Decay of standing foams: drainage, coalescence and collapse

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Abstract

A summary of recent theoretical work on the decay of foams is presented. In a series of papers, we have proposed models for the drainage, coalescence and collapse of foams with time. Each of our papers dealt with a different aspect of foam decay and involved several assumptions. The fundamental equations, the assumptions involved and the results obtained are discussed in detail and presented within a unified framework.

Film drainage is modeled using the Reynolds equation for flow between parallel circular disks and film rupture is assumed to occur when the film thickness falls below a certain critical thickness which corresponds to the maximum disjoining pressure. Fluid flow in the Plateau border channels is modeled using a Hagen–Poiseuille type flow in ducts with triangular cross-section.

The foam is assumed to be composed of pentagonal dodecahedral bubbles and global conservation equations for the liquid, the gas and the surfactant are solved to obtain information about the state of the decaying foam as a function of time. Homogeneous foams produced by mixing and foams produced by bubbling (pneumatic foams) are considered. It is shown that a draining foam eventually arrives at a mechanical equilibrium when the opposing forces due to gravity and the Plateau-border suction gradient balance each other. The properties of the foam in this equilibrium state can be predicted from the surfactant and salt concentration in the foaming solution, the density of the liquid and the bubble radius.

For homogeneous foams, it is possible to have conditions under which there is no drainage of liquid from the foam. There are three possible scenarios at equilibrium: separation of a single phase (separation of the continuous phase liquid by drainage or separation of the dispersed phase gas via collapse), separation of both phases (drainage...
and collapse occurs) or no phase separation (neither drainage nor collapse occurs). It is shown that the phase behavior depends on a single dimensionless group which is a measure of the relative magnitudes of the gravitational and capillary forces. A generalized phase diagram is presented which can be used to determine the phase behavior.

For pneumatic foams, the effects of various system parameters such as the superficial gas velocity, the bubble size and the surfactant and salt concentrations on the rate of foam collapse and the evolution of liquid fraction profile are discussed. The steady state height attained by pneumatic foams when collapse occurs during generation is also evaluated.

Bubble coalescence is assumed to occur due to the non-uniformity in the sizes of the films which constitute the faces of the polyhedral bubbles. This leads to a non-uniformity of film-drainage rates and hence of film thicknesses within any volume element in the foam. Smaller films drain faster and rupture earlier, causing the bubbles containing them to coalesce. This leads to a bubble size distribution in the foam, with the bubbles being larger in regions where greater coalescence has occurred.

The formation of very stable Newton black films at high salt and surfactant concentrations is also explained.

Keywords: Foams, Surfactants, Drainage, Concentrated Emulsions, Stability

Contents

1. Introduction ..................................... 3
2. Theoretical model .................................. 6
   2.1 Foam geometry ................................ 7
   2.2 Film drainage ................................. 8
   2.3 Film rupture .................................. 9
   2.4 Calculation of the disjoining pressure .......... 13
      2.4.1 van der Waals force ...................... 13
      2.4.2 Electrical double layer force .............. 15
      2.4.3 The short range repulsive force .......... 18
      2.4.4 Effect of surfactant concentration on the disjoining pressure
          for ionic surfactants .......................... 21
      2.4.5 Effect of salt concentration on disjoining pressure isotherms
          of ionic surfactants .......................... 24
      2.4.6 Steric repulsion ............................ 25
   2.5 Flow in Plateau border channel ................... 28
2.6 Theoretical model for the drainage and coalescence in foam .. 30
   2.6.1 Conservation equation for drainage .......... 30
   2.6.2 Conservation equation for surfactant .......... 40
   2.6.3 Coalescence ................................ 42
   2.6.4 Movement of the foam/gas interface ........... 49
   2.6.5 Movement of the foam/liquid interface ........ 50
2.7 Drainage equilibrium .................................. 51
2.8 Initial conditions .................................. 52
2.9 Homogeneous foams .................................. 52
   2.9.1 Initial and boundary conditions for homogeneous foams .. 52
1. Introduction

Foams are highly concentrated dispersions of gas (dispersed phase) in a liquid (continuous phase). Since they contain more than 90% gas by volume, the bubbles are usually polyhedral. This is because the highest volume fraction that identical spheres can occupy is 0.74. An increase in the volume fraction of the dispersed phase gas beyond this value is characterized by a departure from spherical geometry. It must be noted, however, that this criterion for determining the onset of polyhedricity is applicable only to monodisperse systems. With polydisperse systems, the bubbles can remain spherical at much higher volume fractions.

Concentrated emulsions (biliquid foams) are a similar class of systems composed of one liquid dispersed in another. In this review, the terms “foams” and “concentrated emulsions” will be used interchangeably, as much of the principles discussed here are equally applicable to both foams and liquid-liquid concentrated emulsions.

Foams are metastable systems. They show a spontaneous tendency to separate into two distinct bulk phases. The time scale for the disintegration, however, varies widely. Foams can persist for a few minutes or several days depending on the conditions.

Foams have several very interesting and unusual properties which make them possible candidates for use in many industrial applications. The large gas/liquid interfacial area available can be exploited in foam fractionation to efficiently separate surface active substances such as proteins from their solutions [1–5]. An often cited example of foam fractionation is beer foam which contains more than 80% of the protein in the beer. Foams are also being considered for use in enhanced oil recovery [6,7], insulation and to reduce the impact of explosions [6]. On
the negative side [8,9], foams can be a major nuisance in the chemical process industry. When they last long enough, they interfere with physical and chemical processes and can adversely impact productivity and efficiency. Liquid-liquid concentrated emulsions have been used in our laboratory to prepare high molecular weight polymers and composites as well as membranes for separation processes [10,11].

To effectively utilize foams and concentrated emulsions in any of these situations, it is important to have some control over their stability. A detailed understanding of the mechanisms involved in foam persistence and decay is therefore desirable.

Unfortunately, much of the work in this area has been rather empirical [12] and most experimental data are rendered useless because important parameters such as bubble size have not been measured. There is therefore a need for reliable theoretical models which can be used to interpret experimental results. A fairly comprehensive review of the theoretical work in this area up to 1990 has been presented by Narsimhan and Ruckenstein [13]. In this paper, we attempt to summarize the work done in this laboratory over the last few years [14–18] on the decay of standing foams.

A standing foam is a simple and convenient system to study foam decay. Typically, a certain volume of foam is prepared and the changes occurring in it are monitored as a function of time. The length of the foam/concentrated emulsion usually decreases; the heavier phase accumulates at the bottom and the lighter phase accumulates at the top. At the same time, the mean size of the bubbles increases resulting in a decrease in the interfacial area. A suitable model for the decay of standing foam should be able to predict the foam length, the bubble size and the composition of the foam (proportion of the two phases) as a function of time.

The continuous phase liquid in a foam is present in the liquid films that are formed between the faces of the polyhedral bubbles and the channels (Plateau border channels) that are formed where neighboring films meet. Figure 1 shows a typical foam column, a polyhedral bubble and the cross-section of a typical Plateau border (PB) channel formed where three films meet. These Plateau border channels form a complex interconnected network through which liquid flows out of the foam under the action of gravity. At the same time, the liquid in the films is sucked into the Plateau border channels. As a result, they become thinner and finally rupture. Film rupture at the foam boundary causes loss of the dispersed phase gas from the foam. When a film ruptures
within a foam, bubbles sharing the film coalesce, leading to an increase in the bubble volume. Drainage of the continuous phase liquid therefore plays a pivotal role in foam decay.

Several models [19–26] for the drainage of standing foams have appeared in literature. The most notable papers are those of Krotov [22] and Narsimhan [23]. Krotov [22] was the first to recognize the effect of Plateau border suction (capillary pressure) on foam drainage and formulated the basic equations and boundary conditions. He showed that drainage in a foam eventually comes to a halt when the gradient of the
capillary pressure, that is set up as drainage proceeds, balances gravity. However, while he formulated the basic equations, he did not attempt to solve them. Narsimhan [23] recognized the importance of the method of foam generation and numerically solved the drainage equations for foams produced by bubbling using a quasi-steady state approximation to simulate the drainage during bubbling. He studied the effect of various parameters including the bubble size and viscosity on foam drainage. In a series of papers [14-18] over the past couple of years, we have studied the problem of standing-foam decay in detail. For pneumatic foams produced by bubbling, we used an unsteady state model [14] to simulate the drainage during bubbling. The results obtained differed significantly from those obtained by Narsimhan using a quasi-steady state approach and in some cases showed better agreement with experiment. In a later paper [15], we also considered the drainage of homogeneous foams. Most of the above models involved the numerical solution of the relevant differential equations. However, some efforts to obtain analytical solutions have been made [26].

These drainage models provided useful insights into the drainage process. However, they did not deal with the larger questions involving foam stability such as the decrease in the foam volume and the interfacial area with time. These phenomena are a direct consequence of film rupture which has traditionally been ignored in drainage models. Film rupture was included in our model [15-18]. This has enabled us to directly evaluate the effect of drainage on the various phenomena associated with foam decay such as bubble coalescence and foam collapse. Each of our papers dealt with a different aspect of foam decay and the basic equations were improved as we learnt more about the system. The aim in this paper is to present our results within a unified framework. We first present in detail the fundamental equations in their most rigorous form. The results for the various cases are presented towards the end.

2. Theoretical model

As mentioned in the previous section, drainage of the continuous phase liquid plays a crucial role in the decay of a standing foam. Two mechanisms are responsible for fluid flow in a foam. Flow in the films is driven by the capillary pressure, while the flow in the Plateau border channels occurs due to gravity. After a brief discussion of foam structure, we will discuss the flow in individual films and Plateau border channels and then formulate the bulk conservation equations.
2.1. Foam structure and geometry

Any theoretical model of foam must necessarily involve assumptions regarding foam structure and geometry, which, needless to say, is extremely complex. Foams are composed of polyhedral bubbles which differ markedly in shape and size. Even among bubbles having the same volume, there is a variation in the number of faces and the number of edges per face. There is some order, however, amidst this apparent chaos. Almost without exception, foams always obey a few simple rules, referred to as Plateau's laws in honor of the Belgian physicist Plateau who first formulated them.

Plateau's laws state:
(1) Three and only three films meet at an edge at an angle of 120.
(2) Four and only four edges (Plateau border channels) meet at a point at an angle of 109.

These rules have been used as a justification for the use of the regular pentagonal dodecahedron as the "idealized" foam bubble. While it is not space filling, the regular pentagonal dodecahedron comes remarkably close to satisfying Plateau's laws. The angle between the faces is about 116 and the angle between the edges is about 108. Indeed, detailed studies of foam structure by Matzke [27] indicate that pentagonal films and dodecahedral bubbles do occur most frequently. Several interesting discussions of foam structure can be found in literature [27–33].

The size of a bubble is expressed in the model in terms of the bubble radius \( R \), which is the radius of a sphere having the same volume as that of the bubble. All other parameters which depend on the bubble size such as area of the films (faces) and the length of the Plateau border channels are expressed in terms of \( R \) as shown below. The volume of a regular pentagonal dodecahedron with edge length \( l \) is:

\[
V = 7.7l^3 \tag{1}
\]

and the area \((A_F)\) of each pentagonal film is:

\[
A_F = 1.72 \; l^2 \tag{2}
\]

Since by definition \( V = (4\pi R^3)/3 \), we have \( l = 0.816R \).

In the model, the pentagonal films are represented by circular disks which have the same surface area. If \( R_F \) is the radius of these circular disks, we have

\[
A_F = \pi R_F^2 \Rightarrow R_F = 0.606R \tag{3}
\]
2.2. Film drainage

Figure 2 shows a cross-section of a draining film. The surface is curved at the edges where neighboring films come together to form a Plateau border channel. Because of this curvature, the pressure is smaller at the edges than at the center of the film and a radial flow is induced leading to a reduction of the film thickness with time.

Film thinning is modeled using a Reynolds [33] type equation for the flow between two circular parallel disks, which gives the rate of film thinning as:

$$\frac{dx_F}{dt} = \frac{2c_f \Delta P x_F^3}{3\mu R_P^2} = V_f$$

In Eq. (4), $t$ is the time, $\mu$ is the viscosity of the continuous phase, $R_P$ is the radius of the disk and $\Delta P$ is the pressure difference causing the flow. The driving force $\Delta P$ is a net result of the suction pressure in the adjacent Plateau border channels and the disjoining pressure ($\Pi$) in the films and is given by

$$\Delta P = \frac{\sigma}{r_p} - \Pi,$$

where $\sigma$ is the surface tension and $r_p$ is the radius of curvature of the Plateau border channels. The coefficient $c_f$ is a correction factor which accounts for the mobility of the film surfaces and is given by [35]:

$$\frac{1}{c_f} = 16 \sum_{n=1}^{\infty} \frac{(6\mu + \eta_s k_n^2 \alpha_s x_F)^2}{(6\mu + 6\mu \alpha_s + \eta_s k_n^2 \alpha_s x_F) \lambda_n^4}$$
In Eq. (5), $\lambda_n$ is the $n$th root of the equation

$$J_0(\lambda_n) = 0, \quad k_n = \frac{\lambda_n}{R_F}, \quad \alpha_s = \frac{-3D\mu}{\Gamma\left(\frac{\partial\sigma}{\partial c_s}\right)} \left[ 1 + \frac{2D_s\left(\frac{\partial\Gamma}{\partial c_s}\right)}{D_F} \right] = -\frac{3D\mu}{\Gamma\left(\frac{\partial\sigma}{\partial c_s}\right)} \cdot$$

$J_0$ is the 0th order Bessel function of the first kind, $D$ is the bulk diffusivity and $D_s$ is the surface diffusivity of the surfactant.

The disjoining pressure ($\Pi$) refers to the repulsive force that arises when the film surfaces are close enough ($x_F < 1000$ Angstroms) to interact with each other. When $\Pi$ is positive (repulsive), it opposes film thinning, while when it is negative (attractive), it increases the driving force ($\Delta P$) and accelerates film thinning. In the most general case, $\Pi$ is computed as a sum of an attractive van der Waals force ($\Pi_{VDW}$), a repulsive force ($\Pi_{DL}$) due to the interaction of the electrical double layers on the two surfaces and a short range repulsive force ($\Pi_{SR}$) which could result from steric interaction when long chained molecules are adsorbed on the surfaces or due to hydration forces that are set up due to the ordering of the water molecules near charged surfaces. The former are not observed with ionic surfactants. They arise only when long-chained nonionic surfactants or polymeric molecules such as proteins are adsorbed on the film surfaces. Thus we have:

$$\Pi = \Pi_{vW} + \Pi_{DL} + \Pi_{SR} \quad (6)$$

Unlike the other two forces which are reasonably well understood within the realm of the DLVO theory, the origin of the short range forces is still a subject of discussion. It is generally agreed that the force decays roughly exponentially with distance.

The plot of $\Pi$ versus $x_F$ is referred to as the disjoining pressure isotherm and plays a crucial role in determining the rate of film thinning and its stability to rupture. Film rupture will be discussed next.

2.3. Film rupture

Rupture of a film occurs when waves generated on the surface due to mechanical and thermal perturbations grow in an unbounded fashion. Whether a surface wave is damped or undergoes catastrophic growth is determined mainly by the shape of the disjoining pressure isotherm. If the repulsive disjoining force increases in response to the local thinning
Fig. 3. Various types of disjoining pressure isotherms.
Fig. 3. Continued.
due to the disturbance, the wave is damped and no rupture occurs. On
the other hand, if the disjoining pressure decreases, the local thinning
is accelerated and leads to rupture. Film rupture can therefore occur
only if the disjoining pressure decreases when the film thickness de-
creases, i.e. when its derivative with respect to film thickness
\( \frac{d\Pi}{dx_F} \) is positive. Figure 3 shows some typical plots of disjoining
pressure (\( \Pi \)) versus film thickness \( x_F \). For the rupture of a thin film to
occur via the growth of instabilities, \( \frac{d\Pi}{dx_F} \) must be positive. Thus, a
thin film with an isotherm like the one in Fig. 3a will rupture only for
\( x_F < x_{Fm} \). A film with an initial thickness \( x_F > x_{Fm} \) can arrive at
thicknesses less than \( x_{Fm} \) only if the capillary pressure \( (\sigma/r_p) \) in the
Plateau borders, which drives film thinning exceeds the maximum
disjoining pressure. It can therefore rupture only if the capillary pres-
sure exceeds the maximum disjoining pressure \( (\Pi_{\text{max}}) \). On the other
hand, a film with an isotherm like that in Fig. 3b will definitely rupture
since \( \frac{d\Pi}{dx_F} \) is always positive. Figure 3c shows an isotherm in which
there are two maxima. The smaller one to the right is primarily due to
the electrical double layer forces, while the other is due to a short range
repulsive force. At high electrolyte concentrations, the electrical double
layer is compressed and the double layer forces are overwhelmed by the
van der Waals forces at all thicknesses. If the short range force is
significant, we will either have an isotherm like Fig. 3a, where the
maximum is mainly due to the short range repulsive forces or like Fig.
3d if the short range forces are large enough to overcome the van der
Waals forces at short distances (few Angstroms).

The latter case corresponds to an extremely stable film because
\( \frac{d\Pi}{dx_F} \) is always negative. We will primarily consider isotherms of the
type shown in Fig. 3a. For this kind of isotherm, the situation regarding
the stability of the film to rupture can be summarized as follows:

\[
\begin{align*}
 x_F > x_{Fm} & \Rightarrow \frac{d\Pi}{dx_F} < 0 \quad \text{(Stable)} \\
n x_F < x_{Fm} & \Rightarrow \frac{d\Pi}{dx_F} > 0 \quad \text{(Unstable)} \\
n x_F = x_{Fm} & \Rightarrow \frac{d\Pi}{dx_F} = 0 \quad \text{(Metastable)}
\end{align*}
\]  

(7)

A number of papers have appeared in the literature that attempt to
predict the lifetime of a film using linear and non-linear stability theory
Fig. 4. Film rupture.

[35–40]. The emphasis in these papers is on computing the time elapsed between the onset of instability (the point at which $d\Pi/dx_F = 0$ & $x_F = x_{Fm}$) and the actual rupture of the film which is deemed to occur when the waves on the surface become large enough for the two film surfaces to touch (Fig. 4). The mean film thickness when film rupture occurs ($x_{Fc}$) is actually smaller than the mean thickness ($x_{Fm}$), when the instability begins, i.e. $x_{Fc} < x_{Fm}$. Needless to say, these theories are extremely complex and it is practically impossible to incorporate them into a global model for foam collapse. We therefore assume that a film ruptures at the moment its surfaces become unstable. In other words, we assume that $x_{Fc} = x_{Fm}$. This assumption is reasonable because the time scale for the growth of the instability is much shorter than the time for film drainage. For an isotherm of the type shown in Fig. 3a, $x_{Fc}$ is therefore the film thickness corresponding to the maximum disjoining pressure ($\Pi_{max}$). The disjoining pressure isotherm and especially the value of the maximum disjoining pressure ($\Pi_{max}$) therefore plays a critical role in our model for foam collapse.

It must be emphasized here that a film can also rupture when it is very thick, much before the film surfaces are close enough to interact. The stability of the film in this situation will be independent of the disjoining pressure and will be determined primarily by the elasticity of the film [41] and the nature of the mechanical perturbations involved. This mechanism of film rupture is not considered in our model.

Details regarding the calculation of the disjoining pressure isotherm are discussed next.

2.4. Calculation of the disjoining pressure

2.4.1 van der Waals force

The attractive van der Waals component of the disjoining pressure ($\Pi_{VDW}$) can be obtained using the expression:

$$\Pi_{VDW} = -\frac{A_h}{6\pi x_F^3}$$  \hspace{1cm} (8)
The Hamaker's constant \( (A_h) \) has a weak dependence on film thickness, but is often taken to be constant. Donners et al. [42] have obtained a simple expression for \( A_h \):

\[
A_h = 6\pi \left[ \frac{b + cx_F}{1 + dx_F + ex_F^2} + q \right]
\]

(9)

where \( b, c, d, e \) and \( q \) are constants which depend on the specifics of the particular system such as the media involved and the thickness \( p \) of the surfactant film (see Fig. 5). In some of our calculations, sodium dodecyl sulfate was used as the model surfactant. For this system, the values available for air–water–air systems with dodecane monolayers \( (p = 0.9 \text{ nm}) \) at the air–water interfaces were used. These values are:

\[
\begin{align*}
    b &= -3.96 \times 10^{-23} \text{ J}, \\
    c &= -2.05 \times 10^{-13} \text{ J/m}, \\
    d &= 8.86 \times 10^7 \text{ J/m}, \\
    e &= 6.61 \times 10^{16} \text{ J/m}^2, \\
    q &= -1.8 \times 10^{-22} \text{ J}.
\end{align*}
\]

It must be emphasized that \( x_F \) refers to the thickness of the aqueous core of the film. Experimentally obtained disjoining pressure isotherms [43,44] are usually presented in terms of the total film thickness which include the thicknesses of the surfactant layer. Thus, a correction (2.3 nm in case of sodium dodecyl sulfate [43]) must be applied to \( x_F \) to make a comparison with experimental results.

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Fig. 5. The three layers involved in the calculation of the van der Waals forces.
2.4.2. Electrical double layer force ($\Pi_{DL}$)

When the film surfaces are charged, a repulsive force arises due to the confinement of ions in the electrical double layer as the film thickness decreases. Calculation of $\Pi_{DL}$ involves the solution of the Poisson–Boltzmann equation to obtain the concentration of ions at the midplane. An approximate power series solution to the Poisson–Boltzmann equation at moderate potentials has been obtained by Oshima and Kondo [45,46]. The potential $\psi$ at a distance $x$ from the midplane is given by:

$$\tanh\left[\frac{e\psi}{k_BT}\right] = \gamma A_1(\kappa x) + \gamma^2 A_2(\kappa x) + \gamma^5 A_3(\kappa x)$$

where:

$$\gamma = \tanh\left(\frac{e\psi_s}{4kT}\right); A_1(x) = \frac{\cosh(\kappa x)}{\cosh(\frac{\kappa F}{2})}$$

$$A_2(x) = \frac{(\kappa x) \sinh(\kappa x) - \frac{\kappa F}{2} \tanh\left(\frac{\kappa F}{2}\right) \cosh(\kappa x)}{\cosh^3\left(\frac{\kappa F}{2}\right)}$$

$$A_3(x) = \frac{A_1(x) - (A_1(x))^3}{4 \cosh^2\left(\frac{\kappa F}{2}\right)} + \frac{3A_2(x)}{4 \cosh^2\left(\frac{\kappa F}{2}\right)} \left[1 - 4 \frac{\kappa F}{2} \tanh\left(\frac{\kappa F}{2}\right)\right] - \frac{A_1(x)\left(\frac{\kappa F}{2}\right)^2 - (\kappa x)^2}{2 \cosh^4\left(\frac{\kappa F}{2}\right)}$$

The mid plane potential ($\Psi_m$) is therefore:

$$\tanh\left[\frac{e\psi_m}{k_BT}\right] = \gamma A_1(0) + \gamma^2 A_2(0) + \gamma^5 A_3(0)$$

and the repulsive force per unit area is given by:

$$\Pi_{DL} = \frac{16e\epsilon RTY_m^2}{(1 - Y_m^2)^2} \approx 16e\epsilon RTY_m^2 [1 + 2Y_m^2 + 3Y_m^4]$$
where \( Y_m = \tanh \left[ \frac{e\psi_m}{k_B T} \right] \) and \( c_{el} \) is the electrolyte concentration. Using Eq. (10), Eq. (13) can therefore be rewritten as:

\[
\Pi_{DL} = 16(c_s + c_v)R_G T \left[ \gamma^2 A_1^2(0) + 2\gamma^4 A_1(0)(A_2(0) + A_3(0)) + \gamma^6(2A_1(0)A_3(0) + 8A_1^2(0)A_2(0) + 3A_1^6(0) + A_2^2(0)) \right] \quad (14)
\]

If the surface potential \( (\psi_s) \) is fixed and known, Eqs. (10–14) suffice for the calculation of \( \Pi_{DL} \). However, the surface potential is often not fixed and depends on the surface charge. For nonionic surfactants, the surface charge arises due to the binding of ions present in the water and is probably independent of surfactant concentration. On the other hand, for ionic surfactants, the surface charge results from the dissociation of the adsorbed surfactant molecules and is likely to be strongly dependent on the surfactant concentration. The calculation of the surface charge and the surface potential for ionic surfactants is discussed below.

