} \alpha = 10^{-2} \text{ N m}^{-1}\).
Conclusions of this work may be summarized as follows:

**VII-1 Axisymmetric Drainage**

- *without disjoining pressure*

1. During film drainage, the ratio of maximum possible curvature in the dimple to the curvature in the meniscus $C_R$ decreases. Initially $C_R$ is larger than 0.7 and the film is nearly "plane-parallel". Later $C_R$ is less than about 0.7 and a dimple forms.

2. The rate of drainage is always less than that predicted by Reynolds' theory because:
   
   a. The pressure drop across the film is less than half of that predicted by Reynolds' theory
   b. There is a significant pressure gradient beyond the nominal film radius for large $C_R$
   c. When the dimple is formed, most of the resistance to flow is in the thin barrier ring

3. If $C_R$ is less than about 0.3, the thickness at the center is in good agreement with that predicted by the approximate theory of Frankel-
Mysels. When \( C_R \) is larger than 0.3, the Frankel -Mysels theory predicts smaller values. A similar statement can be made for the thickness at the barrier ring, except that agreement is achieved only when \( C_R \) is less than or equal to 0.1.

- Influence of disjoining pressure

4 At low electrolyte concentration, the repulsive disjoining pressure inhibits the formation of the thin barrier ring. Thus the film drains relatively fast to a thick uniform equilibrium film.

5 At high electrolyte concentration, the disjoining pressure is dominated by the van der Waals attraction. The result is formation of a thin annular film that forces the dimple into a lens with a finite contact angle. The drainage of the lens is very slow because of the high resistance to flow in the thin annular film.

VII-2. Asymmetric Drainage

1 Asymmetric Drainage is much faster than symmetric drainage.

2 Symmetric drainage is associated with rigid surfaces that permit little or no tangential flow, as indicated by high values of surface shear viscosity.

3 Asymmetric drainage is associated with more mobile surfaces which have low values of surface shear viscosity.
4 The surface viscosity of an ionic surfactant solution, such as SDS, can be increased by adding a small quantity of long chain alcohol.

5 A criterion giving conditions for the onset of instability causing asymmetric drainage in foam films was developed from linear stability analysis.

6 Variation in thickness is necessary for the instability to develop.

7 Numerical simulations were also successful in giving conditions for the onset of instability causing asymmetric drainage and provide a stability condition for situations that are not covered by the linear stability analysis, i.e. cases where either the longitudinal system length $L_x$ or the width of the barrier ring are comparable to or smaller than the critical half wave length $\lambda_{yc}$.

8 Asymmetric drainage is the result of an instability involving surface tension driven flow that is stabilized by surface dilational viscosity, surface diffusivity, system length scale and especially surface shear viscosity.

9 Predictions from the criterion are in good agreement with experimental observations.

10 The criterion is also applicable to marginal regeneration in vertical films, which is produced by the same instability.
APPENDIX A

CLARIFICATION ON FRANKEL-MYSELS THEORY

Frankel and Mysels in reference (38) developed solutions for thicknesses at the center and at the barrier ring of a dimpled film assuming quasi-steady flow in the latter region. Because they did not include various points about the way their results were derived, we present a derivation of their equations.

Frankel and Mysel neglected accumulation in the barrier ring region. Thus, the flow $Q$ through the ring per unit length of periphery is independent of radial location $r$ and in the lubrication approximation is given by:

$$Q = \left( \frac{\sigma}{3\mu} \right) h^3 \frac{d^3h}{dr^3} \quad (A-1)$$

Equation (A-1) can be transformed as follows:

$$\frac{d^3\left( \frac{h}{b} \right)}{d\left( \frac{r-R_f}{a} \right)^3} = \left( \frac{b}{h} \right)^3 \quad (A-2)$$
where \( a = \frac{3\mu Q R_f^4}{16\sigma h_0} \) and \( b = \frac{2h_o a}{R_f} \), \( h_0 \) is the thickness at the film center, \( R \) the film radius, \( \mu \) the bulk viscosity and \( \sigma \) the surface tension.

