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DRAINAGE OF STATIC AND TRANSLATING FOAM FILMS

by

Gurmeet Singh

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IN PARTIAL FULFILLMENT OF THE
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ABSTRACT

DRAINAGE OF STATIC AND TRANSLATING FOAM FILMS

by

Gurmeet Singh

Drainage of a mobile, symmetric, plane-parallel thin liquid film between two gas bubbles (foam film) is studied. An analytical solution for the rate of thinning of such a liquid film with an insoluble surfactant and having both film elasticity and surface viscosity is presented for the first time. Analysis is extended to the more general case of a soluble surfactant and compared with previous analyses. Surfactant material parameters affecting the rate of thinning are identified and grouped into a single dimensionless parameter, the surfactant number which describes the transition from a mobile to an immobile film. Significant deviation from the Reynolds velocity is found when this dimensionless parameter is small.

Since draining foam or emulsion films are generally of nonuniform thickness with a thick region or 'dimple' as the central part and separated from the Plateau border by a thinner 'barrier ring', an analytical solution is not possible. Hence a numerical model was developed. This model simulates the hydrodynamics associated with the drainage of an axisymmetric, dimpled, mobile foam film with an insoluble surfactant. This extends the work of Joye (1994) which was limited to immobile films. Results of the parametric study indicate that the rate of drainage of these films is dependent on surfactant properties viz. elasticity, surface dilatational viscosity, surface shear viscosity and surface diffusivity. These properties are grouped into a single dimensionless parameter which is the same as obtained by our analytical solution for a plane parallel film and which correlates with the rate of drainage of the foam film. This parameter describes the transition from a mobile film to an immobile film. The
simulations indicate considerable motion of the interface for draining mobile foam films.

Foam texture in a porous medium is governed by the hydrodynamics of individual foam films (lamellae) flowing through pores of varying size. The stability of foam in a particular application depends upon the stability of a lamella in the porous medium, especially as the lamella expands in translating from a small pore (pore throat) to a larger pore (pore body). The numerical simulator developed above is extended to translating foam films to model the effect of various parameters on foam stability. The model predicts that the travelling lamella is unstable only for certain ranges of surfactant properties, porous media geometry and flow conditions, for e.g. gas flow rate and capillary pressure. Simulations show that mobile foam films stretch in going from a pore throat to a pore body and may thin down to the critical thickness and break, under certain conditions. In contrast immobile foam films are very stable due to an entrainment effect which occurs as the film expands in going from a pore throat to a pore body. The critical capillary pressure at which a moving lamella will break is determined as a function of film and porous medium properties. Further the concept of asymmetric drainage of foam films in porous media has been explored.
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To my wife

Rajita
Chapter 1

Introduction

Dispersed fluid systems are very important in chemical engineering processes and products; e.g., distillation, lubricating oils, fire-fighting, pulping in paper industry, detergents, shampoos, shaving creams, enhanced oil recovery, soil remediation, and in fermentation processes in the pharmaceutical industry (Bikerman, 1973).

The utility of these dispersed fluid systems, whether they be foams or emulsions depends upon understanding their stability. In our study we concentrate on foam systems for use in fluid displacement in porous media. In a foam system, the continuous liquid phase is bound in a network of thin liquid films and meniscus regions. These thin-liquid films are used as a model to study foam stability. Further, to study the lifetime of a thin liquid film it is essential to know both the rate of drainage and the transition phenomenon when the film reaches a critical thickness. Hence the need to elucidate the hydrodynamics of thin liquid film drainage.

A thin liquid film consists of two surface layers containing adsorbed surfactant separated by a liquid phase containing dissolved the surfactant. The forces that govern the film drainage are the capillary pressure and the disjoining pressure. The resultant pressure causes the liquid in the film to flow out into the meniscus, producing uneven distribution of surfactant on the surface (Huang et al., 1986). This leads to tangential stresses on the interface opposing the bulk liquid flow. It is the interfacial rheological properties, viz., surface elasticity, surface viscosity, surface tension, etc., which play a crucial role in the tangential extensibility of the surface. Thus there is a need to identify surfactants capable of stabilizing or destabilizing the dispersion through indirect knowledge of bulk phase and interfacial properties (Edwards et al.,

Models for thin liquid film drainage have been proposed by numerous researchers dating back to 1886, when Reynolds (Reynolds, 1886) solved for the drainage velocity of the fluid between two plane parallel disks. Flow in thin liquid films is critically dependent on the tangential extensibility of the two interfaces in intimate contact with the thinning film. If neither of the interfaces will support tangential stress, thinning is generally very rapid (i.e. we have mobile film surfaces) in comparison to the situation where either one or both the surfaces is tangentially inextensible (i.e. immobile) (Good, 1974).

Experimental investigators have shown that, during the drainage process, the central part of the film becomes thicker than its periphery, and a lenticular bulge, more commonly referred to as a “dimple” is usually formed.

The complete process of drainage of a thin liquid film can be divided into five stages (Ivanov, 1980): 1) two bubbles approaching each other; 2) hydrodynamic interaction of the slightly deformed bubbles; 3) strong deformation leading to a bell-shaped formation, called a “dimple”; 4) the gradual disappearance of the dimple and formation of an essentially plane parallel film; 5) the plane parallel film thinning down further to critical thickness. Analytical study of the drainage of a thin liquid film considering all the above stages is a difficult task. One thus assumes in the simplest case a plane parallel film and analytically solves the hydrodynamic equations governing the drainage. Ivanov (1980) discusses the effect of surface mobility on the drainage and rupture of plane parallel thin liquid films. Barber and Hartland (1976), Ivanov and Dimitrov (1974) and Radöev et al. (1974), treat the hydrodynamics of plane parallel thin liquid foam films, with a soluble surfactant. The effect of interfacial properties on the mobility of plane parallel emulsion films has been discussed by Malhotra and Wasan (1987), Traykov and Ivanov (1977) and Traykov et al. (1977).

Foam in porous media is defined as a dispersion of gas in a liquid such that the liquid phase is interconnected and at least some of the gas flow paths are blocked by
lamellae (i.e. thin liquid films). In order to relate the thin liquid film dynamics to foam stability in porous media we need to study the hydrodynamics of thin liquid film (lamella) translating in porous media. Nutt et al. (1992) have shown experimentally that foam stability in porous media is related to the lamella stability which in turn is determined by pore geometry, flow rate and the rheological properties of the lamella. Most important is the dynamics of lamella as it expands/stretches in moving from pore throat (small pore radius) to pore body (large pore radius). Dynamic stability of a foam lamella (thin liquid film) flowing through a periodically constricted pore has been studied by Jieménez & Radke (1989). They considered a plane parallel thin liquid film in their analysis and presented a theory to explain the dependence of critical capillary pressure (capillary pressure at which lamella is unstable) in porous media to the foam flow rate. This dependence was first seen experimentally by Khatib et al. (1986). Jieménez & Radke (1989) showed that disjoining pressure was the only dominant variable as regards to lamella stability.

In this thesis we first present a brief summary of the interfacial rheology (Chapter 2) and try to dispel some wrong notions associated with it. We then present derivation of equations governing the drainage of a stationary thin liquid film (Chapter 3) followed by a discussion on the role of parameters appearing in the governing equations (Chapter 4). In Chapter 5 we present a rigourous analytical derivation of the thinning velocity of a plane parallel film for the cases of an insoluble and soluble surfactant. Dimensionless parameters are obtained which alter the mobility of the film and the expression for the thinning velocities have been presented. This is followed by a detailed numerical simulation (Chapter 6) of a dimpled thin liquid film with an insoluble surfactant draining under the action of capillary pressure. Application of thin liquid film hydrodynamics studied above, to foam stability in porous media has been presented in Chapter 7. Here we numerically solve the equations governing hydrodynamics of a lamella translating in porous media. The effect of parameters such as capillary pressure, pore geometry and interfacial rheological preoerties on
foam stability has been studied. Conclusions of the study constitute the last chapter of this thesis.
Chapter 2

Surface Rheology

Before we discuss the governing equations for studying the drainage behavior of thin liquid films we would like to clear some misunderstandings in the rheology of interfaces, especially regarding the dilatational properties. We believe this will help the reader in understanding later sections of this manuscript. We will in this section present analogies between the well understood 3-D rheology and the confusing 2-D rheology so as to make the surface rheology more tractable.

Bulk Fluids:

The behavior of materials (bulk or interface) is described by a constitutive equation, which tells us how the contact forces in a body depend upon the motion and deformation of the body (Slattery, 1981). These constitutive equations satisfy the principles of determinism, frame indifference and local action.

The most general form of the linear constitutive equation, for a bulk Newtonian fluid is given as

\[
T = (-P_T + \lambda \nabla \cdot \mathbf{v}) I + 2 \mu D
\]  

(2.1)

where \( P_T \) is the thermodynamic pressure. Since the physical interpretation of the divergence of the velocity field is that, "it is the relative change of dilatation following a particle path" (Aris, 1989), the coefficient \( \lambda \) should be called the dilatational viscosity of the bulk fluid. For an incompressible fluid the above equation reduces to the following

\[
T = -p I + 2 \mu D
\]  

(2.2)
where \( p \) is the mean pressure of the bulk fluid, more commonly referred as the pressure. The measured pressure in the flow experiments is nothing but the mean pressure, since the thermodynamic pressure is not defined for incompressible fluids. The mean pressure is defined as

\[
p \equiv -\frac{1}{3} \text{tr } \mathbf{T}
\]  

(2.3)

Thus for a compressible Newtonian fluid, the thermodynamic pressure \( P_T \) and the mean pressure \( p \) are related as (Aris, 1989; Joly 1972)

\[
p - P_T = -\chi \nabla \cdot \mathbf{v}
\]  

(2.4)

Where \( \chi \) is the bulk coefficient of viscosity and is given as (Truesdell and Toupin, 1960; Bird et al., 1960; Slattery, 1981; Aris, 1989)

\[
\chi = \lambda + \frac{2}{3} \mu
\]  

(2.5)

Although some authors (Edwards et al., 1991), call \( \chi \) the dilatational viscosity of the bulk fluid, the above relation shows us that \( \chi \) does include the contribution from the shear coefficient of viscosity \( \mu \).

All the above explanation has been done to make way for constructing analogies between the bulk and interfacial rheology. The reason is that we feel most readers are comfortable with bulk (3-D) rheology than with interfacial rheology.

**Surface Fluids:**

Analogous to equation (2.1), the most general linear constitutive equation for an interface, is as follows (Slattery, 1990)

\[
\mathbf{T}' = (\alpha + \lambda^s \nabla_s \cdot \mathbf{v}^s) \mathbf{I}' + 2\mu_s \mathbf{D}^s
\]  

(2.6)

Using the Clausius-Duhem inequality (Slattery, 1990, p819), we have \( \alpha = \sigma \), where \( \sigma \) is the thermodynamic surface tension. Comparing equations (2.1) and (2.6).
one can see that the 2-D analog of pressure is the surface tension. The negative sign in $\sigma$ denotes tension as opposed to $p$ which is usually compressive (Miller and Neogi, 1985). Similar to equation (2.1), the coefficient $\lambda^s$ is associated with the divergence of the surface velocity field, hence it should be rightly called as the surface dilatational viscosity. It will be shown later that surface dilatational viscosity is defined differently in the literature, hence to avoid confusion we will call $\lambda^s$ the coefficient of dilatational viscosity. Analogous to equation (2.3), for 3-D rheology, we define the mean surface tension, $\bar{\sigma}$ as

$$\bar{\sigma} = \frac{1}{2} \text{tr} \ T^s$$

Contrary to most bulk liquids, interfaces are usually compressible. Thus in any analysis of surface flow, we would have both the thermodynamic surface tension $\sigma$ and the dynamic surface tension $\bar{\sigma}$. Hence the need for an expression relating both the properties. The relation between the mean surface tension and the thermodynamic tension for a viscous interface is analogous to eqn. (2.4), and is as follows:

$$\bar{\sigma} = \sigma + \mu_d \ \nabla_s \cdot \mathbf{v}^s$$

where

$$\mu_d \equiv \lambda^s + \mu_s$$

is called the “apparent dilatational viscosity”, or more commonly in the literature the surface dilatational viscosity. We will in our analysis, be consistent with the vast literature, and call $\mu_d$ the surface dilatational viscosity, but it needs to be emphasized that it is actually defined as shown above.

The surface constitutive equation for a Newtonian interface (eqn. 2.6) can thus be written as

$$T^s = \sigma I^s + (\mu_d - \mu_s) \ \nabla_s \cdot \mathbf{v}^s \ I^s + 2 \mu_s \ D^s$$
The above equation is also referred to as the Boussinesq-Scriven equation for a surface. The parameters $\mu_d$ and $\mu_s$ are called the intrinsic surface viscous properties. By intrinsic we mean, properties that can be attributed to an isolated, autonomous interface. The surface stress tensor (eqn. 2.10) for a planar interface of type

$$z = z(x, y) = \text{constant}$$

can be written as follows:

$$\sigma + (\mu_d - \mu_s) \nabla_s \cdot \mathbf{v}^s + 2 \mu_s \frac{\partial v_y^s}{\partial x} \quad \mu_s \left( \frac{\partial v_y^s}{\partial x} + \frac{\partial v_x^s}{\partial y} \right)$$

$$\mu_s \left( \frac{\partial v_y^s}{\partial x} + \frac{\partial v_x^s}{\partial y} \right) \quad \sigma + (\mu_d - \mu_s) \nabla_s \cdot \mathbf{v}^s + 2 \mu_s \frac{\partial v_y^s}{\partial y}$$

The $x$ component of the divergence in cartesian co-ordinates, for the surface described as before is given as

$$\frac{\partial T_{xx}^s}{\partial x} = \frac{\partial \sigma}{\partial x} + (\mu_d + \mu_s) \left( \frac{\partial^2 v_x^s}{\partial x^2} + \frac{\partial^2 v_y^s}{\partial x \partial y} \right) + \mu_s \left( \frac{\partial^2 v_x^s}{\partial y^2} - \frac{\partial^2 v_y^s}{\partial y \partial x} \right)$$

We will now use the simple example of a one dimensional flow and explain how the surface tension gradients introduce an additional viscosity and an elasticity.

**Compositional Effects:**

The $x$ component of the surface stress tensor (eqn. 2.10) for a one-dimensional flow is given as:

$$T_{xx}^s = \sigma + (\mu_d + \mu_s) \frac{d v_x^s}{d x}$$

(2.12)

In problems of surface motion, it is the divergence of the stress tensor that enters the momentum balance equations. Using the above equation we have

$$\frac{d T_{xx}^s}{d x} = \frac{d \sigma}{d x} + (\mu_d + \mu_s) \frac{d^2 v_x^s}{d x^2}$$

(2.13)
We can write the first term on the right hand side \( \frac{d \sigma}{d x} \) as

\[
\frac{d \sigma}{d x} = \frac{d \sigma}{d \ln A} \frac{d \ln A}{d x} \tag{2.14}
\]

where \( A \) is the area of the element of the film. Using the surface Reynolds transport theorem (Edwards et al., 1991) one can show that

\[
\frac{d \ln A}{d x} = \frac{d^2 \xi}{d x^2} \tag{2.15}
\]

where \( \xi \) is the surface displacement. Further, Gibbs (1961) defined the film elasticity as (considering single surface, for two surfaces, we have a factor of 2 multiplying the right hand side)

\[
E_G = \frac{d \sigma}{d \ln A}
\]

In the above definition by Gibbs, \( \sigma \), has been used as a thermodynamic quantity, rather than based on the mean surface tension \( \bar{\sigma} \), as reported by Lucassen-Reynders (1979). Thus eqn(2.14) can be rewritten as

\[
\frac{d \sigma}{d x} = E_G \frac{d^2 \xi}{d x^2} \tag{2.16}
\]

For the special case of an insoluble surfactant monolayer, since there is no diffusional exchange with the bulk, the amount of surfactant present at the interface is constant. Hence

\[
\Gamma a = \text{constant}
\]

\[
d \ln \Gamma = - d \ln a
\]

where \( \Gamma \) and \( a \) are the surface concentration and the surface area per molecule, respectively. Since for an insoluble surfactant we have (Joly, 1982)
\[ d \ln A = d \ln a = -d \ln \Gamma \]

it follows that the Gibbs elasticity for an insoluble monolayer is defined as

\[ E_G \equiv -\frac{d \sigma}{d \ln \Gamma} \quad (2.17) \]

Now if we assume that locally the surface concentration does not deviate much from its equilibrium value, then we can re-write eqn. \((2.17)\) as

\[ E_G \approx E^o \equiv -\left( \frac{d \sigma}{d \ln \Gamma} \right)^o \quad (2.18) \]

Thus equation\((2.13)\) can be rewritten as

\[ \frac{d T^{ss}_{xx}}{d x} = E^o \frac{d^2 \xi}{d x^2} + (\mu_d + \mu_s) \frac{d^2 v^s_x}{d x^2} \quad (2.19) \]

For the general case of a soluble surfactant, equation\((2.14)\) can be decomposed as (Maru et al., 1979)

\[ \frac{d \sigma}{d x} = \left( \frac{d \sigma}{d \Gamma} \right) \left( \frac{d \Gamma}{d x} \right) = E_{dc} \frac{d^2 \xi}{d x^2} + \mu_{dc} \frac{d^2 v^s_x}{d x^2} \quad (2.20) \]

where \(E_{dc}\) and \(\mu_{dc}\) are the compositional elasticity and viscosity respectively. One thus needs an explicit surfactant transport model for evaluating \(\frac{d \Gamma}{d x}\). That is we need to solve for the surfactant concentration gradients in the bulk and at the surface. Thus expressions for \(E_{dc}\) and \(\mu_{dc}\) as were obtained for the insoluble monolayer (\(E_{dc} = E^o, \mu_{dc} = 0\)) are generally not easily obtained for the case of soluble surfactants, although in the analysis of longitudinal wave experiments the use of periodic deformations allows us to solve the conservation equations for the surfactant to obtain simple expressions for \(E_{dc}\) and \(\mu_{dc}\) (Ting et al., 1984).

Equation\((2.13)\) can now be written as

\[ \frac{d T^{ss}_{xx}}{d x} = E_{dc} \frac{d^2 \xi}{d x^2} + (\mu_d + \mu_s + \mu_{dc}) \frac{d^2 v^s_x}{d x^2} \quad (2.21) \]
We now define the net elasticity $E_n$ and the net viscosity $\mu_n$ of the surfactant monolayer as follows

$$E_n \equiv E_{dc} \quad (2.22)$$

and

$$\mu_n \equiv \mu_d + \mu_s + \mu_{dc} \quad (2.23)$$

We think now it should be clear to the reader that even though the interface was assumed to be purely viscous (Newtonian), there is an elastic effect due to the changes in the surface tension. This elasticity is called the *compositional elasticity* (Maru et al., 1979). And further these effects also contribute to the surface viscosity, as the *compositional viscosity* $\mu_{dc}$, which is different from the *intrinsic viscosities* namely $\mu_d$ and $\mu_s$.

The above distinction between the intrinsic and compositional properties was important since researchers usually confuse them, and as a result one is unable to differentiate between the effects of various surface properties on the surface flow.

**Surface Stress vs. Surface Tension:**

Another important point we would like to clear up the misconception of treating the change in surface tension as the surface stress.

Lucassen-Reynders (1979) and Lucassen and van den Tempel (1972), call $\Delta \sigma$ (here $\Delta$ represents the change) as the surface stress, and show that it can be written as the sum of a viscous and an elastic contribution.

We will now show that this misconception introduces an error in the measured values of the overall elasticity $E_n$ and viscosity $\mu_n$.

As remarked earlier the quantity measured during the experiments is the mean surface tension $\overline{\sigma}$ and not the thermodynamic surface tension $\sigma$. Let us highlight the distinction between these two quantities as most often it is not taken into account.
Using equation (2.8) one can now show that the measured change in surface tension is then given as

\[ \frac{d \sigma}{d x} = \frac{d \sigma}{d x} + \mu_d \frac{d^2 v_x^s}{d x^2} \tag{2.24} \]

Using equation (2.20) we have

\[ \frac{d \sigma}{d x} = E_{dc} \frac{d^2 \zeta}{d x^2} + (\mu_d + \mu_{dc}) \frac{d^2 v_x^s}{d x^2} \tag{2.25} \]

Comparing equations (2.21) and (2.25) we can see that using the change in surface tension as the surface stress is not the same as it does not account for the contribution of the surface shear viscosity.

The coupling between the compositional effects and the intrinsic hydrodynamic parameters poses great difficulties in the determination of the dilatational properties. We have seen from equation (2.19) that for the case of an insoluble monolayer such effects can be distinguished without an explicit surfactant transport model.

**Experimental Techniques:**

Techniques for measuring the surface dilatational viscosities have been discussed in Edwards et al. (1991). For the longitudinal wave technique (Lucassen Reinders, 1979) where the surface is subjected to periodic deformations with frequency \( \omega \), equation (2.13) in the most general case of a soluble surfactant can be written as

\[ \frac{d T_{xx}}{d x} = \left[ E^\ast - i \omega (\mu_d + \mu_s) \right] \frac{d^2 \zeta^\ast}{d x^2} \tag{2.26} \]

where \( \zeta^\ast \) is the (complex) displacement and \( E^\ast \) is the complex modulus which can be decomposed as follows

\[ E^\ast = E_{dc} + i \omega \mu_{dc} \]

Equation (2.26) can be rearranged as
\[
\frac{d}{dx} T_{xx} = \left[ E_{dc} - i \omega (\mu_d + \mu_s + \mu_{dc}) \right] \frac{d^2 \zeta^*}{dx^2}
\]  \hspace{1cm} (2.27)

Thus the 'elastic' gain is associated with \(E_{dc}\) and the loss modulus with \(\mu_n\) (eqn. 2.23). On the other hand if the characteristic time of the wave experiment is too short for the surfactant diffusion from bulk to become noticeable (i.e. at high frequencies), the monolayer would behave as insoluble. In fact explicit expressions (Edwards et al., 1991) for \(E_{dc}\) and \(\mu_{dc}\) show that as \(\omega \to \infty\) we have

\[
E_{dc} \to E^0 \text{ and } \mu_{dc} \to 0
\]

In general for a soluble surfactant from the longitudinal wave experiments we get the surface shear and dilatational viscosity as a sum. To get an estimate of the surface dilational viscosity one measures the surface shear viscosity separately using the Mannheimer and Schechter (1970) deep channel viscometer.

**Visco-Elastic Interfaces:**

Until now we have described the interface as a Newtonian (purely viscous) fluid, but viscoelastic interfaces are frequently encountered in practice. In the case of a viscoelastic interface we will have four intrinsic hydrodynamic parameters viz. the surface shear elasticity \(G\), the surface shear viscosity \(\mu_s\), the surface dilatational elasticity \(\Lambda\) and the surface dilatational viscosity \(\mu_d\). One should again be cautious in separating the effects of these intrinsic properties and the compositional properties as discussed before.

An analysis for the viscoelastic interface would be based on the type of spring-dashpot model one assumes to model the behavior of the interface. Maru et al. (1979) and Djabbarah (1978) use the Kelvin-Voight element to model the interface and determine its viscous and elastic properties.

The Kelvin-Voight element is a spring and dashpot arranged in parallel. "Clearly, this arrangement is a model of a solid, since the maximum extension which can be
achieved is limited by the force applied and is independent of the time of application" (Fredrickson, 1964). Thus we believe that the model used by Maru et al. (1979) is for a \textit{elastico-viscous} solid rather than a \textit{visco-elastic} fluid.

Various other models for a visco-elastic interface have been proposed. Among these are the Maxwell-Voight model (Edwards et al., 1991) and a combination of linear Maxwell model (Tambe and Sharma, 1991) for the surface shear elasticity and surface shear viscosity. Gardner et al. (1978) present a network rupture model, which is a 2-D analog of the network rupture theory of Tanner and Simmons (1967) (which in turn is a special case of the KBKZ, i.e. Kaye-Bernstein-Kearsley-Zapas model). This model has been successfully used by Addison and Schechter (1979) to predict shear properties of a viscoelastic interface. The network model of Gardner et al. (1978) provides explicit expressions for the shear properties. Although the network rupture model predicts the dilatational elasticity, it however does not offer any explicit mathematical expression for the dilatational elasticity (Edwards et al., 1991).

The following table summarizes the different variables used in the above section and compares them with other symbols used in the literature.

**Philosophy:**

To conclude, we can say that the confusion and errors in the literature occur because one does not start from the basic physics and rather uses the results derived by others, which may have been derived for a different case. Hence in solving any surface problem, one should follow the philosophy outlined below.