**Calculation of the surface charge and surface potential for ionic surfactants**

In films stabilized by ionic surfactants, the charge on the surface of a film is caused by the adsorbed surfactant molecules that are dissociated. Let us consider a model system of sodium dodecyl sulfate and sodium chloride. If \( \alpha_d \) is the degree of dissociation of the adsorbed surfactant molecules, the surface charge per unit area \( (\sigma_c) \) can be expressed in terms of the surface density \( (\Gamma) \) as:

\[
\sigma_c = -\Gamma \alpha_d e \quad (15)
\]

where \( e \) is the protonic charge and the degree of dissociation \( \alpha_d \) is provided by the equilibrium of the following reaction: \( R-\text{Na} \text{surface} \rightarrow R^- \text{surface} + \text{Na}^+ \text{aqueous phase} \).

Thus, denoting \( K_d \) as the equilibrium constant, we have

\[
K_d = \frac{\alpha_d c_{Na^+}}{(1 - \alpha_d) \Gamma} = \frac{\alpha_d c_{Na^+}}{1 - \alpha_d} \quad (16)
\]

In Eq. (16), the concentration \( c_{Na^+} \) of the sodium ions near the surface can be expressed in terms of the surfactant concentration \( (c_s) \) and the salt \( (\text{NaCl}) \) concentrations \( (c_v) \) in the Plateau border channels as:

\[
c_{Na^+} = (c_s + c_v) \exp \left\{ -\frac{e\psi_s}{k_B T} \right\} \quad (17)
\]
and $\Gamma$ can be computed using the Frumkin adsorption isotherm:

$$b_1 c_{R^-} = \frac{\Gamma}{\Gamma_\infty} \exp\left(-2a_1 \frac{\Gamma}{\Gamma_\infty}\right)$$

(18)

where

$$c_{R^-} = c_s \exp\left(\frac{e\psi_s}{k_BT}\right)$$

is the concentration of the surfactant anions near the interface, $\Gamma_\infty$ is the surface excess at saturation and the constants $a_1$ and $b_1$ are empirical parameters which are available in literature from experiments carried out for air–water interfaces in contact with a large amount of water. The experimental results however, relate $\Gamma$ to the bulk surfactant concentration $c_s$ and not $c_{R^-}$. At large ionic strengths, the double layer is completely compressed and $c_{R^-}$ is equal to the $c_s$. The highest salt (NaCl) concentration for which data on sodium dodecyl sulfate are available [47] is 1 M for which $\Gamma_\infty = 5 \times 10^{-6}$ mol/m$^2$, $a_1 = -1.53$ and $b_1 = 881$ m$^3$/mole. These values were used in our calculations with ionic surfactants. The Frumkin isotherm when combined with the Gibbs adsorption equation provides the following relation for the surface tension:

$$\sigma_0 - \sigma = -\Gamma_\infty R_G T \left[ \log\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) + a_1 \left(\frac{\Gamma}{\Gamma_\infty}\right)^2 \right] +$$

$$\frac{4R_G T(2\varepsilon_d \varepsilon_k R_G T(c_e + c_s))^{1/2}}{N_A e} \left[ \cosh\left(\frac{e\psi_s}{2k_BT}\right) - 1 \right]$$

(19)

The surface charge can also be expressed in terms of the surface potential and the midplane potential as:

$$\sigma_c = \sqrt{2\left\{ \cosh\left(\frac{e\psi_s}{k_BT}\right) - \cosh\left(\frac{e\psi_m}{k_BT}\right) \right\}} \frac{k\varepsilon_d \varepsilon_k k_BT}{e}$$

(20)

Equating the right hand sides of Eq. (20) and Eq. (16) and solving with Eq. (13) we can get the midplane ($\psi_m$) and surface potential ($\psi_s$) in terms of the dissociation constant $K_d$ and electrolyte concentration $c_{el}$. It may
be noted that for ionic surfactants, the electrolyte concentration $c_{el}$ will depend on the surfactant concentration. Thus, if $c_e$ is the concentration of the monovalent salt (e.g. NaCl) and $c_s$ is the concentration of the monovalent ionic surfactant (e.g. NaDS), we have:

$$c_{el} = c_s + c_e$$  \hspace{1cm} (21)

It may be noted that the use of Eq. (17) implies that the effect of the interactions between the adsorbed species has been ignored. Because these interactions provide a positive contribution to the free energy, they decrease the degree of dissociation. These effects have been considered for micelles by Ruckenstein and Beunen [50].

**2.4.3. The short range repulsive force ($I_{SR}$) [17]**

As mentioned earlier, large exponentially decaying repulsive forces arise due to the steric interaction of long-chained molecules or due to the organization of water molecules near charged surfaces. We will first discuss the latter in detail. A short discussion of steric forces is provided in a later section.

**Short range repulsion due to organization of water molecules**

It has been experimentally observed [37] that in many systems, the resistance of a foam to collapse increases sharply at sufficiently high surfactant and salt concentrations. Experimental measurements of the disjoining pressure isotherms of single films containing sodium dodecyl sulfate [43] show that qualitatively different isotherms are obtained depending on the concentration of sodium chloride. As the pressure on a film is increased, its thickness decreases and the repulsive disjoining pressure increases. When the thickness is small enough (about 10 nm), black spots appear which eventually cover the entire film giving rise to a common black film. Further increase in pressure, however, gives rise to different phenomena depending on the salt concentration. At lower salt concentrations, the common black film ruptures, while at higher salt concentrations, there is a sudden transition to a very stable Newton black film. In the latter case, the film rupture predicted by the DLVO theory is prevented by the emergence of a large short range repulsive force. We use a simple model proposed by Schiby and Ruckenstein [51] to compute the short range repulsive force. An electric field is generated by the undissociated surfactant molecules via their dipoles. This electric field organizes the water molecules near the surface and gives rise to the repulsive force. Thus, increased counterion binding at high salt
concentration increases the number of surface dipoles and hence the electric field and makes the short range repulsive force stronger. We show that most effects of salt and surfactant concentration can be qualitatively accounted for by combining this theory with the DLVO theory. Schiby and Ruckenstein derived the expression for the short range repulsive force between two parallel plates using an idealized model in which the water molecules are arranged in a hexagonal close packed configuration in parallel planes separated by a distance $\delta$. They assumed that the electric field generated by the surfaces orients the water molecules in the direction of the field and gives rise to a profile of mean dipole moment. They obtained a simple expression for the polarization (dipole moment per unit volume) profile between the plates and used it to obtain the following expression for the force per unit area ($\Pi_h$) between the plates:

$$\Pi_h = \frac{P_1 \left[ \exp(-2\alpha x_F) - \exp(-\alpha x_F) + \alpha x_F \exp(-\alpha x_F) \right]}{(A' \exp(-\alpha x_F) + B')^2} + \frac{P_2 A' \left[ \exp(-\alpha x_F) - \exp(-3\alpha x_F) - 2\alpha x_F \exp(-2\alpha x_F) \right]}{[A' \exp(-\alpha x_F) + B']^3} + \frac{P_2 \exp(-\alpha x_F)}{[A' \exp(-\alpha x_F) + B']^2} + \frac{P_2 A' \left[ \exp(-2\alpha x_F) \right]}{[A' \exp(-\alpha x_F) + B']^2} \tag{22}$$

where $A', B'$ and $\alpha$ are constants which can be computed (see Eqs.(24–27)) and $P_1$ and $P_2$ are given by:

$$P_1 = n \gamma_p [E^0]^2; \quad P_2 = 2P_1 \alpha \delta \tag{23}$$

In Eq.(23), $n$ is the number of water molecules per unit volume, $\gamma_p$ is the polarizability of water and $E^0$ is the electric field generated by the surface which acts on the first layer of water molecules.

Calculations indicate that the third term is dominant. $\Pi_h$ is therefore primarily an exponentially decaying force with a decay length of $\alpha^{-1}$. The constants $A', B'$ and $\alpha$ in Eq.(22) can be expressed in terms of the distance between adjacent water molecules ($\alpha$) and the distance between the parallel planes of water molecules ($\delta$) as follows:

$$\alpha^2 = \frac{\left[ 1 - \gamma_p (2\Lambda(\delta) + \Lambda(0)) \right]}{\gamma_p \Lambda(\delta) \delta^2} \tag{24}$$

where:
\[ \Lambda(\pm \delta) = \frac{2}{\delta^3} + \frac{6}{(a^2 + \delta^2)^{\frac{3}{2}}} \frac{2\delta^2 - a^2}{\delta^2 + a^2} \]  

(25)

Also,

\[ A' = -1 + \gamma_p[\Lambda(\delta) \exp(\alpha\delta) + \Lambda(0)] \]  

(26)

\[ B' = 1 - \gamma_p[\Lambda(\delta) \exp(-\alpha\delta) + \Lambda(0)] \]  

(27)

For \( \delta = a = 2.8 \, \text{Å}, A' = 0.268, B' = 2.53 \) and \( \alpha = 3.58 \times 10^9 \, \text{m}^{-1} \). The electric field \( E^0 \) however depends on the characteristics of the surface and is computed as shown below.

**Calculation of \( E^0 \)**

The inner surface of the film contains dissociated chains which behave as point charges and undissociated chains which behave as dipoles pointing into the liquid phase. If we consider both surfaces to be of infinite extent, the electric field at any point between the planes due to the surface charges will be 0. The reason for this is that the electric field due to a charged infinite plane is independent of distance. The fields from the charges on the two surfaces therefore cancel each other and \( E^0 \) depends solely on the dipoles present on the surface. The electric field at a distance \( 'z' \) from a semi-infinite plane with a dipole moment per unit area \( u_s \) is given by (see Appendix B):

\[ E = \frac{2u_s}{3\varepsilon_d \varepsilon_0 z} \]  

(28)

Thus, if \( u_s \) is the dipole moment of a single undissociated surfactant molecule we have:

\[ u_s = \Gamma(1 - \alpha_d)N_A \mu_s \]  

(29)

where \( N_A \) is the Avogadro number. Combining Eqs. (28) and (29), we get:

\[ E = \frac{2\Gamma(1 - \alpha_d)N_A \mu_s}{3\varepsilon_d \varepsilon_0 z} \]  

(30)

Since we are dealing with individual water molecules, the medium among them is vacuum and we have \( \varepsilon_d = 1 \). The assumption in that theory is that the external electric field is important only in the first layer of molecules. Thus, if \( d \) is the distance between the plane containing
the surfactant molecules and the first layer of water molecules, we need $E$ at $z = d$. Since $\mu_s/d$ is not known, we use it as a parameter. Thus we write:

$$E^0 = \Gamma(1 - \alpha_d)E_d$$
with $E_d = 2N_A\mu_s/(3e_{d0}d)$ \hspace{1cm} (31)

Since $E_d$ is a parameter to be varied, it is helpful to have a reference value for $E_d$ about which it can be varied. In the model of Schiby and Ruckenstein, the mean dipole moment of the water molecules close to the surface is given by:

$$\mu(0) = \frac{\gamma_p E^0(1 - \exp(-\alpha \chi_F))}{A' \exp(-\alpha \chi_F) + B} = \frac{\gamma_p \Gamma(1 - \alpha_d)E_d(1 - \exp(-\alpha \chi_F))}{A' \exp(-\alpha \chi_F) + B}$$

(32)

Thus:

$$E_d = \frac{\mu(0)(A' \exp(-\alpha \chi_F) + B)}{\gamma_p \Gamma(1 - \alpha_d)(1 - \exp(-\alpha \chi_F))}$$

(33)

Therefore, if $\mu_w$ is the dipole moment of water,

$$E_{d_{\text{ref}}} = \frac{\mu_w(A' + B')}{\gamma_p} = 3.65 \times 10^{15} \text{ N.m}^2/\text{C}$$

serves as a useful reference value.

It may be noted that we assume here that the short range repulsion force and the electric double layer force are additive. An attempt to couple them nonlinearly has been made by Schiby and Ruckenstein [52].

We carried out some sample calculations using expressions presented above for a model system comprising sodium dodecyl sulfate and sodium chloride. Some results are presented in the following sections.

2.4.4 Effect of surfactant concentration on the disjoining pressure for ionic surfactants [17]

Being an ionic surfactant, the bulk concentration of sodium dodecyl sulfate affects the disjoining pressure in two ways:

(a) It affects the surface excess $\Gamma$ and hence affects the surface charge (see Eq.(16)).

(b) It affects the ionic strength and the degree of dissociation and therefore the extent of the electrical double layer. Figures 6 and 7 show the effect of the surfactant concentration on the disjoining pressure.
isotherm for two different values of the dissociation constant $K_d$ viz. $K_d = 158$ moles/$m^3$ and $K_d = 0.316$ moles/$m^3$. In both cases, $E_d/E_{dref}$ was taken 0.04. It is clear that there is a qualitative difference in the effect of surfactant concentration in the two cases. In Fig. 6, since the degree of dissociation is large, the number of dipoles which contribute to the short range repulsive force is small and it is too weak to overcome the van der Waals forces. Thus, the increase in surfactant concentration primarily affects the disjoining pressure by changing the double layer force. This is clear from the fact that the maximum disjoining pressure is very close to that ($\Pi_{max,dl}$) obtained when no short range repulsive force is included (see Table 1). In the system considered in Fig. 7, the smaller degree of dissociation significantly increases the number of surface dipoles and hence the contribution of the short range polarization force. Thus the increase in surfactant concentration causes the

Fig. 6. Effect of surfactant concentration on the disjoining pressure isotherms with $K_d = 158$ moles/$m^3$ and $E_d = 0.04E_{dref}$.
Table 1

Effect of surfactant concentration on system parameters for $E_d = 0.04E_{dref}$ and $c_e = 0$

<table>
<thead>
<tr>
<th>$c_x$ (M)</th>
<th>$K_d$ (moles/m$^3$)</th>
<th>$\Pi_{max}$ (N/m$^2$)</th>
<th>$x_{Fm}$ (nm)</th>
<th>$\Pi_{max,dl}$ (N/m$^2$)</th>
<th>$x_{Fm,dl}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>158</td>
<td>217500</td>
<td>2.624</td>
<td>217200</td>
<td>2.64</td>
</tr>
<tr>
<td>0.003</td>
<td>158</td>
<td>384000</td>
<td>1.855</td>
<td>378000</td>
<td>1.94</td>
</tr>
<tr>
<td>0.005</td>
<td>158</td>
<td>534000</td>
<td>1.402</td>
<td>506000</td>
<td>1.7</td>
</tr>
<tr>
<td>0.001</td>
<td>0.316</td>
<td>30990</td>
<td>3.97</td>
<td>30970</td>
<td>3.97</td>
</tr>
<tr>
<td>0.005</td>
<td>0.316</td>
<td>A)* 106000</td>
<td>0.828</td>
<td>21900</td>
<td>3.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B)* 22000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* There are two maxima.

Fig. 7. Effect of surfactant concentration on the disjoining pressure isotherms with $K_d = 0.316$ moles/m$^3$ and $E_d = 0.04E_{dref}$. 
isotherm to undergo a qualitative change from one containing a single maximum corresponding to the double layer force to one containing two peaks. In Fig. 7, the shorter peak at a larger film thickness is due to the electrical double layer while the steep peak to the left is due to the short range hydration force.

2.4.5 Effect of salt concentration on the disjoining pressure isotherms of ionic surfactants

The concentration of sodium chloride has the following effects: (a) it compresses the electrical double layer by raising the ionic strength, (b) it decreases the degree of dissociation of the adsorbed surfactants (see Eq. (17)) by causing increased binding of the counterions, (c) it affects the concentration of \( R^- \) ions near the interface via the surface potential and hence the surface excess (\( \Gamma \)). In experiments with single thin liquid films, it has been observed by Exerowa et al. [43] that at high salt concentrations, as the capillary pressure is increased, there is, instead of rupture, a sudden transition to very stable Newton black films. Figure 8 shows the effect of salt concentration on a system with \( c_s = 0.001 \) M. With no salt (\( c_e = 0 \)), there is just one peak corresponding to the electrical double layer. As the salt concentration is increased, however, the curve changes first to one in which there are two maxima and then to one having only a short range repulsion. This can be explained as follows: An increase in the salt concentration increases the binding of sodium ions and raises the number of dipoles on the surface. The short range repulsive force therefore increases. At the same time, the double layer is compressed. At intermediate concentrations, the double layer is not too compressed and the increased short range repulsive force gives rise to an additional strongly repulsive force at a smaller thickness. In this case, there is a jump transition when the capillary pressure is raised above the value at point A. However, at high concentrations, the electrical double layer is so compressed that \( \Pi_{DL} \) now has a range comparable to that of the short range polarization force and the two combine to give a single peaked short range repulsion. These results are in qualitative agreement with the observations of Exerowa et al., in the sense that a jump transition is observed as the salt concentration is increased. We would like to point out however that Exerowa et al. [43] observed these jump transitions only at salt concentrations above 0.165 M, much higher than those used in Fig. 8.

While the calculations here have been done for ionic surfactants, the model is applicable in principle to non-ionic surfactants with short head
groups as well. In these systems, the surface charge arises due to ion-binding rather than the dissociation of the adsorbed surfactant molecules as happens with ionic surfactants. The short range force in this case is likely to be independent of electrolyte concentration, since the surface dipole moment would be essentially unchanged by the ion binding. This could be the reason why Newton black films are formed at much lower ionic strengths with non-ionic surfactants [44]. It may be noted, however, that in case of non-ionic surfactants with large head groups, steric forces are likely to play a significant role. A brief discussion of steric forces is given below.

2.4.6 Steric repulsion

Steric forces arise when large molecules (polymers like proteins or surfactants with large head groups) are adsorbed on the film surfaces.
Depending on the interaction between the adsorbed molecules and the film liquid, the free ends of the adsorbed molecules extend a significant distance into the liquid. When the film surfaces approach each other, the entropy of these free ends decreases. This results in a repulsive osmotic pressure that increases as the chains become more confined, i.e. as the film thickness decreases. The steric interactions usually come into play when the film thickness becomes smaller than \( 2L \), where \( L \) is the mean thickness of the adsorbed layer. The value of \( L \) depends on the configuration of the chain. When the chain is fully extended, \( L \) is maximum and is given by \( L = n_s l_s \) where \( n_s \) is the number of segments and \( l_s \) is the length of each segment. The actual value of \( L \) depends on the interaction between the molecule and the film liquid. In a \( \theta \) solvent, in which there is no interaction between various segments, we have:

\[
L \approx L_0 \equiv l_s \sqrt{n_s}
\]

For low surface coverage in a \( \theta \) solvent, Dolan and Edwards [53] have derived a simple expression for the interaction energy per unit area:

\[
W(x_F) = \Gamma k_B T \left( \frac{\pi L^2_n}{6x_F^2} + 1 - \frac{1}{2} \ln \left[ \frac{3x_F^2}{8\pi L^2_n} \right] \right) \quad \text{for} \quad x_F \leq \sqrt[3]{3}L_n
\]

\[
= 2\Gamma k_B T \left( \exp \left( \frac{3x_F^2}{2L^2_n} \right) \right) \quad \text{for} \quad x_F \geq \sqrt[3]{3}L_n
\]

(34)

The force per unit area is therefore given as:

\[
\Pi_{ST} = \Gamma k_B T \left( \frac{2\pi^3 L^2_n}{3x_F^3} - \frac{2}{x_F^2} \right) \quad \text{for} \quad x_F \leq L_n \sqrt{3}
\]

\[
= 12\Gamma k_B T \left( \frac{x_F^2}{L_n^2} \right) \exp \left( -\frac{3x_F^2}{2L^2_n} \right) \quad \text{for} \quad x_F \geq L_n \sqrt{3}
\]

(35)

At high surface coverages, the adsorbed molecules form a brush. The thickness of the brush in a good solvent has been given by Alexander [54] as:

\[
L = \Gamma^{1/2} R_f^{5/2}
\]

(36)

where \( R_f = l_s n_s^{3/5} \) is the Flory radius. The repulsive pressure between two brush-bearing surfaces is given by the Alexander–de Gennes theory [55].
\[ \Pi_{ST} \approx k_BT \left[ \frac{2L}{x_F} \right]^9 - \left( \frac{x_F}{2L} \right)^{10} \] for \( x_F < 2L \) \hspace{1cm} (37)

The first term in Eq.(37) results from the osmotic repulsion while the second term arises from the elastic energy which opposes stretching. Figure 9 shows the disjoining pressure isotherm obtained using Eq. (37) for a typical surfactant with a large head group (polyoxyethylene n-dodecanol) with 12 ethoxy (CH\(_2\)-CH\(_2\)-O) groups. The volume of an ethoxy unit is approximately 63 Å\(^3\). This gives the length of each unit as approximately 0.49 nm. So we have \( n_s = 12 \) and \( l_s = 0.49 \) nm which gives \( L = 3.04 \) nm from Eq. (36). The values of the other parameters used are: \( \psi_s = 20 \) mV, \( A_h = 3.7 \times 10^{-20} \) J and \( c_{el} = 1 \) mM. It is clear that for film thicknesses smaller than \( 2L \), the steric repulsion overcomes the attractive van der Waals forces.

Fig. 9. Theoretical disjoining pressure isotherm for polyoxyethylene n-dodecanol.
This concludes our discussion of single films. The flow in individual Plateau border channels is considered next.