Assume that the dimple is given by a spherical cap having a thickness \( h_0 \) at the center and intersecting the mid-plane at the film radius \( R_f \). (see figure III-13). In the lubrication approximation, the thickness profile in the dimple is given by:

\[
h \approx \left( h_0 - \frac{1}{2} \left( \frac{r^2}{R_d} \right) \right) \quad \text{with} \quad R_d = \frac{R_f^2}{2h_0} \quad (A-3)
\]

Therefore we have

\[
\left( \frac{dh}{dr} \right)_{r=R_f} = \frac{2h_0}{R_f} = \frac{b}{a} \quad (A-4)
\]

Equation (A-2) can be solved numerically using the following boundary conditions:

- asymptotic slope given in the given by (A-4) in the dimple.
- asymptotic pressure in the dimple given by the product of surface tension and the curvature of the spherical cap.
- zero slope at \( r = R_f \) (minimum thickness).

The numerical solution of equation (A-2) was obtained by Frankel and Mysels and is shown in figure A-1.
The asymptotic curvature at the right was found to be 1.22 and must be equal to that of the meniscus $1/R_c$. Therefore we have:

\[
\frac{\left( \frac{d^2 \left( \frac{h}{b} \right)}{d \left( \frac{r - R_f}{a} \right)^2} \right)}{a^2 \left( \frac{d^2 h}{dr^2} \right)} = \frac{a^2}{b} \left( \frac{d^2 h}{dr^2} \right) = \frac{a^2}{b} \left( \frac{2}{R_c} \right) = 1.22 \quad (A-5)
\]

and

\[
a = \frac{1.22 R_c h_o}{R_f} \quad (A-6)
\]

Substituting this expression for $a$ into equation (A-6), the flow rate $Q$ can be expressed as:
\[ Q = \frac{1.22 \cdot 16 \sigma R_c h_o^5}{3 \mu R_f^5} \quad (A-7) \]

Q can also be expressed as the derivative with respect to time of the volume \( V_c \) per unit length of liquid lying under the spherical cap. \( V_c \) is obtain from equation (A-3) and is given by:

\[ V_c = \frac{h_o R_f}{4} \quad (A-8) \]

Since \( Q = -\frac{dV_c}{dt} \), \( h_o \) is the solution to the following differential equation:

\[ \frac{dh_o}{h_o^5} = -\frac{2^6 \cdot 1.22 \sigma R_c}{3 \mu R_f^6} \quad dt \quad (A-9) \]

Integrating equation (A-9) we get:

\[ h_o = \left( \frac{0.0096 \ R_f^6 \mu}{\sigma R_c t} \right)^{\frac{1}{4}} \quad (A-10) \]

From the numerical solution (figure A-1) the minimum thickness \( h_{\text{min}} \) is 1.25 x b. Therefore:

\[ h_{\text{min}} = 3.05 \ \frac{R_c h_o}{R_f^2} = \left( \frac{0.06 \ R_f^6 \mu}{\sigma R_c t} \right)^{\frac{1}{2}} \]
APPENDIX B
LINEAR STABILITY OF A FLAT INTERFACE

Let us consider a flat film interface containing an insoluble monolayer of surfactant which, at rest, has a uniform concentration \( \Gamma_{eq} \). The underlying liquid has a uniform thickness \( h_0 \) and is subject to a constant pressure gradient in the x-direction. Flow of the underlying liquid results in a constant shear stress applied to the interface and equal to \( h_0 \left( \frac{\partial p^{ss}}{\partial x} \right) \).

The steady state solution is the same as that of chapter VI: uniform thickness \( h_0 \), zero surface velocity, and constant surface tension gradient to balance the constant induced shear stress at the surface.