Given a problem one should:

a) define a constitutive equation for both the bulk fluid as well as the interface.

b) define the surface geometry

c) list the assumptions

d) Using all the above satisfy the conservation laws, namely mass balance, mo-
<table>
<thead>
<tr>
<th>Variable</th>
<th>2-D Analog</th>
<th>3-D Analog</th>
<th>Physical Interpretation</th>
<th>Literature name/symbol</th>
<th>Our notation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BULK FLUID</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \lambda )</td>
<td>( \lambda' )</td>
<td>-</td>
<td>It appears as a coefficient of divergence of the velocity field in equation (1.1)</td>
<td>-</td>
<td>Dilatational viscosity of the bulk fluid</td>
</tr>
<tr>
<td>( \mu )</td>
<td>( \mu_s )</td>
<td>-</td>
<td>It is the coefficient of the rate of deformation tensor (eqn. 1.1)</td>
<td>shear coefficient of viscosity ( \mu ) (Slattery, 1981)</td>
<td>Bulk fluid viscosity</td>
</tr>
<tr>
<td>( \chi )</td>
<td>( \mu_d )</td>
<td>-</td>
<td>Relates the thermodynamic and mean pressure (eqn. 1.5) ( \chi \equiv \lambda + 2/3 \mu )</td>
<td>dilatational viscosity of bulk fluid ( \kappa ) (Edwards et al., 1991); coefficient of bulk viscosity (Aris, 1989); bulk coefficient of viscosity (Slattery, 1981)</td>
<td>Bulk coefficient of viscosity</td>
</tr>
<tr>
<td>( P' )</td>
<td>( \sigma )</td>
<td>-</td>
<td>It is the pressure in the general linear constitutive equation</td>
<td>Thermodynamic pressure ( P ) (Slattery, 1981)</td>
<td>Thermodynamic pressure</td>
</tr>
<tr>
<td>( P )</td>
<td>( \sigma )</td>
<td>-</td>
<td>It is the pressure in the Newtonian constitutive equation</td>
<td>pressure, mean pressure ( \beta ) (Aris, 1989)</td>
<td>Fluid pressure</td>
</tr>
<tr>
<td><strong>SURFACE FLUID</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \lambda' )</td>
<td>-</td>
<td>( \lambda )</td>
<td>Appears as coefficient of the divergence of the surface velocity field (eqn. 1.6)</td>
<td>-</td>
<td>surface coefficient of dilatational viscosity</td>
</tr>
<tr>
<td>( \mu_s )</td>
<td>-</td>
<td>( \mu )</td>
<td>Appears as coefficient of the surface rate of deformation tensor</td>
<td>surface shear viscosity ( \kappa ) (Slattery, 1990); ( \mu' ) (Edwards et al., 1991)</td>
<td>surface shear viscosity</td>
</tr>
<tr>
<td>( \mu_d )</td>
<td>-</td>
<td>( \chi )</td>
<td>Relates the thermodynamic and mean surface tension (eqn. 1.9) ( \mu_d \equiv \lambda' + \mu_s )</td>
<td>surface dilatational viscosity ( \mu' ) (Edwards et al., 1991); apparent surface dilatational viscosity ( \kappa ) (Slattery, 1990)</td>
<td>surface dilatational viscosity</td>
</tr>
<tr>
<td>( E_{ds} )</td>
<td>-</td>
<td>-</td>
<td>Elasticity due to surface tension gradient (eqn. 1.19)</td>
<td>Compositional elasticity (Maru et al., 1979)</td>
<td>Compositional elasticity</td>
</tr>
<tr>
<td>( \mu_{ds} )</td>
<td>-</td>
<td>-</td>
<td>Viscosity due to surface tension gradient (eqn. 1.19)</td>
<td>Compositional viscosity (Maru et al., 1979)</td>
<td>Compositional viscosity</td>
</tr>
<tr>
<td>( \mu_n )</td>
<td>-</td>
<td>-</td>
<td>Experimentally measured viscosity</td>
<td>Net surface viscosity ( \mu_n ) (Maru et al., 1979)</td>
<td>Net surface viscosity</td>
</tr>
<tr>
<td>( E_0 )</td>
<td>-</td>
<td>-</td>
<td>Elasticity due to change in surface tension</td>
<td>Gibbs elasticity (Gibbs, 1951)</td>
<td>Gibbs elasticity</td>
</tr>
</tbody>
</table>
momentum balance, moment of momentum balance and the energy balance.

In the next section we present the derivation of the equations governing the drainage of a thin liquid film, based on the philosophy outlined above.
Chapter 3

Governing Equations

A schematic of the thin liquid film is shown in Figure (3.1).

A cylindrical co-ordinate system, with origin at the center of the film is taken, and the local half thickness of the film is denoted by $h(r, t)$. Before we proceed ahead to derive the governing equations, let us list the assumptions we make.

i) The drainage is axisymmetric, i.e. the interfaces bounding the thin liquid film (Figure 3.1), can be written as $z = h(r, t)$.

ii) The bulk liquid is an incompressible Newtonian fluid.

iii) The pressure $p_g$ in the gas (or bubble) phase is constant.

iv) The effect of gravity is neglected.

v) All inertial effects are assumed negligible.

vi) The flow obeys the Reynolds lubrication theory approximation.

vii) 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.

viii) The interface forms a specified contact angle with the capillary wall. When the liquid wets the capillary wall, we assume the contact angle to be small but finite.

ix) The perturbations in the surface concentration are small, so that surface tension is assumed to vary linearly with the surface concentration of the surfactant.

x) The bulk liquid is dilute in surfactant, so that ideal solution conditions are maintained.

xi) The surfactant transport between the bulk fluid and the interface is assumed to be diffusion controlled.
Figure 3.1: Dimpled Thin Liquid Film
xii) The effect of disjoining pressure is neglected.

Thus the equations we need are the following:

a) Bulk continuity equation.

b) Bulk fluid momentum balance.

c) Surfactant mass balance in the bulk fluid.

d) Jump momentum balance at the interface.

e) Surfactant mass balance at the interface.

f) A constitutive equation for the interface, describing its material behavior.

The overall mass balance (or the continuity equation) for the bulk liquid can be written as (Slattery, 1981)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (3.1)$$

From assumptions (i) and (ii) we have

$$\nabla \cdot \mathbf{v} = 0$$

which for the cylindrical geometry (Figure 3.1) considered, reduces to the following

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{\partial v_z}{\partial z} = 0 \quad (3.2)$$

Assumptions (i) to (v), suggest us that we look for a solution of the form

$$v_r = v_r (r, z, t); \quad v_\theta = 0$$

$$v_z = v_z (r, z, t)$$

$$p = p(r, t)$$
Also we have at the interface \( z = h(r, t) \), the following condition

\[
v_z = \frac{D h}{D t} = \frac{\partial h}{\partial t} + v_r \frac{\partial h}{\partial r}
\]  

(3.3)

Although this generalization has also been pointed out by Edwards et al. (1991), in their further analysis they neglect the second term on the right hand side. We show here that, if one integrates equation (3.2), over the film half thickness \( h(r, t) \), using the Leibnitz rule (integration limit being a variable) it is not necessary to neglect this term.

The integration yields

\[
- v_r \frac{\partial h}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} (r h \bar{v}_r) + v_z = 0
\]  

(3.4)

where \( v_r \) and \( V_z \) are evaluated at \( z = h \) and

\[
\bar{v}_r = \frac{1}{h} \int_0^h v_r \, dz
\]

Using equation (3.3), we have

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

(3.5)

With assumptions (i) to (v) and the lubrication approximation, the 'r' and 'z' components of the Cauchy's first law in cylindrical co-ordinates (Slattery, 1981) can be written as

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

(3.6)

\[
\frac{\partial p}{\partial z} = 0
\]  

(3.7)

with the following boundary conditions

\[
\frac{\partial v_r}{\partial z} = 0 \text{ at } z = 0
\]
\[ v_r = v^*_r \text{ at } z = h \]

where \( v^*_r \) is the radial component of the surface velocity.

The above equations are solved for an expression of the bulk velocity as

\[ v_r = \frac{1}{2\mu} \left( \frac{\partial p}{\partial r} \right) (z^2 - h^2) + v^*_r \]  \hspace{1cm} (3.8)

Integrating the above equation over the film half thickness, gives

\[ \bar{v}_r = v^*_r - \frac{h^2}{3\mu} \left( \frac{\partial p}{\partial r} \right) \]  \hspace{1cm} (3.9)

On substitution of equation (3.9) into equation (3.5), one gets

\[ \frac{\partial h}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} (r h v^*_r) + \frac{1}{3\mu} \frac{1}{r} \frac{\partial}{\partial r} \left( r h^3 \left( \frac{\partial p}{\partial r} \right) \right) \]  \hspace{1cm} (3.10)

The next step as mentioned before is to formulate the surfactant mass balance in the bulk fluid. Assumption(x) implies that the velocity distribution in the bulk is independent of the species (surfactant) concentration distribution. This is a very important assumption which researchers most often neglect mentioning. Thus the effects of diffusion induced convection can only be neglected in case of sufficiently dilute solutions (Slattery, 1981). The surfactant mass balance for the prescribed cylindrical geometry and consistent with Fick’s law of binary diffusion is given as:

\[ \frac{\partial c}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r v_r c) + \frac{\partial}{\partial z} (c z) = D \frac{\partial^2 c}{\partial z^2} + D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \]  \hspace{1cm} (3.11)

We now integrate the above equation over the the film half thickness \( h(r, t) \) using the Leibnitz rule, to give

\[ \frac{\partial (h \bar{c})}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r v^*_r h \bar{c}) - \frac{1}{2\mu} \frac{1}{r} \frac{\partial}{\partial r} \left( r h^2 \left( \frac{\partial p}{\partial r} \right) h \bar{c} \right) = D \left( \frac{\partial c}{\partial z} \right)_{z=h} \]
\[-D \left( \frac{\partial c}{\partial r} \right)_{r=h} \frac{\partial h}{\partial r} + D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial (h \bar{c})}{\partial r} \right) - D \frac{1}{r} \frac{\partial}{\partial r} \left( r c^* \frac{\partial h}{\partial r} \right) \quad (3.12)\]

where

\[c^* = c(r, t, z = h)\] is the concentration in equilibrium with the interface and is related to the surfactant concentration at the interface through an equilibrium adsorption isotherm.

We now need to formulate the surfactant mass balance at the interface. The most general form of species mass balance at the interface is given as (Edwards et al., 1991)

\[\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\nu^s \Gamma) + \nabla_s \cdot (I_s \cdot j^s) = R^s + n \cdot \|j\| \quad (3.13)\]

where \(j^s\) is the surface diffusion flux vector

\(n \cdot \|j\|\) is the jump mass balance at the interface

\(R^s\) is the species production rate per unit area.

\(I_s\) is the projection tensor.

For details on interfacial tensor analysis, see Slattery (1990, Appendix A) and Edwards et al. (1991).

The jump mass balance \(n \cdot \|j\|\) under dynamical conditions represents a two step process of surfactant transport. The first is the diffusion of the surfactant from the bulk fluid to the interface followed by 'adsorption' of the surfactant at the interface.

We know that surfactant molecules have a preferred orientation at the interface and thus any surfactant molecule diffusing from the bulk and arriving adjacent to the interface with a random orientation has to rotate into the preferred orientation before it can enter the interface (Slattery, 1990); this step is termed as the 'adsorption' step.

Limiting cases of (a) diffusion controlled and (b) adsorption controlled surfactant transport from the bulk to the interface can be considered in defining an expression for \(n \cdot \|j\|\). For case (a) one needs to choose a particular adsorption equilibrium isotherm and the jump mass balance is given by the diffusional flux to or from the
bulk. In case(b) $n \cdot \| j \|$ is replaced by the appropriate adsorption kinetics. We in our analysis consider case(a), i.e. we assume that the surfactant adsorption at the interface takes place instantaneously and diffusion is the rate controlling step. The jump mass balance is then given as

$$ n \cdot \| j \| = - D \left( \frac{\partial c}{\partial z} \right)_{z=h} $$

Consequently the surfactant mass balance at the interface consistent with Fick's first law of diffusion is

$$ \frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v}^s \Gamma) = D_s \nabla_s \cdot \nabla_s \cdot \Gamma - D \left( \frac{\partial c}{\partial z} \right)_{z=h} \quad (3.14) $$

Due to assumed axisymmetry and the lubrication approximation, we have

$$ \frac{\partial \Gamma}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \mathbf{v}^s \Gamma \right) = D_s \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Gamma}{\partial r} \right) - D \left( \frac{\partial c}{\partial z} \right)_{z=h} \quad (3.15) $$

The stress behavior of the interface, is described using the Boussinesq -Scriven surface fluid constitutive equation (recall Section 2) This relates the surface stress tensor, surface extra stress tensor and the surface rate of deformation tensor (Slattery, 1990 p193), as follows

$$ S^s = T^s - \sigma \mathbf{I}_s = (\mu_d - \mu_s) (\nabla_s \cdot \mathbf{v}^s) \mathbf{I}_s + 2 \mu_s \mathbf{D}^s \quad (3.16) $$

where $\mu_s, \mu_d$ are the surface shear and dilational viscosities respectively. $S^s$ is the surface extra stress tensor.

In view of assumptions (v) and (x), the jump momentum balance at the interface, for an insoluble surfactant, is given as

$$ \nabla_s \sigma + 2 H \sigma \mathbf{n} + \nabla_s \cdot S^s + \left[ \mathbf{T} \cdot \mathbf{n} \right] = 0 \quad (3.17) $$

where $\sigma$ is the thermodynamic surface tension.
\( H \) is the mean curvature

\( \mathbf{n} \) is the unit normal vector at the interface

\( \mathbf{T} \) is the bulk fluid stress tensor

The component form of the above equation for an interface of the form \( z = h(r, t) \), under the lubrication approximation, can be written as follows:

**r component:**

\[
\frac{\partial \sigma}{\partial r} + (\mu_d + \mu_s) \frac{\partial}{\partial r} \left[ \frac{1}{r} \frac{\partial (r v_r^s)}{\partial r} \right] + \tau_{rz} \mid_{z=h} = 0 \tag{3.18}
\]

**z component:**

\[
2 \ H \ \sigma + [ \mathbf{T}_{zz} ] = 0 \tag{3.19}
\]

where

\[
H = \frac{1}{2} \frac{r}{r} \frac{\partial}{\partial r} \left( \frac{r \frac{\partial h}{\partial r}}{1 + \left( \frac{\partial h}{\partial r} \right)^2} \right)^{\frac{1}{2}}
\]

and

\[
[ \mathbf{T}_{zz} ] = p - p_g
\]

Realizing that

\[
\tau_{rz} \mid_{z=h} = -\mu \left( \frac{\partial v_r}{\partial z} \right) \mid_{z=h}
\]

and utilizing assumption (ix) we write the first term in equation(17) as

\[
\frac{\partial \sigma}{\partial r} = \left( \frac{d \sigma}{d \Gamma} \right) \left( \frac{\partial \Gamma}{\partial r} \right)
\]

Using equation (3.8), we can then write the tangential stress balance (r component) at the interface as

**Tangential Stress balance:**
\[-\left(\frac{d\sigma}{d\Gamma}\right)\frac{\partial \Gamma}{\partial r} + (\mu_d + \mu_s) \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial (r v^2_r)}{\partial r}\right) = h \left(\frac{\partial p}{\partial r}\right) \tag{3.20}\]

and the normal stress balance (z component) at the interface as:

Normal Stress (or jump momentum) balance:

\[p_s - p = \sigma \frac{1}{r} \frac{\partial}{\partial r} \left(r \sin \alpha\right) \tag{3.21}\]

where

\[
\sin \alpha = \frac{\frac{\partial h}{\partial r}}{\left[1 + \left(\frac{\partial h}{\partial r}\right)^2\right]^{\frac{1}{2}}}
\]

Plane Parallel Film:

For the case of a plane parallel thin liquid film, i.e. \(h = h(t)\) only, the governing equations (eqns. 3.10, 3.11, 3.15,3.20) reduce to the following

\[V = -\frac{d h}{d t} = \frac{h}{r} \frac{\partial}{\partial r} \left(r U\right) - \frac{h^3}{3 \mu} \frac{1}{r} \frac{\partial}{\partial r} \left(\frac{r}{r} \frac{\partial P}{\partial r}\right) \tag{3.22}\]

where

\[U \equiv v^2_r \text{ and } P = p - p_m\]

\(p\) and \(p_m\) are the pressures in the film phase and the meniscus respectively. \(V\) is the rate of thinning of the thin liquid film.

\[
\frac{\partial h \bar{c}}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left(r v^2_r h \bar{c}\right) - \frac{1}{2 \mu} \frac{1}{r} \frac{\partial}{\partial r} \left(r h^2 \left(\frac{\partial P}{\partial r}\right) h \bar{c}\right) = 0
\]

\[= D \left(\frac{\partial c}{\partial z}\right)_{z=h} + D \frac{1}{r} \left(r \frac{\partial (h \bar{c})}{\partial r}\right) \tag{3.23}\]

\[
\frac{\partial \Gamma}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left(r U \Gamma\right) = D_s \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \Gamma}{\partial r}\right) - D \left(\frac{\partial c}{\partial z}\right)_{z=h} \tag{3.24}\]
The tangential stress balance for a plane parallel film can be re-written using the definition of $E^o$ (eqn. 2.18) as

$$-\frac{E^o}{\Gamma_o} \frac{\partial \Gamma}{\partial r} + \mu_{d+s} \frac{\partial}{\partial r} \left[ \frac{1}{r} \frac{\partial}{\partial r} (r U) \right] = h \left( \frac{\partial P}{\partial r} \right)$$  \hspace{1cm} (3.25)

where

$$\mu_{d+s} \equiv \mu_d + \mu_s$$

For a plane parallel film the normal stress boundary condition (eqn. 3.21) cannot be satisfied locally, therefore we use the global force balance as:

$$F = \int_{0}^{R_f} 2\pi r P \, dr$$  \hspace{1cm} (3.26)

where $R_f$ is the film radius.

From the governing equations, one can identify $E^o, \mu_{d+s}, D$ and $D_s$ as the surfactant specific parameters which affect the drainage of the thin liquid film. In the next section we highlight how these surface parameters affect the rate of thinning of a thin liquid film.
Chapter 4

Parameters Affecting Film Drainage

From the equations governing the drainage of a thin liquid film, in Chapter 3, one can see that the main properties influencing the drainage of thin liquid film are:

1) Elasticity

\[ E^o = \Gamma_o \left( \frac{-d \sigma}{d \Gamma} \right)^o \]

2) Bulk and Surface Diffusivity

\[ D & D_s \]

3) Surface Viscosity

\[ \mu_{d+s} \]

4) Bulk phase Viscosity

\[ \mu \]

4.1 Elasticity

In very simple words, surface elasticity is the increase in tension with extension. This is an important effect influencing the resistance to thinning of thin liquid films. This is now an equilibrium property of the system, and can be estimated, given a surface equation of state. The parameter \( E^o \) is referred to as the limiting elasticity or the limiting modulus (Lucassen-Reynders 1979, Sonin et. al., 1993), and not as the Gibbs elasticity (a dynamical quantity) as called by some authors (Slattery 1990, Edwards et. al, 1991). In this work from now on the word elasticity refers to the aforementioned parameter.
This parameter appears in the equations governing the drainage of thin liquid films, and is indicative of the elastic forces a particular surfactant can generate, subject to surface extension due to adjoining bulk flow. Thus it is a material property which can be varied and its effect on drainage rate recorded.

Elasticity of thin liquid films has been measured experimentally and treated theoretically by Russanov and Prokhorov (1983), Prokhorov and Russanov (1987), Prins et al. (1967), Bianco and Marmur (1993) and Mysels et al. (1961).

Significant differences between the film elasticities of mobile films and rigid films have been reported, with the mobile films being 4 to 20 times more yielding than the rigid films (Mysels et al., 1961).


4.2 Surface Viscosity

The term surface viscosity here is being used for the sum of the surface shear and dilational elasticity, the reason being the way these viscosities appear in the physical equations governing the drainage of the thin liquid film. As we stated before, in the case symmetrical drainage of a thin liquid film, the interfaces are dilated rather than sheared. Therefore it is expected that no important role is played by the surface shear properties in the drainage. Several investigators (Johannes and Whitaker, 1965; Berg, 1972; Maru, 1975) have shown that dilational surface properties are several orders of magnitude higher than the corresponding shear properties of the same surfactant monolayer.

The resistance to thinning of the film due to the surface viscosity has been studied

Ivanov et al. (1985) neglect the contribution of the term involving the surface viscosity in the tangential stress balance. Ivanov and Dimitrov (1974) show that the effect of surface viscosity on the liquid flow strongly depends on the area of film element, hence $\mu_{d+s}$ influences the wave motion in the film while its effect on the thinning rate is considerably weaker. Malhotra and Wasan (1987) in their analysis for a plane parallel film, show that the surface viscosity $\mu_{d+s}$ resists thinning of the film, by retarding the adjoining bulk flow.

Rao et al. (1982) perform experiments to correlate surface viscosity with drainage time, for pure and mixed surfactant systems. They also predict the same behavior, i.e. increasing surface viscosity leads to increased drainage time.

Barber and Hartland (1976) report a dimensionless number, which controls the mobility of film thinning. By mobility is implied how fast is the thinning relative to that predicted by the Reynolds theory. Barber and Hartland (1976) parameter is inversely proportional to the square root of the apparent surface viscosity. Further the apparent surface dilational viscosity parameter $K$ of Barber and Hartland (1976) has both an elastic as well as a viscous contribution, related to mass transfer of the surfactant( Lucassen-Reynders, 1979). Also most of the literature, which refers to the Barber and Hartland (1976) paper, mentions that it treats the insoluble surfactant model, which is a misinterpretation. We would like this to be clear that they treat the mass transfer effect with the bulk through the parameter $K$.

Tambe and Sharma (1991) treat the surfactant covered interface as a viscoelastic interface and show that the effect of surface viscosity is much more pronounced if the interface is modelled as a linear visco-elastic fluid, rather than the more commonly used Newtonian model. They conclude that film thinning predictions are very sensitive to interfacial viscosity and elasticity. They however do not differentiate between the effects of 'intrinsic' elasticity (due to assumption of a viscoelastic interface) and
the surface dilational elasticity due to surfactant mass transfer effects (see Chapter 2).

4.3 Bulk and Surface Diffusivity

The effect of surface tension gradients is "relaxed" (i.e., equilibrated) by the diffusional fluxes of the surfactant. These diffusional fluxes are a) diffusion of the surfactant from the bulk liquid to the interface, b) lateral diffusion of the surfactant already adsorbed at the interface. Thus they act to reduce the effect of stress related to surface tension gradients and thereby increase the rate of thinning of the liquid film.

The effect of bulk and surface diffusion on the rate of film thinning has been examined by Malhotra and Wasan (1987), Zapryanov et al. (1983), Radöev et. al. (1974) and Good (1974).

Radöev et. al. (1974) showed that for "small film thicknesses and strong surfactants, surface diffusion can be more important than the bulk diffusion". As already suggested, Radöev et. al. (1974) found that surface diffusion increased the rate of thinning. Clark et. al (1990) experimentally determined the surface diffusion coefficient of SDS stabilized thin liquid films.

In case of an insoluble monolayer, surface diffusion is the only relaxation mechanism. Ewers and Sutherland (1952) showed that the diffusing surfactant could drag significant amounts of bulk liquid, into the regions of high surface tension, thus causing restoration of uniform film thickness. Ivanov (1980) emphasizes the effect of surface diffusion on the rate of thinning for a mobile film, and shows that it should not be neglected.

4.4 Bulk phase viscosity

The effect of bulk phase viscosity on the thinning velocity of the thin liquid film is very tractable. The base case is that of Reynolds velocity for thinning of a plane parallel
thin liquid film with tangentially inextensible (immobile) surfaces. In this case as expected the rate of thinning is inversely proportional to $\mu$ i.e. the more viscous the bulk liquid the slower the drainage. But in the more general case of mobile surfaces the tangential stress at the interface due to the motion of the bulk fluid is directly proportional to the bulk phase viscosity, and hence the mobility (i.e. the rate of thinning compared to Reynolds velocity) increases with increasing bulk viscosity $\mu$. Good (1974), Barber and Hartland (1976) and Malhotra and Wasan (1987) have studied the effect of bulk phase viscosity on the the mobility of the thinning film, for soluble surfactants.
Chapter 5

Analytical Solutions for thinning of a Plane Parallel Film

In this chapter we present analytical solutions for the simplest case of a plane parallel thin liquid film. These solutions enable us to understand how the properties discussed in previous section affect the thin liquid film dynamics and how we should group these properties into dimensionless parameters. The plane parallel formulation has limitations in that it cannot account for all the physical phenomena associated with a draining thin liquid film, e.g. liquid flow in the meniscus or the Plateau border.