2.5 Flow in a Plateau border channel

As mentioned earlier, the flow of the continuous phase liquid out of a foam takes place through the Plateau border channels. The flow of liquid in a single Plateau border channel must therefore be understood before an attempt to model drainage in a foam is made. An expression for the average velocity \( u \) of the liquid in a vertical Plateau border channel has been derived for a triangular Plateau border cross-section and is given by [56]:

\[
    u = \frac{c_v a_p}{20\sqrt{3} \mu} \left( \rho_c g - \frac{\partial p}{\partial z} \right) \tag{38}
\]

In Eq. (38), \( z \) refers to the vertical space co-ordinate (see Fig. 10) which increases in the downward direction and \( g, \rho_c, \mu \) and \( p \) to the gravitational acceleration, density, viscosity and pressure in the continuous phase. \( a_p \) is the cross-sectional area of a Plateau border channel and can be computed from the radius of curvature of the walls \( (r_p) \) and the film thickness \( (x_F) \) using the expression [57]:

\[
    a_p = \frac{(0.322r_p + 1.732x_F)^2 - 2.721x_F^2}{0.644} \tag{39}
\]

Fig. 10. A plateau border channel.
The factor $c_v$ in Eq. (38) accounts for the effect of finite surface viscosity ($\eta_s$) and has been computed by Desai and Kumar [55] as a function of the inverse of the dimensionless surface viscosity ($\gamma_s = \frac{0.4387\sqrt{\alpha_p}}{\eta_s}$). It must be emphasized that their results for the calculation of $c_v$ is valid only for foams since they neglected the viscosity of the dispersed phase. Equation (38) can be used for liquid–liquid concentrated emulsions only the surfaces are immobile, i.e. when $c_v = 1$. The pressure gradient ($\partial p / \partial z$) can be computed as follows:

If $p_{\text{ref}}$ is the pressure at a position $z_{\text{ref}}$ inside a droplet/bubble, the $p_i$ at any position $z$ inside a droplet is:

$$p_i = p_{\text{ref}} + \rho_D g (z - z_{\text{ref}})$$  (40)

where $\rho_D$ is the density of the dispersed phase. Also, if $\sigma$ is the interfacial tension between the two phases, $p_i - p = \sigma / \rho_p$. Thus, if we assume that the dispersed phase is not compressed, $\rho_D$ is independent of $z$ and Eq. (38) can be rewritten as:

$$u = \frac{c_v \alpha_p}{20\sqrt{3}\mu} \left( (\rho_c - \rho_D) g + \frac{\partial}{\partial z} \left( \frac{\sigma}{r_p} \right) \right) = \frac{c_v \alpha_p}{20\sqrt{3}\mu} \left( \rho g + \frac{\partial}{\partial z} \left( \frac{\sigma}{r_p} \right) \right)$$  (41)

where $\rho = \rho_c - \rho_D$ is the density difference between the two phases. For a foam, in which the dispersed phase is a gas, $\rho_c >> \rho_D$ and $\rho = \rho_c$. The terms in the parentheses represent the driving forces due to gravity ($\rho g$) and the gradient of Plateau border suction ($\frac{\partial}{\partial z} \left( \frac{\sigma}{r_p} \right)$). These forces oppose each other when the latter is negative, i.e. when the liquid fraction is smaller at the top.

Leonard and Lemlich [57] were the first to consider the effect of surface viscosity on drainage in a Plateau border channel. Equation (38), which differs from their equation only by a constant factor however has been used more frequently because Desai and Kumar have provided a very simple equation for $c_v$. Experiments [58] on the flow of fluid in individual Plateau border channels seem to suggest that Eq. (38) appropriately describes the dependence of the velocity on the viscosity and channel dimensions. The usefulness of the factor $c_v$ in describing the effect of surface viscosity is, however, still not clear. In most of our calculations, we have assumed $c_v = 1$. For simulations that were carried
out for sodium dodecyl sulfate foams, an attempt was made to relate the surface viscosity to the surface density ($\Gamma$) of the surfactant. To our knowledge, there is no available theoretical relation between the surface viscosity ($\eta_s$) and $\Gamma$. Experimentally measured [59] values of $\eta_s$ as a function of $c_s$ and of $c_s$ as a function of $\Gamma$ are however available. We therefore combined the two sets to get a piecewise cubic polynomial fit of $\eta_s$ versus $\Gamma$. Figure 11 shows the curve obtained.

2.6. Theoretical model for the drainage and coalescence in foam

2.6.1 Conservation equation for drainage [18]

Modeling of the drainage in a foam essentially involves the formulation of the bulk conservation equations in terms of the expressions for film thinning (Eq. (4)) and Plateau border drainage (Eq. (41)). There are
two ways to approach this problem. In the microscopic approach, each Plateau border channel and film in the foam is considered separately and the liquid content in the foam at any time is computed by summing the liquid content in each Plateau border channel and film in the foam. Typically, this would involve the construction of a detailed polyhedral network in which the position and orientation of each channel and film in the foam would need to be specified. An attempt was made to formulate a microscopic model for foam drainage using Voronoi polyhedra to generate the network. In the non-degenerate case, these polyhedra possess two important structural properties seen in actual foams and concentrated emulsions: four and only four edges (Plateau border channels) meet at a point and three and only three faces (films) meet at an edge. The goal was to solve the partial differential equations arising from the mass balances for each channel with appropriate conditions at the junctions and the top and bottom of the foam. The basic balance equation in a single Plateau border channel is:

\[
\frac{\partial a_p}{\partial t} = -\frac{\partial u_y a_p}{\partial y}
\]

(42)

where \( y \) is the direction of flow and \( u_y \) is the fluid velocity in the \( y \) direction. If a channel is inclined at an angle \( \theta \) to the vertical, \( u_y \) is given by:

\[
u_y = \frac{c_o a_p}{20 \sqrt{3} \mu} \left[ \rho g \cos \theta + \frac{\partial}{\partial y} \left( \frac{\sigma}{r_p} \right) \right]
\]

(43)

Two conditions need to be satisfied at the junctions in the network:

(a) The pressure in the continuous phase is continuous at the junction. Thus, if \( r_{pi} \) and \( r_{pj} \) are the Plateau border radii of channels \( i \) and \( j \) meeting at a junction, we have:

\[
\frac{\sigma}{r_{pi}} = \frac{\sigma}{r_{pj}} \Rightarrow r_{pi} = r_{pj}
\]

(44)

Since there is no accumulation at a junction, the net volumetric flow rate of fluid into the junction is 0. Thus, we have:

\[
\sum c_i a_{pi} u_{yi} = 0
\]

(45)

The summation is over all channels meeting at the junction and \( c_i \) is a constant which takes the values +1 or -1 depending on whether the
channel is above or below the junction. A serious attempt was made to model foam drainage using this microscopic approach. However, an incredible amount of cpu time would be required to get results of any value. Instead, we decided to use the macroscopic approach in which the foam is treated as a continuous fluid. In this approach, one does not concern oneself with details of individual films and Plateau border channels. Rather, one considers the properties of infinitesimal elements of foam, with each element containing a large number of bubbles. The differential element is large enough to contain a large number of bubbles, yet small enough relative to the total volume of the foam for a continuum treatment to be valid. This approach is usually appropriate when the bubble size is much smaller than the length of the foam. Thus, in each element, we consider a mean Plateau border radius ($\bar{r}_p$), a mean film thickness ($\bar{x}_F$) and a mean bubble radius ($\bar{R}$). The ultimate goal is to obtain these quantities as a function of time and position within the foam. Since all quantities of interest such as the liquid volume fraction ($\epsilon$) can be expressed in terms of $\bar{r}_p$, $\bar{x}_F$ and $\bar{R}$, the conservation equations are formulated solely in terms of these quantities. The exact distribution of $x_F$, $r_p$ and $R$ within an element is important only to the extent that it is required to compute these mean quantities. The Plateau border radius $r_p$ can be assumed to be uniform within a volume element because of the tendency of the capillary pressure ($\sigma/r_p$) to equalize due to the flow of liquid from the thicker to thinner channels. This is because the pressure ($p_i - \frac{\sigma}{r_p}$) will be smaller in channels with smaller $r_p$ and liquid will flow from regions of higher pressure (larger $r_p$) to regions of lower pressure (smaller $r_p$). Thus, a “local” equilibrium of the capillary pressure is established in a very short time and one can assume $r_p = \bar{r}_p$. However, the film thickness is not necessarily uniform. Even in a monodisperse foam, the faces of the polyhedral bubbles are not identical [27] and there is a non-uniformity in the film areas ($A_F = \pi R_F^2$). This causes a non-uniformity of film thicknesses because the rate of film thinning depends on $R_F$ (see Eq. (4)). For a given capillary pressure ($\sigma/r_p$), films with smaller $R_F$ drain faster and are therefore thinner. Thus, if $R_{F_{\text{min}}} \leq R_F \leq R_{F_{\text{max}}}$ and $\int dR_F$ is the fraction of films in the element that have radii between $R_F$ and $R_F + dR_F$, the mean film thickness ($\bar{x}_F$) and the mean film area ($\bar{A}_F$) are given by
In an initially monodispersed foam, the bubble size is uniform within an element, i.e. all bubbles within the element have the same radius \( R \) and \( \bar{R} = R \). However, once films start rupturing, coalescence starts and gives rise to a size distribution within the element, i.e. \( \bar{R} \neq R \). The mean bubble radius \( \bar{R} \) increases because neighboring bubbles coalesce to form a larger bubble. The rate at which \( \bar{R} \) increases with time, which in turn depends on the number of films rupturing per unit time and hence depends on the distribution of film areas. This relationship will be discussed after we formulate the conservation equation equations in terms of the mean quantities.

It must be emphasized here that we ignore the increase in the bubble size due to Ostwald ripening, which occurs due to the diffusion of gas from smaller to larger bubbles. In monodisperse foams containing gases like nitrogen, which are sparingly soluble in water, the time scale for Ostwald ripening is likely to be much larger than that for drainage and collapse, so that foam decay can be said to occur in two stages. In the first stage, drainage, coalescence and collapse is dominant, while in the second stage, Ostwald ripening dominates. We consider only the first stage. Ostwald ripening for steady state foams has been considered by Narsimhan and Ruckenstein [61].

Figure 12 shows a schematic of a foam when it is freshly formed (a) and when some decay has taken place (b). The space coordinate \( z \) increases in the downward direction and \( z_1 \) and \( z_2 \) represent the upper and lower boundaries of the foam respectively. The origin \( (z = 0) \) defines the upper boundary of the entire system. In other words, all the gas entering the foam lies between the reference plane \( (z = 0) \) and the foam/liquid interface \( (z = z_2) \). Before collapse, all the gas lies within the foam and \( z_1 = 0 \) (see Fig. 12a). After collapse starts, the foam/gas interface moves down as gas is released from the bubbles at the top due to film rupture and \( z_1 > 0 \) (see Fig. 12b). The gas released from the ruptured bubbles lies between \( z = 0 \) and \( z = z_1 \). The foam volume decreases due to the loss of liquid and the lower boundary of the foam moves up as the drainage occurs and \( z_2 \) decreases with time. It is to be noted that since wall effects are neglected, all quantities are functions of vertical position \( z \) only.

Some variables relevant to the macroscopic approach need to be defined [60,61] before we proceed to formulate the conservation equations.

\[
\bar{x}_F = \int_{R_{fin}}^{R_{f_{\text{max}}}} x_F f dR_F; \quad \bar{A}_F = \int_{R_{fin}}^{R_{f_{\text{max}}}} A_F f dR_F = \int_{R_{fin}}^{R_{f_{\text{max}}}} \pi R_F^2 f dR_F
\]  
(46)
As mentioned earlier, we deal with groups of bubbles rather than individual bubbles. Consider a volume element of foam at a level \( z \). Let \( \varepsilon \) be the volume fraction of liquid in this element. The volume fraction of gas is then \( 1 - \varepsilon \). If \( V \) is the mean bubble volume in this element, the number of bubbles per unit volume \( (N) \) in this element is given by:

\[
N = \frac{1 - \varepsilon}{V} \tag{47}
\]

Let \( n_F \) be the average number of films per bubble. The total number of films per unit volume is then \( Nn_F \) and the amount of liquid in the films per unit volume is \( \frac{R_{F_{\text{max}}}}{f A_{F \alpha F} dR} = Nn_F A_{F \alpha F} \). Similarly, if \( n_p \) is the average number of Plateau border channels per bubble, the total number of Plateau border channels per unit volume is \( Nn_p \) and the amount of liquid in the Plateau border channels per unit volume is \( Nn_p a_p I \) where \( a_p \) is the cross-sectional area of a Plateau border channel in this element and \( I \) is the mean length of a Plateau border channel. We assume that in spite of coalescence, the bubbles maintain their pentagonal dodecahedral geometry and that the geometrical relationships valid for a single bubble are valid for mean values as well. Thus we have:

\[
I = 0.816 \frac{R}{\sqrt[3]{V}} = 0.816 \left( \frac{3}{4\pi} \frac{V}{V} \right)^{1/3} \tag{48}
\]
The values of \( n_F \) and \( n_p \) follow from the fact that there are 12 films and 30 channels in a pentagonal dodecahedral bubble. Since, each film is shared by two bubbles and each Plateau border channel is shared by three bubbles, we have \( n_F = 6, n_p = 10 \). The liquid volume fraction is given by the sum of liquid per unit volume in the Plateau border channels and the liquid per unit volume in the films as:

\[
\varepsilon = N n_p a_p \overline{I} + N n_F \overline{A_F x_F} 
\]

(49)

Combining Eqs. (47) and (49), \( \varepsilon \) can be expressed as:

\[
\varepsilon = \frac{n_p a_p \overline{I} + n_F \overline{A_F x_F}}{V + n_p a_p \overline{I} + n_F \overline{A_F x_F}}
\]

(50)

Each of the variables \( \overline{I}, \overline{A_F x_F}, V \) and \( a_p \) are functions of time and vertical position \( z \).

The variation of \( \varepsilon \) in any volume element with time depends on the net rate at which liquid flows into the volume element. Hence, the volumetric flux of liquid at each \( z \) is required in order to formulate the bulk conservation equations. This will be considered next.

**Calculation of the volumetric flux of liquid**

Liquid flow in a foam takes place in two ways. Firstly, there is gravity drainage through the Plateau border channels. In addition, as the foam becomes drier, there is a net upward movement of bubbles as the volume of the foam decreases (\( z_2 \) decreases) due to the outflow of liquid from the foam. As these bubbles move, they carry with them the liquid in the associated films and Plateau border channels. Thus, an upward convective flow of liquid due to bubble movement is superimposed on the downward gravity-driven flow through the Plateau border channels. We will discuss each of these components of the flux below:

**Gravity drainage through the Plateau border channels** [14]

The flow rate of liquid across any horizontal plane in a foam is given by the sum of the flow rates through all the Plateau border channels that intersect the plane. The flow rate through a Plateau border channel with cross-sectional area \( a_p \) will depend on its orientation. It is highest in a vertical channel and lowest in a horizontal channel. Consider a Plateau border channel inclined at an angle \( \theta \) with the vertical. The average velocity of liquid in this channel is given by:
\[ u_\theta = \frac{c_v a_p}{20\sqrt{3} \mu} \left[ \rho g \cos \theta + \sigma \frac{d}{dz} \left( \frac{1}{r_p} \right) \right] \] 

Comparing Eq. (51) with Eq. (41), we get:

\[ u_\theta = \cos \theta \left[ \frac{c_v a_p}{20\sqrt{3} \mu} \left( \rho g + \sigma \frac{d}{dz} \left( \frac{1}{r_p} \right) \right) \right] = u \cos \theta \]

thus the volumetric flow rate of liquid through this channel is given by:

\[ q_\theta = u_\theta a_p = u a_p \cos \theta \]

If we assume that the Plateau border channels are oriented randomly, the probability that a channel is oriented between \( \theta \) and \( \theta + d\theta \) is \( \sin(\theta)d\theta \) and the average volumetric flow rate per channel is given by:

\[ \bar{q} = \int_0^{\pi/2} q_\theta \sin(\theta) \, d\theta = \frac{u a_p}{2} \]

The total volumetric flux through the Plateau border channels across the plane is therefore given as

\[ q_{PB} = \text{(number of PB channels per bubble intersected by a horizontal plane)} \times \text{(number of bubbles intersected by the horizontal plane per unit area)} \times \text{(mean flow rate through a PB channel)} \]

For a pentagonal dodecahedral bubble, the number of Plateau border channels per bubble intersected by a horizontal plane is \( n_p/5 \). The number of bubbles intersected by a horizontal plane can be obtained as shown below using a technique common in dealing with the flow of fluids in porous media [60,61].

Let \( F(R) \, dR \) be the fractional number of bubbles with radii between \( R \) and \( R + dR \). The number of bubbles with centers at a distance between \( X \) and \( X + dX \) from the plane is \( 2N A F(R) \, dR \, dX \), where \( A \) is the cross-sectional area of the foam. Only those bubbles whose centers are at a distance smaller than their radii (\( X < R \)) will intersect the plane. Therefore, the number of bubbles of radius \( R \) which intersect the plane is

\[ \int_{X=0}^{X=R} 2NF(R) \, dR \, dX = 2NF(R) \, dR \]
where the factor 2 arises due to the fact that bubbles on both sides of the plane are considered. The total number of spheres per unit area intersected by the plane is then given as

\[
R_{\rightarrow 0} \int_{R=0}^{R=\infty} 2NRF(R)dR = 2NR
\]

and the flux of liquid due to gravity drainage through the Plateau border channels is therefore:

\[
q_{PB} = 2NR \left( \frac{n_p}{5} \right) \bar{q} = \frac{3}{15} NRn_p a_p \mu
\]  

(55)

**Calculation of the convective flux**

As mentioned earlier, drainage of the liquid causes a decrease in the foam volume, which leads to an upward movement of the bubbles. We need to know the rate at which the liquid associated with the bubbles moves up. Let \( q_G \) be the volumetric flux of gas due to the convection of the bubbles. The number of bubbles moving per unit area per unit time is then given by \( q_G \sqrt{V} \). Since the amount of liquid per bubble is \( \varepsilon/N \), the rate (\( q_c \)) at which the liquid is convected along with the bubbles (\( q_c \)) is given as:

\[
q_c = \text{Number of bubbles moving up per unit area per unit time} \times \text{Volume of liquid associated with each bubble}
\]

\[
= \frac{q_G \varepsilon}{\sqrt{V} N} = q_G \frac{\varepsilon}{1 - \varepsilon}
\]

The total flow rate of liquid per unit area per unit time (\( q_L \)) is obtained by summing the contribution due to the Plateau border drainage (\( q_{PB} \)) and the convection due to bubble movement (\( q_c \)) and is given as:

\[
q_L = q_{PB} + q_c = q_{PB} + q_G \left( \frac{\varepsilon}{1 - \varepsilon} \right)
\]  

(57)

However, we still do not know \( q_G \). When the foam drains, the convective motion of the bubbles occurs in the upward direction as the foam volume decreases, i.e. \( q_G \) is negative. Also, since this movement occurs due to drainage in the Plateau border channels, it is natural to expect \( q_G \) to be related to \( q_{PB} \). The relation between these two quantities is derived as follows.
Since the rate of accumulation of liquid in a volume element equals the net flow rate into the volume element, the conservation equation for the liquid is:

\[
\frac{\partial \varepsilon}{\partial t} = -\frac{\partial q_L}{\partial z}
\]

(58)

If the dispersed gas phase is assumed to be incompressible, a similar conservation equation can be written for the gas phase as:

\[
\frac{\partial}{\partial t} (1 - \varepsilon) = -\frac{\partial q_G}{\partial z}
\]

(59)

i.e.

\[
\frac{\partial \varepsilon}{\partial t} = \frac{\partial q_G}{\partial z}
\]

(60)

Comparing Eq. (58) and Eq. (60) we have:

\[-q_L = q_G
\]

(61)

Combining Eqs. (56) and (60), \(q_L\) and \(q_G\) can be expressed in terms of \(q_{PB}\) as:

\[
q_G = -(1 - \varepsilon)q_{PB}
\]

(62)

\[
q_L = (1 - \varepsilon)q_{PB}
\]

(63)

Thus, the total flux \(q_L\) is smaller than the flux \(q_{PB}\) due to Plateau border drainage alone because bubble convection moves some liquid upward.

Equation (58) can therefore be rewritten as:

\[
\frac{\partial \varepsilon}{\partial t} = -\frac{\partial (1 - \varepsilon)q_{PB}}{\partial z}
\]

(64)

Equation (64) is the conservation equation for the liquid in which the quantities \(\varepsilon\) and \(q_{PB}\) can be expressed in terms of \(r_p\), \(A_p\) and \(R\) using Eq. (48), Eq. (49) and Eq. (50). It is to be noted that Eq. (64) is valid whether coalescence occurs or not. Coalescence occurring in a volume element does not by itself change the amount of liquid in the element.
It only causes a redistribution of liquid from the ruptured films and Plateau border channels to the remaining Plateau border channels within the element. The change in the amount of liquid in the element occurs only due to drainage. The effect of coalescence is felt through $\overline{R}$. When coalescence occurs, the local $\overline{R}$ increases. The expressions for the change in $\overline{R}$ due to coalescence are derived later.

The two boundary conditions required for Eq. (64) are presented next.

**Boundary conditions**

When the foam is collapsing, i.e. when $\frac{dz_1}{dt} > 0$, the liquid released from the collapsed bubbles reenters the foam. The amount of liquid released depends on the rate of foam collapse ($\frac{dz_1}{dt}$). Equating the rate at which liquid is released from the collapsed bubbles ($\varepsilon \frac{dz_1}{dt} \big|_{z_1}$) to the flow rate of liquid at the foam gas interface ($q_L \big|_{z_1}$) gives the boundary condition at the foam/gas interface ($z = z_1$):

$$ q_L \big|_{z_1} = \varepsilon \frac{dz_1}{dt} \big|_{z_1} $$ (65)

The other boundary condition follows from the fact that the bubbles are spherical at the foam/liquid interface:

$$ r_p \big|_{z_2} = \overline{R} \big|_{z_2} $$ (66)

Since coalescence never occurs at the foam/liquid interface, $\overline{R} \big|_{z_2} = R_0$, where $R_0$ is the radius of a bubble in the freshly formed monodisperse foam.

It may be noted that the effect of bubble convection was ignored in our earlier papers [14–17]. While this does not affect the computed liquid profiles much, it cannot be ignored when the conservation equations for the surfactant are formulated, since bubble convection produces a significant movement of the surface area and hence of the adsorbed surfactant. The balance equations for the surfactant are considered next.
2.6.2 Conservation equations for surfactant

Part of the surfactant in the foam is present in dissolved form in the liquid in the films and Plateau border channels while the rest is adsorbed on the film surfaces. Thus, the amount of surfactant per unit volume of the foam is given by \( \varepsilon c_s + (2Nn_F \Gamma A_F) \), where the first term \( \varepsilon c_s \) represents the surfactant dissolved in the liquid contained in the films and the Plateau border channels and the second term corresponds to the adsorbed surfactant on the film surfaces. The term

\[
\frac{R_{F \max}}{2n_F \Gamma A_F} = \int f \Gamma A_F dR_F
\]

is the mean value of the surfactant adsorbed on the surface of a film. The mass flux of the surfactant contains three contributions:

(a) from the flow of liquid in the Plateau border channels \( (q_{Lc_s}) \);

(b) from the dispersion \( -\varepsilon D \frac{\partial c_s}{\partial z} \) where \( D \) is the apparent diffusivity;

(c) from the movement of the adsorbed surfactant due to the convection of bubbles \( \left( \frac{q_G}{\Gamma} 2n_F \Gamma A_F \right) \) where \( \frac{q_G}{\Gamma} \) is the number of bubbles per unit area per unit time moving in the downward direction and \( 2n_F \Gamma A_F \) is the surfactant adsorbed per bubble.