The stability analysis of the steady state solution is investigated by considering small perturbations in concentration and surface velocity around the steady state solution. Perturbations in thickness are not considered because the interface is assumed to remain flat.

\[
\tilde{\Gamma} = \Gamma - \Gamma^{ss} \tag{B-1}
\]

\[
\tilde{v}_{sx} = v_{sx} - 0 \tag{B-2}
\]

\[
\tilde{v}_{sy} = v_{sy} - 0 \tag{B-3}
\]
Governing equations are equations (6-4), (6-5) and (6-6) given in chapter VI. Neglecting second order terms, the equations of change for the perturbations are linearized. In the lubrication approximation, the equations are as follows:

\[
\frac{\partial \tilde{v}}{\partial t} = -\Gamma_{eq}\left(\frac{\partial \tilde{v}_{sx}}{\partial x} + \frac{\partial \tilde{v}_{sy}}{\partial y}\right) - \frac{\partial \Gamma^{ss}}{\partial x} \tilde{v}_{sx} + D_s \left(\frac{\partial^2 \tilde{v}^2}{\partial x^2} + \frac{\partial^2 \tilde{v}^2}{\partial y^2}\right) \quad (B-4)
\]

\[-\alpha \frac{\partial \tilde{v}}{\partial x} + (\mu_d + \mu_s) \frac{\partial^2 \tilde{v}_{sx}}{\partial x^2} + \mu_s \frac{\partial^2 \tilde{v}_{sx}}{\partial y^2} + \mu_d \frac{\partial^2 \tilde{v}_{sy}}{\partial x \partial y} = 0 \quad (B-5)
\]

\[-\alpha \frac{\partial \tilde{v}}{\partial y} + (\mu_d + \mu_s) \frac{\partial^2 \tilde{v}_{sy}}{\partial y^2} + \mu_s \frac{\partial^2 \tilde{v}_{sy}}{\partial x^2} + \mu_d \frac{\partial^2 \tilde{v}_{sx}}{\partial x \partial y} = 0 \quad (B-6)
\]

Equations (B-4), (B-5) and (B-6) can be made dimensionless by using the following dimensionless quantities:

\[
X = \frac{x}{L_x}, \quad Y = \frac{y}{L_x}, \quad U = \frac{v_{sx}}{V_o}, \quad V = \frac{v_{sy}}{V_o}, \quad T = \frac{t}{t_o}, \quad W = \frac{\Gamma}{\Gamma_o}
\]

with

\[
t_o = \frac{\mu_d + \mu_s}{h_0 \frac{L_x}{\frac{-\partial p^{ss}}{\partial x}}}, \quad \frac{V_o}{\mu_d + \mu_s} = \frac{h_0 \frac{L_x}{\frac{-\partial p^{ss}}{\partial x}}}{\alpha}, \quad \frac{\Gamma_o}{\alpha} = \frac{h_0 \frac{L_x}{\frac{-\partial p^{ss}}{\partial x}}}{\alpha}
\]
Equations of change become:

\[
\frac{\partial \bar{W}}{\partial T} = -N_2 \left( \frac{\partial \bar{U}}{\partial X} + \frac{\partial \bar{V}}{\partial Y} \right) - \bar{U} + N_3 \left( \frac{\partial^2 \bar{W}}{\partial X^2} + \frac{\partial^2 \bar{W}}{\partial Y^2} \right)
\]  
(B-7)

\[
- \frac{\partial \bar{W}}{\partial X} + \frac{\partial^2 \bar{U}}{\partial X^2} + N_4 \frac{\partial^2 \bar{U}}{\partial Y^2} + N_5 \frac{\partial^2 \bar{V}}{\partial X \partial Y} = 0
\]  
(B-8)

\[
- \frac{\partial \bar{W}}{\partial Y} + \frac{\partial^2 \bar{V}}{\partial Y^2} + N_4 \frac{\partial^2 \bar{V}}{\partial X^2} + N_5 \frac{\partial^2 \bar{U}}{\partial X \partial Y} = 0
\]  
(B-9)

where

\[
N_2 = \frac{\Gamma_{eq} \alpha}{h_0 L_x \left( -\frac{\partial p_{ss}}{\partial X} \right)}, \quad N_3 = \frac{D_s (\mu_d + \mu_s)}{h_0 \left( -\frac{\partial p_{ss}}{\partial X} \right) L_x^3}
\]

\[
N_4 = \frac{\mu_s}{(\mu_d + \mu_s)}, \quad N_5 = \frac{\mu_d}{(\mu_d + \mu_s)}
\]