Analytical solutions, for a soluble surfactant have been presented by Barber and Hartland (1976) for foam films; Good (1974) for emulsion films; and Ivanov and Jain (1980), Ivanov and Dimitrov (1974), Radöev et al. (1974), for foam and emulsion films. Radöev et al. (1974) study the relative importance of bulk diffusion and surface diffusion on film thinning while the effect of surface viscosity is neglected. Ivanov (1980) derives an expression for the mobility of the thin liquid film, but neglect surface viscosity. We will however show show that surface viscosity does play a major role in determining the rate of thinning. On the other hand, Barber and Hartland (1976) do the analysis for a soluble surfactant, but the dimensionless parameter they present does not include the surface elasticity effect explicitly. In the present analysis we treat each surface property explicitly, and solve for the thinning velocity in terms of these properties.

Our analysis of thinning with an insoluble surfactant is the most complete available treatment of this situation. For a soluble surfactant our analysis is the first to incorporate radial transport of the surfactant by convection in the bulk film. In
both cases we use an improved boundary condition on surface velocity at the film periphery and demonstrate how the material parameters can be grouped into a single dimensionless number which combines the effects of surface elasticity and viscosity.

5.1 Insoluble Surfactant

The governing equations for the drainage of a plane parallel thin liquid film with an insoluble surfactant are eqns. (3.22), (3.24) without the bulk contribution (i.e. $D(\frac{\partial \xi}{\partial z})$, (3.25) and (3.26).

The first step is to find an expression for $\partial \Gamma/\partial r$, using the surfactant mass balance at the interface (eqn. 3.24) to be used in equation (3.25).

The surfactant mass balance for the insoluble case is as follows:

$$\frac{\partial \Gamma}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r U \Gamma) = D_s \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Gamma}{\partial r} \right)$$ (5.1)

It is assumed that all variables depend implicitly on time through the film thickness (Ivanov (1980); Ivanov et al. (1985); Good (1974)). This is called the quasi-steady state assumption, and thus the transient term $\partial \Gamma/\partial t$ is neglected.

Equation (5.1) can then be written as

$$U \frac{\partial \Gamma}{\partial r} + \frac{\Gamma}{r} \frac{\partial}{\partial r} (r U) = D_s \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Gamma}{\partial r} \right)$$ (5.2)

Now assuming that

$$\Gamma = \Gamma_o + \Gamma_1$$

where

$$\Gamma_1 \ll \Gamma_o$$

i.e. deviations from the equilibrium are small the surfactant mass balance (eqn. 5.2) simplifies to
\[
\frac{\Gamma_o}{r} \frac{\partial}{\partial r} (r \ U) = \frac{D_s}{r} \frac{\partial}{\partial r} \left( r \ \frac{\partial \Gamma}{\partial r} \right)
\]  
(5.3)

Integrating eqn. (5.3) and using the condition that flux at the center of the film is zero, i.e.

\[ U = 0 \quad \text{at} \quad r = 0 \]

and

\[ \frac{\partial \Gamma}{\partial r} = 0 \quad \text{at} \quad r = 0 \]

we have

\[
\frac{\partial \Gamma}{\partial r} = U'(r) \ \frac{\Gamma_o}{D_s}
\]  
(5.4)

Integrating eqn.(3.22) with the boundary condition that

\[ \frac{\partial P}{\partial r} = 0 \quad \text{at} \quad r = 0 \]

we have

\[
\frac{\partial P}{\partial r} = \frac{3 \mu}{h^3} \left[ h \ U'(r) - \frac{r}{2} \ V \right]
\]  
(5.5)

Substituting eqns(5.4) and (5.5) in eqn (3.25), it follows that

\[
-\frac{E_o}{D_s} U(r) + \mu d_{+s} \frac{\partial}{\partial r} \left[ \frac{1}{r} \frac{\partial}{\partial r} (r \ U) \right] = \frac{3 \mu}{h^2} \left[ h \ U(r) - \frac{r}{2} \ V \right]
\]  
(5.6)

De-dimensionlizing equation(5.6) we get

\[- N_r N_o U^* + N_u N_o \frac{\partial}{\partial r^*} \left[ \frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* \ U^*) \right] = U^* \ - \ \frac{r^* \ V^*}{2}
\]  
(5.7)
where

\[ r^* = \frac{r}{R_f} \]

\[ V^* = \frac{V}{V_{Re}} \]

\[ U^* = \frac{U}{U_o} \]

\[ N_\Gamma = \frac{\Gamma^0 \left( -\frac{d \sigma}{d \Gamma} \right)^0 R_f}{3 \mu D_s} = \frac{E^0 R_f}{3 \mu D_s} \quad (5.8) \]

\[ N_\mu = \frac{\mu d + s}{3 \mu R_f} \quad (5.9) \]

\[ N_\alpha = \frac{h}{R_f} \quad (5.10) \]

\[ V_{Re} = \frac{8 h^3 F}{3 \pi \mu R_f^4} \]

The parameter \( N_\Gamma \) represents the ratio of elastic effect to surface diffusion and \( N_\mu \) is the ratio of surface viscous traction to bulk viscous traction. \( V_{Re} \) is Reynolds result for rate of thinning of a fluid layer between two rigid plane parallel circular disks (Reynolds, 1886).

De-dimensionlizing eqn.(3.22) using \( V_{Re} \) as the characteristic thinning velocity and \( U_o \) as the characteristic surface velocity and then making dimensionless groups equal
to unity, will enable us to define characteristic quantities like \( U_o \) and \( P_o \) as

\[
U_o = \frac{8 \hbar^2 F}{3 \pi \mu_R f^3}
\]

\[
P_o = \frac{8 F}{\pi R_f^2}
\]

With the substitution, \( x = \sqrt{\theta} \; r^* \), eqn.(5.7) can be rewritten as

\[
x^2 U^{\prime\prime} + x U^\prime - \left(x^2 + 1\right) U^* + \frac{x^3}{2 N_m N_\alpha \theta^{3/2}} V^* = 0 \quad (5.11)
\]

where

\[
\theta = \frac{N_r N_\alpha + 1}{N_m N_\alpha} \quad (5.12)
\]

The homogeneous part of eqn (5.11) is the familiar ‘Bessel’s differential equation’ (Kreyszig, 1990).

The general solution of eqn. (5.11) can be written as

\[
U^*(x) = U_h^*(x) + \hat{U}^*(x)
\]

where \( U_h^*(x) \) and \( \hat{U}^*(x) \) are the homogeneous and particular solutions respectively of eqn. (5.11).

The particular solution \( \hat{U}^*(x) \) is

\[
\hat{U}^*(x) = \frac{x}{2 N_m N_\alpha \theta^{3/2}} V^* \equiv \frac{r^*}{2 \left(N_r N_\alpha + 1\right)} V^* \quad (5.13)
\]

The homogeneous solution is the well known Bessel function solution (Kreyszig, 1990) Thus the general solution is given as:

\[
U^*(r^*) = a_1 I_1 \left(\sqrt{\theta} \; r^*\right) + a_2 K_1 \left(\sqrt{\theta} \; r^*\right) + \frac{r^*}{2 \left(N_r N_\alpha + 1\right)} V^* \quad (5.14)
\]
where $I_1$ and $K_1$ are the modified Bessel functions of order one, and of first kind and second kind respectively (Abramowitz and Stegun, 1982).

Using the boundary condition, mentioned earlier on the surface velocity at the center of the film, i.e.

$$U^* = 0 \quad \text{at} \quad r^* = 0$$

we have $a_2 = 0$.

The other constant can be determined by the condition that the surface velocity attains a maximum at the film periphery (this will be discussed later in detail, also see Chapter 6), i.e.

$$\frac{\partial U^*}{\partial r^*} = 0 \quad \text{at} \quad r^* = 1$$

(5.15)

$$a_1 = \left( \frac{V^*}{2 \left( N_{T} N_{o} + 1 \right)} \right) \frac{1}{I_1 \left( \sqrt{\theta} \right) - \sqrt{\theta} I_0 \left( \sqrt{\theta} \right)}$$

(5.16)

Let's define $a_1^*$ such that

$$a_1^* = a_1^*(\theta) = \frac{1}{I_1 \left( \sqrt{\theta} \right) - \sqrt{\theta} I_0 \left( \sqrt{\theta} \right)}$$

The final solution is then given as

$$U^* = \frac{V^*}{2 \left( N_{T} N_{o} + 1 \right)} \left[ a_1^* I_1 \left( \sqrt{\theta} \, r^* \right) + r^* \right]$$

(5.17)

De-dimensionlizing equation(5.5) we have

$$\frac{\partial P^*}{\partial r^*} = U^* - \frac{r^* \, V^*}{2}$$

(5.18)

where

$$P^* = \frac{P}{P_o}$$
Substituting for $U^*(r)$ (eqn.(5.17)) in the above equation and integrating with the boundary condition that

$$P^* = 0 \text{ at } r^* = 1$$

we get

$$P^*(r^*) = \frac{V^*}{2} \left[ \frac{a_i^2}{(N_r N_\alpha + 1) \sqrt{\theta}} \left( I_0 \left( \sqrt{\theta} \, r^* \right) - I_0 \left( \sqrt{\theta} \right) \right) \right]$$

$$- \frac{1}{2} \left( N_r N_\alpha + 1 \right) \left( r^{*2} - 1 \right) - \frac{1}{2} \left( r^{*2} - 1 \right) \right]$$

(5.19)

Further the global force balance eqn. (3.26) can be re-written in terms of the dimensionless variables as

$$\int_0^1 r^* P^* d r^* = \frac{1}{16}$$

(5.20)

Using eqns(5.19) and (5.20), and rearranging we have the mobility factor $V/V_{Re}$ as

$$V^* = \left[ \frac{4 N_\mu N_\alpha}{(N_r N_\alpha + 1)^2} \frac{2 I_1 \left( \sqrt{\theta} \right) - \sqrt{\theta} I_0 \left( \sqrt{\theta} \right)}{I_1 \left( \sqrt{\theta} \right) - \sqrt{\theta} I_0 \left( \sqrt{\theta} \right)} \right]$$

$$- \frac{1}{(N_r N_\alpha + 1) + 1} \right]^{-1}$$

(5.21)

where $\theta$ is given by eqn.(5.12).

We can see that the above equation is dependent on only three dimensionless parameters, namely $N_\mu$, $N_r$ and $N_\alpha$ (eqns. 5.8, 5.9 and 5.10). As $N_\mu, N_r \to \infty$, i.e. as $\mu_{d+s}, E^o \to \infty$, eqn. (5.21) shows that the mobility factor $V/V_{Re}$ approaches unity, which was expected since the interface becomes immobile (note that for $\mu_{d+s} \to \infty$ we have $\theta \to 0$, the term with Bessel functions approaches 0.25 $\theta$).
The form of equation (5.21) is similar to that presented by Barber and Hartland (1976). However our results cannot be directly compared to theirs because we believe that the boundary condition used by them is in error. They “assume for simplicity that the shear stress at the surface drops to zero at the film periphery, where \( r = R \) and remains so for \( r > R \).” But the shear stress at the surface is given by \( h \left( \frac{d \psi}{dr} \right) \). Our detailed numerical simulations of film drainage (Chapter 6), which allow for variations in film thickness, do not predict a zero pressure gradient at \( R_f \).

Since the plane parallel film model cannot predict changes resulting from change in curvature, it cannot make clear the correct boundary conditions at \( r = R_f \). We have used the boundary condition which is observed in our numerical simulations (Chapter 6), i.e. \( \frac{\partial U^*}{\partial r} = 0 \). In fact, this boundary condition was considered by Barber and Hartland (1976) but thought to be less realistic than that of the proceeding paragraph. In Appendix A we show how using the Barber and Hartland (1976) boundary condition gives counter-intuitive results (i.e. film mobility increasing with increasing surface viscosity and elasticity respectively in some regions of parameter space). We re-derive the thinning velocity for their case by setting \( N_\alpha = 0 \) in eqn. (5.21):

\[
\left( \frac{V}{V_{Re}} \right)_{new,BH} = \left( \frac{\sqrt{\phi} \, R_f}{4} \right)^2 \left[ \frac{\sqrt{\phi} \, R_f \, I_0 \left( \sqrt{\phi} \, R_f \right) - I_1 \left( \sqrt{\phi} \, R_f \right)}{\sqrt{\phi} \, R_f \, I_0 \left( \sqrt{\phi} \, R_f \right) - 2 \, I_1 \left( \sqrt{\phi} \, R_f \right)} \right] \tag{5.22}
\]

where

\[
\varphi = \frac{3 \, \mu}{\mu_{d+s} \, h}
\]

Also one can show that

\[
\sqrt{\phi} \, R_f = \left( \frac{1}{N_\mu \, N_\alpha} \right)^{1/2} \tag{5.23}
\]

This result could be used as a limiting case check on our analysis, for zero elasticity. A comparison between this new result and the original Barber and Hartland (1976) result has been presented in Appendix B. In the limit of \( E^* \to 0 \) eqn.(5.21) reduces
Table 5.1: Mobility Ratio ($V/V_{Re}$) under various conditions

<table>
<thead>
<tr>
<th>General</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{4 N_r N_o}{(N_r N_o + 1)^2} \left[ \frac{2 I_1 (\sqrt{\theta}) - \sqrt{\theta} I_0 (\sqrt{\theta})}{I_1 (\sqrt{\theta}) - \sqrt{\theta} I_0 (\sqrt{\theta})} \right] - \frac{1}{(N_r N_o + 1)} + 1 \right]^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\mu_{d+s} \to 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 + \frac{1}{N_r N_o}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E^o \to 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{(\sqrt{\theta} R_f)^2}{4} \left[ \frac{\sqrt{\theta} R_f I_o (\sqrt{\theta} R_f) - I_1 (\sqrt{\theta} R_f)}{\sqrt{\theta} R_f I_o (\sqrt{\theta} R_f) - 2 I_1 (\sqrt{\theta} R_f)} \right]$</td>
</tr>
</tbody>
</table>

to eqn. (5.22) as expected. Further for negligible surface viscosity, the form of the expression for the thinning velocity (eqn. 5.21) for an insoluble surfactant is given as

$$\left( \frac{V}{V_{Re}} \right)_{\mu_{d+s} \to 0} = 1 + \frac{1}{N_r N_o}$$ \hspace{1cm} (5.24)

where $N_r$ and $N_o$ are the dimensionless parameters as defined earlier. Table 5.1 lists the expressions for the mobility ratio of a thin liquid film, under different conditions.

Next we do a parametric study of the thinning velocities and show that indeed the dimensionless parameters described above control the rate of drainage of thin liquid film. We also show that our general result (eqn. 5.21) reduces to the limiting cases
Table 5.2: Parameter Values

<table>
<thead>
<tr>
<th>$E^o$ (mN/m)</th>
<th>$\mu_{d+s}$ (kg/s)</th>
<th>$D_s$ (m$^2$/s)</th>
<th>$\mu$ (kg/m$\cdot$s)</th>
<th>$R_f$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 $\cdot$ 10$^{-4}$</td>
<td>2.0 $\cdot$ 10$^{-4}$</td>
<td>4.0 $\cdot$ 10$^{-9}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>0.023</td>
</tr>
</tbody>
</table>

mentioned above.

5.1.1 Results and Discussion

In this section we carry out a parametric study on the mobility factor $V/V_{Re}$ (note some authors call this as the interfacial mobility which we feel is a misnomer since $V/V_{Re}$ does not represent any tangential interfacial motion) by recording the effects of parameters outlined in Section 3 and grouped into dimensionless parameters (eqns. 5.8-10). A wide range of values for these parameters can be achieved for different surfactants depending upon their chemical structure (Rosen, 1978) and concentration. Table (5.2) lists some of the typical values of these physical parameters used in the analysis (Djabbarah, 1978).

Parametric Study:

Figure (5.1) illustrates the effect of surface viscosity $\mu_{d+s}$ on the mobility factor as a function of film thickness. It is evident that the rate of thinning approaches the Reynolds velocity at large thicknesses. Further the plot shows that even at moderate values of surface viscosity, a mobile film thins much faster compared to the Reynolds solution. Also, the mobility factor approaches unity at all values of film thickness for high surface viscosity. This is due to the fact that at such high surface viscosity the surfaces become rigid (immobile). Figure (5.2) displays the same information but at a higher value of elasticity thus the interface is now more immobile and hence we do not see any large deviation from the Reynolds model of film thinning. Thus as
contemplated an increase in surface viscosity decreases the rate of drainage and thus leads to more stable foam.

The effect of varying the elasticity of the surfactant on the rate of drainage has been depicted in Figure (5.3). Again large deviations from the Reynolds theory can be seen. Since elasticity is a measure of the tangential stresses generated due to the surface tension gradients, it was expected that increased elasticity would lead to tangentially inextensible (immutable) surfaces. As can be seen from Figure (5.3) the mobility factor is close to unity at high values of elasticity. Figure (5.4) displays essentially the same information but at a high value of surface viscosity and as expected the values of the mobility factor are close to unity.

From the discussion in Section 3 we know that surface diffusion is the "relaxation" mechanism, i.e. it tends to eliminate the surface tension gradients and hence negates the tangential stresses opposing the bulk flow of the liquid. Figure (5.5) tells us the same story.

Even though the Reynolds velocity is inversely proportional to bulk viscosity, the mobility factor increases with increasing bulk viscosity as is shown in Figure (5.6). This is due to the fact that the shear stress exerted on the surface due to the flow of bulk liquid is directly proportional to bulk viscosity.

The next step in this study was to see if indeed dependence of the mobility factor on aforementioned parameters can be grouped as suggested by the dimensionless numbers in eqn.(5.20). Properties were varied in a way so as to keep \( N_\mu, N_\Gamma \) constant and the mobility factor was recorded as a function of \( N_\alpha \) (film thickness). No changes in the mobility factor were observed, thus validating our hypothesis that only three independent dimensionless parameters \( (N_\Gamma, N_\mu, N_\alpha) \) control the rate of thinning.

**Dimensionless Parameters:**

Until now we have seen that \( N_\Gamma \) and \( N_\mu \) are the two dimensionless parameters which contain surfactant specific information and determine the rate of thinning,
Figure 5.1: Effect of surface viscosity on $V/V_{Re}$ at a low value of elasticity
Figure 5.2: Effect of surface viscosity on $V/V_{Re}$ at a high value of elasticity
Figure 5.3: Effect of elasticity on $V/V_{Re}$ at a low value of surface viscosity.

- $a$: $E^0 = 10^{-5} \text{ N/m}$
- $b$: $E^0 = 10^{-4} \text{ N/m}$
- $c$: $E^0 = 10^{-3} \text{ N/m}$
- $d$: $E^0 = 10^{-2} \text{ N/m}$

$\mu_{d+s} = 10^{-5} \text{ kg/s}$
$\mu = 10^{-3} \text{ kg/m-s}$
$D_s = 4.0 \cdot 10^{-9} \text{ m}^2/\text{s}$
Figure 5.4: Effect of elasticity on $V/V_{Re}$ at a high value of surface viscosity
Figure 5.5: Effect of surface diffusivity on $V/V_{Re}$
Figure 5.6: Effect of bulk viscosity on $V/V_{Re}$

- a: $\mu = 2 \cdot 10^{-3}$ kg/m·s
- b: $\mu = 1 \cdot 10^{-3}$ kg/m·s
- c: $\mu = 0.5 \cdot 10^{-3}$ kg/m·s

- $\mu_{d+s} = 10^{-5}$ kg/s
- $E^0 = 4.0 \cdot 10^{-4}$ N/m
- $D_s = 4.0 \cdot 10^{-9}$ m²/s
but we have no clue whatsoever as to how these dimensionless parameters interact among themselves. For example, in Good's (1974) analysis for emulsion films with a soluble surfactant these parameters are shown to interact additively. Since both the parameters $N_\Gamma$ and $N_\mu$ show similar trends in their effect on the mobility factor, we hypothesize that the thinning velocity depends on the weighted linear combination of the dimensionless parameters $N_\Gamma$ and $N_\mu$. We can then write

$$\frac{V}{V_{Re}} = f \left( N_\mu + w N_\Gamma , N_\alpha \right) \quad (5.25)$$

For a given value of $N_\alpha$ we can write the above equation as

$$f^{-1} \left( \frac{V}{V_{Re}} \right)_{N_\alpha=const} = N_\mu + w N_\Gamma \quad (5.26)$$

Therefore if we plot the contours of $V/V_{Re}$ for varying $N_\mu$ and $N_\Gamma$ we should obtain straight lines with a slope equal to negative of $1/w$. Recall eqn. (5.21) and observe that the three dimensionless parameters $N_\Gamma$, $N_\alpha$ and $N_\mu$ occur as $N_\Gamma N_\alpha$ and $N_\mu N_\alpha$. We computed the contour plots of $V/V_{Re}$ as a function of $N_\Gamma N_\alpha$ and $N_\mu N_\alpha$ and got straight line contours with a constant slope $w = 0.27$ (Fig. 5.7). This implies that the two parameters do not act independently but as a single dimensionless parameter $N_R$:

$$N_R = N_\mu + 0.27 N_\Gamma \quad (5.27)$$

Some insight as to why the surface viscosity and the elasticity effects combine as shown in eqn. (5.27) may be obtained from Figure (5.7) that both $N_\mu N_\alpha$ and $N_\Gamma N_\alpha$ are small for mobile films. Under these conditions $\theta$ is rather large and the ratio of the terms involving Bessel functions in eqn.(5.21) approaches unity. It is readily seen that in the limit $\theta \rightarrow \infty$, $V^*$ becomes inversely proportional to $N_\mu + 0.25 N_\Gamma$. Apparently for a wide range of conditions where this limit is not reached but where $\theta$
Figure 5.7: Contour Plot of mobility ratio $V/V_{Re}$
Figure 5.8: Variation of mobility ratio $V/V_{Re}$ with $N_\alpha$. 
is still rather large, the behavior of $V^*$ is well represented by considering it a function of the single variable $N_R$.

Figure (5.8) shows the variation of mobility factor with film thickness for different values of $N_R$. Further the mobility factor was recorded as a function of $N_R$ at different values of the parameter $N_\alpha$ (Figure 5.9). One can see that all the curves are equidistant indicating that $N_\alpha$ acts in a multiplicative manner with $N_R$.

Finally we can now combine all the results of this study of a plane parallel film with an insoluble surfactant in a single plot (Figure 5.10). For a thin liquid film with given surfactant properties one can see how the rate of thinning varies with thickness by following the arrows in Figure (5.10). To see how the mobility affects the surface velocity we plot profiles of this variable in Figure (5.11).

It is evident that as $N_R$ increases the surface becomes more less mobile and thus the surface velocity $U^*$ decreases. Further it is seen from the definitions of the parameters $N_T$ and $N_\mu$ that the relative importance of elasticity and surface viscosity depends on the film radius $R_f$.

**Drainage Time**

The quantity of most practical interest is the time it takes for a thin liquid film to drain from an initial thickness of $h_i$ to a final thickness $h_f$. This drainage time is given as follows

$$\tau = - \int_{h_i}^{h_f} \frac{d h}{V}$$

(5.28)

To get a general result it would be better to de-dimensionlize the drainage time, the choice of the characteristic drainage time being none other than the one based on Reynolds velocity of thinning.
Figure 5.9: Variation of mobility ratio $V/V_{Re}$ with $N_R$

- a: $h/R_q = 1.3 \times 10^{-4}$
- b: $h/R_q = 2.6 \times 10^{-4}$
- c: $h/R_q = 5.2 \times 10^{-4}$
- d: $h/R_q = 10.4 \times 10^{-4}$
- e: $h/R_q = 20.8 \times 10^{-4}$
Figure 5.10: Contour Plot of mobility ratio $V/V_{Re}$ as a function of parameters $N_R$ and $N_\alpha$. 

Arrow indicates a typical experimental run.
Figure 5.11: Surface velocity for different values of $N_R$.
\[ \tau_{Re} = \frac{3 \pi \mu R_f^2}{16 F} \left( \frac{1}{h_f^2} - \frac{1}{h_i^2} \right) \]  

(5.29)

Thus we have

\[ \tau^* \equiv \frac{\tau}{\tau_{Re}} = \frac{-2}{\left( \frac{1}{N_{a_f}} - \frac{1}{N_{a_i}} \right)} \int_{N_{a_i}}^{N_{a_f}} \frac{d N_a}{V^* N_a^3} \]  

(5.30)

The integral was evaluated using a Sigma Plot transform. Varying values of \( dN_a \) were used in evaluating this integral because at small values of film thicknesses the function \( 1/V^* N_a^3 \) changes rapidly. Hence any analysis which integrates the above integral using a constant value of \( dN_a \) will not be accurate.