It must be emphasized that \( D \) is different from the molecular diffusivity and depends on the degree of local mixing. \( D \) is actually different in different portions of the foam. We have, however, assumed \( D \) to be constant in order to avoid complexity. The net flux of surfactant \( (q_{cs}) \) is then given as:

\[
q_{cs} = q_{Lc_s} = \varepsilon D \frac{\partial c_s}{\partial z} + \frac{q_G}{\Gamma} (2n_F \Gamma A_F) = q_{Lc_s} - \varepsilon D \frac{\partial c_s}{\partial z} - \frac{q_L}{\Gamma} (2n_F \Gamma A_F)
\]  

(67)

and the conservation equation for the surfactant can be written as:

\[
\frac{\partial}{\partial t} (\varepsilon c_s + 2Nn_F \Gamma A_F) = -\frac{\partial q_{cs}}{\partial z} = -\frac{\partial}{\partial z} \left[ q_{Lc_s} - \varepsilon D \frac{\partial c_s}{\partial z} - \frac{q_L}{\Gamma} (2n_F \Gamma A_F) \right]
\]  

(68)

This equation is also second order in space and we need two boundary conditions for the surfactant concentration \( c_s \).
Boundary conditions for surfactant

Before collapse starts, there is no surfactant entering the system at the top. In other words, the surfactant flux at the foam/gas interface \((z = z_1)\) is 0. The boundary condition at the top before collapse is therefore:

\[
q_{cs} \bigg|_{z_1} = q_{LCs} - \varepsilon D \frac{\partial c_s}{\partial z} - \frac{q_L}{V} \left(2n_P\overline{\Gamma F}\right) \bigg|_{z_1} = 0
\]  

(69)

Now, since from Eq. (65), \(q_L \big|_{z_1} \) is 0 before collapse starts, Eq. (69) becomes:

\[
\frac{\partial c_s}{\partial z} \bigg|_{z_1} = 0
\]  

(70)

On the other hand, once collapse starts, the surfactant in the collapsed bubbles is released into the foam. If \(A\) is the cross-sectional area of the foam, the number of bubbles collapsing when the front moves with a velocity \(\frac{dz_1}{dt} = \frac{A}{V} \frac{dz_1}{dt}\). Also, the surfactant associated with a bubble includes the amount adsorbed on the film surfaces and that dissolved in the liquid in the films and Plateau border channels and is given by \((n_p\alpha_p\overline{I} + n_P\overline{A_Fx_F})c_s + 2n_P\overline{\Gamma F}\big|_{z_1}\). Thus, the flux of surfactant into the system due to collapse is given by:

\[
\text{(number of bubbles collapsing per unit area per unit time)} \times \text{(amount of surfactant per bubble)} = \frac{1}{V \big|_{z_1} dt} \left[(n_p\alpha_p\overline{I} + n_P\overline{A_Fx_F})c_s + 2n_P\overline{\Gamma F}\right]_{z_1}
\]

Equating this to the flux of surfactant at the foam/gas interface from Eq. (67), we get the boundary condition:

\[
-\varepsilon D \frac{\partial c_s}{\partial z} \bigg|_{z_1} + \left[q_{LCs} - \frac{q_L}{V} \left(2n_P\overline{\Gamma F}\right) \right]_{z_1} = \frac{1}{V \big|_{z_1} dt} \left[(n_p\alpha_p\overline{I} + n_P\overline{A_Fx_F})c_s + 2n_P\overline{\Gamma F}\right]_{z_1}
\]  

(71)

Using Eq. (65) to eliminate \(\frac{dz_1}{dt}\) and simplifying we get:
\[
\varepsilon D \frac{\partial c_s}{\partial z} \bigg|_{z_1} + q_L \left[ \frac{\varepsilon}{1 - \varepsilon} c_s + \frac{1 + \varepsilon}{V \varepsilon} \left( 2n_F \bar{A}_F \right) \right] \bigg|_{z_1} = 0
\] (72)

The other boundary condition is obtained from the fact that at the foam/liquid interface, the concentration is that of the original foaming solution \((c_{s0})\)

\[
c_s \bigg|_{z_2} = c_{s0}
\] (73)

The basic conservation equations for the continuous phase liquid and the surfactant have now been formulated. However, several additional details are required to specify the system completely. Expressions are needed for the movement of the boundaries \(z_1\) and \(z_2\). Furthermore, the mean values \(\bar{F}, \bar{A}_F\) and \(R\) depend on the degree of coalescence. We shall first discuss coalescence and then formulate expressions for the movement of the boundaries.

### 2.6.3 Coalescence [18]

When a film ruptures within a foam, the bubbles sharing the film coalesce. Coalescence results in a decrease in the number of bubbles in the element and an increase in the mean bubble volume in the element. The assumption made in our model is that coalescence within any volume element in the foam occurs because the faces (films) of the polyhedral bubbles are not identical. Since the films differ in size \((R_F)\), they drain at different rates (see Eq. (4)) and rupture at different points in time. The film radii \((R_F)\) are assumed to lie between two limiting values \(R_{Fmin}\) and \(R_{Fmax}\) and the distribution of \(R_F\) about a mean value \(R_{F0} = 0.606R_0\) within these limits is assumed to be given by the function

\[
\bar{f} = \frac{\exp \left[ -\left( \frac{R_F - R_{F0}}{2s} \right)^2 \right]}{\int_{R_{Fmin}}^{R_{Fmax}} \exp \left[ -\left( \frac{R_F - R_{F0}}{2s} \right)^2 \right] dR_F}
\] (74)

Note that \(\int \bar{f} dR_F = 1\). Thus, \(\bar{f} dR_F\) is the fraction of the films in the \(R_{Fmin}\) element that have radii between \(R_F\) and \(R_F + dR_F\). It must be mentioned
that this does not imply a variation in bubble volumes. The foam is assumed to be initially monodispersed, i.e. all the bubbles have the same volume. A bubble size distribution arises only after coalescence starts.

It is clear from Eq. (4) that, since all the films are subjected to the same capillary pressure \( (r_p = r_p') \), films with smaller \( R_F \) will drain faster and hence will rupture earlier. Thus, if we monitor a freshly formed group of films in a certain volume element, films with the smallest \( R_F \) will rupture first, followed by films that are slightly larger and so on until all the films at this level have either ruptured or have stopped draining.

Before coalescence starts, \( R_{F_{\text{min}}} \) is constant and equal to \( R_{F_{\text{min}0}} \) (the value of \( R_{F_{\text{min}}} \) in freshly formed foam; an input parameter). The distribution in any volume element in the foam before coalescence starts is therefore the same as that when the foam is just formed and is given by

\[
f_0 = f|_{t=0} = \frac{\exp \left[ \left( \frac{R_F - R_{F_0}}{2s} \right)^2 \right]}{\int_{R_{F_{\text{min}}}}^{R_{F_{\text{max}}}} \exp \left[ -\left( \frac{R_F - R_{F_0}}{2s} \right)^2 \right] dR_F}
\]

Once coalescence starts, however, the value of \( R_{F_{\text{min}}} \) in an element is not a constant and increases as coalescence proceeds (see Fig. 13). As \( R_{F_{\text{min}}} \) increases, the number of bubbles decreases and the mean bubble volume \( (\bar{V}) \) increases. At the same time, liquid and surfactant from the ruptured films are distributed among the remaining Plateau border channels. It may be noted that we assume \( R_{F_{\text{max}}} \) to be a constant. This is not strictly true. It is possible that geometrical rearrangements occurring during coalescence will give rise to films larger than \( R_{F_{\text{max}}} \). It may also be noted that \( f \) and \( R_{F_{\text{min}}} \) and hence the mean bubble volume are functions of only the vertical position \( (z) \) and time \( (t) \). This is because, if wall effects are neglected, the capillary pressure \( (\sigma/r_p) \) at a given level \( (z) \) is independent of the radial position and any volume element at a given level will have the same distribution of film radii. On the other hand, at any time \( t \) and at each \( z \), we need to know the film thickness \( x_F \) corresponding to each \( R_F \) so that we can determine when coalescence starts at each level and how quickly coalescence proceeds. Thus we need to compute \( x_F \) as a function of three variables, viz. \( t \), \( z \) and \( R_F \) using Eq. (4). This is a moving boundary problem, since one of the boundaries in \( R_F \) space \( (R_F = R_{F_{\text{min}}}) \) moves when coalescence starts and both boundaries
Fig. 13. The distribution $f$ of $R_E$ before and after coalescence.

in $z$ space ($z = z_1$ and $z = z_2$) move when foam collapse starts. The computation is simplified considerably if the various boundaries are immobilized by carrying out a transformation from $t, R_F, z$ space to $t, r, \xi$ space where:

$$\xi = \frac{z - z_1}{z_2 - z_1}, \quad r = \frac{R_F - R_{F\text{min}}}{R_{F\text{max}} - R_{F\text{min}}}$$

With this transformation, the variables $\xi$ and $r$ lie between 0 and 1 and the Reynolds equation (Eq. (4)) can be written in $t, r, \xi$ space as:

$$\frac{dx_F}{dt} \bigg|_{R_{p,z}} = -V_f = \frac{\partial x_F}{\partial t} \bigg|_{r,\xi} + \frac{\partial x_F}{\partial r} \bigg|_{t,\xi} \frac{dr}{dt} \bigg|_{R_{p,z}} + \frac{\partial x_F}{\partial \xi} \bigg|_{t,r} \frac{d\xi}{dt} \bigg|_{R_{p,z}}$$

where:

$$\frac{d\xi}{dt} \bigg|_{R_{p,z}} = \frac{1}{z_2 - z_1} \left[ (\xi - 1) \frac{dz_1}{dt} - \xi \frac{dz_2}{dt} \right]$$
\[ \frac{dr}{dt} \bigg|_{R_F} = \frac{(r - 1)}{(R_{F_{\text{max}}} - R_{F_{\text{min}}})} \frac{dR_{F_{\text{min}}}}{dt} \bigg|_{z} = \frac{(r - 1)}{(R_{F_{\text{max}}} - R_{F_{\text{min}}})} \left[ \frac{\partial R_{F_{\text{min}}}}{\partial t} \bigg|_{z} + \frac{\partial R_{F_{\text{min}}}}{\partial \xi} \frac{d\xi}{dt} \right] \]

Using Eqs. (78) and (79), Eq. (77) becomes:

\[ -V_f = \frac{\partial x_F}{\partial t} \bigg|_{r, \xi} + b_1 \frac{\partial R_{F_{\text{min}}}}{\partial t} \bigg|_{z} + b_2 \frac{dz_1}{dt} + b_3 \frac{dz_2}{dt} \]

where

\[ b_1 = \frac{\partial x_F}{\partial r} \frac{(r - 1)}{(R_{F_{\text{max}}} - R_{F_{\text{min}}})} \]

\[ b_2 = \frac{\xi - 1}{z_2 - z_1} \left[ \frac{\partial x_F}{\partial \xi} + \frac{(r - 1)}{(R_{F_{\text{max}}} - R_{F_{\text{min}}})} \frac{\partial R_{F_{\text{min}}}}{\partial \xi} \right] \]

and

\[ b_3 = \frac{-\xi}{z_2 - z_1} \left[ \frac{\partial x_F}{\partial \xi} + \frac{(r - 1)}{(R_{F_{\text{max}}} - R_{F_{\text{min}}})} \frac{\partial R_{F_{\text{min}}}}{\partial \xi} \right] \]

In order to specify the system completely, expressions for the rate of movement of the various boundaries (\(z_1\) and \(z_2\) in \(z\) space and \(R_{F_{\text{min}}}\) in \(R_F\) space) are required. The expression for \(dR_{F_{\text{min}}}/dt\) is derived below.

**Expression for \(dR_{F_{\text{min}}}/dt\)**

Before coalescence starts, the value of \(R_{F_{\text{min}}}\) is constant throughout the foam and is given by \(R_{F_{\text{min}0}}\) which is an input parameter. Coalescence begins at a given \(z\) when the thinnest films at that \(z\) (those with \(R_F = R_{F_{\text{min}0}}\)) become critical \((x_F = x_{Fc})\) and rupture. Once this happens, \(R_{F_{\text{min}}}\) starts increasing. Since the capillary pressure and the disjoining pressure isotherm are different in different parts of the foam, the degree of coalescence and hence the value of \(R_{F_{\text{min}}}\) will be different in different portions of the foam. Thus \(R_{F_{\text{min}}}\) is a function of time \(t\) and vertical position \(z\). As long as coalescence occurs, \(R_{F_{\text{min}}}\) increases and the rate of increase is obtained by recognizing that \(x_F\big|_{z,R_{F_{\text{min}}}}\), i.e. \(x_F\big|_{\xi, \tau=0}\) always corresponds to the critical thickness \((x_{Fc})\) which in turn is a function of the surfactant concentration \((c_s)\) at that \(\xi\). Thus coalescence at a given \(\xi\) is characterized by the following conditions.
\[ x_F \bigg|_{\xi, r=0} = x_{F_c} \bigg|_{\xi} \]  \hspace{1cm} (84)

i.e.

\[ -V_f \bigg|_{r=0, \xi} = -V_f \bigg|_{x_{F_c}(c_s \xi)} \]  \hspace{1cm} (85)

Differentiating Eq. (84) with respect to time, we get

\[ \frac{\partial x_F}{\partial t} \bigg|_{\xi, r=0} = \frac{\partial x_{F_c}}{\partial t} \bigg|_{\xi} = \frac{\partial x_{F_c}}{\partial c_s} \frac{\partial c_s}{\partial t} \bigg|_{\xi} \]  \hspace{1cm} (86)

Combining Eq. (86) with Eq. (80) for \( r = 0 \), we get

\[ -V_f \bigg|_{r=0, \xi} = -V_f \bigg|_{x_{F_c}(c_s \xi)} = \frac{\partial x_{F_c}}{\partial c_s} \frac{\partial c_s}{\partial t} \bigg|_{\xi} + b_1 \bigg|_{r=0, \xi} \frac{\partial R_{F_{\text{min}}}}{\partial t} \bigg|_{\xi} \]

\[ + b_2 \bigg|_{r=0, \xi} \frac{dz_1}{dt} + b_3 \bigg|_{r=0, \xi} \frac{dz_2}{dt} \]  \hspace{1cm} (87)

which can be rewritten as:

\[ \frac{dR_{F_{\text{min}}}}{dt} \bigg|_{\xi} = \frac{-V_f \bigg|_{x_{F_c}(c_s \xi)}}{-b_1 \bigg|_{r=0, \xi}} - \frac{\partial x_{F_c}}{\partial c_s} \frac{\partial c_s}{\partial t} \bigg|_{\xi} - b_2 \bigg|_{r=0, \xi} \frac{dz_1}{dt} - b_3 \bigg|_{r=0, \xi} \frac{dz_2}{dt} \]  \hspace{1cm} (88)

Before we proceed further, some features of Eq. (88) need to be noted. The rate \( \left( \frac{dR_{F_{\text{min}}}}{dt} \right) \) at which coalescence proceeds at any level depends strongly on the film velocity \( (V_f) \) corresponding to the critical thickness \( (x_{F_c}) \) at that level. Since \( b_1 < 0 \), \( dR_{F_{\text{min}}}/dt \) increases as the film velocity corresponding to the critical thickness increases. On the other hand, since \( \frac{dx_{F_c}}{dc_s} < 0 \), the coalescence rate will decrease if the local surfactant concentration increases, i.e. if \( \frac{dc_s}{dt} > 0 \).

As mentioned earlier, coalescence gives rise to a bubble size distribution in an initially monodispersed foam. The number of bubbles decreases and the mean bubble volume increases. Owing to the complexity involved in computing the evolution of the bubble size distribution, we
restrict our treatment to the calculation of the mean bubble volume $V$ which is required in the formulation of the bulk conservation equations. This is considered next.

**Calculation of the mean bubble volume**

Before coalescence begins, $V$ is the same throughout the foam and equal to the volume of the bubble as it is first formed ($V_0 = \frac{4}{3} \pi R_0^3$). As coalescence starts, i.e. as $R_{F_{\min}}$ starts increasing, $V$ increases because the rupture of a film causes coalescence of the neighboring bubbles that share the film and the same volume of gas is distributed among a smaller number of bubbles. Consider a certain volume element. If $f_0$ is the distribution of film radii in this element before coalescence starts (see Eq. (75)), the following relationship is always satisfied:

Number of films in the element at any time $t = (\text{Initial number of } R_{F_{\max}}\text{ films in the element}) \times \int_{R_{F_{\min}(t)}}^{R_{F_{\max}}} f_0 dR_F \quad (89)$

It may be noted that

$$\int_{R_{F_{\min}(t=0)}}^{R_{F_{\max}}} f_0 dR_F = 1$$

and $f_0$ is only a function of $R_F$ and is independent of time. As films rupture and disappear, $R_{F_{\min}(t)}$ increases and

$$\int_{R_{F_{\min}(t)}}^{R_{F_{\max}}} f_0 dR_F$$

decreases (see Fig. 14). Since the number of bubbles in this element is proportional to the number of films, we have from Eq. (89):

Number of bubbles in the element at any time $t =$

$$\text{Initial number of bubbles in the element} \times \int_{R_{F_{\min}(t)}}^{R_{F_{\max}}} f_0 dR_F \quad (90)$$
Fig. 14. The area under the $f_0$ curve is proportional to the degree of coalescence.
Mean bubble volume in element = \( \frac{\text{Volume of gas in element}}{\text{Number of bubbles in element}} \)  \( (91) \)

Now since the volume of gas in this element remains unchanged, the mean bubble volume in the element at any time is inversely proportional to the number of bubbles in the element. In other words:

\[
\frac{\text{Number of bubbles in element before coalescence}}{\text{Number of bubbles in element after coalescence}} = \frac{\text{Mean bubble volume after coalescence}}{\text{Initial bubble volume}}
\]  \( (92) \)

Thus we have:

\[
\frac{V(t)}{V(t = 0)} = \frac{\int f_0 dR_F}{\int f_0 dR_F} = \frac{1}{\int f_0 dR_F} = \frac{R_{Fmax}}{R_{Fmax}}
\]  \( (93) \)

All the equations dealing with coalescence have now been formulated. Expressions for the movement of the two foam boundaries (\( z_1 \) and \( z_2 \)) are presented next.

2.6.4 Movement of the foam/gas interface

When \( R_{Fmin} \) at any \( z \) becomes equal to \( R_{Fmax} \), all the films at this \( z \) are critical and rupture simultaneously. When this happens at the foam/gas interface (\( z = z_1 \)), all the bubbles at the top of the foam collapse and the interface moves downward i.e. \( z_1 \) starts increasing. In other words, the boundary starts moving when the distribution function \( f \) at the top becomes a Dirac-delta function. The moving interface is, therefore, always characterized by \( R_{Fmin} = R_{Fmax} \) = constant, i.e.

\[
\frac{\partial R_{Fmin}}{\partial t} \bigg|_{\xi=0} = 0
\]

Using this condition in Eq. (88) with \( \xi = 0 \), we get:
\[
0 = \frac{-V_f \frac{dx_{Fc}}{dc_s} \frac{dc_s}{dt} \bigg|_{\xi=0} - b_2 \frac{dz_1}{dt} - b_3 \frac{dz_2}{dt}}{b_1 \bigg|_{r=0, \xi=0}}
\]

Since \( b_3 \big|_{\xi=0} \), Eq. (94) can be rewritten as:

\[
\frac{dz_1}{dt} = \frac{-V_f \bigg|_{x_{Fc}(c_s, z=0)} - \frac{dx_{Fc}}{dc_s} \frac{dc_s}{dt} \bigg|_{\xi=0}}{b_2 \bigg|_{r=0, \xi=0}}
\]  

(95)

Since it is not possible numerically to deal with the Dirac delta function, collapse was deemed to occur when the distribution was narrow enough, i.e. when \( R_{F_{min}} \) became equal to \( R_{Fc} \) where \( R_{Fc} \) is slightly smaller than \( R_{F_{max}} \) and is given by \( R_{Fc} = R_{F_{max}}/1.001 \).

It may be noted that when the critical thickness \( (x_{Fc}) \) is independent of the surfactant concentration, as is probably the case with non ionic surfactants, Eq. (95) reduces to:

\[
\frac{dz_1}{dt} = \frac{-V_f \big|_{x_{Fc}}}{{b_2} \bigg|_{r=0, \xi=0}}
\]

(96)

Furthermore, if there is no variation in film area, the terms involved with \( R_F \) space disappear from the above equations and we have:

\[
\frac{dz_1}{dt} = \frac{-V_f \big|_{x_{Fc}}}{z_2 - z_1 \frac{d x_F}{d \xi} \bigg|_{\xi=0}}
\]

(97)

Equation (97) was used in our earlier papers [16,17] in which coalescence was ignored.

2.6.5 Movement of the foam/liquid interface

The foam/liquid interface moves up \( (z_2 \) decreases) as liquid drains out of the foam at the bottom. This upward movement occurs because the volume of the foam decreases as liquid leaves the foam. Thus, the rate at which this interface moves up is equal to the rate at which the height of the liquid pool at the bottom increases, which in turn depends on the flow rate of liquid through the Plateau border channels at the bottom. Therefore, if \( A \) is the cross-sectional area of the foam:
The system is now completely specified and with the appropriate initial conditions, the conservation equations can be solved with equations for the change of $R$, $R_{Fmin}$, $z_1$ and $z_2$. Before we proceed with the formulation of the initial conditions and the solution of the differential equations, we will briefly discuss the phenomenon of drainage equilibrium.

2.7 Drainage equilibrium

It has been experimentally observed that a draining foam usually arrives at a metastable mechanical equilibrium in which all processes associated with drainage come to a halt. This equilibrium is characterized by the following properties:

(1) There is no flow in the Plateau border channels, i.e. $u = 0$ throughout the foam. This happens when the gradient in capillary pressure balances gravity, i.e. when $\rho g = -\frac{\partial}{\partial z} \left( \frac{\sigma}{r_p} \right)$. Indeed, experimental measurements [62] of the pressure in a draining foam indicate that after a sufficiently long time, the pressure profile becomes linear with a slope equal to $\rho g$.

(2) There is no film thinning, i.e. $\frac{dx_F}{dt} = 0$ throughout the foam. This occurs when the repulsive disjoining pressure ($\Pi$) in the films balances the capillary pressure ($\frac{\sigma}{r_p}$). In other words, $\frac{\sigma}{r_p} = \Pi$ throughout the foam.