Let us consider the following perturbations:

\[
\bar{W} = \hat{W} \exp \left( \beta' T + i \left( K_x X + K_y Y \right) \right)
\]  
(B-10)

\[
\bar{U} = \hat{U} \exp \left( \beta' T + i \left( K_x X + K_y Y \right) \right)
\]  
(B-11)

\[
\bar{V} = \hat{V} \exp \left( \beta' T + i \left( K_x X + K_y Y \right) \right)
\]  
(B-12)
where \( \hat{W} \), \( \hat{U} \), \( \hat{V} \) are constants, \( K_X \) \( K_Y \) are the dimensionless wave number in the \( x \) and \( y \) direction and \( \beta' \) is the dimensionless growth factor. Substitution of the above expressions for the perturbations \( \hat{W} \), \( \hat{U} \), \( \hat{V} \) into the differential equations yields the following set of equations:

\[
\left( \beta' + N_3 \left( K_X^2 + K_Y^2 \right) \right) \dot{W} + (iN_2 K_X + 1) \dot{U} + iN_2 K_Y \dot{V} = 0 \quad (B-13)
\]
\[
iK_X \dot{W} + \left( K_X^2 + N_4 K_Y^2 \right) \dot{U} + N_5 K_X K_Y \dot{V} = 0 \quad (B-14)
\]
\[
iK_Y \dot{W} + N_5 K_X K_Y \dot{U} + \left( K_Y^2 + N_4 K_X^2 \right) \dot{V} = 0 \quad (B-15)
\]

In order to have a nontrivial solution for \( \hat{W} \), \( \hat{U} \), \( \hat{V} \), the determinant of the above set of equations must be equal to zero. This yields a linear equation in \( \beta' \) with complex coefficients. \( \beta' \) is complex and given as follows:

Real part:

\[
\text{Re} \beta' = \frac{-N_2 \left( \frac{K_X^2 \left( \left( K_Y^2 + N_4 K_X^2 \right) - N_5 K_Y^2 \right) + K_Y^2 \left( \left( K_X^2 + N_4 K_Y^2 \right) - N_5 K_X^2 \right) \right)}{\left( \left( K_X^2 + N_4 K_Y^2 \right) \left( K_Y^2 + N_4 K_X^2 \right) - N_5^2 K_X^2 K_Y^2 \right)} \right)}{-N_3 \left( K_X^2 + K_Y^2 \right)} \quad (B-16)
\]
Imaginary part:

\[ \text{Im} \beta' = \frac{K_x \left( (K_y^2 + N_4 K_x^2) - N_5 K_x^2 \right)}{\left( (K_x^2 + N_4 K_y^2) \right) \left( (K_y^2 + N_4 K_x^2) - N_5^2 K_x^2 K_y^2 \right)} \]  \hspace{1cm} (B-16)

Since \( R_5 \) is less than unity, the real part of \( \beta' \) is always negative. Any perturbation will decay in time and the system is stable.

Consider the following cases:

- \( K_x = K_y = K \)
  \[ \begin{align*}
  \text{Re} \beta' &= -2 \left( \frac{N_2}{1 + N_4 + N_5} \right) + N_3 K_x^2 \\
  \text{Im} \beta' &= \frac{1}{K(1 + N_4 + N_5)}
  \end{align*} \]

- \( K_y = 0 \)
  \[ \begin{align*}
  \text{Re} \beta' &= -\left( N_2 + N_3 K_x^2 \right) \\
  \text{Im} \beta' &= \frac{1}{K_x}
  \end{align*} \]

- \( K_x = 0 \)
  \[ \begin{align*}
  \text{Re} \beta' &= -\left( N_2 + N_3 K_y^2 \right) \\
  \text{Im} \beta' &= 0
  \end{align*} \]
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