The dimensionless drainage time \( \tau^* \) has been plotted for a wide range of surfactant properties and for three different film radii in Figure (5.12). \( h_f \) was taken as a typical half critical thickness (\( \approx 15 \text{ nm} \)) of a thin liquid film (Ivanov, 1980) while \( h_i \) was chosen high enough such that any higher value gave no change in the value of \( \tau^* \). (The critical thickness is also an important material parameter which affects the drainage time of a thin liquid film. It depends on the surfactant and the electrolyte concentration through the disjoining pressure isotherm. However we neglect such effects in our study.) It indicates that at a value of \( N_R > 10^5 \) the surfaces become immobile and the thinning follows the Reynolds solution. Further we see that films with a large radius show greater deviation from the Reynolds solution.

5.2 Soluble Surfactant

In this section, we extend the analytical solution of previous section to the more general case of a surfactant soluble in the liquid phase. Nearly all the previous analyses (Radöev et al., 1974; Malhotra and Wasan, 1987; Jain and Ivanov, 1980) neglect the effect of surface viscosity on the rate of drainage of a thin liquid film. The one previous analysis where both the film elasticity and surface viscosity are
Figure 5.12: Dimensionless Drainage Time $\tau^*$ as a function of $N_R$

\[ N_R = N_{\mu} + 0.27 N_{\Gamma} \]

- a: $N_{\mu} = 2.61 \cdot 10^{-3}$
- b: $N_{\mu} = 0.65 \cdot 10^{-3}$
- c: $N_{\mu} = 0.163 \cdot 10^{-3}$
considered (Ivanov and Dimitrov, 1974) neglects the effect on surfactant transport of radial convection in the bulk fluid due to the capillary suction. It also uses yet another boundary condition on $U$ at $r = R_f$, viz., no surface expansion ($\frac{1}{r} \frac{\partial}{\partial r} (r U) = 0$).

In our analysis we include both radial diffusion and radial convection of the surfactant in the bulk fluid. This makes the bulk surfactant mass balance equation difficult to solve analytically compared to the well known Laplace equation used by previous workers where the radial convection was neglected. We will in the succeeding section show how the governing equations can be manipulated to avoid solving for the bulk concentration distribution and yet get an analytical solution for the rate of film thinning. Further we will show that the the solution so obtained reduces to the insoluble surfactant solution under limiting conditions.

### 5.2.1 Analytical Solution

The governing equations are the ones presented in Chapter 3 and are as follows:

Rearranging the left hand side (L.H.S.) eqn. (3.23)

\[
\bar{\eta} \left[ \frac{\partial}{\partial t} \left( \frac{h}{r} \frac{\partial}{\partial r} (r U) \right) - \frac{h^3}{3 \mu} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial P}{\partial r} \right) \right] + h \frac{\partial \bar{\eta}}{\partial t}
\]

\[
+ \left[ U - \frac{h^2}{2 \mu} \left( \frac{\partial P}{\partial r} \right) \right] h \frac{\partial \bar{\eta}}{\partial r} - \frac{\bar{\eta}}{6 \mu} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{h^3}{r} \frac{\partial P}{\partial r} \right)
\]

(5.31)

Using eqn.(5.5) and eqn.(3.23) this expression simplifies to

\[
h \frac{\partial \bar{\eta}}{\partial t} - h \frac{\partial \bar{\eta}}{\partial r} \frac{U}{2} - \frac{h \bar{\eta}}{2} \frac{1}{r} \frac{\partial}{\partial r} (r U) + \frac{r V}{2} \frac{\partial \bar{\eta}}{\partial r} + \frac{V}{4} \frac{1}{r} \frac{\partial}{\partial r} (r^2 \bar{\eta})
\]

(5.32)

We now follow exactly the same methodology as we did in the insoluble surfactant case, i.e. we assume that all variables depend implicitly on time through the film thickness (Good, 1974; Ivanov and Dimitrov, 1974). This is called the quasi-steady state assumption. The time derivative terms are thus neglected. Further we assume
that the average bulk surfactant concentration and the surface surfactant concentration can be written as a perturbations from their respective initial values as:

\[ \Gamma = \Gamma_0 + \Gamma_1 \text{ and } \Gamma_1 \ll \Gamma_0 \]

and

\[ \bar{c} = c_0 + \bar{c}_1 \text{ and } \bar{c}_1 \ll c_0 \]

(Note that before drainage begins the bulk concentration is uniform and equal to \( c_0 \) hence \( \bar{c}_0 = c_0 \)).

With these assumptions we have

\[
h \frac{\partial \bar{c}}{\partial t} = h \frac{\partial \bar{c}}{\partial h} \frac{\partial h}{\partial t} = -V h \frac{\partial \bar{c}}{\partial h} \frac{\partial h}{\partial t} = -V h \frac{\partial \bar{c}}{\partial h} \sim \frac{h U}{R_f} (\bar{c} - c_0) = \frac{h U}{R_f} \bar{c}_1
\]

(here we have used eqn. (3.23), which implies that \( V \sim \frac{h U}{R_f} \))

Similarly we can show that the second, fourth and the fifth terms in equation (5.32) are of the same order. In contrast it is clear that the third term is of order \( \frac{h U}{2 R_f} c_0 \) and thus much larger than the other terms.

Substituting the final form of eqn. (5.32) into eqn. (5.23) and using the above assumptions, we have an equation similar to that for an insoluble surfactant (eqn. 6). The resultant surfactant mass balances at the surface and in the bulk are then given as

\[
\frac{\Gamma_0}{r} \frac{\partial}{\partial r} (r U) = \frac{D_s}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Gamma}{\partial r} \right) - D \left( \frac{\partial c}{\partial z} \right)_{z=h} \tag{5.33}
\]

\[
- \frac{h c_0}{2 r} \frac{\partial}{\partial r} (r U) = \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h \bar{c}}{\partial r} \right) + D \left( \frac{\partial c}{\partial z} \right)_{z=h} \tag{5.34}
\]

We know that the surface surfactant concentration is related to the bulk surfactant concentration at the surface through an adsorption isotherm (e.g. Langmuir, Frumkin etc.) as follows
\[
\frac{d \Gamma}{d r} = \frac{d \Gamma}{d c_s} \frac{d c_s}{d r}
\]

Assuming that the adsorption and diffusion across the film are very fast such that the interface is approximately in equilibrium with the bulk liquid in the film (this results from \(h/R_f \ll 1\)), implies

\[c_s \approx \bar{c}\]

We can then write

\[
\frac{\partial \bar{c}}{\partial r} \approx \left(\frac{d \bar{c}_o}{d \Gamma_o}\right) \frac{\partial \Gamma}{\partial r} \equiv \frac{1}{\beta} \frac{\partial \Gamma}{\partial r}
\]

where

\[\beta = \frac{d \Gamma_o}{d c_o}\]

Adding eqns(5.33) and (5.34) and utilizing the above relation we have

\[
\left(\Gamma_o - \frac{h c_o}{2}\right) \frac{1}{r} \frac{\partial}{\partial r} (r U) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \left(D_s + \frac{D h}{\beta}\right) \frac{\partial \Gamma}{\partial r}\right)
\]

Integrating the above equation with the following boundary conditions,

\[U = 0 \text{ at } r = 0\]

\[\frac{\partial \Gamma}{\partial r} = 0 \text{ at } r = 0\]

gives

\[
\frac{\partial \Gamma}{\partial r} = \frac{\Gamma_o - \frac{h c_o}{2}}{(D_s + D h/\beta)} U(r)
\]

Substituting eqn. (5.37) into eqn. (3.25), leads to
\[- E^o \left( \frac{1 - \frac{h e_o}{2 \Gamma_o}}{D_s + D h / \beta} \right) U(r) + \mu_{d+s} \frac{\partial}{\partial r} \left[ \frac{1}{r} \frac{\partial}{\partial r} (r U) \right] = h \left( \frac{\partial P}{\partial r} \right) \] (5.38)

Using eqn. (5.5) and re-arranging we get

\[- \frac{E^o}{D_s} \left( \frac{1 - \frac{h e_o}{2 \Gamma_o}}{1 + \frac{D}{D_s} \frac{h}{\beta}} \right) U(r) + \mu_{d+s} \frac{\partial}{\partial r} \left[ \frac{1}{r} \frac{\partial}{\partial r} (r U) \right] = \frac{3 \mu}{h^2} \left[ h U(r) - \frac{r}{2} V \right] \] (5.39)

We assume that the film is not very thick so that \(hc_o/2\Gamma_o < 1\) because we have neglected the surfactant accumulation \((V c_o)\) in the bulk compared to the convection in the bulk. This will not hold strictly in case of very thick films where accumulation is of the same order as convective terms.

Comparing equations (5.39) and (5.6) it is clear that in the soluble surfactant case the effective elasticity is now a function of the film half thickness \(h\), the bulk to surface diffusivity ratio \(D/D_s\), the ratio of the bulk and surface surfactant concentration \(c_o/\Gamma_o\) and the adsorption isotherm coefficient \(\beta\).

Thus as the film thins the elasticity increases because the bulk surfactant reservoir is getting depleted and after a while the elasticity approaches the insoluble surfactant limit. Further as seen by Radöev et al., (1974) surface diffusion becomes important for thinner films and with stronger surfactant, i.e. large \(\beta\). This dependence of elasticity on the film thickness has been shown based on thermodynamic arguments by Prins et al. (1967) and Rusanov and Prokhorov (1983).

The subsequent analysis is the same as that for the insoluble surfactant, the only difference being that now the new dimensionless elasticity number is a function of film thickness.

De-dimensionlizing eqn. (5.39) in the same way as before we have

\[- N^T \frac{\partial}{\partial r^*} \left[ \frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* U^*) \right] = U^* - \frac{r^* V^*}{2} \] (5.40)
where $N'_\Gamma$ is the new dimensionless elasticity number and is given as

$$
N'_\Gamma = \frac{E^o \left(1 - \frac{k}{2} \Gamma_o\right)}{3 \mu D_s \left(1 + \frac{D_s}{D_s} \frac{1}{\beta}\right)} = \frac{N_\Gamma \left(1 - N_a N_c\right)}{(1 + N_{D\beta} N_a)}
$$

(5.41)

Here $N_\Gamma$ is the same as defined earlier in the insoluble surfactant analysis and $N_c$ and $N_{D\beta}$ are defined as follows

$$
N_{D\beta} = \frac{D}{D_s} \frac{R_l}{\beta}
$$

$$
N_c = \frac{c_o R_l}{\Gamma_o}
$$

One can now follow exactly the same methodology as for the insoluble surfactant case and arrive at the following result for the mobility factor for a plane parallel thin liquid film with a bulk soluble surfactant.

$$
V'^{ss} = \left[ \frac{4 N_on_a}{\left(\frac{N_r N_o (1 - N_o N_c)}{1 + N_o N_{D\beta}} + 1\right)^2} \right] \frac{2 I_1 \left(\sqrt{\theta^s}\right) - \sqrt{\theta^s} I_0 \left(\sqrt{\theta^s}\right)}{I_1 \left(\sqrt{\theta^s}\right) - \sqrt{\theta^s} I_0 \left(\sqrt{\theta^s}\right)}
$$

$$
+ \frac{1}{\left(\frac{N_r N_o (1 - N_o N_c)}{1 + N_o N_{D\beta}} + 1\right)}
$$

$$
\left(\frac{N_r N_o (1 - N_o N_c)}{1 + N_o N_{D\beta}} + 1\right)^{-1}
$$

(5.42)

where

$$
\theta^s = \frac{N_r N_o (1 - N_o N_c)}{N_o N_{D\beta}} + 1
$$

The above expression reduces to eqn.(5.21) in the insoluble surfactant limit, i.e. $\beta \rightarrow \infty$ ( $N_{D\beta} \rightarrow 0$). Physically $\beta \rightarrow \infty$ implies that whatever surfactant is in the bulk at the start gets adsorbed at the surface and thus we have the insoluble behavior.

We now compare our analytical solution with those of previous researchers. Raddey et al. (1974) have studied the case of negligible surface viscosity (neglecting the convective terms in the bulk) and their expression for $V/V_{Re}$ using the definitions of $N_\beta$ and $N_\Gamma$ is as follows:
\[
\left( \frac{V}{V_{Re}} \right)_{\text{Radóev}} = 1 + \frac{1 + \frac{N_{DB}}{N_{\Gamma}} \frac{N_{\alpha}}{N_{\alpha}}}{1 - \frac{N_{\alpha}}{N_{c}}} \tag{5.43}
\]

This can be compared to our analysis for the limiting case of \( \mu_{d+s} \to 0 \). We have
\[
\left( \frac{V}{V_{Re}} \right)_{\mu_{d+s} \to 0} = 1 + \frac{1 + \frac{N_{DB}}{N_{\Gamma}} \frac{N_{\alpha}}{N_{\alpha}}}{1 - \frac{N_{\alpha}}{N_{c}}} \tag{5.44}
\]

One can see that we have an extra term \( 1 - \frac{N_{\alpha}}{N_{c}} \) which appeared because we took into account the radial convection of the surfactant along with the radial diffusion (eqn. 5.36). For \( N_{\alpha} \to 0 \) the equations become identical. But for thicker films Radóev et al. (1974) predict a slower rate of drainage compared to eqn. (5.44).

Ivanov and Dimitrov (1974) have presented an expression for the mobility factor considering the effect of both the elasticity and the surface viscosity. Re-writing their result in terms of the dimensionless parameters and using the mathematical identity that for \( J_0(\lambda_n) = 0 \)

\[
\frac{J_2(\lambda_n)}{J_1(\lambda_n)} = \frac{2}{\lambda_n}
\]

we have
\[
\left( \frac{V}{V_{Re}} \right)_{\text{Ivan-Dim}} = \frac{1}{16} \left[ \sum_{n=1}^{\infty} \left[ \frac{1 + \frac{N_{\mu}}{N_{\Gamma}} \left( 1 + \frac{N_{DB}}{N_{\Gamma}} \frac{N_{\alpha}}{N_{\alpha}} \right) \lambda_n^2}{1 + \frac{1 + \frac{N_{DB}}{N_{\Gamma}} \frac{N_{\alpha}}{N_{\alpha}}}{1 + \frac{N_{\mu}}{N_{\alpha}} \lambda_n^2}} \right] \right]^{-1} \tag{5.45}
\]

Here too the effect of radial transport of surfactant due to convection in the bulk film has been neglected, so that no terms in \( N_{c} \) appear. But since \( N_{c} \) occurs as a product with \( N_{\alpha} \) in eqn. (5.42), the effect of radial convection is more important at large \( N_{\alpha} \) (i.e. thicker film) and becomes negligible as the film thins down. This suggests that the small Peclet number assumption made by Ivanov and Dimitrov (12) (whereby one neglects the convection terms) will hold for sufficiently thin films.
Table 5.3 - Parameter Values for Soluble Surfactant

<table>
<thead>
<tr>
<th>$E^o$ (mN/m)</th>
<th>$\mu_{d+s}$ (kg/s)</th>
<th>$D_s$ (m$^2$/s)</th>
<th>$D$ (m$^2$/s)</th>
<th>$\beta$ (m)</th>
<th>$\mu$ (kg/m $\cdot$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.0 \cdot 10^{-4}$</td>
<td>$2.0 \cdot 10^{-4}$</td>
<td>$5.5 \cdot 10^{-9}$</td>
<td>$5.5 \cdot 10^{-9}$</td>
<td>$1.0 \cdot 10^{-5}$</td>
<td>$1.0 \cdot 10^{-3}$</td>
</tr>
</tbody>
</table>

5.2.2 Results and Discussion

In this section we present the results for the more general case of a surfactant soluble in the bulk phase. Some typical values used in our study have been listed in Table (5.3).

The mobility factors as predicted by equations (5.42) and (5.45) have been plotted in Figure (5.13) for different values of the parameter $N_c$. The difference in the two solutions for $N_c = 0$ is due to the use of different boundary conditions for the surface velocity $U$ at $r = R_f$. We feel more confident with the boundary condition that the surface velocity reaches a maximum (i.e. $\frac{\partial U}{\partial r} = 0$) because that is what we see from our numerical simulations (Chapter 6). Figure (5.13) illustrates that including the effect of radial convection in the bulk fluid leads to increased mobility factor $V/V_{Re}$ for thicker films. It was also seen that the effect of $N_c$ on the mobility factor was more pronounced when the dimensionless elasticity number $N_T$ dominated over the dimensionless surface viscosity number $N_\mu$.

Contour plots of $V/V_{Re}$ for different set of values of the dimensionless parameters $N_T$ (not $N_T'$ because this is a function of film thickness $N_\alpha$) and $N_\mu$ for a constant value of $N_D\beta$ and $N_c$ were computed. These contours were straight lines with the same slope as we obtained for insoluble surfactant. Hence for the soluble surfactant we can group $N_T$ and $N_\mu$ into the same dimensionless parameter $N_R$.

Soluble vs. Insoluble:
Figure 5.13: Comparison of the mobility factor $V/V_{Re}$ as predicted by equations (5.42) and (5.45)
Figure (5.14) compares the mobility factor $V/V_{Re}$ for a thin liquid film with an insoluble surfactant and a soluble surfactant. As expected the mobility factor in the case of a soluble surfactant is greater due to the relaxation of the surface tension gradients by mass transfer of surfactant from the bulk fluid to the surface. One can see that for low values of the parameters $N_{DB}$ and $N_c$ the soluble surfactant solution as expected approaches that for the insoluble case.

We have seen from equations (5.21) and (5.42) that the only difference in the insoluble surfactant and soluble surfactant case is that the dimensionless elasticity number $N_{T}$ for the former is replaced by an effective dimensionless elasticity number $N'_{T}$ for the latter. Further from eqn.(5.41) we see that the effective elasticity number $N'_{T}$ is a function of the film thickness $N_{o}$. Figure (5.15) shows how $N'_{T}$ changes with film thickness for various values of the parameters $N_{DB}$ and $N_{c}$. The insoluble case $N_{T}$ has been plotted for reference. One can see that for low values of $N_{DB}$ and $N_{c}$ the elasticity number for the soluble surfactant $N'_{T}$ approaches that of the insoluble case $N_{T}$. Another thing to be noted is that as the film thins ($N_{o}$ decreases) the soluble case elasticity approaches the insoluble case. This is because ‘effective elasticity’($N'_{T}$) increases as the the bulk surfactant reservoir gets depleted due to the thinning of the film.

**Drainage Time**

The drainage times were calculated in the same manner as before using eqn.(5.30). Although the choice of the final film thickness is arbitrary we follow the literature in choosing $h_{f}$ equal to the average half critical thickness of the film $h_{cr}$ ($\approx 15nm$). The integral in eqn. (5.30) was calculated using a Sigma Plot transform with variable size of $dN_{o}$.

Figure (5.16) shows how the dimensionless drainage time $\tau^{*}$ varies with the surfactant properties denoted by $N_{R}$ for different values for the parameter $N_{DB}$. Negligible difference in the values of $\tau^{*}$ was found for values $N_{c}$ in the range of experimental
Figure 5.14: Comparison of the mobility factor $V/V_{Re}$ for an insoluble surfactant and a soluble surfactant.
Figure 5.15: Comparison of the dimensionless elasticity number $N_f'$ for soluble surfactant and $N_f$ for insoluble surfactant.
data. Also we have plotted the corresponding drainage times for an insoluble surfactant (which corresponds to the limit of $N_{DB} \rightarrow 0$ and $N_c \rightarrow 0$). From figure (5.16) one can see that as the parameter $N_{DB}$ decreases the soluble surfactant results approach that of the insoluble surfactant, as was anticipated.

Figure (5.17) compares the drainage times predicted by the present analytical solution (eqn. 5.42) with that of Ivanov and Dimitrov (1974) (eqn. 5.45). The experimental results of Djabbarah (1978) for films with purified SDS have also been plotted on Figure (5.17). The experimental data on the elasticity, surface viscosity and drainage times was grouped into the dimensionless parameters. Typical values of the parameters used are listed in Table 5.3 The comparison is good considering the limitations of the plane parallel model. Most important is that trends are same as seen in the experimental results. Figure (5.17) also shows that the drainage time is insensitive to $N_R$ beyond some high value of $N_R$ indicating that the surfaces have been rendered immobile.

Even though Figure (5.17) shows considerable difference between the mobility factors as predicted by equations (5.42) and (5.45) respectively, we see that the predicted dimensionless drainage times in Figure (5.17) don't show much difference. The reason for this lies in the definition of the dimensionless drainage time $\tau^*$ (eqn. 5.30) according to which $\tau^*$ is dominated by small $N_\alpha$. But the effect of the parameter $N_c$ becomes negligible at small $N_\alpha$. Thus one expects that the contribution of the parameter $N_c$ to the dimensionless drainage time $\tau^*$ is small at low values of $N_\alpha$. The difference between the predictions shown in Figure (5.17) is due to the different boundary conditions on $U$ mentioned previously.
Figure 5.16: Dimensionless drainage times for different set of parameters for the soluble surfactant compared with the insoluble case.

- Insoluble Surfactant
- Soluble Surfactant

- Insoluble Surfactant curves:
  - $N_c = 23$
  - $N_{\alpha_i} = 8.7 \cdot 10^{-2}$
  - $N_{\alpha_f} = 6.65 \cdot 10^{-4}$

- Soluble Surfactant curves:
  - a: $N_{DB} = 460$
  - b: $N_{DB} = 1840$
  - c: $N_{DB} = 7360$
Figure 5.17: Comparison of the drainage times as predicted by eqn. (5.42), eqn. (5.45) and the experimental data of Djabbarah (1978)
Chapter 6

Numerical Simulation of a Dimpled Thin Liquid Film with an Insoluble Surfactant

In this chapter we solve the nonlinear partial differential equations governing the drainage of a dimpled thin liquid film with an insoluble surfactant (Chapter 3). We in this study simulate the entire process of dimple formation and drainage in thin liquid film (Chapter 1).

The relevant equations are eqn. (3.10)(thickness equation), eqn. (3.15)(surfactant surface mass balance) without the term accounting for mass transfer from the bulk liquid, the normal stress balance, eqn.(3.21) and the tangential stress balance, (eqn.3.20).

These equations along with the following boundary conditions specify the problem completely in view of the assumptions made.

At \( r = 0 \) we have

\[
\frac{\partial h}{\partial r} = 0
\]

\[
\frac{\partial p}{\partial r} = 0
\]

\[
\frac{\partial \Gamma}{\partial r} = 0
\]

\[
v_r^s = 0
\]
and at \( r = R_c \) we have

\[
\frac{\partial h}{\partial r} = s = \text{specified slope}
\]

\[
- \frac{2\pi R_c h^3}{3\mu_f} \left( \frac{\partial p}{\partial r} \right) = Q \quad \text{for } 0 < t < t_1
\]

\[
\frac{\partial p}{\partial r} = 0 \quad \text{for } t > t_1
\]

\[
\frac{\partial \Gamma}{\partial r} = 0
\]

\[
v_r^* = 0
\]

where

\( t_1 \) is the withdrawal time, \( Q \) is the withdrawal flow rate. \( R_c \) is the bubble radius (radius of the glass cell, Joye et al., (1992)).

In the next section we present the numerical procedure and the methodology used to solve the above equations.

### 6.1 Numerical Simulation Methodology

The above equations and the boundary conditions are made dimensionless using the following

\[
T = \frac{t \sigma}{3 \mu R_c} \quad V = \frac{3 \mu v^*_r}{\sigma}
\]

\[
P = \frac{(p - p_2)}{\sigma} \quad H = \frac{h}{R_c} \quad R = \frac{r}{R_c}
\]

\[
\Gamma = \frac{\Gamma}{\Gamma_o}
\]
and rearranged to give us the following set of governing equations, which we use in our numerical analysis of thin liquid film drainage.

\[
\frac{\partial H}{\partial T} = -\frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial H}{\partial R} \right) + \frac{1}{R} \frac{\partial}{\partial R} \left( R^3 \frac{\partial P}{\partial R} \right) \tag{6.1}
\]

\[
P = -\frac{1}{R} \frac{\partial}{\partial R} \left( R \sin \alpha \right) \tag{6.2}
\]

\[
\sin \alpha = \frac{\frac{\partial H}{\partial R}}{\left[ 1 + \left( \frac{\partial H}{\partial R} \right)^2 \right]^{\frac{1}{2}}}
\]

\[
\frac{\partial \Gamma}{\partial T} = -\frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \Gamma}{\partial R} \right) + M_4 \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \Gamma}{\partial R} \right) \tag{6.3}
\]

\[
-M_2 \frac{\partial \Gamma}{\partial R} + M_3 \frac{\partial}{\partial R} \left( \frac{1}{R} \frac{\partial (R \frac{\partial \Gamma}{\partial R})}{\partial R} \right) - H \left( \frac{\partial P}{\partial R} \right) = 0 \tag{6.4}
\]

where \( M_2, M_3, M_4 \) are dimensionless parameters, given as

\[
M_2 = \frac{\Gamma^\circ \left( -\frac{\partial}{\partial \Gamma} \right)^\circ}{\sigma} \equiv \frac{E^\circ}{\sigma}
\]

\[
M_3 = \frac{\mu \kappa_{s}}{3 \mu R_c}
\]

\[
M_4 = \frac{3 \mu D^s}{\sigma R_c}
\]

here \( E^\circ \) is the elasticity due to the surface tension gradients (Chapter 4).