(3) The surfactant concentration does not change with time. There is no diffusion ($\frac{\partial c_s}{\partial z} = 0$) and there is no convection ($u = 0$).

(4) There is no movement of the boundaries, i.e. there is no collapse at the top ($\frac{dz_1}{dt} = 0$) and no drainage at the bottom ($\frac{dz_2}{dt} = 0$). This actually follows from conditions (1) and (2). If there is no drainage, $r_p$ will not change and the capillary pressure cannot increase to overcome the maximum disjoining pressure ($\Pi_{max}$) and cause collapse. Thus, in an equilibrated foam, $\frac{\sigma}{r_p} \leq \Pi_{max}$ and $x_F \geq x_{Fc}$.

The initial conditions are formulated in the next section.
2.8. Initial conditions

The extent of drainage and collapse that occurs in time will depend on the difference in the amount of liquid in the foam initially and at equilibrium. The larger this difference, the larger is the amount of drainage that will occur. The state of the foam (distribution of liquid) at the start of the experiment therefore plays an important role in determining its drainage and collapse behavior. The initial distribution of liquid, however, depends on the manner in which the foam is produced. Foams can be divided into two categories depending on the method of generation: (1) homogeneous foams, and (2) pneumatic foams.

Homogeneous foams are usually produced by vigorous agitation of surfactant solutions. As the name suggests, the distribution of liquid is uniform in such foams. Pneumatic foams, on the other hand, are produced by bubbling a gas through a surfactant solution. As the bubbling proceeds and the length of the foam increases, there is drainage of liquid in the foam and a profile of liquid fraction develops. The foam is drier (liquid fraction is lower) higher up in the foam where the bubbles are older and more drainage has occurred.

We will first discuss homogeneous foams in detail and then consider pneumatic foams. Before we proceed further, it must be mentioned that several assumptions were involved in obtaining most of the results that will be presented in the following sections:

1. Coalescence was ignored [14–17]. The films areas were assumed to be the same and the film thickness was only a function of the vertical position ‘z’.

2. The surfactant concentration was assumed to be uniform, i.e. the surface potential and surface tension were assumed to be constant.

3. In our first two papers [14,15], film drainage was ignored.

These assumptions were relaxed as we learned more about the system. However, most of our results (which were qualitative in any case) remain valid. In fact, an analysis of the results obtained using these simplifying assumptions actually improves our understanding of the system. The results and the simplifying assumptions are presented below.

2.9. Homogeneous foams [15]

2.9.1. Initial and boundary conditions for homogeneous foams

As mentioned earlier, homogeneous foams are characterized by a uniform initial liquid fraction. The initial condition for homogeneous foams therefore is:
At $t = 0$, $\varepsilon = \varepsilon_0$ for all $z$  

The other distinguishing property of homogeneous foams is that they do not start draining immediately. Some time usually elapses before some continuous phase liquid appears at the bottom of the foam. This is in contrast to pneumatic foams which are always in contact with the continuous phase liquid at the bottom. It has also been noted [63] that in homogeneous foams, phase separation occurs only when $\varepsilon$ at the bottom exceeds a certain minimum ($\varepsilon_b$) (the exact value though has not been specified). We postulate that for a "monodisperse" foam/concentrated emulsion, this value corresponds to the point when the amount of liquid at the bottom becomes large enough for the bubbles at the bottom to become spherical ($r_p = R_0$). The liquid fraction $\varepsilon$ at this point corresponds to that for close-packed spheres, i.e. $\varepsilon = 0.26 = \varepsilon_b$. The reasoning behind this can be understood as follows: Consider a foam/concentrated emulsion with a uniform initial continuous phase fraction of $\varepsilon_0 < \varepsilon_b$ (say $\varepsilon_0 = 0.15$). The bubbles at the bottom will be polyhedral (see Fig. 15a). As time passes, the Plateau border channels at the top drain into those below, so that $\varepsilon$ decreases at the top and increases at the bottom. Suppose, at a given point in time, $\varepsilon$ at the bottom just exceeds 0.26. At this instant, (see Fig. 15b) the bubbles at the bottom will cease to be in contact and become spherical. (Implicit in this argument is the assumption that droplet radius is much smaller than the capillary length ($R >> \sqrt{\sigma/\rho g}$.) However, due to buoyancy, these bubbles will rise and arrange themselves in a compact fashion ($\varepsilon = 0.26$) (see Fig. 15c) causing the excess continuous phase to accumulate at the bottom as a separate phase. As drainage proceeds, this process continues and the interface rises ($z_2$ increases), always maintaining $\varepsilon = 0.26$ at the bottom till a drainage equilibrium is established. Thus, there is no flow at the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mechanism.png}
\caption{Mechanism of continuous phase separation.}
\end{figure}
bottom as long as \( \varepsilon \big|_{z=z_2} < \varepsilon_b \) and \( \varepsilon \big|_{z=z_2} \) does not change once it attains the value \( \varepsilon_b \). The appropriate boundary condition at the bottom is therefore:

\[
t < t_b \Rightarrow u \big|_{z=z_2} = 0, \quad t > t_b \Rightarrow \varepsilon = \varepsilon_b
\]

where \( t_b \) is the time when \( \varepsilon \) at the bottom just becomes \( \varepsilon_b \).

Thus, for a homogeneous foam, there are two critical conditions: one for the separation of the dispersed phase \( (x_F = x_{F_0}) \) and the other for the separation of the continuous phase \( (r_p = R_0 \text{ or } \varepsilon = \varepsilon_b = 0.26) \). Four scenarios are therefore possible for a foam/concentrated emulsion with a certain initial uniform continuous phase volume fraction \( (\varepsilon_0) \) depending on whether one or both these critical conditions are achieved before equilibrium:

(a) Only the continuous phase separates out at the bottom;
(b) Only the disperse phase separates out at the top;
(c) Both phases separate out;
(d) There is no phase separation.

By analyzing the equilibrium state of a foam in relation to its initial state, it is possible to determine, at the outset, which of the above situations arise. In the following sections, we will discuss the equilibrium state in detail and show that by making suitable approximations, it is possible to determine analytically the phase behavior from the initial conditions.

The system can be simplified considerably, if films are neglected. In this section, we will discuss the equilibrium in detail using simplified equations that are obtained when films are neglected. Film drainage is important in determining the kinetics of foam collapse (see Eq. (95)). However, since most of the liquid in a foam is stored in the Plateau border channels, films can be ignored when computing the liquid volume fraction. Our main concern in this section is with the drainage equilibrium. This assumption is therefore valid. This assumption was made in our first two papers \([14,15]\) and proved to be useful in obtaining insights into many features of foam decay. Also, in an equilibrated foam, the bubble radius is uniform and equal to the initial bubble radius \( (R_0) \) because no coalescence has occurred in foam that remains at equilibrium. When films are neglected, the liquid fraction \( \varepsilon \) depends only on the local Plateau border radius \( r_p \) and the various macroscopic variables can be expressed as
Let us re-examine the condition for foam collapse within the framework of this assumption.

Since film rupture can occur only if the capillary pressure \( \frac{\sigma}{r_p} \) exceeds the maximum disjoining pressure \( \Pi_{\text{max}} \), it is possible to define a critical Plateau border radius \( r_{pc} \) given by:

\[
r_{pc} = \frac{\sigma}{\Pi_{\text{max}}} \tag{102}
\]

For film rupture to occur, the Plateau border radius \( r_p \) must be less than \( r_{pc} \). When a collapsing foam arrives at an equilibrium, i.e. when \( \frac{dz}{dt} \) decreases to 0, \( r_p = r_{pc} \) at the foam/gas interface. This is because (see Eqs. (95–97)) when collapse comes to a halt:

\[
V_f \bigg|_{z = z_1} = 0 \quad \text{i.e.} \quad \frac{\sigma}{r_p} = \Pi_{\text{max}} \quad \text{at} \quad z = z_1
\tag{103}
\]

i.e.

\[
\varepsilon \bigg|_{z = z_1} = \varepsilon_c
\tag{104}
\]

where \( \varepsilon_c \) is the liquid volume fraction corresponding to \( r_p = r_{pc} \). Let us now consider the equilibrium state in more detail.

### 2.9.2 Drainage equilibrium in homogeneous foams

Since at equilibrium, \( u = 0 \) for all \( z \), we have:

\[
\frac{d}{dz} \left( \frac{1}{r_p} \right) = -\frac{\rho g}{\sigma} \tag{105}
\]

Using Eq. (101), Eq. (105) can be written in terms of \( \varepsilon \) at equilibrium \( (\varepsilon_{eq}) \) as:

\[
\sqrt{\frac{3(0.161) n_p 0.816}{4\pi}} \frac{1}{R_0} \frac{d}{dz} \sqrt{\frac{1 - \varepsilon_{eq}}{\varepsilon_{eq}}} = -\frac{\rho g}{\sigma} \tag{106}
\]

Now let us define:
Integration of Eq. (106) gives:

\[ \sqrt{\frac{1 - \varepsilon_{eq}}{\varepsilon_{eq}}} = -\frac{K\rho g R_0 z}{\sigma} + c \]  

(107)

where "c" is a constant of integration. Equation (107) can be rewritten as:

\[ \varepsilon_{eq} = \frac{1}{1 + \left( c - \frac{K\rho g R_0 z}{\sigma} \right)^2} \]  

(108)

Let \( z_1 = z_{1e} \) and \( z_2 = z_{2e} \) at equilibrium. The volume of the continuous phase per unit cross-section at equilibrium is then given by:

\[ V_{eq} = \int_{z_{1e}}^{z_{2e}} \varepsilon_{eq} \, dz \]  

(109)

Substituting the expression for \( \varepsilon_{eq} \) from Eq. (108) into Eq. (109) and integrating, we get:

\[ V_{eq} = \frac{\sigma}{K\rho g R_0} \left[ \tan^{-1} \left( c - \frac{K\rho g R_0 z_{1e}}{\sigma} \right) - \tan^{-1} \left( c - \frac{K\rho g R_0 z_{2e}}{\sigma} \right) \right] \]  

(110)

If \( L_0 \) is the initial foam length, the volume of liquid per unit area initially present in the foam is \( L_0 \varepsilon_0 \). The distance moved by the lower boundary by the time equilibrium is established is equal to the loss of continuous phase per unit cross-section. Thus:

\[ L_0 - z_{2e} = L_0 \varepsilon_0 - V_{eq} \]  

(111)

Combining Eq. (110) and Eq. (111) gives:

\[ L_0 - z_{2e} = L_0 \varepsilon_0 - \frac{\sigma}{K\rho g R_0} \left[ \tan^{-1} \left( c - \frac{K\rho g R_0 z_{1e}}{\sigma} \right) - \tan^{-1} \left( c - \frac{K\rho g R_0 z_{2e}}{\sigma} \right) \right] \]  

(112)
To accurately determine the conditions at equilibrium, we need to evaluate the constant of integration \( c \), i.e. we require \( \varepsilon_{eq} \) at one of the boundaries. There are four possible scenarios for the state of the foam/concentrated emulsion at equilibrium. Each is discussed below.

**Case a: The equilibrated foam is in contact with the continuous phase at the bottom**

In this case, since there is no collapse, we have \( z_{le} = 0 \) and since the foam is in contact with liquid at the bottom, \( \varepsilon_{eq} \Big|_{z=z_{2e}} = \varepsilon_b = 0.26 \). Using these conditions in Eq. (107) gives the integration constant for this case:

\[
c = \sqrt{\frac{1-\varepsilon_b}{\varepsilon_b}} + \frac{K\rho g R_0 z_{2e}}{\sigma}
\]

Using this expression for \( c \), Eq. (110) and Eq. (112) gives:

\[
V_{eq} = \frac{\sigma}{K\rho g R_0} \left[ \tan^{-1} \left( \frac{1-\varepsilon_b}{\varepsilon_b} + \frac{K\rho g R_0 z_{2e}}{\sigma} \right) - \tan^{-1} \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \right]
\]

\[
L_0 - z_{2e} = L_0 \varepsilon_0 - \frac{\sigma}{K\rho g R_0} \left[ \tan^{-1} \left( \frac{1-\varepsilon_b}{\varepsilon_b} + \frac{K\rho g R_0 z_{2e}}{\sigma} \right) - \tan^{-1} \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \right]
\]

**Case b: The equilibrated foam is in contact with the separated disperse phase at the top**

In this case, since no drainage of liquid from the foam has taken place, the lower boundary does not move and \( z_{2e} = L_0 \). Also, since a collapsing foam arrives at equilibrium with \( r_p = r_{pc} \) at the top, \( \varepsilon \Big|_{z=z_{1e}} = \varepsilon_c \). The constant of integration is given by:

\[
c = \sqrt{\frac{1-\varepsilon_c}{\varepsilon_c}} + \frac{K\rho g R_0 z_{le}}{\sigma}
\]

Substituting the expression for \( c \) in Eqs. (112) and (110) we get:
\[
L_0 \varepsilon_0 - \frac{\sigma}{K\rho g R_0} \left[ \tan^{-1} \left( \frac{1-\varepsilon_c}{\varepsilon_c} \right) - \tan^{-1} \left( \frac{1-\varepsilon_c}{\varepsilon_c} - \frac{K\rho g R_0}{\sigma} (L_0 - z_{1e}) \right) \right] = 0
\]

(117)

\[
V_{eq} = \frac{\sigma}{K\rho g R_0} \left[ \tan^{-1} \left( \frac{1-\varepsilon_c}{\varepsilon_c} \right) - \tan^{-1} \left( \frac{1-\varepsilon_c}{\varepsilon_c} - \frac{K\rho g R_0}{\sigma} (L_0 - z_{1e}) \right) \right]
\]

(118)

**Case c: Both phases separate**

In this case, since both drainage and collapse has taken place, \(z_{1e} > 0\) and \(z_{2e} < L_0 \varepsilon|_{z=z_{1e}} = \varepsilon_c\) and \(\varepsilon|_{z=z_{2e}} = \varepsilon_b\). Thus from Eq. (107) we have:

\[
c = \sqrt{\frac{1-\varepsilon_b}{\varepsilon_b} + \frac{K\rho g R_0 z_{2e}}{\sigma}}
\]

(119)

Also, we have:

\[
c = \sqrt{\frac{1-\varepsilon_c}{\varepsilon_c} + \frac{K\rho g R_0 z_{1e}}{\sigma}}
\]

(120)

Combining Eqs. (119) and (120), we have:

\[
z_{2e} - z_{1e} = \frac{\sigma}{K\rho g R_0} \left[ \sqrt{\frac{1-\varepsilon_c}{\varepsilon_c}} - \sqrt{\frac{1-\varepsilon_b}{\varepsilon_b}} \right] \equiv L_{max}
\]

(121)

In Eq. (121), \(z_{2e} - z_{1e}\) is the length of the foam at equilibrium. Since the right hand side of Eq. (121) is a constant for a given system, it is clear that when both phases separate, the final length \((z_{2e} - z_{1e})\) of the equilibrated column is fixed and given by \(L_{max}\).

An important point to be noted is that the length of a foam cannot increase. When one or more phases separate, the length of the foam has to decrease. If there is no loss of liquid or gas, there is no change in the foam length. Thus, the following condition always holds:

\[
z_{2e} - z_{1e} \leq L_0
\]

(122)
Thus, if \( L_0 < L_{\text{max}} \), it is not possible to have an equilibrium with both phases separating. In other words, when \( L_0 < L_{\text{max}} \) only one phase will separate. The initial composition (\( e_0 \)) of the system determines which phase separates. If during drainage, \( e \) at the bottom exceeds \( e_b \) before the films at the top rupture, the continuous phase separates and Eqs. (113–115) are valid. On the other hand if film rupture occurs first, collapse occurs at the top and Eqs. (116–118) are valid. If, however, \( u \) becomes zero before either of the above occur, no phase separation takes place. The initial state of the foam \( (L_0, e_0) \) therefore plays a crucial role in determining the phase behavior. The effect of the initial condition on phase separation is discussed next.

2.9.3. Effect of initial condition on phase separation

Based on the initial state of a foam/concentrated emulsion, it is possible to determine at the outset which of the two phases separates out. As has been discussed earlier, if \( L_0 < L_{\text{max}} \), only one phase will separate out. Two situations are possible in this case. Each is discussed separately.

Case 1: Separation of the continuous phase

Let us define a critical volume:

\[
V_c = \frac{\sigma}{KpgR_0} \left[ \tan^{-1}\left( \sqrt{\frac{1-e_b}{e_b}} + \frac{KpgR_0 L_0}{\sigma} \right) - \tan^{-1}\left( \sqrt{\frac{1-e_b}{e_b}} \right) \right] \tag{123}
\]

A comparison with Eq. (114) indicates that \( V_c \) is the volume of the continuous phase per unit cross-section in an equilibrated foam/concentrated emulsion when \( z_{2e} = L_0 \) (see Fig. 16). Thus, if \( e_0 L_0 = V_c \), the continuous phase will redistribute itself until an equilibrium is established with \( e|_{z=x_2} = e_b \). However, if \( e_0 L_0 > V_c \), some continuous phase has to separate out before an equilibrium can be established. To understand the reasoning behind this, consider Fig. 17a. The curve HAFB represents the equilibrium profile of \( e \) in a column of length \( L_{\text{max}} \). Consider a column of length \( L_0 < L_{\text{max}} \) with an initial profile represented by the horizontal line EFG. Thus:

\[
L_0 = \text{length}(EG); \quad \text{Area}(CDEG) = e_0 L_0 \tag{124}
\]

Also note that for this system, the volume of continuous phase per
Fig. 16. Profile of liquid fraction ($\varepsilon_{eq}$) in an equilibrated foam of length $L_{\max}$ in contact with the continuous phase at the bottom and the dispersed phase at the top. $V_c$ is the volume of continuous phase per unit area in an equilibrated foam of length $L_0$ with $\varepsilon = 0.26$ at the bottom. $V_D$ is the volume of the dispersed phase per unit area in an equilibrated foam of length $L_0$ with $\varepsilon = \varepsilon_c$ at the top.

unit cross-section in an equilibrated column of length $L_0$ is given by $\text{Area(ABCD)}$. Thus:

$$V_c = \text{Area(ABCD)}$$  \hspace{1cm} (125)

It is clear from the figure that the part of the emulsion from E to F has an excess of continuous phase given by $V_1 = \text{Area(AEF)}$, while the part of the foam from F to G has a deficiency of continuous phase given by $V_2 = \text{Area(BFG)}$. Thus:

$$\varepsilon_0 L_0 - V_c = V_1 - V_2$$  \hspace{1cm} (126)

Now if $V_1 = V_2$, i.e. if $V_c = \varepsilon_0 L_0$, the amount of continuous phase that the upper part (EF) loses as it attains equilibrium is just equal to the
amount the lower part needs. Thus, at equilibrium, the $\varepsilon$ profile is given by curve(AFB) and the length of the column remains unchanged. On the other hand, if $V_1 > V_2$, i.e. if $\varepsilon_0 L_0 > V_c$ (see Fig. 17b), the upper part must lose a greater amount of liquid than the lower part requires, i.e., the

![Diagram](image)

(a)

![Diagram](image)

(b)

Fig. 17. A pseudo-phase diagram for continuous phase separation: (a) $V_1 = V_2$ and (b) $V_1 > V_2$.
lower part will gain more continuous phase liquid than it can hold. As a result, the excess separates out and the column length decreases. The final profile is now given by curve A1FB and the equilibrium length is given by length(D1C). One may note that \( \text{length(DD1)} = V_1 - V_2 \). Princen [64-67] has treated the problem of continuous phase separation using osmotic pressure considerations.

**Case 2: Separation of the dispersed phase**

As in the previous case, it is possible to define a critical volume for disperse phase separation:

\[
V_D = \frac{\sigma}{K\rho g R_0} \left[ \tan^{-1}\left( \frac{1 - \varepsilon_c}{\varepsilon_c} \right) - \tan^{-1}\left( \frac{1 - \varepsilon_c - K\rho g R_0 L_0}{\sigma} \right) \right]
\]  

(127)

It may be noted that Eq. (127) is a special case of Eq. (118) with \( z_{1e} = 0 \) (see Fig. 16). Consider Fig. 18. The initial profile in this case is given by segment EFG. It is clear that \( V_D = \text{Area(ABCD)} \). Thus, the excess continuous phase in the upper part is \( V_1' = \text{Area(AEF)} \) and the deficiency in the lower part is \( V_2' = \text{Area(BGF)} \). Now, if \( V_1' = V_2' \) we have \( \varepsilon_0 L_0 = V_D \) and the continuous phase will simply redistribute so as to attain a final equilibrium profile given by curve AFB. However, if \( V_1' < V_2' \), the lower part (FG) requires more continuous phase than can be provided by the upper part (EF), so that \( \varepsilon \) at the top falls below \( \varepsilon_c \) and the disperse phase separates out. This causes the length of the foam to decrease and the final profile is given by curve(AFB1). In this case, the change in length is given by length(CC1).

The discussion in the above sections can be summarized as follows (see Fig. 16):

- **when** \( L_0 < L_{\text{max}} \):
  - \( L_0 \varepsilon_0 < V_D \Rightarrow \) separation of the disperse phase
  - \( \varepsilon_0 L_0 > V_c \Rightarrow \) separation of the continuous phase

- If \( V_D < \varepsilon_0 L_0 < V_c \), equilibrium is established before \( \varepsilon \) at either end can reach \( \varepsilon_c \) or \( \varepsilon_b \) and no phase separation takes place.

**Separation of both phases**

As mentioned earlier, when both phases separate, the length of the column at equilibrium is fixed and given by \( L_{\text{max}} \). Thus, separation of
both phases can occur only if $L_0 > L_{\text{max}}$. However, $L_0 > L_{\text{max}}$ does not necessarily imply that both phases separate. Using a reasoning similar to that used above, it is possible to determine the conditions under which both phases separate.

The volume of continuous phase per unit cross-section in an emulsion in equilibrium with two phases ($V_{\text{eq}}$) is given by (see Fig. 19):

$$V_{\text{eq}} = \frac{\sigma}{K \rho g R_0} \left[ \tan^{-1}\left(\frac{1 - \varepsilon_c}{\varepsilon_c}\right) - \tan^{-1}\left(\frac{1 - \varepsilon_b}{\varepsilon_b}\right) \right]$$  \hspace{1cm} (128)

$$V_{\text{Deq}} = L_{\text{max}} - V_{\text{eq}}$$  \hspace{1cm} (129)
Fig. 19. Profile of liquid fraction ($\varepsilon_{eq}$) in an equilibrated foam of length $L_{max}$ in contact with the continuous phase at the bottom and the dispersed phase at the top. $V_{ceq}$ is the volume of continuous phase per unit area and $V_{Deq}$ is the volume of the dispersed phase per unit area in an equilibrated foam of length $L_{max}$ with $\varepsilon = \varepsilon_c$ at the top and $\varepsilon = 0.26$ at the bottom.