The dimensionless boundary conditions are given as:

At \( R = 0 \) we have

\[
\frac{\partial H}{\partial R} = 0
\]
\[
\frac{\partial P}{\partial R} = 0
\]

\[
\frac{\partial \Gamma}{\partial R} = 0
\]

\[V = 0\]

and at \(R = 1\) we have

\[
\frac{\partial H}{\partial R} = s = \text{specified slope}
\]

\[-H^3 \left( \frac{\partial P}{\partial R} \right) = Q^* \text{ for } 0 < T < T_1\]

\[
\frac{\partial P}{\partial R} = 0 \text{ for } T > T_1
\]

\[
\frac{\partial \Gamma}{\partial R} = 0
\]

\[V = 0\]

where \(Q^*\) is defined as the dimensionless withdrawal flow rate, given as

\[
Q^* = \frac{Q}{Q_o}; \quad Q_o = \frac{2\pi R_c^3}{(3\mu R_c)}
\]

One can see that \(Q_o\) is the ratio of characteristic volume to characteristic time.

The set of partial differential equations controlling the drainage of the mobile dimpled axisymmetric thin liquid film (eqns 6.1-4) are coupled. Hence to determine the spatio-temporal evolution of the film thickness \(H\), the surfactant surface concentration \(\Gamma\) and the interfacial velocity \(V\), these equations need to be solved simultaneously. For solving the equations we use the finite difference method. The entire flow domain
is divided into gridblocks, i.e. a "block centered" grid is employed rather than the usual "point-centered" grid. The dependent variable is defined at the center of the gridblock and the fluxes are evaluated at the faces separating the gridblocks. The divergence of the flux in a gridblock, expressed in finite difference is the net efflux from the gridblock. The advantage is that this formulation is mass conservative and convenient for problems with flux boundary conditions.

Semi-implicit procedure was used for these equations i.e. the non-linear terms were linearized using the Taylor series expansion. Single point upstream weighting was used for the convective terms to avoid the numerical oscillations associated with standard central differencing. By making appropriate assumptions regarding evaluation of coefficients, it is possible to decouple the finite difference representation of equations (Anderson et al., 1987), i.e. the equations are solved in a loosely coupled manner. Thus the coefficients ($V$ and $\Gamma$) in the finite difference form of equations (6.1 and 6.2), are calculated at old time level ‘n’, to solve for intermediate value of film half thickness $H^\ast$. Similarly equations (6.3) and (6.4) are solved simultaneously for intermediate values $V^\ast$ and $\Gamma^\ast$, using thickness values at time level ‘n’. Using these values, the coefficients are then updated to solve for $H, V, \Gamma$ at the next time level, by use of simple iterative updating procedures. This procedure of loosely coupling and updating the coefficients is known as "lagging" coefficients method (Anderson et al., 1987). In our case, linearizing and lagging the coefficients worked well, and just one iteration was required. Anderson et al. (1987) points out that its better to go for smaller step sizes to reduce truncation error, rather than utilizing computation time to iterate for this sake. Also that smaller step size reduces the truncation error associated with the derivatives in the marching co-ordinate.

The coefficient matrix for the film half thickness $H$ turns out to be pentadiagonal in form, while a block tridiagonal coefficient matrix is achieved for the surfactant mass balance and the tangential stress balance at the interface. A non-uniform mesh was used, with 50% of the grids located in the film region. Grid size independence of
the numerical solution was tested. As regards the time step size, an automatic time step selector was used, such that the maximum relative change per time step did not exceed a given value (typically 5%). The numerical code was validated by doing a mass balance analysis. The flow rate at the outlet \( R_c \) was calculated from the pressure profile, based on the last 10 grid blocks and matched with the specified flow rate \( Q \). All simulations were performed on the IBM RISC 6000 computer. A typical run took less than a minute.

### 6.2 Results and Discussion

In this section we first present the results of a typical numerical simulation followed by a detailed parametric study. Next we choose a series of simulations to see whether the parameters effecting the rate of drainage can be grouped into dimensionless parameters as suggested by the analytical solution (Chapter 5, Singh et al., 1996).

#### Typical Simulation

To simulate the film formation and drainage according to the experimental procedure, a thin liquid film is formed by withdrawing fluid at a constant rate \( Q \), during a time \( t_1 \). Then the liquid withdrawal is stopped and the film drains due to the capillary suction. The entire drainage process was simulated and profiles of film thickness, surfactant surface concentration and interfacial velocity were recorded. In the initial stage of the drainage process the film radius changes rapidly and then reaches a final radial location. The film radius \( R_f \) defined as the location of the minimum film thickness ( barrier ring ) is calculated using quadratic interpolation.

Figure (6.1) shows that during withdrawal the meniscus advances radially and after the drainage has stopped (i.e. film now drains under ‘capillary suction’) the barrier ring reaches a final radial location corresponding to the film radius \( R_f \). Another interesting observation in Figure (6.1) is that a plateau is formed in the film
thickness between the dimple and the barrier ring. These are known as “welts”. As we had remarked earlier the process of fluid withdrawal to form a thin liquid film is depective of the process of two bubbles suspended in the media moving towards each other (stages a to c, see Introduction). Thus one expects considerable motion on the interface during this process. Figures (6.2) and (6.3) illustrate this point well enough.

Figure (6.2) shows how the interfacial velocity changes during withdrawal. The peaks in the profile denote the position of the minimum thickness (barrier ring). The peak shifts during withdrawal until a final radial location $R_f$ is attained. The interfacial velocities during withdrawal are much higher compared to the values when the liquid drains under capillary suction.

Profiles of the surfactant surface concentration during withdrawal have been illustrated in Figure (6.3). Initially the surfactant was distributed uniformly over the film surface with a concentration of $10^{-6}$ mol/m$^2$. Considerable motion during withdrawal causes the surfactant to be swept away from the center of the film into the meniscus region as can be seen from the profiles. Also note that large gradients are observed in the film radius region and that the magnitude of these gradients is significantly reduced once the withdrawal is stopped and capillary suction takes over.

All the above tells us that the process of film formation is a very important dynamic process and that surface tension gradients giving rise to Marangoni stresses have been set up even before the thin liquid film starts draining under the action of capillary pressure.

Figure (6.4) shows the thickness profiles during drainage for a different set of parameters. One can see that the location of the barrier ring is constant during the drainage process. Further Figure (6.5) shows that at the barrier ring we have large interfacial velocities (this explains the choice of boundary condition for the surface velocity at $R_f$ used in the analytical solution (Chapter 5) which progressively decrease in magnitude as the film drains since the surface tension gradients responsible for this motion are getting equilibrated with time (see Figure 6.6).
Figure 6.1: Film Half Thickness Profiles; withdrawal time=4.0 s

\[ E^0 = 10^{-4} \text{ N/m}; \mu_{d+s} = 5.24 \times 10^{-5} \text{ kg/s} \]
\[ \mu = 10^{-3} \text{ kg/m/s}; D_s = 4.0 \times 10^{-9} \text{ m}^2/\text{s} \]
\[ R_f = 0.597 \text{ mm} \]
Figure 6.2: Interfacial Velocity Profiles; withdrawal time=4.0 s

\[ E^0 = 10^{-4} \text{ N/m}; \mu_{d+s} = 5.24 \times 10^{-5} \text{ kg/s} \]
\[ \mu = 10^{-3} \text{ kg/m-s}; \, D_S = 4.0 \times 10^{-9} \text{ m}^2/\text{s} \]
\[ R_f = 0.597 \text{ mm} \]
Figure 6.3: Surfactant Surface Concentration Profiles; withdrawal time=4.0s
Figure 6.4: Film Half Thickness Profiles; withdrawal time=0.625s
**Parametric Study**

Although the entire drainage process was simulated, from now onwards we just concentrate on the film drainage under capillary suction (i.e. after the withdrawal has been stopped). We did not take into account the effects of disjoining pressure but the simulation can be extended very easily to include them.

We now want to see how the surfactant properties affect the motion on the interface and thus alter the rate of drainage. The main properties are i) elasticity \( E^o \), ii) surface viscosity \( \mu_{d+s} \), iii) surface diffusivity \( D_s \), iv) bulk viscosity \( \mu \). Figures (6.7) and (6.8) show the effect of elasticity on the interfacial velocity and surfactant surface concentration respectively. As expected increasing elasticity dampens the motion on the interface and makes it less extensible.

One can see a large reduction in the peaks (Figure 6.7) of the interfacial velocity as the elasticity is increased. Figure (6.8) illustrates a similar effect, i.e. the surface concentration gradients get damped with increase in elasticity. This is because a surfactant with high elasticity \( E^o \) implies that for the same perturbation in the surface concentration due to the bulk liquid flow, the corresponding perturbation in the surface tension is high giving rise to large Marangoni stresses which reduce the extensibility (mobility) of the surface.

Surface viscosity is a rheological property of the interface which resists the motion of the interface. Thus one expects the surface to become more inextensible (immobile) at high surface viscosities. The effect of increasing surface viscosity on the interfacial velocity during drainage has been depicted in Figure (6.9). The peaks decrease in magnitude as the surface viscosity is increased. Similarly in Figure (6.10) the gradients in the surfactant surface concentration are reduced.

If we imagine an extended spring to represent the elastic forces generated due to the surface tension gradients then the spring tries to relax and thus generates interfacial tangential stresses (so called Marangoni stresses) which oppose the flow.
Figure 6.5: Interfacial Velocity Profiles; withdrawal time = 0.625s

Withdrawal Time = 0.625 s

- $E^o = 4.0 \times 10^{-3} \text{ N/m}$
- $\mu = 1.0 \times 10^{-3} \text{ kg/m-s}$
- $\mu_{d+s} = 4.36 \times 10^{-5} \text{ kg/s}$
- $D_s = 4.0 \times 10^{-9} \text{ m}^2/\text{s}$
- $R_f = 0.1155 \text{ mm}$
Figure 6.6: Surfactant Surface Concentration Profiles; withdrawal time = 0.625s
Figure 6.7: Effect of Elasticity on Interfacial Velocity; sampling time=100s
Figure 6.8: Effect of Elasticity on Surfactant Surface Concentration; sampling time=100s
Figure 6.9: Effect of Surface Viscosity on Interfacial Velocity; sampling time=100s
Figure 6.10: Effect of Surface Viscosity on Surfactant Surface Concentration; sampling time=100s
of the liquid in the bulk. These tangential stresses get damped due to the surface diffusion of the surfactant which acts as a dashpot in series with the spring. Thus high surface diffusivity implies that the tangential stresses opposing the bulk would be reduced, leading to increased mobility. The above point is clearly illustrated in Figures (6.11) and (6.12), where we see that the interfacial velocities and surface tension gradients increase with increase in surface diffusivity.

Although in most cases of practical interest the bulk viscosity of the liquid phase will not change much, but for simulation sake we try and see the effect bulk viscosity has on the interfacial motion. Since increase in bulk phase viscosity means higher drag at the interface consequently we see an increase in the interfacial velocity and the surfactant surface concentration gradient (Figures 6.13 and 6.14).

**Dimensionless Parameters**

The hydrodynamics of film thinning are described by equations (6.1-4) and the corresponding boundary conditions. From these equations we can identify the dimensionless parameters affecting the rate of film thinning $V$ as follows:

\[ M_2 = \frac{E^g}{\sigma} \]

\[ M_3 = \frac{\mu_{d+s}}{3 \mu R_c} \]

\[ M_4 = \frac{3 \mu D_s}{\sigma R_c} \]

Contrary to the case of a plane parallel axisymmetric thin liquid film, the rate of thinning of a dimpled axisymmetric thin liquid film depends on the radial location 'r'. Two main locations of interest are i) the barrier ring, $V_{ring}$ (i.e. location of minimum thickness, $r = R_f$); ii) the center of the film, $V_{center}$ ($r = 0$). The rate of thinning at
Figure 6.11: Effect of Surface Diffusivity on Interfacial Velocity; sampling time=100s
Figure 6.12: Effect of Surface Diffusivity on Surfactant Surface Concentration; sampling time=100s
Figure 6.13: Effect of Bulk Viscosity on Interfacial Velocity; sampling time=100s
Figure 6.14: Effect of Bulk Viscosity on Surfactant Surface Concentration; sampling time=100s
these locations is normalized with respect to the Reynolds velocity (Reynolds, 1886) $V_{Re}$.

The normalized rate of thinning at the center $V_{center}/V_{Re}$ was computed for different set of parameters $E^\circ, \mu_{d+s}, \sigma, D_s, \mu$ and $R_c$ and it was found that indeed these parameters could be grouped into the dimensionless parameters $M_2$, $M_3$ and $M_4$ as described before.

Joye et al. (1992) showed that the rate of thinning at the barrier ring $V_{ring}$ approaches the Reynolds velocity $V_{Re}$ at small film thicknesses. Thus $V_{ring}$ can be used to compare the numerical simulation results with those predicted by the analytical solution (Chapter 5). Further from the analytical solution of palne parallel film we saw that the dimensionless rate of film thinning $V/V_{Re}$ depends on the dimensionless parameters $N_\Gamma$ and $N_\mu$, given as

$$N_\Gamma = \frac{E^\circ}{3} \frac{R_f}{\mu D_s}$$

$$N_\mu = \frac{\mu_{d+s}}{3} \frac{R_c}{R_f}$$

A close look reveals that these parameters are related to the dimensionless parameters $M_2$, $M_3$ and $M_4$ as follows

$$N_\Gamma = \frac{M_2}{M_4} \frac{R_f}{R_c}$$

$$N_\mu = M_3 \frac{R_c}{R_f}$$

From the numerical simulation $V_{ring}/V_{Re}$ was computed for different set of parameters $E^\circ, \mu_{d+s}, \sigma, \mu, D_s, R_f$ and $R_c$ and it was found that the normalized rate of thinning at the barrier ring depends on two dimensionless parameters $N_\Gamma$ and $N_\mu$ very much like the analytical solution (Chapter 5).

The next question is can we group the dimensionless parameters $N_\mu$ and $N_\Gamma$ in an additive manner as done for plane parallel film case. To do this we get contour
plots of the mobility factor $V/V_{Re}$ at the barrier ring for different combinations of $N_\mu$ and $N_\Gamma$. We carried out 100 simulations by varying $N_\mu$ and $N_\Gamma$ in an arithmetic progression at a fixed value of dimensionless film thickness $N_\alpha = h/R_f$. Figure (6.15) shows such a contour plot.

Straight lines indicate that $N_\mu$ and $N_\Gamma$ do interact additively in a linear fashion. Thus we can now combine these dimensionless parameters into one as follows

$$N_R = N_\mu + w N_\Gamma$$  \hspace{1cm} (6.5)

(Note that the contour lines are not exactly straight, this is due to the numerical problems of interpolation associated with contouring. While 10,000 runs were carried out in the analytical solution (Chapter 5) such a task will be time exhaustive for the numerical solution.)

These 100 simulations were repeated for five different values of $N_\alpha$. Contours of the mobility factor were plotted and the value of the coefficient $w$ determined for each case. Table 6.1 lists the value of $w$ for different $N_\alpha$.

Recall that in the plane parallel case the coefficient $w$ was constant over a wide range of $N_\alpha$ and had a numerical value of 0.27. Taking an average of the values in the table we have $w = 0.278$. Certainly the difference is not substantial and could be due to the numerics. Nevertheless both the analytical and the numerical solutions predict similar dependence of the mobility factor $V/V_{Re}$ on the dimensionless parameters $N_\Gamma$ and $N_\mu$.

**Rate of Thinning**

In the absence of disjoining pressure Joye et al. (1996) correlated the rate of thinning/drainage of an immobile dimpled axisymmetric film in terms of a single dimensionless parameter $C_R$. They obtained a universal curve for the normalized rate of thinning at the center and the barrier ring as a function of $C_R$ for the range of film radii investigated. This parameter is called as the curvature ratio and is defined
Figure 6.15: Contours of the mobility factor $\frac{V}{V_{Re}}$

$N_\alpha = 7.0 \cdot 10^{-5}$
as

$$C_R = \frac{1/R_d}{1/R_c} \approx \frac{2h_o}{R_c^2}$$ (6.5)

where \(h_o\) is the height of the dimple (i.e. film half thickness at the center), \(1/R_d\) is the curvature in the dimple and \(1/R_c\) is the curvature in the meniscus. As the authors (Joye et al., 1992) state "a physical interpretation can be made for the curvature ratio 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".

We will therefore plot the rate of thinning at the center and the barrier ring normalized with respect to the Reynolds velocity \(V_{Re}\) as a function of \(C_R\) and see how it departs from the immobile case studied by Joye et al. (1992). Simulations were carried out and it was seen that for a mobile film the rate of thinning at the barrier ring and at the film center were much higher than that predicted for the immobile film.

Figure (6.16) shows the normalized rate of thinning \(V/V_{Re}\) (mobility ratio) correlated with the parameter \(N_R\). A range of values of \(N_R\) were investigated by varying it in a geometric progression. One sees that at low values of \(N_R\) the film is quite mobile while at higher values the mobility factor approaches the result of Joye et al. (1992) for an immobile film.

**Drainage Time**

The quantity of most practical interest is the time it takes for a thin liquid film to drain from an initial thickness \(h_i\) to a final thickness \(h_f\). The final thickness is usually taken to be the critical thickness \(h_{cr}\) (Although the critical thickness \(h_{cr}\) depends on the surfactant and the electrolyte concentration through the disjoining pressure isotherm, we neglect such effects in our analysis).
Figure 6.16: Mobility factor $V/V_{Re}$ as a function of $C_R$ for different values of the parameter $N_R$.
Since the barrier ring will reach the critical thickness first, we concentrate on the drainage time based on the barrier ring film thickness. The critical half thickness was chosen to be 15nm (Djabbarah, 1978). The initial film thickness $h_i$ is the thickness at the start of the drainage due to the capillary suction (i.e. once the liquid withdrawal has been stopped). These drainage times have been plotted in Figure (6.17) for three different values of the film radius $R_f$ as a function of the material parameter $N_R$. Results are in qualitative agreement with the experimental observations of Djabbarah (1978) and the results of the analytical solution. Also it is seen that the limiting $N_R$ value (i.e. value of $N_R$ above which the film behaves as immobile) is of the same order ($N_R > 10^4$) for both this numerical study and the analytical solution.

**Numerical vs. Analytical**

We have seen that both the numerical and the analytical solution agree as to what dimensionless parameters control the rate of thinning at the barrier ring and the critical value of $N_R$ at which the surfaces become immobile. We now need to compare the drainage times predicted by these two solutions. The idea is to investigate if we can replace the cumbersome numerical simulation with the simple analytical solution for some regions of parameter space.

The dimensionless drainage time $\tau^*$ is the drainage time normalized with respect to drainage time predicted by the Reynolds theory $\tau_{Re}$ for a film thinning down from an initial thickness $h_i$ to a final thickness $h_f$. From Joye et al. (1992) we have seen that the numerical study results approach Reynolds theory at low values of film thickness (low $C_R$). This is probably because the quasi-steady state assumption holds well at large time i.e. small film thickness. Hence for comparison between the dimensionless drainage time obtained from the numerical simulation $\tau_{num}$ and that from analytical solution $\tau_{ana}$, we concentrate in this region of low $C_R$. Further we know that $R_f/R_e$ is the factor which quantifies the deviation from plane-parallel films to a dimpled film (see Appendix C). Hence we plot are results as a function of the parameter $R_f/R_e$.

The simulations show that the agreement between the numerical and the analytical
Figure 6.17: Dimensionless Drainage Time based on the barrier ring film thickness as a function of the material parameter $N_R$. 

- $R_f = 0.0459$ mm
- $R_f = 0.0325$ mm
- $R_f = 0.023$ mm

$h_f = 15$ nm
improve as the dimensionless parameter $R_f/R_e$ becomes small, with the numerically predicted values being twice as much as those predicted by the analytical solution. Figure (6.18) shows such a comparison at a constant value of $N_R$ and the dimensionless film thickness at the barrier ring $N_{\alpha_f}$. Further it is seen that the discrepancy in the numerical and the analytical solution reduces as the film becomes more immobile. Figure (6.19) shows that the solutions approach each other as the parameter $N_R$ increases.
Figure 6.18: Ratio of Dimensionless Drainage Time obtained from Numerical Simulation to that predicted by the Analytical Solution as a function of the ratio $R_f/R_c$. 

- $(R_f/R_c) \times 10^3$
  - a: 2.03
  - b: 4.20
  - c: 6.89
  - d: 9.43
  - e: 12.9

- $N_R = 348$
- $N_{\alpha r} = 7.47 \cdot 10^{-5}$
Figure 6.19: Ratio of Dimensionless Drainage Time obtained from Numerical Simulation to that predicted by the Analytical Solution as a function of the material parameter $N_R$

$R_f / R_c = 6.89 \cdot 10^{-3}$

$N_{\alpha} = 7.47 \cdot 10^{-5}$
Chapter 7

Foam Film in Porous Media

7.1 Introduction

Falls et al. (1988) define foam in porous media as a “dispersion of gas in liquid such that the liquid phase is interconnected and at least some of the gas flow paths are blocked by lamellae” (i.e. thin liquid films). Foams are classified into two main categories, namely a) continuous, where there exists at least one flow path for gas that is not blocked by lamellae, b) discontinuous, where all the flow paths for gas are blocked by these lamellae, and thus gas flows as bubbles encapsulated by these lamellae (Rossen, 1995; Kovscek and Radke, 1994).

In our study we concentrate on discontinuous foam where foam in porous media is composed of individual liquid lamella each straddling a pore body or throat and separated from each other by at least a pore length. Each of these lamellae consists of curved regions known as Plateau borders which connect lamellae to the pore wall.

Foam texture in porous media depends on creation and destruction of these lamellae (thin liquid films). Foam generation has been discussed in detail by Gauglitz and Radke (1986) and Chambers and Radke (1992). Foam destruction is due to lamella rupture and diffusion of gas out of small bubbles. Rossen (1995) emphasizes that foam destruction due to diffusion is insignificant in porous media, “because lamella curvature is not so directly and inversely related to bubble volume”.

Experimental observations of Nutt et al. (1992) show that foam flow in porous media is a dynamic process, in which “foam lamellae continually undergo rupture and reconstruction during their passage along the pore system, at rates which are determined by pore geometry, as well as foam quality, foam flow rate and rheological
properties of lamellae". Hence in this work we study the dynamics of the foam lamella as it moves in the pore system, and elucidate the parameters which affect the stability of these lamellae. Most important are the dynamics of a lamella moving from pore throat to pore body.

Jiménez & Radke (1989) have studied the dynamic stability of a foam lamella flowing through a periodically constricted pore. They propose that the lamella stability depends on the capillary pressure of the medium as originally proposed and verified experimentally by Khatib et al. (1986). Jiménez & Radke (1989) present a hydrodynamic theory to explain the dependence of the critical capillary pressure on the gas velocity. In their model they assumed a foam lamella with plane parallel surfaces and thus they were able to use the Reynolds expression for the thinning of the film (lamella).

We in our study will show that the above is just one regime in the dynamic behavior of the foam lamella as it moves through a periodically constricted pore. First we carry out numerical simulations to predict the evolution of film thickness as the film with an insoluble surfactant moves from a pore throat to a pore body at a constant flow rate $Q$. A generalized model is developed which accounts for the mobility of film surfaces (see chapter 6) and reduces to the immobile case (rigid surfaces) under limiting conditions.

### 7.2 Governing Equations

The equations governing the hydrodynamics of the foam film (lamella) (see Chapter 3) as it traverses a porous medium are as follows:

**Thickness Equation:**

$$
\frac{\partial h}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} (r h v_r^2) + \frac{1}{3 \mu} \frac{1}{r} \frac{\partial}{\partial r} \left( r h^3 \left( \frac{\partial p}{\partial r} \right) \right) \quad (7.1)
$$
where \( h \) is the film half thickness, \( v^*_r \) is the interfacial velocity and \( p \) is the pressure in the film.

**Pressure Equation:**

\[
p_g - p = \sigma \frac{1}{r} \frac{\partial}{\partial r} \left( r \sin \alpha \right) + \Pi
\]  

(7.2)

where

\[
\sin \alpha = \frac{\frac{\partial}{\partial r} \left( \frac{h}{r} \right)}{\left[ 1 + \left( \frac{\partial}{\partial r} \left( \frac{h}{r} \right) \right)^2 \right]^{1/2}}
\]

and \( \Pi = \Pi (h) \) is the disjoining pressure which is a sum of three different terms:

\[
\Pi = \Pi_{vdW} + \Pi_{el} + \Pi_{sr}
\]  

(7.3)

\( \Pi_{vdW} \) is the van der Waals attraction term and is given as:

\[
\Pi_{vdW} = -\frac{A}{48 \pi h^3}
\]

where \( A \) is the Hamaker constant. \( \Pi_{el} \) is the pressure due to the electrostatic repulsion and can be expressed as:

\[
\Pi_{el} = 64 n k T \phi^2 e^{-2} \kappa (h - \delta)
\]

this can be written as

\[
\Pi_{el} = \Pi_{el}^0 e^{-2} \kappa (h - \delta)
\]

\[
\phi = \tanh \left( \frac{z e \psi}{4 k T} \right)
\]

\[
\kappa^{-1} = \left( 2 e^2 z^2 n/\epsilon k T \right)^{-1/2}
\]

where \( n \) is the number of counterions per cubic centimeter in the bulk solution, \( \delta \) is the thickness of the adsorbed monolayer, \( z \) is the valence, \( \epsilon \) the electronic charge,
\( \epsilon \) the dielectric constant for the solvent, \( \psi \) the electric potential at the interface, and 
\( \kappa^{-1} \) is the Debye-Hückel characteristic length. \( \Pi_{sr} \) is the short range repulsion term and is expressed as

\[
\Pi_{sr} = C_1 \exp\left(-C_2 (2h)\right)
\]

\( C_1 \) and \( C_2 \) are constants and are chosen such that the disjoining pressure curve has almost an infinite slope at a thickness \( 2h \) of \( 30A^o \) corresponding to typical thickness \( 2\delta \) (\( h_{ads} = \delta \)) of a Newton Black film. Figure (7.1) shows the plot of disjoining pressure as a function of thickness for a typical set of parameters.

**Surface Surfactant Mass Balance:**

\[
\frac{\partial \Gamma}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r v_r^+ \Gamma) = D_s \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Gamma}{\partial r} \right)
\]  

(7.4)

where \( \Gamma \) is the surfactant surface concentration and \( D_s \) is the surface diffusivity.

**Tangential Stress Balance at the Interface:**

\[
- \left( \frac{-d\sigma}{d\Gamma} \right)^a \frac{\partial \Gamma}{\partial r} + \mu_{d+s} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial (r v_r^+)}{\partial r} \right) = h \left( \frac{\partial p}{\partial r} \right)
\]

(7.5)

where \( \mu_{d+s} \) is the sum of the surface dilatational viscosity \( \mu_d \) and the surface shear viscosity \( \mu_s \).

The corresponding boundary conditions are:

At \( r = 0 \) we have

\[
\frac{\partial h}{\partial r} = 0
\]

\[
\frac{\partial p}{\partial r} = 0
\]
Figure 7.1: Disjoining Pressure $\Pi$ as a function of film half thickness $h$ as determined by equation (7.3)

\[ C_{el} = 6 \cdot 10^{-4} \text{ mol/L} \]
\[ A_{yw} = 8 \cdot 10^{-19} \text{ J} \]
\[ \psi = 94 \text{ mV} \]
\[ h_{\text{adsorbed}} = 1.5 \text{ nm} \]
\[ \frac{\partial \Gamma}{\partial r} = 0 \]

\[ v_r^z = 0 \]

and at \( r = R_p \) i.e. pore radius, we have

\[ \frac{\partial h}{\partial r} = s = \text{specified slope} \]

\[ \frac{\partial \Gamma}{\partial r} = 0 \]

\[ v_r^z = 0 \]

\[ P = P_{c,s} = \text{Capillary Pressure of medium} \]

where \( P_{c,s} \) is the medium capillary pressure and is specified for a particular simulation.

Constant capillary pressure boundary condition is imposed because in a realistic porous medium the grooves and channels permit liquid transport to equalize any local gradients in \( P_c \) and thus it is expected that the capillary suction pressure exerted in the Plateau borders is very close to the \( P_c \) of the medium.

The pore geometry is given by the equation for the pore radius as (see Figure 7.2)

\[ R_p (x) = R_t \left[ (1 + \beta) - \beta \cos \left( \frac{\pi x}{L} \right) \right] \]  

(7.6)

where

\[ \beta = 0.5 \left( \frac{R_b}{R_t} - 1 \right) \]
Figure 7.2: Schematic of a periodically constricted pore
\( R_b \) and \( R_t \) are the pore body and pore throat radii respectively. \( L \) is the axial distance between the pore throat and the pore body; we prefer calling it the pore length.

Realize that there is a one to one correspondence between the axial location \( x \) and the time \( t \). The local interstitial velocity \( \nu(x) \) is given as:

\[
\frac{d x}{d t} = \nu(x) = \frac{Q}{\pi R_p(x)^2}
\]

Thus replacing \( t \) by \( x \) in equations (7.1,7.4) we de-dimensionize (see Appendix E) eqns(7.1-5), using \( R_p(x) \) as the characteristic radial length. The dimensionless equations now are

\[
\frac{\partial H}{\partial X} = \frac{1}{Ca_x} \frac{1}{R} \frac{\partial}{\partial R} \left( R H^3 \frac{\partial P}{\partial R} \right) - \frac{1}{R_p} \frac{d R_p}{d X} \left( H - R \left( \frac{\partial H}{\partial R} \right) \right) \tag{7.7}
\]

\[
P = -\frac{1}{R} \frac{\partial}{\partial R} (R \sin \alpha) + \Pi \tag{7.8}
\]

\[
\sin \alpha = \frac{\frac{\partial H}{\partial R}}{\left[1 + \left(\frac{\partial H}{\partial R}\right)^2\right]^{\frac{1}{2}}}
\]

\[
\frac{\partial \Gamma}{\partial X} + \frac{1}{R} \frac{\partial}{\partial R} (R V \Gamma) = \frac{M_4}{Ca_x} \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \Gamma}{\partial R} \right) + \frac{1}{R_p} \frac{d R_p}{d X} R \left( \frac{\partial \Gamma}{\partial R} \right) \tag{7.9}
\]

\[-M_2 \frac{\partial \Gamma}{\partial R} + M_3 \frac{\partial}{\partial R} \left( \frac{1}{R} \frac{\partial (R V)}{\partial R} \right) - H \left( \frac{\partial P}{\partial R} \right) = 0 \tag{7.10}
\]

where the parameters \( M_2, M_3 \) and \( M_4 \) are the same as presented in Chapter 6 and are given as:

\[
M_2 = \frac{E_o}{\sigma}, \quad M_3 = \frac{\mu_{d+s}}{3 \mu R_p(x)}, \quad M_4 = \frac{3 \mu D_s}{\sigma R_p(x)}
\]
with

\[ H = \frac{h}{R_p(x)}, \quad R = \frac{r}{R_p(x)}, \quad P = \frac{p - p_0}{P_o(x)}, \quad X = \frac{x}{L} \]

\[ \Pi = \frac{\Pi}{P_o(x)}, \quad V = \frac{v_s}{v_o}, \quad \Gamma = \frac{\Gamma}{\Gamma_o} \]

Since the structural contribution \( \Pi_{sr} \) of disjoining pressure comes into play at very small thicknesses \((h < h_{cr})\), we assume it to be negligible. Then the dimensionless disjoining pressure isotherm is given as:

\[ \Pi = \frac{1}{P_o(x)} \frac{-A}{48 \pi R_p(x)^3 H^3} + \frac{\Pi_{el}^o e^{-2 \kappa R_p(x)} H}{P_o(x)} \]

thus we have

\[ \Pi = \left( \frac{\Pi_{el}^o}{P_o(x)} \right) \left[ -\frac{1}{\theta_x H^3} + e^{-\alpha_x H} \right] \quad (7.11) \]

where \( \theta_x \) can be termed as the ratio of electrical double layer forces to van der Waals forces and \( \alpha_x \) is dimensionless debye length.

The boundary conditions in terms of dimensionless variable are:

At \( R = 0 \) we have

\[ \frac{\partial H}{\partial R} = 0 \]

\[ \frac{\partial P}{\partial R} = 0 \]

\[ \frac{\partial \Gamma}{\partial R} = 0 \]

\[ V = 0 \]
and at $R = 1$ we have

$$\frac{\partial H}{\partial R} = s$$

$$P = -\frac{P_{c,s}}{P_o}$$

$$\frac{\partial \Gamma}{\partial R} = 0$$

$$V = 0$$

### 7.3 Dimensionless Parameters

Before we go into the numerical solution of the above defined problem let us list the dimensionless parameters present in the governing equations.

From eqn. 7.7 we have the following parameters:

$$Ca_x = \frac{3 \mu Q}{\pi \sigma L R_p(x)}, \quad \beta = \frac{1}{2} \left(a - 1\right), \quad a = \frac{R_b}{R_i}$$

The parameter $\beta$ comes from the term $\frac{1}{R_p} \frac{d R_p}{d X}$ in equation (7.7) which is given as (using eqn. 7.6):

$$\frac{\beta \pi \sin(\pi X)}{1 + \beta \left(1 - \cos(\pi X)\right)}$$

Since this is a moving boundary problem the dimensionless parameters as they appear in the equations are dependent on axial location $X$ in the pore. In order to study the effect of these parameters on hydrodynamics of foam film we use the axially independent counterpart of these parameters. We now define the above parameters as:
\[ C_{a_x} = \frac{C}{f(x)} ; \quad f(x) = \omega (1 - 0.5\omega - 0.5\omega \cos(\pi X)) ; \quad \omega = \frac{2\beta}{\beta + 0.5} \quad (7.12) \]

where

\[ C = \frac{3\mu Q'}{\pi \sigma R_b L} \left(1 - \frac{R_t}{R_b}\right) \]

Hence from equation (7.7) we have two dimensionless parameters namely \( C \), the capillary number and \( a \), the aspect ratio.

Equations (7.8) and (7.11) have the following dimensionless parameters:

\[ \theta_x, \alpha_x, \frac{\Pi_{ei}^o}{P_o(x)} \]

These parameters can be written as

\[ \theta_x = \theta g(x)^3, \quad g(x) = 1 - 0.5\omega - 0.5\omega \cos(\pi X) \quad (7.13) \]

where

\[ \theta = \frac{4S \pi R_b^2 \Pi_{ei}^o}{A} \]

and

\[ \alpha_x = \alpha g(x) \quad (7.14) \]

where

\[ \alpha = 2\kappa R_b \]

and

\[ \frac{\Pi_{ei}^o}{P_o(x)} = \frac{\Pi_{ei}^o R_b}{\sigma} g(x) \quad (7.15) \]

Thus the axially independent dimensionless parameters are

\[ \theta, \alpha, \frac{\Pi_{ei}^o R_b}{\sigma} \]
Similarly from equations (7.9 and 7.10) the axially independent dimensionless parameters are

\[ M_2 = \frac{E^0}{\sigma}, \quad M_3 = \frac{\mu_{d+s}}{3 \mu R_b}, \quad M_4 = \frac{3 \mu D_s}{\sigma R_b} \]

Further note that (see also Chapter 6)

\[ N_\Gamma = \frac{M_2}{M_4}, \quad N_\mu = M_3 \] (7.16)

We also showed in Chapters 5 and 6 that these parameters act in a linear additive manner and can be grouped into a single dimensionless parameter \( N_R \) such that

\[ N_R = N_\mu + 0.27 N_\Gamma \] (7.17)

The other dimensionless parameters appear in the boundary conditions and are given as

\[ s, \quad \frac{P_{c,s}}{P_0(x)} = \frac{P_{c,s} R_b}{\sigma} g(x) \]

where the parameter \( 's' \) determines the geometry of the lamella and does not play any role in the foam film stability.

Let us now summarize the dimensionless parameters we encounter in the governing equations, they are:

\[ Ca, \quad a, \quad \theta, \quad \alpha, \quad \frac{\Pi_{e}\frac{R_b}{\sigma}}, \quad N_R, \quad \frac{P_{c,s} R_b}{\sigma} \]

We know that a static foam film is unstable at a critical capillary pressure \( (P_{cr}) \) which equals the maximum in the disjoining pressure curve (see Figure 7.1) \( \Pi_{max} \). Further \( \Pi_{max} \) depends on surfactant formulation and electrolyte concentration, i.e. the parameters \( \theta, \alpha \) and \( \frac{\Pi_{e}\frac{R_b}{\sigma}}{\sigma} \). Thus the parameter \( P_{cr} = \Pi_{max}(\theta, \alpha, \frac{\Pi_{e}\frac{R_b}{\sigma}}{\sigma}) \) is defined by the these three parameters and hence for our study we group these parameters and \( \frac{P_{c,s} R_b}{\sigma} \) into a single dimensionless parameter \( 'm' \) such that
\[ m = \frac{P_{c,s}}{P_{cr}(= \Pi_{max})} \] (7.18)

This parameter quantifies the capillary pressure in medium for a foam film with respect to the critical capillary pressure of a static foam film. Thus for values of \( m << 1 \) the foam film will be stable.

Finally we have four dimensionless parameters which affect the hydrodynamics of foam film (lamella) in porous medium, viz.

\[ Ca, \quad a, \quad N_R, \quad m \]

### 7.4 Initial Conditions

The initial conditions for the film thickness are based on the capillary pressure of the medium \( P_{c,s} \). For \( P_{c,s} > P_{trans} \), where

\[ P_{transition} = \frac{2 \sigma}{R_t} \]

there is a lamella at the pore throat and for \( P_{c,s} < P_{trans} \) we have a slug of liquid, i.e., a lens at the pore throat. Further we make sure that \( P_{c,s} \) is greater than \( \sigma/R_t \) which is the condition for snap off (Gauglitz and Radke, 1986).

**Lens at Pore Throat:**

If the capillary pressure of the porous medium \( P_{c,s} \) is less than the transition pressure \( P_{trans} \), then the initial profile at the pore throat is that of a pair of hemispherical menisci of radius \( R_s = \frac{\sigma}{\Pi_{c,s}} \) separated by a distance \( 2 h_i \). The initial half thickness is calculated from geometric consideration as:

\[ h_i = \frac{L}{\pi \cos^{-1}} \left( 1 - 2 \left( \frac{R_s/R_t - 1}{(R_b/R_t - 1)} \right) - R_s \right) \] (7.19)
We will not be considering this case in our study.

**Lamella at Pore Throat**

For $P_{c,s} > P_{\text{trans}}$, we have a lamella at the pore throat. Under conditions of static equilibrium this implies that the thickness of the film is governed by the disjoining pressure isotherm $\Pi = \Pi (h)$

**Determination of Initial Film Profile:**

The initial film profile in this case is that of a flat film of thickness $h_i$ and radius $R_f$ associated with a meniscus with a radius of curvature corresponding to the capillary pressure in the medium (Figure 7.3)

At the equilibrium film thickness the capillary pressure exerted in the Plateau borders equals the disjoining pressure in the film, hence $h_i = h_{eq}$ is given as

$$\Pi (h_{eq}) = P_{c,s}$$

Thus for a given $P_{c,s}$ and a given disjoining pressure isotherm (eqn 7.3), the equilibrium thickness is determined by solving the above non-linear equation using a hybrid algorithm of Newton-Raphson and the bisection method. From figure (7.1) one can see that in general three distinct roots are possible, but the root of interest is the one of maximum thickness as the middle root is unstable and the minimum root corresponds to a Newton black film.

Young-Laplace equation is assumed for the thickness profile in the meniscus region, i.e.

$$\frac{d^2 h}{d r^2} \left(1 + \left(\frac{d h}{d r}\right)^2\right)^{3/2} + \frac{1}{r} \frac{dh}{dr} \left(1 + \left(\frac{d h}{d r}\right)^2\right)^{1/2} = \frac{P_{c,s}}{\sigma} \quad (7.20)$$
Figure 7.3: Initial Film Thickness Profile of a thin liquid film (Lamella) in a pore
with the boundary conditions:

\[
\frac{d h}{d r} = 0 \quad \text{at} \quad r = R_f
\]

\[
h = h_i \quad \text{at} \quad r = R_f
\]

\[
\frac{d h}{d r} = s \quad \text{at} \quad r = R_i
\]

Integrating the above equation once and using the boundary condition at \( R_f \) we have

\[
R_f = R_i \left[ 1 - \frac{2 \sigma}{P_{c,s}} \frac{s}{R_i (1 + s^2)^{1/2}} \right]^{1/2}
\]

(7.21)

The initial profile for the lamella is then computed numerically by solving the Young-Laplace equation using a fourth order Runge-Kutta method.

### 7.5 Numerical Method

With the above initial conditions and the respective boundary conditions the set of partial differential equations (7.7-10) are solved numerically by a finite difference method. One has to take note that this is a moving boundary problem. We used the so called "semi-implicit" procedure, where the spatial differences for the flux terms were evaluated with a linear approximation to the new axial level using unknown values of the dependent variable \( H \). The governing equations are transformed into a system of linear equations, where the unknowns are the change in film half thickness at each grid block. The resulting equations are pentadiagonal. The system was solved using an LU(lower and upper) decomposition and then an upper and lower back substitution.
We adopted an automatic time step size selection such that the maximum relative change in $H$ and $R_p$ per axial step did not exceed a given value of 5% and 0.5% respectively.

### 7.6 Results and Discussion

As stated earlier foam stability in porous media depends on how film thickness changes as the lamella traverses the pore, especially as it expands in going from a pore throat to a pore body.

Before we go any further we will like to clear the difference between ‘stretching’ and ‘expansion’. The lamella as it goes from a small pore (pore throat) to a larger pore (pore body) undergoes an ‘expansion’ as it conforms to the pore wall. On the other hand if the lamella were very mobile such that it thins uniformly we term it as ‘stretching’. Thus stretching is a subset of expansion and both the terms are not equivalent. The expansion in turn depends on the pore aspect ratio `$a$`, which determines the amount of expansion, and pore length $L$ and flow rate $Q$ which determine the rate of expansion.

Also important are the capillary suction forces which tend to drain/fill the lamella. Foam stability thus depends on an interplay of all these aforementioned parameters. For a given pore geometry, medium capillary pressure and flow rate if the film thins down to the critical thickness it becomes unstable and breaks.

Previous researchers (Jiménez & Radke, 1989) have used a plane parallel model ($\frac{\partial}{\partial z} \frac{H}{R} = 0$) to examine the effect of flow rate, capillary pressure and aspect ratio on foam stability. Although they have used the Reynolds model for film thinning with a correction factor ($\alpha_s$) for a mobile film, nearly all their results are for a rigid (immobile, $\alpha_s = 0$) film. The values used in our simulations are based on the typical values reported by Chambers and Radke (1992) in their experiments on foam flow in porous medium. Chambers and Radke (1992) report frontal advance rates (interstitial
Table 7.1: Parameter Values

<table>
<thead>
<tr>
<th>$u$(m/day)</th>
<th>$Q$(m$^3$/s)</th>
<th>$R_v$(µm)</th>
<th>$R_s$(µm)</th>
<th>$L$(µm)</th>
<th>$P_{c,s}$(kPa)</th>
<th>$Ca$</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>$2.6 \cdot 10^{-10}$</td>
<td>100</td>
<td>200</td>
<td>100</td>
<td>7.0</td>
<td>$2 \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

velocities) ranging from $30 - 300m/day$. Typical widths of pore bodies ranged from $150 - 300µm$ while the widths of pore throats vary between $25 - 125µm$. Similar data has also been reported by Rossen (1995). Table 7.1 lists some of values used in our study and the corresponding dimensionless parameter values.

7.6.1 Immobile Film

We will first present the results for an immobile film as it moves down the pore. We had shown earlier in the study of hydrodynamics of stationary mobile foam films (Chapter 6) that the parameter $N_R$ determines the mobility of the film and that for $N_R$ sufficiently large ($> 10^4$) the film is immobile. Hence for an immobile film we carried out simulations at high $N_R$. As mentioned earlier an initial lamella profile is calculated under given conditions and the simulator is allowed to move the lamella through a series of pore throat and pore body configurations. The results are recorded when a periodic behavior in change of lamella thickness (as it goes from throat to body) is observed. It is seen that periodicity is achieved sooner ($\approx 10$ pore lengths) at low capillary number ($Ca$) while at high $Ca$ it may take around 600 pore lengths.

The film thickness changes were computed for a given disjoining pressure isotherm (Figure 7.1), pore geometry and constant medium capillary pressure $P_{c,s}$. Figure (7.4) shows the film thickness profiles at a low capillary number $Ca$, as the lamella moves from pore throat to pore body. The axial locations in the pore have been posted. One can see that the film expands at a constant thickness (i.e. the equilibrium thickness).
As is evident from equation (7.7) at such a low capillary number the film thickness is governed by the disjoining pressure $\Pi$. The profiles of film thickness as the lamella moves form the pore body to pore throat are shown in Figure (7.5).

Contrary to results of Jiménez & Radke (1989), Figure (7.6) shows that the film gets thicker rather than thinner as the capillary number (flow rate) is increased. Film half thickness profiles as the lamella moves from pore throat to pore body have been illustrated. It shows the entrainment of liquid into the film rather than thinning as the film expands.

Bretherton (1961) developed an approximate asymptotic solution for the thickness of the liquid film laid down at the front and rear menisci of a long advancing bubble in a capillary tube. Bretherton showed that film thickness is directly proportional to the capillary number (flow velocity) raised to the $2/3$ power. The film thickness at the front of bubble is given as:

$$h_{Br} = 0.643 \ R_p \left( \frac{3 \mu \ U}{\sigma} \right)^{2/3} = 0.643 \ R_p \ C a^{2/3} \quad (7.22)$$

where $R_p$ is the radius of the curvature (i.e. the pore radius) and $U$ is the bubble velocity and for our case is given as:

$$U_z(x) = \frac{d \ R_p}{d \ t} = \frac{d \ R_p}{d \ x} \ \frac{Q}{\pi \ R_p^2}$$

Being consistent with our definition of axially independent dimensionless parameters we define

$$U = U_z(X = 1)$$

we then have

$$\frac{3 \mu \ U}{\sigma} \approx \frac{3 \mu \ Q}{\pi \ \sigma \ R_b} \ \frac{1}{R_b} \ \frac{(R_b - R_t)}{L} = C a$$

Indeed the thickness of the film laid down as predicted by our simulations (see Figure 7.6) was found to be approximately proportional to Bretherton's expression (equation 7.22) and is given as follows:
Figure 7.4: Film Half Thickness Profiles at low $Ca$ and high $N_R$ as the lamella moves from pore throat to pore body; axial location is posted.
Figure 7.5: Film Half Thickness Profiles at low $Ca$ and high $N_R$ as the lamella moves from pore body to pore throat; axial location is posted.
\[ h_{film} = 0.16 \, R_b \left( \frac{3 \mu \, U}{\sigma} \right)^{2/3} \]

substituting for \( U \) from above and realizing our definition for the capillary number we have

\[ \left( \frac{h_{film}}{R_b} \right) = 0.16 \, Ca^{2/3} \quad (7.23) \]

Thus film thickness is predicted well by the thickness at front of bubble moving in a capillary tube. Further it is seen that film thickness profiles as the lamella moves from pore body to pore throat look similar to those observed at the back of a bubble moving in a capillary tube. Figure (7.7) shows that the film dimples as it goes from pore body to pore throat. This is what is seen at the back of a bubble in a capillary tube.

Figure (7.8) compares the film thickness predicted by our simulations to that predicted by equation (7.23). It shows that for a lamella with immobile surfaces, as the capillary number (flow rate \( Q \)) increases the film entrains liquid and becomes thicker rather than thinning down to critical thickness and breaking as proposed by Jiménez and Radke (1989) based on their plane parallel model.

### 7.6.2 Mobile Film

The simulations above were done for an immobile film (i.e. high \( N_R \)). We now study the effect of film mobility (changing \( N_R \)) on the film thickness with varying capillary number \( Ca \). Simulations were carried out for various combinations of the capillary number \( Ca \) and the surfactant number \( N_R \) and the ratio of minimum film thickness to equilibrium thickness \( h_{min}/h_{eq} \) was recorded, as the lamella traverses the pore. Figure (7.9) illustrates a contour plot of \( h_{min}/h_{eq} \) for various different regimes of
Figure 7.6: Film Half Thickness Profiles at medium Ca and high NR as the lamella moves from pore throat to pore body; axial location is posted.
Figure 7.7: Film Half Thickness Profiles at medium $Ca$ and high $N_R$ as the lamella moves from pore body to pore throat; axial location is posted.
Figure 7.8: Comparison of Film Thickness predicted by numerical simulation to Bretherton type thickness (eqn. 7.23)
the capillary number $Ca$ and the surfactant number $N_R$. It shows that for high $N_R$ (immobile film) the ratio $h_{\text{min}}/h_{eq}$ increases with capillary number $Ca$. Further at low capillary number(s) the ratio is nearly equal to one indicating that disjoining pressure is dominating. However as $Ca$ increases we see the Bretherton effect coming into play. In fact we can quantitatively describe the capillary number at which the transition from disjoining pressure controlled to the Bretherton effect occurs, through the following equation

$$\frac{h_{eq}}{R_b} = \frac{h_{\text{film}}}{R_b}$$

This represents the intersection of equilibrium thickness line with the curve for equation (7.23).