The volume per unit cross-section of the disperse phase ($V_{Deq}$) in this situation is given by, i.e.:

$$V_{Deq} = \frac{\sigma}{KpgR_0} \left[ \frac{1 - \varepsilon_c}{\varepsilon_c} - \frac{1 - \varepsilon_b}{\varepsilon_b} - \tan^{-1} \left( \frac{1 - \varepsilon_c}{\varepsilon_c} \right) + \tan^{-1} \left( \frac{1 - \varepsilon_b}{\varepsilon_b} \right) \right]$$

(130)

Clearly, $V_{ceq}$ and $V_{Deq}$ are fixed for given $R_0$, $\sigma$ and $\rho$. Thus, if the volumes per unit cross-section of the two phases in the initial emulsion exceed $V_{ceq}$ and $V_{Deq}$ i.e. if $\varepsilon_0 L_0 > V_{ceq}$ and $(1 - \varepsilon_0) L_0 > V_{Deq}$ both phases separate out. If any one of these conditions are not satisfied, only one phase will separate. The final length will then be less than $L_{max}$ and the situation is the same as that discussed earlier.
A generalized “phase” diagram

The condition for the separation of the continuous phase can be written as:

\[ \varepsilon_0 L_0 > V_c \quad \text{for} \quad L_0 < L_{\text{max}} \]  
\[ \varepsilon_0 L_0 > V_{\text{ceq}} \quad \text{for} \quad L_0 > L_{\text{max}} \] (131) (132)

Using Eq. (123), Eq. (131) can be written as:

\[ \varepsilon_0 > \frac{\sigma}{K \rho g R_0 L_0} \left[ \tan^{-1} \left( \frac{1 - \varepsilon_b}{\varepsilon_b} + \frac{K \rho g R_0 L_0}{\sigma} \right) - \tan^{-1} \left( \frac{1 - \varepsilon_c}{\varepsilon_c} \right) \right] \] (133)

And using Eq. (128), Eq. (132) can be written as:

\[ \varepsilon_0 > \frac{\sigma}{K \rho g R_0 L_0} \left[ \tan^{-1} \left( \frac{1 - \varepsilon_c}{\varepsilon_c} \right) - \tan^{-1} \left( \frac{1 - \varepsilon_b}{\varepsilon_b} \right) \right] \] (134)

Similarly, using Eq. (127), the condition for disperse phase separation can be written as:

\[ \varepsilon_0 < \frac{\sigma}{K \rho g R_0 L_0} \left[ \tan^{-1} \left( \frac{1 - \varepsilon_c}{\varepsilon_c} \right) - \tan^{-1} \left( \frac{1 - \varepsilon_c}{\varepsilon_c} - \frac{K \rho g R_0 L_0}{\sigma} \right) \right] \] \quad \text{for} \quad L_0 < L_{\text{max}} \] (135)

\[ \varepsilon_0 < 1 - \frac{\sigma}{K \rho g R_0 L_0} \left[ \sqrt{\frac{1 - \varepsilon_c}{\varepsilon_c}} - \sqrt{\frac{1 - \varepsilon_b}{\varepsilon_b}} - \tan^{-1} \left( \frac{1 - \varepsilon_c}{\varepsilon_c} \right) + \tan^{-1} \left( \frac{1 - \varepsilon_b}{\varepsilon_b} \right) \right] \] \quad \text{for} \quad L_0 > L_{\text{max}} \] (136)

Let us define a dimensionless number:

\[ P \equiv \frac{\sigma}{K \rho g R_0 L_0} \]

The above conditions can then be written in terms of \( P \) as follows:

Continuous phase separates when
\[ \varepsilon_0 > P \left[ \tan^{-1}\left( \frac{1-\varepsilon_b}{\varepsilon_b} + \frac{1}{P} \right) - \tan^{-1}\left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \right] \quad \text{for } L_0 < L_{\text{max}} \tag{137} \]

\[ \varepsilon_0 > P \left[ \tan^{-1}\left( \frac{1-\varepsilon_c}{\varepsilon_c} \right) - \tan^{-1}\left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \right] \quad \text{for } L_0 < L_{\text{max}} \tag{138} \]

Dispersed phase separates where

\[ \varepsilon_0 < P \left[ \tan^{-1}\left( \frac{1-\varepsilon_c}{\varepsilon_c} \right) - \tan^{-1}\left( \frac{1-\varepsilon_c}{\varepsilon_c} - \frac{1}{P} \right) \right] \quad \text{for } L_0 < L_{\text{max}} \tag{139} \]

\[ \varepsilon_0 < 1 - P \left[ \sqrt{\frac{1-\varepsilon_c}{\varepsilon_c} - \frac{1-\varepsilon_b}{\varepsilon_b} - \tan^{-1}\left( \frac{1-\varepsilon_c}{\varepsilon_c} \right) + \tan^{-1}\left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) } \right] \quad \text{for } L_0 > L_{\text{max}} \tag{140} \]

It can be seen from Eqs. (137–140) that for a given \( \varepsilon_0 \), the occurrence of phase separation is determined entirely by the value of \( P \). Figure 20 shows the right hand sides of Eqs. (137–140) plotted versus \( P \) for \( \varepsilon_c = 0.00826 \). The curves AB (Eq. (140)) and BC (Eq. (139)) show the lower limit of \( \varepsilon_0 \) below which the disperse phase separates and curves DB (Eq. (138)) and BE (Eq. (137)) represent the upper limit for \( \varepsilon_0 \) beyond which the continuous phase separates. Point B corresponds to \( L_0 = L_{\text{max}} \). At this point there is no phase separation and at equilibrium \( \varepsilon = \varepsilon_b \) at the bottom and \( \varepsilon = \varepsilon_c \) at the top. The region ABD corresponds to those initial conditions \( (L_0 > L_{\text{max}}) \) for which both phases separate. Figure 20 is also useful in understanding the effect of initial column height \( (L_0) \) and bubble radius \( (R_0) \) on the stability of a concentrated emulsion. The influence of these two parameters is determined entirely by their effect on \( P \). For a given pair of fluids we have

\[ P \propto \frac{1}{L_0 R_0} \]

Consider an emulsion with \( \varepsilon_0 = 0.025 \). Now if its length and bubble size are such that the initial condition is represented by H it is unstable.
However, if its length and/or bubble size are decreased so that it is characterized by point G, it is stable and no phase separation will take place.

2.9.4. Simulation results for homogeneous foams/concentrated emulsions

To demonstrate the results of our model, we carried out simulations for a typical oil in water concentrated emulsion. The following values for the physical parameters were used:
\[ \sigma = 20 \text{ mN/m}, \rho_D = 0.7 \text{ gm/cc}, \rho_c = 1 \text{ gm/cc}, \mu = 1 \text{ cP}, R_0 = 0.2 \text{ mm}, L_0 = 10 \text{ cm}, \] 
Hamaker constant \((A_h) = 0.41 \times 10^{-20} \text{ J},\) ionic strength \((c_{el}) = 0.01 \text{ M},\) surface potential \((\psi_s) = 10 \text{ mV}.\)

For these conditions we get \(\Pi_{\text{max}} = 615.95 \text{ N/m}^2\) and \(\varepsilon_c = 0.00826.\) In this case, \(P = 0.19045\) and \(L_{\text{max}} = 17.65 \text{ cm}.\) Since \(L_0 < L_{\text{max}}\) only one phase separates if at all. From the phase diagram, it is clear that for \(\varepsilon_0 >\)

---

**Fig. 21.** Evolution of the \(\varepsilon\) profile when the continuous phase separates. The system parameters are: \(\mu = 1 \text{ cP}, \rho_c = 1 \text{ gm/cc}, \rho_D = 0.7 \text{ gm/cc}, R_0 = 0.2 \text{ mm}, A_h = 0.41 \times 10^{-21} \text{ J}, L_0 = 10 \text{ cm}, \varepsilon_0 = 0.125\) and \(\psi_s = 10 \text{ mV}.\)
0.0746, the continuous phase separates; for \( \epsilon_0 < 0.0157 \), the disperse phase separates and for \( 0.0746 < \epsilon_0 < 0.0157 \) there is no phase separation. Figure 21 shows the evolution of \( \epsilon \) with time for \( \epsilon_0 = 0.125 \). The continuous curve represents the equilibrium \( \epsilon \)-profile in this system. The other curves represent the profiles at \( t = 0 \), \( t = 108 \) s, \( t = 890 \) s and \( t = 4050 \) s. Note that for \( t = 890 \) s and \( t = 4050 \) s the length of the column decreases indicating that the continuous phase separates out. Figure 22 shows the evolution of \( \epsilon \) for \( \epsilon_0 = 0.01 \). In this case, the interface with \( z \big|_{t=0} = 0 \) moves indicating that the disperse phase separates out. Figure
23 shows the evolution of $\varepsilon$ for $\varepsilon_0 = 0.05$. It is clear that the positions of the two interfaces do not change with time. There is merely a redistribution of the continuous phase before equilibrium is established, no phase separation.

Figure 24 shows the evolution of the $\varepsilon$ profiles for $L_0 = 22.5$ cm and $\varepsilon_0 = 0.09$. The phase diagram indicates that both phases separate out. Indeed, Fig. 24 shows that both interfaces move.


Fig. 24. Evolution of the $\varepsilon$ profile when both phases separate ($L_0 = 22.5$ cm and $\varepsilon_0 = 0.09$). Other parameters are the same as those for Fig. 21.

**Lag time in homogeneous foam drainage**

Kann [63] has presented some experimental data on the lag time of homogeneous foams. We made an attempt to check if our model qualitatively predicts the experimental trends. There are two main results in that paper:

(a) For a given $\varepsilon_0$ the lag time for drainage, i.e. the time required for the first drop of liquid to appear at the bottom decreases as the initial foam height ($L_0$) increases (Fig. 2 in Ref. [63]).

(b) For a given height, the lag time increases as the $\varepsilon_0$ decreases (Fig. 4 in Ref. [63]).
Simulations were carried out with the following values of the parameters:

$R_0 = 0.5 \text{ mm}$, $\sigma = 10 \text{ mN/m}$, $\mu = 1 \text{ cP}$ and $\rho = 1 \text{ gm/cc}$.

Figure 25 shows the simulated drainage curves $\frac{L_0 - z}{\varepsilon_0 L_0}$ for $L_0 = 10 \text{ cm}$ and three values of $\varepsilon_0$. Clearly, the lag time increases as $\varepsilon_0$ decreases. Figure 26 shows the effect of initial foam height ($L_0$) on the drainage curves for $\varepsilon_0 = 1/70$. Figure 27 shows a plot of lag time ($\tau$) versus $L_0$ for this system. One can see that the lag time decreases with an increase in $L_0$ for smaller heights but remains unchanged with height for larger
heights. Figure 27 is very similar to Fig. 3 in Ref. [63]. An explanation for this trend in lag times can be given as follows:

The lag time is essentially the time required for \( \varepsilon \) at the bottom to become equal to \( \varepsilon_b \). If \( \varepsilon_0 \) is constant, the amount of liquid that the lower portion of the foam must receive for \( \varepsilon \) to become \( \varepsilon_b \) is fixed. The time lag is therefore determined by the flow rate of liquid into the bottom Plateau border. The flow rate is initially the same throughout the column (since \( \varepsilon = \varepsilon_0 \) throughout the foam). However, since there is no input of liquid at the top, the Plateau borders at the top contract thereby decreasing the flow into the Plateau borders below them and so on. For longer foams, the effect of the contraction at the top takes a longer time to reach the bottom. Thus, beyond a certain height, \( \varepsilon \) at the bottom becomes equal
Fig. 27. Effect of the initial foam length ($L_0$) on the drainage lag time for the system of Fig. 26.

to $\epsilon_b$ before the influence of the upper boundary becomes significant, so that the flow rate in the lower portion is essentially independent of foam height and the lag time remains more or less constant. The sharp rise in lag times is simply due to the fact that as we decrease $L_0$, we are approaching the point at which no phase separation takes place (i.e. the lag time is infinite).

When $L_0$ is fixed (Fig. 25), as $\epsilon_0$ decreases, the amount of liquid required by the lower part increases and the flow rate decreases resulting in an increase in lag time.

Pneumatic foams will be considered next.
2.10. Pneumatic foams

2.10.1. Drainage and collapse during bubbling

Figure 28 shows a schematic diagram of a typical experimental setup used to produce foam by bubbling. An inert gas is bubbled at a fixed volumetric flow rate through a porous frit into the surfactant solution. Foam is formed and moves up at a rate which depends on the superficial gas velocity. As the foam moves up, drainage of liquid occurs from the upper to the lower portions of the foam and by the time the gas supply is stopped, a profile of liquid fraction ($\varepsilon$) develops. The upper portions of the foam are drier (lower $\varepsilon$) because more drainage has taken place there. In order to compute this profile, the drainage equations need to be solved during foam formation. The basic equations are the same as those presented earlier. However, as the foam moves up, an observer at the origin sees the foam/liquid interface moving away from him (i.e. $z_2$ increases) at a rate which depends on the superficial gas velocity. Thus Eq. (98) is not valid during bubbling and a new expression needs to be formulated.

![Figure 28](image)

Fig. 28. A pneumatic foam being generated by bubbling; (a) no collapse, (b) collapse has occurred.
Depending on the collapse occurring at the top of the foam, part of the gas resides in the foam, while the rest escapes from the top due to collapse. Since, we have defined the reference plane to be such that all the escaped gas resides between it and the foam/gas interface (i.e. between \( z = 0 \) and \( z = z_1 \)), a mass balance for the bubbling gas can be written as:

\[
GA = \frac{d}{dt} \int_{z_1}^{z_2} A(1 - \varepsilon)dz + A \frac{dz_1}{dt} \tag{141}
\]

In Eq. (141), \( A \) is the cross-sectional area and \( G \) is the superficial gas velocity. The first term represents the gas in the foam, while the second term corresponds to the gas escaped from the collapsed bubbles. Simplifying Eq. (141), one obtains:

\[
G = \frac{dz_2}{dt} - \frac{d}{dt} \int_{z_1}^{z_2} \varepsilon dz \tag{142}
\]

Applying Leibnitz's rule and using the fact that:

\[
\frac{\partial \varepsilon}{\partial t} = \frac{\partial [(1 - \varepsilon)q_{PB}]}{\partial z} \tag{143}
\]

we have:

\[
G = (1 - \varepsilon) \left| \frac{dz_2}{dt} \right|_{z_2} + (1 - \varepsilon)q_{PB} \left| \frac{dz_1}{dt} \right|_{z_2} + \varepsilon \left| \frac{dz_1}{dt} \right|_{z_1} - (1 - \varepsilon)q_{PB} \left| \frac{dz_1}{dt} \right|_{z_1} \tag{144}
\]

Eliminating \( \frac{dz_1}{dt} \) using Eq.(65), yields:

\[
\frac{dz_2}{dt} = \left| \frac{G - (1 - \varepsilon)q_{PB}}{1 - \varepsilon} \right|_{z_2} \tag{145}
\]

When the gas supply is shut off, \( G = 0 \) and we get \( \frac{dz_2}{dt} = -q_{PB} \big|_{z_2} \), which is the same as Eq. (98). As long as there is no collapse at the top during generation, the motion of the foam/gas interface is determined by the bulk movement of the foam. However, as soon as the thickness of the liquid films at the top decreases to a critical value, collapse starts at the
top and a downward component is superimposed on the bulk movement of the foam. As a result, the net upward velocity of the foam/gas interface decreases. In case of less stable foams, it is possible to have a steady state in which the foam length does not change with time because the rate of foam collapse at the top becomes equal to the rate of foam generation, i.e. \( \frac{dz_1}{dt} = \frac{dz_2}{dt} \) and the foam length \((z_2 - z_1)\) does not change with time. This steady state has been used to characterize the stability of short-lived foams.

In the sections that follow, we shall present some of our results for pneumatic foams. These results are reproduced from our papers and reflect the improvements with time. We first present results for foam drainage where there is no collapse. Here [14] films are neglected and a comparison is made with some experimental data [68] and the results from the quasi-steady state model for foam drainage proposed by Narasimhan [23]. Results are then presented for the model in which film drainage and rupture are accounted for but coalescence and the change in surfactant concentration are ignored. The effect of various parameters on the steady-state height are examined. Finally, results are presented for our most detailed model [18] in which coalescence and the variation of surfactant concentration are taken into account.

2.10.2. Simulation results for pneumatic foams

Narasimhan [23] has used a quasi-steady state model to compute the initial liquid fraction in a pneumatic foam. Instead of solving the drainage equations using moving boundaries as we have done, he computes the distribution of liquid assuming that the downward flow rate of liquid per unit cross-section due to gravity drainage \((q_{PB})\) is compensated by the liquid entrained by the rising bubbles \((q_B = G\eta_p a_p l/V)\), so that quasi-steady state material balances can be written along the length of the foam. The quasi-steady state balance is written as:

\[
\frac{d}{dz} \left( \frac{G\eta_p a_p l}{V} \right) = \frac{d}{dz} (q_{PB}) \tag{146}
\]

This ordinary differential equation is solved using the boundary conditions:

\( u = 0 \) for \( z = z_1 = 0 \); at \( \varepsilon = 0.26 \) for \( z = z_2 \) \tag{147}
Fig. 29. Liquid fraction profiles in a pneumatic foam when the gas supply is shut off. $L_0 = 5 \text{ cm}$, $\mu = 1 \text{ cP}$, $R_0 = 0.2 \text{ mm}$, $G = 0.001 \text{ m/s}$, $\rho = 10^3 \text{ kg/m}^3$, $\eta_s = \infty$ and $\sigma = 50 \text{ mN/m}$.

Presented below are comparisons of our results with those from the quasi-steady state model.

Figure 29 shows a comparison of the profiles of the initial liquid fraction (profile of $\varepsilon$ when the gas supply is shut off) obtained from the two models for $L_0 = 5 \text{ cm}$ and $G = 10^{-3} \text{ m/s}$. It is clear that the profiles are qualitatively different. The total amount of liquid in the foam per unit cross-section ($V_0$) when the gas supply is just shut off, i.e. when $z_2 - z_1 = L_0$, is the area under the $\varepsilon$ vs $z$ curve and is given by:

$$V_0 = \int_{0}^{L_0} \varepsilon \, dz$$

(148)
Fig. 30. Variation of the fractional change in foam length with time ($t'$) for the system of Fig. 29.

It is clear that the quasi-steady state model predicts a higher $V_0$. Figure 30 shows the evolution of the fractional change in foam height with time $t'$ for the above system. Here $t'$ is the time elapsed after the gas supply is shut off. Note that the curves flatten out indicating that the drainage practically ceases after a given time and the foam height remains almost constant. When the quasi-steady state model is used to compute the initial distribution, the change in the height is about 70% greater than that obtained from our model. Since the two models differ only in the way the initial distribution is computed, it is clear that the initial distribution strongly affects the drainage process. Figures 31–33 show comparisons of the theoretical predictions of the two models with the experimental data.
Fig. 31. Fractional change in foam length versus time ($t'$) for two bubble sizes with $G = 0.0578$ cm/s, $L_0 = 19.8$ cm, $\mu = 1$ cP, $\rho = 1000$ kg/m$^3$ and $\eta_0 = \infty$: (a) $R_0 = 0.153$ mm.

Fig. 31 shows the effect of bubble size, while Fig. 32 shows the results for 3 viscosities. It is clear that our model shows significantly better agreement with the data. Figure 33 shows the effect of initial foam height ($L_0$) on the drainage. Our model shows reasonable agreement for the smallest height ($L_0 = 10.61$ cm). However the theoretical drainage curves do not change to the same extent with height as the experimental curves. At larger heights, the foam is drier at the top and the film thickness is very thin. It is thus possible that bubble collapse which was ignored in our model causes the discrepancy. Before we proceed further, some qualitative features need to be noted in the figures. The extent and rate of drainage is greater when the bubble size is smaller and
the viscosity is higher. With smaller bubble sizes (i.e., smaller PB cross-sectional area) and higher viscosities, the downward fluid velocity is smaller. This means that a smaller amount of liquid drains out of the foam during bubbling. A greater amount of liquid is therefore present in the foam when the gas supply is shut off. This in turn means that the foam is farther from equilibrium when the gas supply is shut off. The change in foam height is therefore larger. It must be emphasized here that film drainage was ignored [14] in obtaining the curves shown in Figs. 31–33.

Film drainage was incorporated into the model in a subsequent paper [16]. This, however, brought to the fore, a new issue regarding the boundary conditions at the foam/liquid interface during foam formation.
In foams formed by bubbling, new bubbles are continuously introduced into the system at the foam/liquid interface. Thus, when the foam is being generated, the boundary condition at the bottom is a statement about the condition of the bubbles as they enter the foam. When films were neglected [14,15], the boundary condition at the bottom was simply the condition for close-packed spheres (ε = 0.26). This was sufficient since there was only one variable (ε). However, with the inclusion of films into the model, there are two independent variables (r_p and x_p) and information is needed about the distribution of liquid between the films and the Plateau border channels. Since the differential equation
for $x_F$ is first order in time, an initial condition is needed. In other words, the value of $x_F$ at the foam/liquid interface during bubbling ($x_{F0}$) is required. We have no physical arguments to specify the film thickness. In order to identify the effect of its value, we carried out simulations with several values of $x_{F0}$. It was found that this value has practically no effect on the drainage [16], since, for thicker films, most of the drainage takes place within a very short distance from the bottom. Figure 34 shows the liquid fraction profiles in a freshly formed foam of height 7.5 cm. In one case, the film thickness at the bottom was 1000 nm and in the other the value was 100 nm. The curves practically coincide indicating that the value one takes for the film thickness at the
bottom is largely irrelevant. Thus, as long as the foam is being generated (gas is being pumped in), the condition at the bottom is:

\[ x_F \bigg|_{z_2} = x_{F0} = \text{constant} \]  

(149)

Once the gas supply is stopped, the films at the bottom simply obey Reynolds equation with Eq. (149) as the initial condition. For the present calculations, \( x_{F0} \) was taken to be 500 nm.

The emphasis in that paper [16] was to theoretically model the effect of various parameters on the steady state height and collapse half life of pneumatic foams. However, since the assumption regarding the neglect
of the liquid in the films was first relaxed here, it would be instructive to make a comparison with results obtained using the earlier models in which only the drainage through the Plateau borders was taken into account.

In a more approximate earlier model [15], it was assumed that films were always in equilibrium with the adjacent Plateau border channels and that the fraction of liquid in the films was negligible. Collapse was deemed to start when the capillary pressure at the foam/gas interface exceeded the maximum disjoining pressure, i.e. when the Plateau border radius became smaller than a critical value \( r_{pc} \) given by Eq. (102).