Substituting from equation (7.23) we have

$$Ca_{\text{transition}} = \left(\frac{h_{eq}}{0.16 R_b}\right)^{3/2}$$

For the medium capillary pressure $P_{c,s}$ and the disjoining pressure isotherm used for calculation in figure (7.9) we have $Ca_{\text{transition}} = 7.48 \cdot 10^{-5}$. This is about what we see from our simulations (see Figure 7.9). Also note that higher values of $Ca$ where the Bretherton effect is important are achieved for realistic conditions (Table 7.1).

The contour plot shows the remarkable effect of the surface mobility ($N_R$) on the hydrodynamics of the lamella. For low values of $N_R$ we see that the ratio $h_{\text{min}}/h_{\text{eq}}$, decreases as the capillary number (or flow rate $Q$) increases, and thus we expect the lamella to thin down to its critical thickness at some high $Ca$ and break or form a Newton black film. This effect of increasing $Ca$ on foam stability is in direct contrast to the behavior see above for high $N_R$ (immobile film). It is observed that for low $N_R$ (mobile films) the dimensionless minimum film half thickness $h_{\text{min}}/h_{eq}$ decreases with increasing capillary number $Ca$ until it reaches a minimum for fixed $N_R$ and then starts to increase with $Ca$ as entrainment (Bretherton effect) sets in.
Figure 7.9: Contours of Dimensionless Minimum Film Half Thickness ($h_{min}/h_{eq}$) as a function of capillary number $Ca$ and surfactant number $N_R$, for $m = 0.07$ and $a = 2$
The profiles of film half thickness $h$ as a lamella moves from pore throat to pore body for low $N_R$ have been shown in Figure (7.10). As shown it stretches and thins down below its equilibrium thickness. At high enough $Ca$ or at a high dimensionless capillary pressure $m$ the lamella could thus thin down to its critical thickness and break. Figure (7.11) shows profiles for the above case as the lamella goes from pore body to pore throat. The dimpling observed is similar to the waviness in film observed at the back of a bubble moving in a capillary tube.

The above observed behavior of film stretching is in qualitative agreement with the results of Jiménez & Radke (1989) who assumed the lamella to be plane parallel, i.e. the film stretches and consequently thins as it goes from pore throat to pore body. Thus we see that a plane parallel model is probably appropriate if the lamella is highly mobile rather than an immobile film as assumed by Jiménez & Radke (1989). The reason for this is that the plane parallel model is unable to account for the entrainment effect (Figure 7.6). The dimensionless minimum film half thickness ($h_{min}/h_{eq}$) as predicted by our simulations has been compared with the results of Jiménez & Radke (1989) in Figure 7.12. It illustrates that for a highly mobile film (low $N_R$) reasonable agreement is achieved between the two models. Quantitatively one expects both results to match in the limit of vanishing $N_R$ i.e. for an infinitely mobile film which will stretch/squeeze as a plane parallel film. Nevertheless our analysis is more complete and hence better for quantitative work.

Figures (7.13) and (7.14) illustrate the film thickness profiles for a different set of $Ca$ and $N_R$. One sees the same effect of the film thinning without any entrainment. Note that the film is nearly plane parallel as it expands in going from a pore throat to a pore body.

The contour plot thus suggests that there exists a surfactant number $N_R$ at which the transition occurs from film thinning to entrainment. To see this effect we recorded film thickness profiles at a medium $Ca$ and $N_R$ as the lamella traverses the pore. For
Figure 7.10: Film Half Thickness Profiles at high $Ca$ and low $N_R = 23.33$ as the lamella moves from pore throat to pore body; axial location is posted.
Figure 7.11: Film Half Thickness Profiles at high Ca and low \( N_R = 23.33 \) as the lamella moves from pore body to pore throat; axial location is posted.
Figure 7.12: Comparison of film thickness between our simulation and Jiménez & Radke (1989) as the lamella moves from pore throat to pore body.
Figure 7.13: Film Half Thickness Profiles at high $Ca$ and low $N_R = 46.66$ as the lamella moves from pore throat to pore body; axial location is posted.
Figure 7.14: Film Half Thickness Profiles at high Ca and low $N_R = 46.66$ as the lamella moves from pore body to pore throat; axial location is posted.
given conditions we see from Figure (7.15) that both the effects are present, i.e. not only the film thins down but there is entrainment (Bretherton effect). Figure (7.16) shows the corresponding profiles with dimples as the lamella goes from pore body to pore throat.

Thus from our simulations we see that, depending on the capillary number \( Ca \) and the surfactant number \( N_R \), we could be in completely different regimes of lamella hydrodynamics. It was observed that the lamella is susceptible to breaking at low values of \( N_R \) and high capillary number \( Ca \) while at high values of \( N_R \) it becomes more stable with increasing \( Ca \) due to the Bretherton effect.

We now discuss the implications of the results presented above, especially those of Figure 7.9. The dependence of film thickness on \( N_R \) and \( Ca \) suggests two different regimes for the stability of moving and stationary lamellae for foam flowing at the limiting capillary pressure. (a) When \( N_R \) is large the moving lamellae (larger \( Ca \) ) maybe more stable than the stationary lamellae (smaller \( Ca \)). If this is the case, the moving lamellae trains will switch paths as stationary lamella rupture and new paths of least resistance appear. This maybe the mode of foam flow when it is desired to contact as much of the porous medium as possible with the flowing discontinuous-gas foam. (b) When \( N_R \) is small the stationary lamellae will be more stable than the moving lamellae. In this case, the foam breakage maybe catastrophic. The rupture of moving lamella in a train will reduce the resistance of the train. The reduced resistance will lead to a higher velocity and thus higher \( Ca \). This higher \( Ca \) will further destabilize the lamellae. In this case, the foam, if it is flowing, maybe a continous-gas foam.

Now that we have a good insight into lamella hydrodynamics, lets see if we can explain the dependence of critical medium capillary pressure on the capillary number \( Ca \) (flow rate \( Q \)) with regard to foam stability in porous media.

For given disjoining pressure isotherm, surface rheological properties (i.e. surfactant number \( N_R \)), pore geometry (aspect ratio \( a \)) and flow rate \( Q \) (capillary number
Figure 7.15: Film Half Thickness Profiles at medium $Ca$ and medium $N_R$ as the lamella moves from pore throat to pore body; axial location is posted.
Figure 7.16: Film Half Thickness Profiles at medium Ca and medium NR as the lamella moves from pore body to pore throat; axial location is posted.
we record the film thickness profiles (as lamella traverses pore throats and bodies) for varying medium capillary pressure. The capillary pressure at which the film thins down to the critical thickness and breaks is termed as the critical capillary pressure $P_{c,s}$. Figure (7.17) illustrates the results of various simulations carried out for different sets of $Ca$ and $N_R$. For a given $Ca$, $N_R$ and fixed disjoining pressure isotherm II and aspect ratio we observed the lamella thickness as it traverses the pore for different sets of capillary pressure $P_{c,s}$. The critical capillary pressure was identified as the pressure at which the lamella thinned down to the critical thickness $h_{cr}$ corresponding to a maximum in the disjoining pressure isotherm (e.g. Figure 7.1). A bisection type approach was used to zero in on the critical capillary pressure value.

The effect of flow rate $Q$ (capillary number $Ca$) on the critical capillary pressure $P_{c,s}$ (made dimensionless with respect to the critical capillary pressure for a static film) has been shown at different values of the surfactant number $N_R$. Note that such an instability can occur under realistic conditions (Table 7.1). It shows that the experimentally observed behavior of decreasing $P_{c,s}$ with increasing $Ca$ (Khatib et al., 1988) is characteristic of lamella with high mobility (low $N_R$).

Figure (7.18) illustrates the evolution of minimum film half thickness for a couple of conditions presented in Figure (7.17). It shows that for $P_{c,s} \geq P_{c,s}^{*}$ the film stretches and thins down to its critical thickness where it may become unstable and break.

Figure (7.19) shows the effect of aspect ratio on foam stability (critical capillary pressure $P_{c,a}$) for different values of $Ca$, at low $N_R$. As expected higher $a$ leads to increased stretching of a lamella as it goes from pore throat to pore body leading to a more unstable foam. A given porous medium will have a distribution of pore throat and pore body sizes. Hence for a given flow rate (capillary number $Ca$) and capillary pressure the lamella will break at constrictions were the aspect ratio $a$ exceeds the value shown in Figure (7.19). These sites are then termed as termination sites.
Figure 7.17: Critical Capillary Pressure $P_{c,s}^*$ as a function of Capillary number $Ca$ at different values of surfactant number $N_R$. 
Figure 7.18: Dimensionless minimum film half thickness $h_{min}/h_{eq}$ as the lamella traverses the pore for $P_{c,s} \geq P_{c,s}^*$.
Figure 7.19: Effect of Pore Aspect Ratio $a$ on critical Capillary Pressure $P_{c,s}$ at different capillary numbers $Ca$
7.6.3 Asymmetric Drainage

Until now we have discussed foam stability in porous media by studying axisymmetric drainage of a foam lamella. Previous researchers (Joye 1994) have conducted experiments by forming thin films in glass cells of approximately 1 mm radius and observed a type of drainage which is asymmetric and much more rapid than axisymmetric drainage discussed above. Joye et al. (1994) showed that the primary mechanism of this fast drainage was an instability caused by surface tension driven flow and presented a stability criterion (based on linear stability analysis) which predicts when such behavior will occur.

We now want to apply the criterion to foam films in a porous medium and determine the conditions under which it affects foam stability in a porous medium. The criterion in terms of dimensionless parameters is given as follows (see also Appendix F)

\[ \Theta = \frac{N_p}{64 \phi^2} \left[ 1 + N_f N_o + N_\mu N_o \right] \]  

(7.24)

where

\[ N_p = \frac{\mu_s \sigma D_s}{P_c^2 R_f^4} \]

and asymmetric drainage occurs for \( \Theta < 1 \).

Also note that for small films i.e. with \( R_f/R_c << 1 \) we have

\[ P_c = \frac{2 \sigma}{R_c} \]

Then the dimensionless parameter \( N_p \) is rewritten as

\[ N_p = \frac{\mu_s \sigma D_s}{P_c^2 R_f^4} = \frac{\mu_s D_s}{4 \sigma R_f^2} \left( \frac{R_c}{R_f} \right)^2 \]

Note that \( N_p \) is inversely proportional to the film radius \( R_f \) to the second power while equation F.2 (Appendix F) shows this proportionality to the sixth power. This
is because the film radius dependence of the pressure gradient has been included in the above equation.

The main premise in Joye et al.'s (1994) theory was that in a dimpled mobile foam film this instability occurs in the barrier ring region. Since the above experiments were done in a glass cell of radius an order of magnitude greater than typical pore size, the question arises whether this will still be the case in a porous medium. This has been answered in Appendix D where simulations for a miniature glass cell show that under certain conditions dimple formation can occur in pores. Another drawback of Joye et al.'s (1994) theory is that they did not account for disjoining pressure in the stability analysis while from our simulations (Appendix D) we see that this effect becomes important at porous medium scale.

From our simulations (Figures 7.6, 7.7, 7.12-15) we have seen that dimple formation occurs in films with large \( N_R \) and is also present when the film moves from pore body to pore throat. Recall that such a motion is identical to the back of a bubble flowing in a long cylindrical capillary (Bretherton, 1961). Thus for given porous medium and specified capillary pressure we can estimate the film radius \( R_f \) using equation (7.21) to be used in the criterion above. Another thing to note is that the asymmetric drainage criterion was developed for static films and thus one must display caution in invoking this criterion except near the pore throat or the pore body where expansion/compression is small. Table 7.2 lists results under various conditions:

We see that even though the criterion predicts less chance of asymmetric drainage to occur as pore size \( R_t \) decreases such an instability could occur if either the medium capillary pressure \( P_c \) is high or the film is very mobile, i.e. low \( N_R \). Further note that asymmetric drainage occurs even at very high values of the parameter \( N_R \), this is because surface shear viscosity \( \mu_s \) plays a dominant role in asymmetric drainage. Experiments have shown that the surface dilatational viscosity \( \mu_d \) is usually orders of magnitude higher than the surface shear viscosity \( \mu_s \) thus \( N_R \) may be large due to a large \( \mu_d \) but asymmetric drainage may occur due to a low surface shear viscosity \( \mu_s \).
Table 7.2: Asymmetric Drainage Criterion

<table>
<thead>
<tr>
<th>$P_c$ (kPa)</th>
<th>$R_t$ ($\mu$m)</th>
<th>$R_f$ ($\mu$m)</th>
<th>$\mu_s$ (kg/s)</th>
<th>$N_R$</th>
<th>$\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>1000</td>
<td>91.4</td>
<td>$3 \cdot 10^{-8}$</td>
<td>$4.0 \cdot 10^5$</td>
<td>$1.4 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>0.70</td>
<td>100</td>
<td>23.9</td>
<td>$10^{-7}$</td>
<td>$3.5 \cdot 10^3$</td>
<td>$1.9 \cdot 10^{-2}$</td>
</tr>
<tr>
<td>7.0</td>
<td>10</td>
<td>2.4</td>
<td>$10^{-7}$</td>
<td>$1.8 \cdot 10^5$</td>
<td>$1.8 \cdot 10^2$</td>
</tr>
<tr>
<td>7.0</td>
<td>10</td>
<td>2.4</td>
<td>$10^{-8}$</td>
<td>$1.3 \cdot 10^4$</td>
<td>$6.1 \cdot 10^{-1}$</td>
</tr>
<tr>
<td>7.0</td>
<td>10</td>
<td>2.4</td>
<td>$10^{-8}$</td>
<td>$1.4 \cdot 10^2$</td>
<td>$3.0 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>13.0</td>
<td>10</td>
<td>7.2</td>
<td>$10^{-7}$</td>
<td>$9.6 \cdot 10^4$</td>
<td>$2.1 \cdot 10^{-1}$</td>
</tr>
</tbody>
</table>

The asymmetric drainage criterion thus predicts that an immobile foam film can be unstable due to such a mechanism due to dimple formation even though axisymmetric drainage study done in previous section predicts otherwise. Further a mobile foam film which may survive the stretching as it goes from pore throat to pore body can be unstable due to asymmetric drainage in the pore body to pore throat travel.
Chapter 8

Conclusions and Future Recommendations

Conclusions of this study have been presented below:

8.1 Plane Parallel Film Drainage

1) For the drainage of a plane parallel thin liquid film with an insoluble surfactant the thinning velocity has been correlated to the surfactant properties through a single dimensionless parameter $N_R$. This parameter is a linear combination of dimensionless surface elasticity ($N_\Gamma$) and surface viscosity ($N_\mu$) numbers.

2) The dimensionless elasticity number $N_\Gamma$ is directly proportional to the film radius $R_f$ while the dimensionless surface viscosity number $N_\mu$ is inversely proportional to the film radius. Thus the relative importance of elasticity and surface viscosity depends on the film radius.

3) The dimensionless drainage time for a thin liquid film with an insoluble surfactant has been correlated with the dimensionless parameter $N_R$. For low values of the parameter $N_R$ the rate of thinning is very high compared to the Reynolds velocity i.e. $V/\nu Re >> 1$, leading to very small drainage times. On the other hand for $N_R$ greater than $\approx 10^4$ the Reynolds solution for an immobile film is approached.

4) In the case of a soluble surfactant there are two additional parameters, namely $N_{D\theta}$ which includes the effect of bulk diffusion and adsorption and $N_c$ which is basically the ratio of surfactant bulk to surface concentration. These parameters can be grouped into a revised dimensionless elasticity number $N'_\Gamma$. In particular $N_c$ reflects
the contribution of radial convection of the surfactant transport in the bulk film, an effect neglected in all previous analyses. It is important for relatively thick films. For very thin films the soluble surfactant solution approaches the insoluble surfactant solution.

8.2 Dimpled Film Drainage

1) Hydrodynamics of the foam film drainage has been studied numerically. Profiles of surfactant surface concentration and interfacial velocity indicate considerable motion of the interface in the barrier ring region, which depends on the surfactant properties viz. elasticity, surface viscosity and surface diffusivity.

2) The rate of drainage of the foam film has been correlated to two dimensionless parameters $C_R$ and $N_R$. The parameter $C_R$ is a function of film thickness and changes as the film drains. The parameter $N_R$ is comprised of the surfactant properties and is a linear combination of the surface elasticity ($N_T$) and the surface viscosity ($N_v$) numbers.

3) Drainage times were correlated with the parameter $N_R$ and it was seen that for low values of the parameter $N_R$ the rate of thinning is very high compared to the Reynolds velocity (i.e. $V/V_{Re} \gg 1$) leading to very small drainage times. On the other hand for $N_R$ greater than $\approx 10^6$ the Reynolds solution for an immobile film is approached. This is in accordance with the results of the analytical solution.

4) Drainage times predicted by the numerical solution were compared with those calculated from the analytical solution for a plane parallel film. Better agreement is obtained for small values of the parameter $R_f/R_c$. The agreement improves as $N_R$ increases (i.e. higher immobility).
8.3 Foam Film in Porous Media

1) The film hydrodynamics in porous media strongly depend on the parameters $Ca$ (the capillary number) and $N_R$ the surfactant number. Based on the values of these parameters the behavior of the lamella, as it goes from a pore throat to pore body, can be divided into different regimes.

2a) For large values of $N_R$ (immobile film) the ratio $h_{min}/h_{eq}$ increases with increasing capillary number $Ca$ (or flow rate) indicative of Bretherton effect. The capillary number above which this effect becomes dominant has been quantified.

2b) For low values of $N_R$ the behavior is opposite, i.e. the ratio $h_{min}/h_{eq}$ decreases with increasing capillary number $Ca$ (or flow rate). Also seen is that $h_{min}/h_{eq}$ goes through a minimum with increasing $Ca$ and starts to increase due to the entrainment effect setting in.

3a) At low $N_R$ (mobile film) the lamella may thin down to its critical thickness and break. Thus the dependence of limiting capillary pressure $P^*_c$ on the flow rate $Ca$ (capillary number) with respect to foam stability is accounted for.

3b) For large $N_R$ (immobile film) it is shown that contrary to Jiménez & Radke (1989) whose analysis does not include the entrainment effect, the film will not break unless the capillary pressure $P^*_c$ corresponds to the maximum in disjoining pressure isotherm $\Pi_{max}$.

4) The effect of the pore shape (aspect ratio $a$) on the foam stability in terms of the critical capillary pressure of the porous medium has been presented. As expected it is seen that large pore body to pore throat ratios are detrimental to foam stability and such sites in a porous medium are termed as termination sites for the foam film.

5) The presence of asymmetric drainage in foam films in porous media was shown to occur under different conditions. It is seen that foam film may be unstable due to this mechanism even though the axisymmetric drainage predicts otherwise.
8.4 Recommendations

Drainage of a thin liquid film and its pertinence to foam stability in a porous medium have been studied. Although in this study we assumed an insoluble surfactant, future work can be done for a soluble surfactant. One can include both the surfactant adsorption kinetics and diffusion in the model and based on time scales of these two processes decide which one is dominant under given conditions.

Once such a model has been developed for a static film it should be extended to a model foam film translating in a porous medium. With this model an analysis similar to the one performed in this thesis can be done to predict foam stability. Also one could include in the model a term to account for loss of surfactant in the porous medium due to adsorption. Further all the above analyses could be repeated for a film containing a polymer and surfactant mixture. Analysis could be done to predict the relative effects of polymer and surfactant properties on foam stability.

As regards foam in a porous medium this thesis addressed the problem of a lamella translating through the pore while the other possibility of a lens (liquid slug) was not pursued. Future work could be done to extend this model to account for flow of both lamella and lens. Most interesting would be to predict the lamella/lens transitions as the foam film traverses the heterogeneous porous medium.
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NOMENCLATURE

Notation

\( a \)  Aspect Ratio

\( A \)  Surface area of the film

\( c \)  Surfactant bulk concentration

\( \bar{c} \)  Average surfactant bulk concentration

\( c_s \)  Surfactant bulk concentration in equilibrium with the surface

\( c_o \)  Initial surfactant bulk concentration

\( Cu \)  Capillary number

\( Ca_x \)  Axially dependent Capillary number

\( C_R \)  Dimensionless parameter for dimpled film

\( D \)  Bulk diffusivity

\( D_s \)  Surface diffusivity

\( D \)  Bulk rate of deformation tensor

\( D_s \)  Surface rate of deformation tensor

\( E_{dc} \)  Compositional elasticity

\( E_G \)  Gibbs elasticity
\( E_n \)  Net elasticity

\( E^o \)  Elasticity

\( F \)  Force thinning the film

\( G \)  Intrinsic surface shear elasticity

\( h \)  Film half thickness

\( h_b \)  Film half thickness at the barrier ring

\( h_{Br} \)  Bretherton Film thickness

\( h_{cr} \)  Critical Film half thickness

\( h_d \)  Film half thickness of the dimple

\( h_{eq} \)  Equilibrium Film Half Thickness

\( h_f \)  Final Film half thickness

\( h_i \)  Initial Film half thickness

\( I \)  Bulk identity tensor

\( I_0 \)  Modified Bessel function of the first kind and of order zero

\( I_1 \)  Modified Bessel function of the first kind and of order one

\( I_s \)  Projection tensor

\( j^s \)  Surface diffusion flux vector

\( K \)  Steady state viscosity

\( L \)  Distance between pore throat and pore body

\( m \)  Dimensionless medium capillary pressure

\( N_p \)  Dimensionless parameter in Asymmetric Drainage
\( N_\alpha \)  Dimensionless Film Half Thickness
\( N_\mu \)  Dimensionless surface viscosity number
\( N_\Gamma \)  Dimensionless surface elasticity number
\( p \)  Bulk fluid pressure
\( p_g \)  Pressure in the gas phase
\( p_m \)  Pressure in the meniscus
\( P_{c,s} \)  Capillary pressure in porous medium
\( P_{c,s}^* \)  Critical capillary pressure
\( P_o \)  Characteristic pressure
\( P_T \)  Thermodynamic pressure
\( R_b \)  Pore Body radius
\( R_c \)  Cell radius
\( R_f \)  Film radius
\( R_p \)  Pore radius
\( R_t \)  Pore throat radius
\( S \)  Extra stress tensor
\( S^* \)  Surface extra stress tensor
\( T \)  Bulk stress tensor
\( T^* \)  Surface stress tensor
\( U \)  Radial component of surface velocity
\( v_r \)  Radial component of bulk fluid velocity
$v_r^2$  Radial component of surface velocity

$V_{Re}$  Reynold’s velocity for film thinning

$w$  Weighting factor

$X$  Dimensionless axial location in pore

**Greek Letters:**

$\beta$  Adsorption isotherm parameter

$\Gamma$  Surfactant surface Concentration

$\Gamma_o$  Initial surfactant surface concentration

$\theta$  Parameter in the insoluble case analytical solution

$\theta^s$  Parameter in the soluble case analytical solution

$\Theta$  Asymmetric drainage criterion

$\omega$  Factor in pore radius

$\phi$  Parameter in asymmetric drainage

$\mu$  Bulk shear viscosity

$\mu_d$  Surface dilatational viscosity

$\mu_{d+s}$  Surface viscosity

$\mu_s$  Surface shear viscosity

$\rho$  Bulk density

$\sigma$  Thermodynamic surface tension

$\bar{\sigma}$  Mean surface tension

$\tau$  Film drainage time
$r^*$ Dimensionless film drainage time

$\Pi$ Disjoining Pressure

$\Pi_{el}$ Electrical component of Disjoining pressure

$\Pi_{max}$ Maximum in the Disjoining pressure

$\Pi_{sr}$ Steric component of Disjoining pressure

$\Pi_{vdW}$ van der Waals component of Disjoining pressure

**Superscripts:**

$\circ$ Limiting value

$r$ Radially dependent

$s$ Soluble surfactant

$ss$ Steady state solution

**Subscripts:**

$b$ Barrier ring

$c$ Cell

$d$ Dimple

$f$ Film

$i$ Initial condition

$o$ Characteristic value

$p$ Pore variable

$x$ Axially dependent
List of Accents

- Average value

* Dimensionless variable
Appendix A

Correction to Barber and Hartland's (1976) solution

The contours of the mobility factor $V/V_{Re}$ as a function of $N_r$ and $N_{\mu}$ using the boundary condition used by Barber and Hartland (1976) have been plotted in Figure(A.1).

One can see that the contours curve sharply near the axes and show that in certain regions the mobility factor increases with increasing $N_{\mu}(constant\ N_r)$ and similarly for increasing $N_r(constant\ N_{\mu})$. This is counter-intuitive since we expect that increasing either the elasticity or surface viscosity should make the surfaces less mobile and thus decreased mobility factor.

The Barber and Hartland (1976) solution has been re-derived using the proper boundary conditions at $r = R_f$ and the comparison between the two solutions has been presented in Figure(A.2).
Figure A.1: Contour Plots of mobility factor $V/V_{Re}$ using Barber & Hartland (1976) boundary condition
Figure A.2: Comparison of Original and modified Barber & Hartland (1976) solution.
Appendix B

Estimation of Adsorption Isotherm Parameter $\beta$

The Gibbs adsorption equation for an ideal nonionic surfactant solution is given as

$$-d\sigma = RT \Gamma d\ln c$$  \hspace{1cm} (B.1)

where

$\sigma$ is the surface tension, $\Gamma$ is the surfactant surface concentration and $c$ is the surfactant bulk concentration. The above equation can be integrated to provide a relationship between $\sigma$ and $c$ depending upon the choice of the adsorption isotherm used to relate $\Gamma$ and $c$.

For example if we use the Langmuir adsorption isotherm i.e.

$$\Gamma = \frac{\Gamma_{\infty} c}{c + a}$$  \hspace{1cm} (B.2)

we have

$$\sigma_w - \sigma = RT \Gamma_{\infty} \ln \left(1 + \frac{c}{a}\right)$$  \hspace{1cm} (B.3)

where $\sigma_w = \sigma \mid_{c=0}$ is the surface tension of pure water. The above equation is called the Szyszkowski equation of state.

Experimentally one records the surface tension $\sigma$ as a function of the surfactant bulk concentration $c$. One can then fit the data to eqn.(B.3) to get the parameters $\Gamma_{\infty}$ and $a$.

The value of the parameter $\beta = \frac{d\Gamma}{dc}$ can then be estimated using eqn.(B.2) as follows
\[ \beta = \frac{a \Gamma_{\infty}}{(c_\alpha + a)^2} \]  

(B.4)
Appendix C

Note on Linearizing Non-Linear Terms in the Governing Equations

The dimensionless film thickness equation (eqn.6.1) is given as:

\[
\frac{\partial H}{\partial t} = -\frac{1}{R} \frac{\partial}{\partial R} (R^n V^n) + \frac{1}{R} \frac{\partial}{\partial R} \left( R^3 \frac{\partial P}{\partial R} \right) \tag{C.1}
\]

Using finite difference and being implicit in \(H\) and explicit in \(V\) we have

\[
\frac{H_{i}^{n+1} - H_{i}^{n}}{DT} = -\frac{1}{R} \frac{\partial}{\partial R} \left( R^n V^n H^{n+1} \right)_i + \frac{1}{R} \frac{\partial}{\partial R} \left( R^{n+1} \frac{\partial P^{n+1}}{\partial R} \right)_i \tag{C.2}
\]

where \(i\) is the spatial location and \(n\) and \(n+1\) are time levels. Further we have

\[
P = -\frac{1}{R} \frac{\partial}{\partial R} \left( \frac{R \frac{\partial H}{\partial R}}{1 + \left( \frac{\partial H}{\partial R} \right)^2} \right)^{1/2} \tag{C.3}
\]

From equations (C.2) and (C.3) we see that the term

\[
H^{3n+1} \left( \frac{\partial P}{\partial R} \right)^{n+1} \tag{C.4}
\]

is a non-linear term.

In our numerical simulator we use a semi-implicit method, i.e. we linearize the non-linear terms using a Taylor series expansion. Previously Joye (1994) performed
this linearization incorrectly leading to numerical problems especially in the meniscus region where the curvature terms become more important. Equation (C.4) was linearized as follows:

\[ H^{3n+1} \left( \frac{\partial P}{\partial R} \right)^{n+1} \]

\[ = H^{3n} \left( \frac{\partial P}{\partial R} \right)^n + 3 H^{2n} \left( \frac{\partial P}{\partial R} \right)^n DH + H^{3n} \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial R} \right)^n DT \]  

(C.5)

Note that we can write

\[ \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial R} \right) = \frac{\partial}{\partial R} \left( \frac{\partial P}{\partial T} \right) \]

Joye (1994) approximated the above terms as follows (using eqn. C.3):

\[ \frac{\partial P}{\partial T} = \frac{R \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial R} \right)}{\left[ 1 + \left( \frac{\partial H}{\partial R} \right)^2 \right]^{1/2}} \]  

(C.6)

This is incorrect and we will now show that such an approximation was not needed. Although Joye (1994) performed this approximation to avoid lengthy partial derivatives (and later on the derivatives of these derivatives) of the denominator, we will now show that even though such a procedure might seem tedious the end result is very neat and simple.

We define

\[ \epsilon = \frac{\partial H}{\partial R} \]

then we have

\[ P = \frac{R \epsilon}{(1 + \epsilon^2)^{1/2}} \]

Thus the partial derivative w.r.t. time \( T \) is given as:
\[
\frac{\partial P}{\partial T} = \frac{R \frac{\partial \xi}{\partial T} (1 + \xi^2)^{1/2} - R \xi^2 \frac{\partial \xi}{\partial T} \frac{1}{(1 + \xi^2)^{1/2}}}{(1 + \xi^2)^{1/2}} \tag{C.7}
\]

Simplifying the above equation we have

\[
\frac{\partial P}{\partial T} = \frac{R \frac{\partial \xi}{\partial T}}{(1 + \xi^2)^{3/2}} \tag{C.8}
\]

Thus the only change (compared to eqn. C.6) is that the denominator is now raised to 3/2 power instead of 1/2. The simulator did not show any numerical problems once the above changes were made.
Appendix D

Dimple Formation in Foam Films in Glass Cells

Drainage of thin liquid films is an important factor influencing stability of emulsions and foams. Some years ago Scheludko and Exerowa (1959) developed an experimental technique which has been widely used to study such films. For the case of a foam film, some aqueous surfactant solution is deposited in a small, horizontal, glass circular cell of radius $R_c$ placed on a microscope stage (see Figure D.1). Fluid is withdrawn through a small tube in the side of the cell until a thin film of surfactant solution forms. Once withdrawal is stopped, the film drains until it breaks or reaches an equilibrium state. The film profile during drainage can be determined as a function of time using interference techniques.

In the conventional Scheludko-Exerowa cell $R_c$ is of order $1\text{mm}$, and one typically sees that the film develops a reverse curvature at its center during drainage to form a “dimple” entrapped by a thinner “barrier ring”. Some workers have reported, however that no dimple occurs when the film radius $R_f$ is sufficiently small, i.e. when withdrawal is stopped soon after film formation begins (Platikanov, 1964; Manev et al., 1984).

Recently Velev et al. (1995) have developed a miniature Scheludko-Exerowa cell with $R_c$ of order of $0.1\text{mm}$. They did not observe any dimples with this cell using the interference method. As they pointed out, the electrical component of disjoining pressure was sufficiently large in their films that the equilibrium thickness was reached during withdrawal and maintained as the film expanded. We simulate such behavior below and further show that a dimple would be expected in the miniature cell in the
Figure D.1: Cross sectional view of the Scheludko-Exerowa cell; $R_c$ is the cell radius; $R_f$ is the film radius
absence of a repulsive disjoining pressure. However interference fringes would not be observed because film thickness throughout the dimple would be below one fourth the wavelength of visible light.

**Conventional Cell (No Disjoining Pressure):**

Numerical simulation of thin film drainage in a conventional Scheludko-Exerowa cell was carried out by Joye et al. (1992) for the case of immobile surfaces. Provided that no reverse curvature developed during the initial fluid withdrawal step and that the film thickness remained thick enough to neglect disjoining pressure effects, the simulations showed that dimple formation began when the following dimensionless parameter $C_R$ fell below a value of about 0.6:

$$C_R = \frac{2 h_d R_c}{R_f^2}$$  \hspace{1cm} (D.1)

where $h_d$ is the dimple thickness (i.e. the half thickness at the center of the film). $C_R$ is equal to the ratio of $(2 h_d/R_f^2)$, the approximation to the curvature in the film region ($r < R_f$), to $(R_c)^{-1}$, the approximation to the curvature in the region just outside the film. Since both these regions have radial extents of order $R_f$ and since the curvature at the barrier ring is small, $C_R$ represents the ratio of the driving force for flow from the center of the film to the periphery, to that from the film periphery to the meniscus. Thus, when the order of magnitude of $C_R$ drops below unity, there is a net outflow of liquid at the film periphery $r = R_f$, and film thickness decreases there, forming a barrier ring with an accompanying dimple.

Since $R_c$ is constant and $R_f$ fixed once fluid withdrawal ends, $C_R$ as given by eqn. (D.1) decreases as the film thins. As indicated above, the simulations (Joye et al., 1992) showed that a dimple began to form when $C_R$ was less than 0.6 and became more pronounced as $C_R$ continued to decrease.

The extent of dimpling can be quantified by the ratio of the film half thickness at the ‘barrier ring’ (periphery) to the half thickness of the dimple, i.e. $h_b/h_d$. Small
values of this ratio indicate pronounced dimpling while values close to unity indicate an essentially plane parallel film. Using our numerical simulator for drainage of thin liquid films, we found that drainage of a given film becomes very slow at long times \( t \approx 1000s \) with both \( h_b/h_d \) and \( C_R \) approaching limiting values (see Figure D.2).

For \( R_f \) and \( R_c \) ranging from 1\( \mu m \) -100\( \mu m \) and 0.1\( mm \) – 10\( mm \) respectively, the relationship between these limiting values is shown in Figure D.3 (filled circles). Also shown in Figure D.3 (squares and triangles) is the relationship between \( h_b/h_d \) and \( C_R \) during drainage of films having fixed values of \( R_f \) and \( R_c \). One sees that all the results indicate a unique relationship between \( h_b/h_d \) and \( C_R \). For \( C_R > 0.6 \) we can say that the film thins without dimpling.

Platikanov (1964) presented an expression relating dimple thickness to the flat film thickness, based on the Frankel-Mysels theory (Frankel and Mysels, 1962), which in terms of the parameter \( C_R \) is written as

\[
\frac{h_b}{h_d} = 1.533 \; C_R; \quad \text{for} \quad C_R \leq \frac{1}{1.533} = 0.65 \quad (D.2)
\]

(note: film thickness \( h_d \) is assumed infinite at start)

This relationship is shown by the straight line in Figure D.3 and is in agreement with the results of our simulations for \( C_R < 0.1 \). It is also in agreement with our finding that dimpling does not seem to occur for large \( C_R \). Since \( C_R \) varies during drainage it is useful to present the results in terms of a dimensionless parameter which is constant for a given experiment. From equation (D.1) we see that the appropriate parameter is \( R_f/R_c \). Figure D.4 (filled circles) shows the results of the simulations carried out for the same ranges of \( R_f \) and \( R_c \) as mentioned above and the corresponding limiting values of the ratio \( h_b/h_d \). Figure D.4 does show a trend between the parameter \( h_b/h_d \) and the parameter \( R_f/R_c \). Simulations were also carried out for given \( R_c \) and \( R_f \), and transient values of \( h_b/h_d \) were plotted at various times during drainage (Figure D.4, squares and triangles). The films start close to plane
Figure D.2: $h_b/h_d$ as a function of time $t$ for three different sets of $R_f$ and $R_c$
parallel but approach the curve of limiting values of the ratio \( h_b/h_d \). Figure D.4 also indicates that the film remains essentially plane parallel for small values of \( R_f/R_c \). This is in agreement with the experimental observations (Manev et al., 1984) and the theoretical results of Buevich and Lipkina (1975) who show that with \( R_f/R_c \ll 1 \) the film can thin without dimpling. Figure D.5 illustrates the film half thickness profiles at various times during drainage for a low value of \( R_f/R_c \), and in the absence of disjoining pressure.

**Miniature Cell (No disjoining pressure):**

A similar simulation of film drainage in a miniature Scheludko-Exerowa cell (\( R_c = 0.14 \) mm) is shown in Figure D.6 for the case of \( R_f/R_c = 0.134 \) and no disjoining pressure. We see that the film dimples as expected from Figure D.4 for the relatively large value of \( R_f/R_c \). Further note that a large region having reverse curvature has developed even before fluid withdrawal is stopped at \( t = 3.25s \) and that \( C_R \) is 0.008 at this time, i.e. two orders of magnitude below the value for incipient dimple formation given above. Thus in contrast to Figure D.5 for the conventional cell where the withdrawal step mainly serves to determine \( R_f \), withdrawal has a major effect on how film shape evolves for the miniature Scheludko-Exerowa cell.

According to Figure D.6, \( (h_b/h_d) \) falls rapidly to quite small values once withdrawal ends, so that film thickness becomes even more nonuniform. In fact, at \( t = 10s \) the curvature reverses three times as \( r \) increases although the more common situation of one curvature reversal is regained for \( t = 50s \) and 100s. The simulations indicate that \( (h_b/h_d) \) decreases toward that given by equation (D.2). However, it never reaches that limit as \( h_b \) would have to shrink to the physically unrealistic values of 0.08 and 0.06 nm for values of \( h_d \) at \( t = 10s \) and 100s respectively.

Especially noteworthy in the results of the Figure D.6 for the miniature cell is that the film half thickness when withdrawal ends is less than 10 nm and thus well below
Figure D.3: Variation of the ratio $h_b/h_d$ with the parameter $C_R$
Figure D.4: Variation of the ratio $h_b/h_d$ with the parameter $R_f/R_c$
Figure D.5: Film half thickness profiles during drainage in a conventional cell; $R_c = 1.8\text{mm}$, $R_f = 0.0018\text{mm}$
Figure D.6: Film half thickness profiles during drainage in a miniature cell; \( R_c = 0.14 \text{mm} \), \( R_f = 0.0188 \text{ mm} \)

Withdrawal rate = \(2 \times 10^{-13} \text{ m}^3/\text{s}\)
Withdrawal time = 3.25 s
Initial half thickness = 5 \( \mu \text{m} \)
the thickness at which interference fringes would occur. These low film thicknesses can also be perceived from Bretherton’s theory (Bretherton, 1962; Joye et al., 1992) which gives the film half thickness during withdrawal as

\[ h_{Br} \approx 0.643 \, R_c \left( \frac{3 \mu U}{\sigma} \right)^{2/3} \quad \text{with} \quad U = \frac{d \, R}{dt} \]

Thus smaller the cell radius \( R_c \), the thinner the film.

**Miniature Cell (With disjoining pressure):**

The thicknesses shown in Figure D.6 and those found during other simulations for the miniature cell are small enough that disjoining pressure effects should be considered, even during the withdrawal step. Indeed, the electrical component of the disjoining pressure is dominant for a film with an ionic surfactant and a low counterion concentration during withdrawal, as may be seen from Figure D.7.

Basically, the film increases in diameter during withdrawal, maintaining an almost uniform thickness near the equilibrium value. Again these thicknesses are below the range where fringes occur. Similar behavior was reported for some experiments with the miniature cell (Velev et al., 1995). In contrast, if London dispersion forces dominate, non-uniformities in film thickness will be enhanced because regions of small thickness will thin faster.

**Conclusions:**

1) Simulations show that in the miniature cell the films become very thin during withdrawal.

2) Disjoining pressure has a significant influence on the initial evolution of film shape in the miniature cell, including whether dimple formation occurs.

a) When a long-range repulsive contribution to disjoining pressure exists, the film expands during withdrawal at nearly a constant thickness, in agreement with the
Figure D.7: Film half thickness profiles during drainage in a conventional cell; \( R_c = 1.8 \text{mm}, R_f = 0.0018 \text{mm} \)

- \( R_c = 0.14 \text{ mm} \)
- \( R_f = 0.044 \text{ mm} \)
- \( Q = 2\times10^{-13} \text{ m}^3/\text{s} \)
- \( t_{\text{withdrawal}} = 7.25 \text{ s} \)
- \( h_{\text{initial}} = 5 \mu\text{m} \)
- \( C_{\text{electrolyte}} = 5\times10^{-4} \text{ M} \)
experimental observations (Velev et al., 1995)

b) However, if these repulsive disjoining pressure effects are small, a dimple can develop although it would not be detected with the usual interference methods because film thickness is well below one fourth of the wavelength of visible light.

3) In the absence of disjoining pressure effects the film would thin without dimpling for very small values of the parameter $R_f/R_e$ for either the conventional or the miniature cell.
Appendix E

Derivation of Governing Equations

The film thickness equation (7.1) is nothing but an integrated form of continuity equation (see Chapter 3) and is given as:

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

In chapter 7 since the thin liquid film is translating in the pore it also depends on the axial location \(x\) other than the variables \(t\) (time) and \(r\) (radial location). But there exists a one to one correspondence between the axial location \(x\) and the time \(t\) through the local interstitial velocity \(\nu\) of the lamella (thin liquid film) as:

\[
\frac{dx}{dt} = \nu(x) = \frac{Q}{\pi R_p^2}
\]

thus replacing \(t\) by \(x\) in equation (E.1) we de-dimensionlize eqn (E.1), using \(R_p(x)\) as the characteristic radial length. The de-dimensionlizing step has to be done with caution as now \(R = r/R_p\) is a function of the axial location \(x\) which means we need to account for this in the partial derivatives \(\frac{\partial h}{\partial x}\). Thus we have

\[
\frac{\partial h}{\partial t} = \left( \frac{\partial h}{\partial x} \right)_R \frac{\partial x}{\partial t} + \frac{1}{\pi R_p^2} \frac{d R_p}{dx} \frac{Q}{R_p}
\]

Replacing \(r\) with \(R = R(x, r)\) and substituting for \(dx/dt\) we have

\[
\frac{\partial h}{\partial t} = \left( \frac{\partial h}{\partial x} \right)_R \frac{Q}{\pi R_p^2} - R \left( \frac{\partial h}{\partial r} \right) \frac{1}{\pi R_p} \frac{d R_p}{dx} \frac{Q}{\pi R_p}
\]  \hspace{1cm} (E.2)

Further realizing that
\[
\left( \frac{\partial h}{\partial x} \right)_R = R_p \left( \frac{\partial H}{\partial x} \right) + H \frac{d R_p}{d x}
\]

where \( H = h/R_p \) is the dimensionless film half thickness.

Substituting now for other dimensionless variables, e.g. \( X = x/L \) we have

\[
Ca_x \frac{\partial H}{\partial X} + Ca_x H \left( \frac{1}{R_p} \frac{d R_p}{d X} \right) - R \left( \frac{\partial H}{\partial R} \right) \frac{1}{R_p} \frac{d R_p}{d X} Ca_x
\]

\[
= -\frac{v_o 3 \mu}{\sigma} \frac{1}{R} \frac{\partial}{\partial R} (R V H) + \frac{1}{R} \frac{\partial}{\partial R} \left( R H^3 \frac{\partial P}{\partial R} \right) \tag{E.3}
\]

where \( v_o \) is the characteristic surface velocity. For \( v_o = \frac{\sigma}{3 \mu} \) and dividing through by \( Ca_x \) we get equation (7.1) in Chapter 7 as the governing equation for lamella thickness as it translates in porous media.

Similar procedure is followed in de-dimensionlizing the other equations, namely the surfactant surface mass balance (eqn. 7.4).
Appendix F

Asymmetric Drainage

Until now we have discussed foam stability in porous media by studying axisymmetric drainage of foam lamellae. Previous researchers (Joye et al., 1994, 1996) have shown experimentally and theoretically that a different type of drainage which is asymmetric and much more rapid occurs when the film surface is sufficiently mobile. Joye et al. (1994) showed that the primary mechanism of this fast drainage was an instability caused by surface-tension-driven flow and presented a stability criterion (based on linear stability analysis) which describes the transition from axisymmetric to asymmetric drainage.

We in this study try to relate Joye et al.'s (1994) stability criterion to foam stability in porous media. The stability criterion developed is as follows:

\[
\Theta = \frac{\mu_s \sigma}{\left( -\frac{\partial \tau_{\alpha}}{\partial r} \right)^2} \left[ \left( D_s + \frac{\hbar_o}{3 \mu} \frac{\partial \sigma}{\partial \Gamma} \right) \left( \frac{2 \pi}{\lambda_y} \right)^6 + \left( D_s (\mu_d + \mu_s) \hbar_o \right) \left( \frac{2 \pi}{\lambda_y} \right)^8 \right]
\]

(F.1)

for \( \Theta < 1 \) we have asymmetric drainage.

Here \( \lambda_y \) and \( \frac{\partial \tau_{\alpha}}{\partial r} \) are the wavelength of the transverse perturbation and the steady state pressure gradient at the barrier ring respectively. Other variables are same as described in earlier chapters.

Rewriting the above equation in terms of dimensionless parameters \( N_\mu, N_\Gamma \) and \( N_\alpha \) we have, for \( \lambda_y = 2 \pi R_f \), chosen because this is the largest possible wavelength (thus least stable).
\[ \Theta = \frac{\mu_\alpha \sigma D_s}{(-\frac{\partial P^*}{\partial r})^2 \overline{R_f}} [1 + N_\mu N_\alpha + N_\Gamma N_\alpha] \quad (F.2) \]

The parameter \( N_\mu N_\alpha + N_\Gamma N_\alpha \) is very similar to the surfactant number \( N_R \) we have developed earlier to explain the hydrodynamics of axisymmetric film drainage (Chapter 5). Note that the analysis in Chapter 5 is for a radial geometry while the stability criterion presented above was developed for a 2-D cartesian geometry (see Joye (1994)) with the assumption that the radial extent of the barrier ring is much smaller than the film radius \( R_f \). This might be the reason that the value of coefficient \( \psi \) (eqn. 5.27) is 1.0 compared to 0.27 in the radial analysis. We thus redefine the surfactant number \( N_R \) in this case as:

\[ N_R = N_\mu + N_\Gamma \quad (F.3) \]

Further note that for different wavelengths \( \lambda_y \) the coefficient in \( N_R \) changes but the fact that the parameters \( N_\mu N_\alpha \) and \( N_\Gamma N_\alpha \) interact in a linear additive fashion is true as we discovered earlier in our analytical and numerical solutions.

The expression for pressure gradient at the barrier ring location is given approximately by that in a mobile plane parallel thin liquid film with insoluble surfactant (eqn. 5.19). It is written as:

\[ \left( \frac{d P^*}{d r^*} \right)_{r^*=1} = \frac{V^*}{2} \left[ \frac{1}{N_\Gamma N_\alpha + 1} \left( \frac{2 I_1 (\sqrt{\theta}) - \sqrt{\theta} I_0 (\sqrt{\theta})}{I_1 (\sqrt{\theta}) - \sqrt{\theta} I_0 (\sqrt{\theta})} \right) - 1 \right] \quad (F.4) \]

The right hand side of the above equation is just a function of the dimensionless parameters \( N_\Gamma N_\alpha \) and \( N_\mu N_\alpha \). Note that for given value of these parameters we can determine \( V^* \) from equation (5.21). We will thus represent this whole term as \( \phi = \phi(N_\Gamma N_\alpha, N_\mu N_\alpha) \).

With \( P^* = P/P_o \) where \( P_o = \frac{8F}{\pi R_f^2} = 8P_c \) and \( r^* = r/R_f \) we have
\[
\left( \frac{d P^{ss}}{d r} \right) = \frac{8 \phi P_c}{R_f} \tag{F.5}
\]

Substituting in equation (F.2) we have an expression for \( \Theta \) as:

\[
\Theta = \frac{N_p}{64 \phi^2} \left[ 1 + N_r N_\alpha + N_\mu N_\alpha \right] \tag{F.6}
\]

where

\[
N_p = \frac{\mu_s \sigma D_s}{P_c^2 R_f^4}
\]

Further for small films i.e. with \( R_f/R_c \ll 1 \) we have

\[
P_c = \frac{2 \sigma}{R_c}
\]

then the dimensionless parameter \( N_p \) is redefined as:

\[
N_p = \frac{\mu_s D_s}{4 \sigma R_f^2} \left( \frac{R_c}{R_f} \right)^2 \tag{F.7}
\]

The final form of the criterion is as follows:

\[
\Theta = \frac{N_p}{64 \phi^2} \left[ 1 + N_\mu N_\alpha + N_r N_\alpha \right] \tag{F.8}
\]

Thus for given rheological properties \( \mu_d, \mu_s \) etc. and film thickness \( h_o \) one can calculate the pressure gradient and hence the value of the parameter \( \Theta \). This will then tell us whether the drainage will be axisymmetric or asymmetric.