Fig. 33. Fractional change in foam length for three values of \( L_0 \) with \( \mu = 0.9632 \) cP, \( \sigma = 59.4 \) dyn/cm, \( G = 0.0375 \) cm/s, \( \rho = 1000 \) kg/m\(^3\) and \( \eta_s = \infty \): (a) \( L_0 = 22.78 \) cm, \( R_0 = 0.203 \) mm.
In order to compare the results from these two approaches, a sample calculation was carried out. The foam was produced with a superficial gas velocity of 0.0001 m/s and the gas supply was shut off when a foam of length 7.5 cm was obtained. Figure 35 shows the profiles of liquid fraction (ε) in the foam when the gas supply is just shut off. Figure 36 shows the evolution of foam height (z₂ − z₁) as a function of time. Here the difference is much more significant. The reason for this is that while films do not influence the drainage process much, they play a crucial role in determining the characteristics of foam collapse. The older model predicts an earlier onset of collapse and a quicker decrease in foam length. This can be explained as follows. In the previous model, the
collapse starts the moment $r_p \big|_{z_1} = \frac{\sigma}{\Pi_{\max}}$. In the current model, collapse begins when $x_F = x_F \big|_{\Pi_{\max}}$. Under these circumstances, $r_p \big|_{z_1} < \frac{\sigma}{\Pi_{\max}}$. Because collapse begins in the new model at a lower value of $r_p$, it starts later. Also the current model predicts a slower collapse because the smaller Plateau border radius at the collapsing front is smaller which in turn implies a smaller rate of collapse (see Eq. (65)).

The results of some simulations done to examine the effect of various parameters on the steady-state height are discussed below.
Effect of superficial gas velocity on the steady-state height [16]

It is practical to use the steady-state height as a measure of foam stability only for relatively short-lived foams. For extremely stable foams, it is possible that the height of the foam when collapse starts will be too large to be conveniently measured in a laboratory. It is also obvious that the superficial gas velocity used to generate the foam will have a significant impact on the steady-state height. Figure 37 shows the steady-state height ($H_0$) as a function of the superficial gas velocity ($G$). It is clear that the steady-state height increases with $G$. The slope of the curve increases and seems to become unbounded for $G = 0.00035$ m/s, indicating that there is an upper limit on the superficial gas velocity beyond which a steady-state foam height will never be achieved. Some explanation for this can be provided as follows. From Eq. (65) it can be seen that the rate of foam collapse is determined by $q_{PB} \frac{1}{z_1}$. Since the
Fig. 35. A comparison of the liquid-fraction profiles in a freshly generated pneumatic foam of height 7.5 cms obtained using two models. Film drainage is included in one (new) and neglected in the other (old). The values of the parameters used are: $\rho = 1000 \text{ kg/m}^3$, $\mu = 1 \text{ cP}$, $G = 0.0001 \text{ m/s}$, $\psi_f = 20 \text{ mV}$, $R_0 = 0.2 \text{ mm}$, $T = 298 \text{ K}$, $A_h = 3.7 \times 10^{-20} \text{ J}$, $c_{in} = 0.005 \text{ M}$, $\Pi_{max} = 473.79 \text{ N/m}^2$ and $\sigma = 40 \text{ mN/m}$.

Film thickness at the collapsing front is fixed, $q_{PB}$ is determined primarily by the value of the Plateau border radius at the top. However, since collapse can occur only if the capillary pressure at the top exceeds the maximum disjoining pressure, there is an upper limit to the Plateau border radius at the top given by:

$$r_{pmax} = \frac{\sigma}{\Pi_{max}}$$  \hspace{1cm} (150)
Fig. 36. Variation of foam height with time for the system of Fig. 35.

In other words, there is an upper limit on the value of \( q_{PB} \) at \( z_1 \), given by:

\[
q_{PB_{\text{max}}} = \frac{3}{15} N n_p \alpha_p R_0 \frac{a_p \rho g}{20 \sqrt{3} \mu} \left| \frac{r_p = r_{p_{\text{max}}}}{x_p = x_{F_c}} \right|
\]  \hspace{1cm} (151)

This means that there is an upper limit to the value of \( \frac{dz_1}{dt} \), given by:

\[
\frac{dz_1}{dt} = \frac{q_{PB_{\text{max}}} (1 - \epsilon) \left| \frac{r_p = r_{p_{\text{max}}}}{x_p = x_{F_c}} \right|}{\epsilon \left| \frac{r_p = r_{p_{\text{max}}}}{x_p = x_{F_c}} \right|}
\]  \hspace{1cm} (152)
Fig. 37. Effect of superficial gas velocity \((G)\) on the steady state height. The values of the parameters used are: \(\rho = 1000 \text{ kg/m}^3\), \(\mu = 1 \text{ cP}\), \(\psi_s = 18 \text{ mV}\), \(R_0 = 0.2\text{ mm}\), \(T = 298 \text{ K}\), \(A_h = 3.7 \times 10^{-20} \text{ J}\), \(c_{el} = 0.001 \text{ M}\), \(\Pi_{max} = 227.23 \text{ N/m}^2\) and \(\sigma = 40 \text{ mN/m}\).

Thus for values of \(G\) for which \(\frac{dz_2}{dt}\) (Eq. (145)) is larger than the maximum value given by Eq. (152), \(\frac{dz_2}{dt}\) will always be larger than \(\frac{dz_1}{dt}\) and a steady-state height (for which \(\frac{dz_1}{dt} = \frac{dz_2}{dt}\)) will never be achieved.

Effect of electrolyte concentration on foam collapse [16]

The concentration of electrolyte in the surfactant solution plays a crucial role in determining the stability of a foam due to its effect on the
repulsive electrical double layer forces in a film. The primary effect of an increase in electrolyte concentration is to compress the electrical double layer, i.e. the Debye length decreases. The lower the value of $\Pi_{\text{max}}$, the smaller is the capillary pressure required to cause collapse. On the other hand, the smaller the critical thickness, the larger is the residence time required for the film to become critical. Figures 38 and 39 show the variation of $\Pi_{\text{max}}$ and the critical thickness ($x_{\text{Fe}}$) with electrolyte concentration. At small concentrations, the double layer is not too compressed. The maximum of the disjoining pressure therefore corresponds to large film thicknesses for which the van der Waals forces are not very large. An increase in the electrolyte concentration therefore...

Fig. 38. Effect of electrolyte concentration ($c_w$) on the maximum disjoining pressure ($\Pi_{\text{max}}$). The values of the other parameters used are: $\psi_s = 19 \text{mV}$, $T = 298 \text{K}$, and $A_h = 3.7 \times 10^{-20}$. 
Fig. 39. Effect of electrolyte concentration \( (c_{el}) \) on the critical thickness \( (x_{Pl}) \) for the system of Fig. 38.

raises \( \Pi_{DL} \) without affecting \( \Pi_{VDW} \) much and raises \( \Pi_{max} \). At higher electrolyte concentrations, the double layer is compressed and \( \Pi_{max} \) corresponds to very small thicknesses at which the van der Waals force is significant. \( \Pi_{max} \) now decreases with an increase in electrolyte concentration because \( \Pi_{VDW} \) rises sharply with a decrease in the film thickness. \( \Pi_{max} \) therefore increases, attains a maximum and then decreases as the electrolyte concentration increases. The position of this maximum however moves to smaller film thicknesses. This means that the critical thickness decreases with an increase in electrolyte concentration. It is therefore reasonable to expect that as the electrolyte concentration increases, the stability of the foam as quantified by the
steady state height ($H_0$) increases at first, achieves a maximum and then decreases. Figure 40, which presents the effect of salt concentration on $H_0$, shows that this indeed is the case.

It has been observed experimentally [69] that plots of $(z_2 - z_1)/H_0$ versus log($t/t_{1/2}$) practically coincide and at lower salt concentrations are linear. To check if our model predicts this feature (see Fig. 41) such plots were generated for six different values of the electrolyte concentration ($c_{el}$). While the curves are not linear, they seem to coincide quite well, especially at higher concentrations. The shape of the curve is more similar to the data provided in the above paper at higher concentrations.
Fig. 41. Effect of electrolyte concentration ($c_{el}$) on the dimensionless plots of $(z_2-z_1)/H_0$ versus $\log(t/t_{in})$. The values of the parameters are the same as in Fig. 40.

(labeled by these authors as “not so nice data”). The slope of the linear portion of the theoretical curves is reasonably close to the universal experimental line provided by these authors. A more direct comparison with the above experiments is not possible because there is no information on the bubble size used in the above experiments.

The concentration of the electrolyte also plays an important role in determining whether the foam collapses completely or arrives at a drainage equilibrium. Figure 42 shows the variation in foam height with time for two systems which differ only in the electrolyte concentration. The initial foam height is 4 cm and the values of the other parameters used are: $\rho = 1000$ kg/m$^3$, $\mu = 1$ cP, $\psi_s = 19$ mV, $R_0 = 0.2$ mm, $A_h = 3.7\times10^{-20}$, $\sigma = 40$ mN/m and $G = 0.0001$ m/s. The foam with $c_{el} = 0.003$ M equilibrates at a height of about 1.85 cm, while the foam with $c_{el} = 0.007$ M collapses completely. This can be explained as follows: The
capillary pressure has its smallest value \((\sigma/R_0)\) at the bottom of the foam, which in this case is 200 N/m\(^2\). For \(c_{el} = 0.003\) M, \(\Pi_{max} = 380.85\) N/m\(^2\) while for \(c_{el} = 0.007\) M, it is about 150 N/m\(^2\). Since in the latter case the smallest capillary pressure possible in the system exceeds the maximum disjoining pressure, the foam collapses completely.

**Effect of bubble size**

Figure 43 shows the effect of bubble radius \((R_0)\) on \(H_0\) for a system with the following parameters: \(\psi_s = 19\) mV, \(\sigma = 40\) mN/m, \(G = 0.0001\) m/s, \(c_{el} = 0.005\) M, \(T = 298\) K. Clearly, \(H_0\) increases with bubble size.
Fig. 43. Effect of the bubble radius $R_0$ on the steady state foam height. The values of the parameters used are: $\rho = 1000 \text{ kg/m}^3$, $\mu = 1 \text{ cP}$, $\psi_s = 19 \text{ mV}$, $T = 298K$, $A_h = 3.7 \times 10^{-20} \text{ J}$, $\sigma = 40 \text{ mN/m}$, $c_{el} = 0.005 \text{ M}$ and $G = 0.0001 \text{ m/s}$.

This can be explained as follows: In general, in a foam column draining under gravity, the curvature of the Plateau border channels ($r_p$) is the largest and the capillary pressure the smallest at the foam/liquid interface where $r_p = R_0$. For a given $\Pi_{\text{max}}$, the smaller the bubble size, the smaller is the decrease in $r_p$ required for the capillary pressure to rise to $\Pi_{\text{max}}$. This means that collapse starts at smaller heights resulting in smaller values of $H_0$. Figure 44 shows a plot of $z_2 - z_1$ versus time for two bubble sizes. It is clear that there is a qualitative difference since the foam with $R_0 = 0.3 \text{ mm}$ collapses to reach an equilibrium height, while the foam with $R_0 = 0.125 \text{ mm}$ collapses completely. This is because
Fig. 44. Variation of foam height with time for a foam with an initial length of 3 cm. With $R_0 = 0.125$ mm, complete collapse occurs, while with $R_0 = 0.3$ mm an equilibrium height is attained. The values of the parameters used are: $\rho = 1000$ kg/m$^3$, $\mu = 1$ cP, $\psi_s = 19$ mV, $T = 298$K, $A_h = 3.7 \times 10^{-20}$ J, $\sigma = 40$ mN/m, $c_{el} = 0.005$ M and $G = 0.0005$ m/s.

$(\sigma/R_0)$ is less than $\Pi_{\text{max}}$ for the former and greater than $\Pi_{\text{max}}$ for the latter. Figure 45 shows a comparison of the dimensionless plots for three bubble sizes with the universal experimental curve. The electrolyte concentration used here is 0.005 M. The other parameters remain the same. Again the agreement is fair. In an attempt to improve the overlap in the later stages of collapse, we made plots of $[(z_2-z_1) - (z_2-z_1)_{eq}] / [H_0-(z_2-z_1)_{eq}]$ versus log(t/t_{0.5}) (see Fig. 46), where $t_{0.5}$ is the time required for $[(z_2-z_1) - (z_2-z_1)_{eq}] / [H_0-(z_2-z_1)_{eq}]$ to become 0.5. The rationale for this was that this would force all the curves to become 0 at long times. It is seen from Fig. 46 that there is some improvement.
Coalescence and enrichment in foam [18]

In all the results discussed thus far, coalescence has been ignored. It was assumed that the film thickness was a function of only the vertical position 'z'. Thus film rupture at any level implied complete collapse of the foam at that level. In reality, however, all films at a given level do not rupture at the same time. There is usually a distribution of film thicknesses. The thinner films rupture first leading to a local increase in bubble size due to coalescence of the neighboring bubbles. Complete collapse occurs only when all the films at a given level rupture. The other important aspect that was ignored thus far was the variation of the
A. Bhakta, E. Ruckenstein / Adv. Colloid Interface Sci. 70 (1997) 1-124

Fig. 46. Effect of bubble radius ($R_o$) on the dimensionless plots of \((z_2-z_1)-(z_2-z_1)_c\) vs. \(\log(t/t_0.5)\). The values of the parameters are the same as in Fig. 45.

surfactant concentration. The surfactant concentration was assumed to be uniform throughout the foam and equal to the concentration in the foaming solution. Thus there was a single $\Pi_{\text{max}}$ and a single critical thickness ($x_{F_c}$) for a given foam. However, coalescence and collapse leads to a local increase in the surfactant concentration because the adsorbed surfactant on the film surfaces is released into the liquid in the Plateau border channels. Thus, depending on the transport properties, a profile of surfactant concentration is set up which in turn leads to a variation of $x_{F_c}$ and $\Pi_{\text{max}}$. $\Pi_{\text{max}}$ is higher and the films are more stable in regions where the surfactant concentration is higher. Thus coalescence and collapse can actually stabilize the remaining films. This effect is probably more significant for ionic surfactants where the disjoining pressure
isotherm is more sensitive to the surfactant concentration. Some of the results obtained when coalescence and surfactant transport are included are presented below.

**Results for coalescence and collapse**

In this section, results of simulations done to examine the effect of various parameters such as the apparent diffusivity \(D\), the concentration of surfactant \(c_{s0}\) and salt \(c_e\) in the foaming solution and the initial distribution of film radii \(f\) will be discussed.

The initial distribution \(f_0\) was assumed to be a truncated normal distribution given by:

\[
 f_0 = \frac{\exp\left[ -\frac{(R_F - R_{F0})^2}{s^2} \right]}{\int_{R_{Fmin0}}^{R_{Fmax}} \exp\left[ -\frac{(R_F - R_{F0})^2}{s^2} \right] dR_F} 
\]  

(153)

The mean film radius was taken to be \(R_{F0} = 0.606 R_0\), where \(R_0\) is the bubble radius (taken to be 0.2 mm) in the monodispersed foam before coalescence starts. The standard deviation \(s\) was taken to be 0.5 \(R_{F0}\) and \(R_{Fmin0}\) and \(R_{Fc}\) were taken to be 0.99 \(R_{F0}\) and 1.01 \(R_{F0}\), respectively, except when their effects on the results were examined. This represents a deviation of about 1% from the mean value. These values are arbitrary as we have no way of identifying what the exact distribution is. Unless otherwise specified, the apparent diffusivity is taken as \(D = 5 \times 10^{-5} \text{ m}^2/\text{s}\). This value is apparent and is much higher than the molecular diffusivity which has a value of \(10^{-10} \text{ m}^2/\text{s}\). In reality, \(D\) will vary throughout the foam depending on the fluid velocity and will be higher in regions where significant coalescence (which results in greater mixing) occurs. The values of the other parameters used were \(G = 0.0001 \text{ m/s}, c_s = 8 \text{ moles/m}^3, R_0 = 0.2 \text{ mm}, \mu = 1 \text{ cP}, T = 298 \text{ K}, c_{s0} = 0.012 \text{ moles/m}^3\) and \(K_d = 0.156 \text{ moles/m}^3\).

**Effect of diffusivity**

To examine the effect of the apparent diffusivity \(D\) on foam collapse, simulations were carried for two values of \(D\), viz. \(D = 5 \times 10^{-5} \text{ m}^2/\text{s}\) and \(D = 5 \times 10^{-6} \text{ m}^2/\text{s}\). Figure 47 shows the variation in foam length with time.
Fig. 47. Variation of foam length with time for two values of the apparent diffusion coefficient $D$. The values of the other parameters used are $c_{a0} = 0.012$ moles/m$^3$, $c_e = 8$ moles/m$^3$, $R_0 = 0.2$ mm, $R_{F0} = 0.606 R_0$, $R_{Fmin0} = 0.99 R_{F0}$ and $R_{Fp} = 1.01 R_{F0}$.

for these two cases. Points A and B indicate the onset of foam collapse. The foam with the higher diffusivity starts collapsing earlier and collapses at a much higher rate. This can be explained as follows: Coalescence leads to a release of surfactant from the ruptured films and hence leads to a local accumulation of surfactant. This local increase of the surfactant concentration tends to stabilize the remaining films since the maximum disjoining pressure increases with surfactant concentration, i.e. a film becomes more stable as the surfactant concentration increases. Further coalescence depends strongly on the rate at which the surfactant is transported away. With low diffusivity, the transport of
surfactant away from the region is slower and the local accumulation is higher. The films are therefore stabilized to a greater extent and the rate of coalescence is much smaller. Thus it takes longer for $R_{F_{\text{min}}}$ to approach $R_{F_{\text{max}}}$ and foam collapse starts much later. A similar explanation applies to the rate of foam collapse. A higher $D$ means that the surfactant released due to collapse quickly diffuses away without significantly stabilizing the films and the foam collapses at a much faster rate. Figure 48 shows a comparison of the surfactant concentration profiles at different times. The rise in surfactant concentration in the upper levels of the foam is primarily due to coalescence and collapse. However, the surfactant concentration throughout the foam is always
higher when the diffusivity is smaller. Figure 49 shows the profiles of the dimensionless bubble radius $\bar{R}/R_0$ at three different times: when the gas supply is just off ($t' = 0$), 10 minutes later ($t' = 600$ s) and 30 minutes later ($t' = 1800$ s). Here $t'$ represents the time elapsed after the gas supply is shut off. At $t' = 0$, there is no coalescence and the bubble size throughout the foam is uniform and equal to the initial bubble radius, i.e. $\bar{R}/R_0 = 1$. At other times however there is a sharp increase in the bubble radius in the upper portion of the foam. This can be explained as follows: due to drainage, the liquid content is lowest at the top of the foam. In other words, at $z = z_1 = 0$, $r_p$ is the smallest and the capillary pressure ($\sigma/r_p$) is the largest which in turn means that for a given $R_F$, 

Fig. 49. Profiles of the dimensionless bubble radius $(\bar{R}/R_0)$ at different times for the system of Fig. 47.
films at the top of the foam drain most rapidly and rupture the earliest. Coalescence therefore starts first at the top of the foam and propagates down the foam with the passage of time. It is clear from the figure that for both values of $D$, there are regions in which coalescence has taken place at $t' = 600 \text{ s}$ and $t' = 1800 \text{ s}$. However, for larger $D$, significantly more coalescence has occurred and the foam/gas interface has moved farther for reasons already outlined earlier in this section.

**Effect of the initial distribution**

To examine the effect of the initial distribution ($f_0$), a simulation was carried out using a different $f_0$ with a larger width, i.e. with $R_{F_{\text{min}}0} = 0.95 R_{F0}$ and $R_{Fc} = 1.05 R_{F0}$, a variation of about 5% about the mean. Figures 50 and 51 show the results for this case. With the broader distribution, coalescence occurs in a larger portion of the foam and foam collapse starts later. Both these effects are consequences of a smaller $R_{F_{\text{min}}0}$. Since films with a smaller $R_F$ drain quicker, a smaller $R_{F_{\text{min}}0}$ means that the corresponding films are thinner at any given time and hence rupture earlier, resulting in the earlier onset of coalescence. On the other hand, since $R_{F_{\text{max}}}$ is larger, it takes longer for $R_{F_{\text{min}}}$ to approach $R_{F_{\text{max}}}$ and foam collapse starts later.

**Effect of surfactant concentration**

An increase in surfactant concentration usually stabilizes a foam by increasing $\Pi_{\text{max}}$ and the surface viscosity. A larger $\Pi_{\text{max}}$ has two consequences: firstly this implies that a larger capillary pressure is required to rupture a film. This means that greater drainage must occur and a longer time must elapse before films at the top with $R_F = R_{F_{\text{min}}0}$ rupture and bubbles start coalescing. A later onset of coalescence means that foam collapse will start much later since it takes a longer time for $R_{F_{\text{min}}}$ to approach $R_{F_{\text{max}}}$. The other important impact of the initial surfactant concentration is on the characteristics of the foam when a mechanical drainage “equilibrium” is achieved. At “equilibrium”, there is no flow in the Plateau Border channels ($\frac{\partial}{\partial z} \left( \frac{\sigma}{r_p} \right) = - \rho g$), no film drainage ($\frac{\sigma}{r_p} = \Pi$), no diffusion of surfactant ($\frac{\partial c_s}{\partial z} = 0$) and no foam collapse ($\frac{dz_1}{dt} = 0$). Thus in an equilibrated foam, the concentration of surfactant throughout the foam is the same and equal to that of the foaming
solution \((c_{s0})\). By integrating the equation \(\frac{\partial}{\partial z} \left( \frac{\sigma}{r_p} \right) = -\rho g\) using the conditions \(\frac{\sigma}{r_p} \bigg|_{z_1} = \Pi_{\text{max}}(c_{s0})\) and \(r_p \bigg|_{z_2} = R_0\), the length of the equilibrated foam is given by:

\[
(z_2 - z_1)_{\text{eq}} = L_{\text{max}} = \frac{-\frac{\sigma}{R_0} + \Pi_{\text{max}}(c_{s0})}{\rho g}
\]
The subscript "max" indicates that this is the largest length a foam can have without undergoing collapse. Figures 52 and 53 show the results for two values of $c_{s0}$, viz. 0.012 moles/m$^3$ and 0.015 moles/m$^3$. $L_{\text{max}}$ for the latter is 3.67 cm as opposed to 1.81 cm for the former. Thus in the latter case, collapse slows down as the foam length approaches 3.67 cm. Such a slowdown is not in evidence in the former case and collapse continues well below $(z_2 - z_2) = 3.67$ cm. The opposite effect is seen when the salt concentration is raised to 8.245 moles/m$^3$. Raising the salt concentration compresses the electrical double layer and lowers $\Pi_{\text{max}}$, thereby lowering $L_{\text{max}}$ from 3.67 cm to 2.07 cm. Figures 54–56 show the effect of salt concentration on a foam with $c_{s0} = 0.015$ moles/m$^3$. With
higher salt concentration, coalescence and foam collapse start earlier and occur at a faster rate. This is further emphasized by the profiles of surfactant concentration. With higher salt, greater coalescence results in a much larger amount of surfactant being released into the bulk leading to higher surfactant concentrations.

Before we proceed with the conclusions, we will discuss briefly the phenomenon of inter-bubble gas diffusion (Ostwald ripening) which has been ignored in our model.

3. Inter-bubble gas diffusion (Ostwald Ripening)

When the pressure in the foam bubbles varies significantly, there is a transfer of gas from bubbles with higher pressure to those with lower pressure. This transfer occurs by diffusion through the liquid films.
separating the bubbles and is driven by the difference in the concentration of the dissolved gas at the two film surfaces. Since these concentrations are proportional to the pressure at the interfaces (Henry’s law) the transport of gas is faster when the pressure difference is higher. The other important factor is the solubility of the gas in the liquid. Interbubble diffusion increases dramatically as the solubility of the gas increases. This is the main reason why CO₂ foams are less stable than N₂ foams. The pressure inside a bubble is determined by its volume when it is just formed. Since the bubble is initially spherical, the pressure inside the bubble is given by:

\[ P_i = P_{pool} + \frac{2\sigma}{R} \]  

(155)

where \( R \) is the bubble radius and \( P_{pool} \) is the pressure in the liquid pool. Thus, the pressure is higher in the smaller bubbles. This means that gas is transferred from smaller to larger bubbles causing the smaller bubbles to get smaller and the larger bubbles to get larger. This is very
similar to the phenomenon of Ostwald ripening observed in supersaturated solutions, where the larger particles grow in size at the expense of smaller ones. Hence inter-bubble diffusion is also referred to as Ostwald ripening.

The first theoretical treatment of inter-bubble diffusion was provided by Clark and Blackman [70], who showed that the rate of growth of a bubble of radius \( R \) is given by the expression:

\[
\frac{dR}{dt} = C \left( \frac{1}{R_m} - \frac{1}{R} \right)
\]  

(156)
Fig. 55. Profiles of dimensionless bubble radius ($\bar{R}/R_0$) at different times for the system of Fig. 54.

where $R_m = \frac{\sum N_i R_i^2}{\sum N_i R_i}$ is a certain mean radius such that bubbles with $R < R_m$ shrink and those with $R > R_m$ grow. Typically, a population balance equation is solved using Eq. (156) to obtain the evolution of the bubble size distribution. A pivotal assumption made in deriving Eq. (156) which has been made in all subsequent papers [61,71–73] dealing with this phenomenon is that the pressure inside a bubble of radius $R$ is given by $p_i = p_{atm} + \frac{2\sigma}{R}$, where $p_{atm}$ is the atmospheric pressure. The pressure difference between two bubbles with radii $R_1$ and $R_2$ is then
This relationship is true only for spherical bubbles. It is not clear how the pressure changes with size in polyhedral bubbles. Equation (156) may therefore not be valid for polyhedral foams. Probably the only option for polyhedral foams is to use a microscopic approach in which the curvature and area of each film is a function of time and changes as the pressure in the bubbles sharing the film changes. This approach has been used to simulate the evolution of a two-dimensional foam [31–33]. Using this approach for three dimensional foam and integrating it with drainage and coalescence is likely to be extremely difficult. A model which incorporates drainage, coalescence and
inter bubble gas diffusion has been proposed by Narsimhan and Ruckenstein [60,61] for steady-state foams. However, drainage is treated assuming pentagonal dodecahedral geometry and inter bubble gas diffusion is treated assuming spherical bubbles. Given the complexity of the system, such assumptions are probably inevitable. Even with these assumptions, extending this model to unsteady state standing foams would be very difficult.

The results of our model are therefore valid only for initially mono-dispersed foams composed of gases that are sparingly soluble in the continuous phase liquid.

4. Conclusions

A detailed model is formulated for the drainage, coalescence and collapse of aqueous foams. Simulations have provided several insights into the kinetics of foam collapse and drainage. New insights into the metastable equilibrium established in foams have also been obtained.

The foam is assumed to be composed of identical pentagonal dodecahedral bubbles. Drainage of the liquid in the films is modeled using the Reynolds equation for flow between circular parallel disks. This flow is driven by the capillary pressure generated due to the curvature of the adjacent Plateau border channels and is opposed by the disjoining pressure that arises between the two film surfaces. The disjoining pressure isotherm (which expresses the relationship between the disjoining pressure and the film thickness) plays a crucial role in determining the characteristics of film drainage and rupture. Since the disjoining pressure is composed of attractive van der Waals and repulsive electrical double layer and hydration forces, the isotherm often has a maximum. The film thickness corresponding to this maximum is the critical thickness of film rupture. Film with thicknesses smaller than this critical thickness rupture because of the unbounded growth of disturbances on the film surfaces. On the other hand, films with thicknesses larger than this thickness are stable because any waves on their surfaces are damped.

Whether a film arrives to this critical thickness depends on the relative magnitudes of the capillary pressure and the disjoining pressure. If the capillary pressure exceeds the maximum disjoining pressure, the film will drain to the critical thickness and rupture; if the capillary pressure is less than the maximum disjoining pressure, the
film will arrive at a stable equilibrium thickness at which the capillary pressure and the disjoining pressure are equal. The capillary pressure must therefore exceed a critical in order to cause film rupture. In other words, there is a critical Plateau border radius (which depends on the local surface tension) below which a film drains to its critical thickness and ruptures.

The capillary pressure is different in different portions of the foam and varies with time depending on the liquid content in the foam. When the liquid content is larger, the Plateau border radius is larger, the capillary pressure is smaller and hence the foam is more stable. The local liquid content in a foam is largely determined by the gravity driven flow in the network of Plateau border channels. While the liquid flows out of the foam through the channels at the bottom, the channels in the upper portion of the foams drain into the channels below. Thus, with the passage of time, there is a redistribution of liquid in the foam with the upper portions becoming progressively drier. This sets up a pressure gradient within the foam which opposes gravity and hence slows down the flow in the foam leading eventually to a drainage equilibrium in which the liquid content in the various portions of the foam no longer changes with time. If this equilibrated state is reached before the capillary pressure exceeds the maximum disjoining pressure, no foam collapse occurs. If not, foam collapse occurs until an equilibrium height is reached.

Foams can be distinguished into two categories depending on the method employed to generate them. Pneumatic foams are produced by bubbling a gas through a solution of surfactant. Foam is formed at the surface of the liquid and rises as more gas is bubbled into the system. The foam length increases till the gas supply is shut off. The drainage that occurs as the foam moves up leads to a distribution of liquid in the freshly formed foam. On the other hand, in homogeneous foams which are produced by vigorous agitation of the surfactant solution, the liquid content is uniform throughout the foam. The other important difference between the two types is that pneumatic foams are always in contact with the foaming solution, while with homogeneous foams, there is a time lag before some liquid appears at the bottom of the foam. Both kinds of foams are modeled in this work.

The model successfully predicts the trend of lag times observed in the drainage of homogeneous foams. For a foam of a given length, the lag time decreases as the initial volume fraction of continuous phase ($\varepsilon_0$) increases and for a given $\varepsilon_0$, the lag time decreases as the foam length
increases. It is shown that based on certain properties of a homogeneous foam such as the bubble radius ($R_0$), column height ($L_0$), interfacial tension ($\sigma$) and density difference between the two phases ($\rho$), it is possible to determine whether phase separation (separation of the continuous phase liquid via drainage or the separation of the dispersed phase gas via collapse). It is also possible to determine which of the two phases (if not both) will separate out before equilibrium is established. Two-phase separation (collapse as well as drainage) is possible only if the column length exceeds a certain value, which for a given pair of fluids depends only on the bubble radius ($R_0$). A generalized “phase” diagram is presented which makes it possible to determine the phase behavior of a concentrated emulsion based on the value of a single dimensionless number ($P = \frac{\sigma}{\rho g K R_0 L_0}$).

In the case of pneumatic foams, the superficial velocity of the bubbling gas plays an important role in determining the liquid content in the foam. Foams produced with a higher superficial gas velocity contain a greater amount of liquid and hence drain at a faster rate. Simulations were carried out to examine the effect of the initial foam length, the bubble radius and the viscosity of the foaming solution on the drainage of liquid from foams in which no film rupture occurs. The results were in good agreement with experimental data.

When foam collapse starts during the generation of a pneumatic foam, the foam often attains a steady state height when the rate at which the foam is produced equals the rate at which the foam is destroyed. The model accounts for the collapse of the foam during generation by bubbling and is therefore able to predict the steady state height attained by such foams. The effect of various parameters such as superficial gas velocity, salt concentration and bubble size on the steady state height and collapse half-life (time required for a foam to collapse to half the steady state height) was examined. For a given system, there is an upper limit on the superficial gas velocity beyond which a steady state height will not be attained. With increasing salt concentration, the stability of a foam (as determined by the steady state height and collapse half life) first increases, attains a maximum and then decreases. The steady state height and the collapse half life decreases with a decrease in bubble size due to an increase in the capillary pressure. Also, for a given system there is an upper limit to the salt concentration and a lower limit to the bubble size beyond which no drainage equilibrium is possible and
complete collapse of the foam occurs. Dimensionless plots of \((z_2 - z_1)/H_0\) versus \(\log(t/t_{1/2})\) where \(H_0\) is the steady state height and \(t_{1/2}\) is the half life, coincide for most of the period of foam collapse even when the electrolyte concentration and bubble size are changed.

It has been observed experimentally that with some foams, the stability of a foam increases sharply at high salt concentrations due to the formation of very stable Newton black films. An attempt is made to explain this phenomenon by considering, in addition to the van der Waals and the electrical double layer forces, a short range repulsive force due to the organization of water molecules near the surfaces. The electrical double layer is a result of the surface charge due to the dissociated adsorbed surfactant molecules, while the short range repulsive force is caused by the dipole moments of the undissociated adsorbed surfactant molecules. It is shown that depending on the values of the parameters used, it is possible to have a disjoining pressure isotherm with two maxima at sufficiently high salt and surfactant concentrations. Under these conditions, instead of film rupture, there is a jump transition to very stable Newton black films. These results are in qualitative agreement with experimental observations.

It is experimentally observed that in some foams, there is often significant coalescence of bubbles which results in an increase in the bubble volume. A model is presented that includes the effect of coalescence in standing foams. Coalescence is assumed to result from the non-uniformity of film sizes within a volume element. This leads to a non-uniformity of drainage rates and hence of film thicknesses within the element. Smaller films drain faster and hence rupture first, causing bubble coalescence. Thus a bubble size distribution is set up within the foam, which evolves with time. The model is also able to predict the variation of the surfactant concentration profile as it changes due to coalescence and collapse. Simulations were performed to examine the effect of various parameters including the apparent diffusion coefficient, the distribution of film sizes and the concentrations of surfactant and salt in the foaming solution. A high diffusion coefficient results in faster coalescence and an earlier onset of foam collapse. This is because the surfactant released due to coalescence and collapse is transported away before it can accumulate and stabilize the films. An increase in the width of the initial distribution of film sizes results in a later onset of foam collapse, because a greater amount of coalescence needs to occur before all the films at the top become critical and rupture. The concentration of surfactant and salt in the foaming solution primarily affects the
equilibrium length at which a collapsing foam must necessarily arrive. A higher surfactant concentration increases the surface charge, raises the maximum disjoining pressure and hence increases the equilibrium foam length. On the other hand, an increase in salt concentration compresses the electrical double layer and has the opposite effect.

**Nomenclature**

\( a = \) Distance between adjacent water molecules
\( A' = \) Constant in the expression for the short range repulsive force
\( A_h = \) Hamaker constant
\( a_p = \) Average cross-sectional area of a Plateau border channel
\( a_1 = \) Empirical parameter in the Frumkin adsorption equation
\( A_1, A_2, A_3 = \) Functions used in the calculation of the electrical double layer force
\( A_F = \) Area of the surface of a film
\( R_{F_{\text{max}}} = \int_{R_{F_{\text{min}}}} f A_F dR_F = \) Mean surface area of a film at any level
\( B' = \) Constant in the expression for the short range repulsive force
\( b_1 = \) Empirical parameter in the Frumkin adsorption equation
\( b_1, b_2, b_3 = \) Variables defined in Eqs. (81–83)
\( b = \) Empirical constant used in the calculation of the van der Waals force
\( c = \) Empirical constant used in the calculation of the van der Waals force; constant of integration
\( c_f = \) Correction factor for Reynolds equation accounting for the mobility of the film surfaces
\( c_v = \) Concentration of salt in the foam
\( c_{\text{el}} = \) Electrolyte concentration
\( c_s = \) Concentration of dissolved surfactant
\( c_{s0} = \) Surfactant concentration in the foaming solution
\( c_{R^-} = \) Concentration of surfactant anions near the surface
\( c_{sNa^+} = \) Concentration of \( Na^+ \) ions near the surface
\( c_v = \) Coefficient accounting for the mobility of the walls of a Plateau border channel
\( C = \) Constant used in Eq. (156)
\( D = \) Apparent diffusivity
\[ D_s = \text{Surface diffusivity} \]
\[ E = \text{Electric field} \]
\[ E^0 = \text{Electric field due to the surface acting on the first layer of water molecules} \]
\[ E_d = \text{Parameter used in the calculation of the short range repulsive force} \]
\[ E_{d\text{ref}} = \text{Reference value for } E_d \]
\[ e = \text{Protonic charge; also empirical constant used in the calculation of the van der Waals force} \]
\[ f = \text{Distribution of film radii} \]
\[ f_0 = \text{Initial distribution of film radii} \]
\[ G = \text{Superficial gas velocity} \]
\[ g = \text{gravity} \]

\[ K = \sqrt{\frac{4\pi}{2(0.161)n_p0.816}} \]

\[ K_d = \text{Dissociation constant of the adsorbed surfactant molecules} \]
\[ k_B = \text{Boltzmann constant} \]
\[ l = \text{Average length of a Plateau border channel} \]
\[ l_s = \text{Length of a segment} \]
\[ L = \text{Thickness of brush} \]
\[ L_0 = \text{Initial length of foam/concentration; Chain length in a theta solvent} \]
\[ L_{\text{max}} = \text{Minimum height of the foam/concentrated emulsion for collapse as well as drainage to occur} \]
\[ n = \text{Number of water molecules per unit volume} \]
\[ n_s = \text{Number segments in molecule} \]
\[ N = \text{Number of bubbles per unit volume} \]
\[ n_p = \text{Number of PB channels per bubble} \]
\[ n_F = \text{Number of films per bubble} \]
\[ N_A = \text{Avogadro's number} \]
\[ p = \text{Pressure in liquid} \]
\[ p_{\text{ref}} = \text{Reference pressure in liquid} \]
\[ p_i = \text{Pressure inside bubble/droplet} \]
\[ \Delta P = \text{Pressure difference driving film drainage} \]

\[ P = \text{Dimensionless number given by } \frac{\sigma}{KpgR_0L_0} \]

\[ P_1, P_2 = \text{Variables used in the calculation of the short range repulsive force} \]
\[ q_\theta = \text{Volumetric flow rate through a Plateau border channel inclined at an angle } \theta \text{ to the vertical} \]
\( q = \) Empirical constant used in the calculation of the van der Waals force
\( q_{PB} = \) Volumetric flux of liquid due to drainage of liquid through the PB channels
\( q_c = \) Volumetric flux of liquid due to bulk movement of bubbles
\( q_L = \) Total flux of liquid
\( q_G = \) Volumetric flux of gas
\( q_{cs} = \) Flux of surfactant
\( r = (R_F - R_{F_{\min}})/(R_{F_{\max}} - R_{F_{\min}}) = \) Dimensionless co-ordinate in \( R_F \) space
\( R = \) Bubble radius
\( R_0 = \) Bubble radius in the initially monodispersed foam
\( \bar{R} = \left( \frac{3}{4\pi} V \right)^{1/3} = \) Mean bubble radius
\( R_m = \) A mean radius used in models for inter-bubble gas diffusion
\( R_F = \) Radius of a film
\( R_{F_{\min}} = \) Smallest value of the film radius at a given level
\( R_{F_{\max}} = \) Largest value of the film radius
\( R_{F_c} = \) The upper limit for \( R_{F_{\min}} \) beyond which the distribution is assumed to be Dirac delta
\( r_p = \) Plateau border radius
\( \bar{R}_G = \) Molar gas constant
\( s = \) Standard deviation
\( T = \) Absolute temperature
\( t = \) time
\( t' = \) time elapsed after gas supply is shut off
\( u = \) Average velocity in a PB channel; also dipole moment
\( u_\theta = \) Average velocity in a PB channel inclined at an angle \( \theta \) to the vertical
\( u_s = \) Dipole moment per unit area
\( V_c = \) Volume of continuous phase per unit area in an equilibrated foam of length \( L_0 \) which is in contact with continuous phase at the bottom
\( V_{eq} = \) Volume of continuous phase per unit area at equilibrium
\( V_{eq} = \) Volume of continuous phase per unit area in an equilibrated foam of length \( L_{\max} \)
\( V_{Deq} = \) Volume of dispersed phase per unit area in an equilibrated foam of length \( L_{\max} \)
\( V_D = \) Volume of dispersed phase per unit area in an equilibrated foam of length \( L_0 \) in which the films at the top are critical
\( \bar{V} = \) Mean bubble volume
\[ V_F = \text{Rate of film thinning} \]
\[ W = \text{Interaction energy} \]
\[ x = \text{Distance from the mid-plane} \]
\[ x_F = \text{Film thickness} \]
\[ x_{F_{\text{max}}} = \frac{\int f x_F dx_F}{R_{F_{\text{min}}}} = \text{Mean film thickness at a given level} \]
\[ x_{F_c} = \text{Critical thickness of film rupture} \]
\[ x_{F_{\text{m}}}, x_{F_{\text{m},\text{dl}}} = \text{Film thickness corresponding to the maximum disjoining pressure} \]
\[ x_{F_{\text{m},\text{dl}}} = \text{Film thickness corresponding to the maximum disjoining pressure when only electrical double layer forces are present} \]
\[ z = \text{Space co-ordinate} \]
\[ z_1 = \text{Co-ordinate of the foam/gas interface} \]
\[ z_{1e} = \text{Co-ordinate of the foam/gas interface at equilibrium} \]
\[ z_{2e} = \text{Co-ordinate of the foam/liquid interface at equilibrium} \]
\[ z_2 = \text{Co-ordinate of the foam/liquid interface} \]

**Greek Letters**
\[ \alpha = \text{Reciprocal decay length of the short range repulsive force} \]
\[ \alpha_d = \text{Degree of dissociation of the adsorbed surfactant molecules} \]
\[ \xi = (z-z_1)/(z_2-z_1) = \text{Dimensionless coordinate in } z \text{-space} \]
\[ \delta = \text{Distance between adjacent planes of water molecules} \]
\[ \varepsilon_d = \text{Dielectric constant; Liquid fraction} \]
\[ \varepsilon = \text{Liquid fraction} \]
\[ \varepsilon_{\text{eq}} = \text{Liquid fraction at equilibrium} \]
\[ \varepsilon_b = \text{Liquid fraction at the foam/liquid interface} \]
\[ \varepsilon_c = \text{Liquid fraction at the foam/gas interface when collapse occurs} \]
\[ \varepsilon_0 = \text{Initial liquid fraction} \]
\[ \varepsilon_{d0} = \text{Permittivity of free space} \]
\[ \gamma_p = \text{Polarizability of water} \]
\[ \gamma_s = \text{Inverse of dimensionless surface viscosity} \]
\[ \eta_s = \text{Surface viscosity} \]
\[ \kappa = \text{Reciprocal Debye length} \]
\[ \lambda_n = \text{nth root of the equation } J_0(\lambda_n) = 0 \]
\[ \mu = \text{Bulk viscosity} \]
\[ \mu_s = \text{Dipole moment of an adsorbed surfactant molecule} \]
\[ \mu_w = \text{Dipole moment of a water molecule} \]
\( \rho_c = \) Density of the continuous phase
\( \rho_D = \) Density of the dispersed phase
\( \rho = \) Density difference between the continuous phase and the dispersed phase
\( \sigma = \) Surface tension
\( \sigma_c = \) Surface charge per unit area
\( \sigma_0 = \) Surface tension of pure water
\( \psi_s = \) Surface potential
\( \psi = \) Potential
\( \psi_m = \) Mid-plane potential
\( \Gamma = \) Surface density of surfactant
\( \Gamma = \) Mean surface density of surfactant at a given level. It taken to be a function of the mean film thickness and the surfactant concentration
\( \Gamma_w = \) Surface density at saturation
\( \Pi = \) Disjoining pressure
\( \Pi_h = \) Contribution to the disjoining pressure due to organization of water molecules
\( \Pi_{\text{max}} = \) Maximum disjoining pressure
\( \Pi_{\text{DL}} = \) Electrical double layer force per unit area
\( \Pi_{\text{SR}} = \) Short range repulsive force per unit area
\( \Pi_{\text{ST}} = \) Steric repulsive force per unit area
\( \Pi_{\text{VDW}} = \) van der Waals force per unit area
\( \Pi_{\text{max,dl}} = \) The maximum disjoining pressure when no short range repulsive forces are present

References

[34] O. Reynolds, Phil. Trans. R. Soc. Lond., A, 177 (1886) 157.
Appendix A

Calculation of velocity coefficient

Desai and Kumar [56] have expressed the velocity coefficient \( c_v \) as a function of the dimensionless surface viscosity \( \gamma_s = \frac{0.438 \eta \sqrt{\alpha \gamma}}{\eta_s} \) as:

\[
c_v = b_{i0} + b_{i1}(\gamma_s - \gamma_i) + b_{i2}(\gamma_s - \gamma_i)^2 + b_{i3}(\gamma_s - \gamma_i)^3
\]  

(A1)

where \( \gamma_i \leq \gamma_s \leq \gamma_{i+1} \) are constants. The values of the coefficients \( b_{ij}, j = 0\text{--}3 \) can be found elsewhere in the literature [56].
Appendix B

Calculation of the electric field due to dipoles on the surface

The component of the electric field at the point P in a direction perpendicular to the plane due to a dipole of moment ‘u’ at point A is given by:

\[ E = \frac{2uc\cos^2(\alpha)}{4\pi\varepsilon_0y^3} \]  

(B1)

If \( u_s \) is the dipole moment per unit area, the electric field at the point P due to a ring of radius \( r \) and thickness \( dr \) is given as:

\[ dE = \left[ \frac{2u_s(2\pi r dr)\cos^2(\alpha)}{4\pi\varepsilon_0y^3} \right] \] 

(B2)

Since \( \cos(\alpha) = r/y \) and \( y^2 = r^2 + z^2 \), we have:

\[ dE = \frac{2\mu_s}{4\pi\varepsilon_0y^3} \left( \frac{2\pi r dr}{(r^2 + z^2)^{3/2}} \right) \frac{r^2}{y^2} \] 

(B3)

Thus the total electric field at P is given as:

\[ E = \frac{u_s}{\varepsilon_0} \int_{0}^{\infty} \frac{r^2}{(r^2 + z^2)^{5/2}} dr = \frac{u_s}{3\varepsilon_0z} \] 

(B4)

Fig. B.1. Schematic diagram for the computation of the electric field.