THE INSTABILITY OF THIN LIQUID FILMS
IN RELATION TO COALESCENCE

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by
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ABSTRACT

The behaviour of the liquid in thin films is examined theoretically and experimentally with special attention given to the influence of intermolecular forces and surface active agents on the stability of such systems. The effect of these forces on the instability of thin liquid films has been observed experimentally by employing an optical interference technique.

The influence of a surface wave on the hydrodynamic instability of a thin liquid film in which intermolecular forces are important is developed theoretically in Section I. The derived equations show that the surface elasticity of the film exerts a considerable damping effect on the growth rate of an unstable wave and it is shown to be a major factor in influencing the stability of foams. The relevance of the results to foam stability is discussed.

In Section 2, experiments were performed to determine interferometrically the draining and rupture process of a thin aqueous film formed between a bubble and a hydrophobic surface. The interferograms observed have been recorded photographically. The results indicate the action of a long range surface force extending to thicknesses of up to 20,000 Å. The barrier ring formed initially is shown to be unstable and rupture proceeds via local thinning on a small area of the barrier ring. The results are discussed in relation to ore flotation and the local thinning mechanism is suggested as an explanation to Padday's remarkable critical rupture thicknesses on low energy surfaces. Photographs are also presented to show the coalescence, in glycerol, of a bubble with an attached surface bubble. The photographs show two different processes, both of which depend upon bubble tilt and asymmetric flow.
Section 3 is concerned with the prediction of the profile of a draining microscopic circular film with particular reference as to why these films appear plane parallel to the dimensions observed. The equations derived produce results which predict plane parallel films of much smaller radii than those seen experimentally. In order to account for this discrepancy the effect of an unstable wave on the surfactant concentration, has been shown, to a first order approximation, to predict a discontinuity at radial distances which are short compared to the wavelength. The presence of such a discontinuity could lead to significant changes in the local film properties.
"If science tends to thicken the crust of ice on which, as it were, we are skating, it is all right. If it tries to find, or professes to have found, the solid ground at the bottom of the water, it is all wrong".  

Samuel Butler (1835-1902)
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NOMENCLATURE

A  film area, London-Hamaker constant

\( c \)  velocity of light in vacuo

\( C \)  concentration of electrolyte

\( D_s \)  surface diffusivity

\( e \)  surface electric charge density

\( F_{h,\infty} \)  Free energy of a film of thickness \( h \) and a thick film respectively.

\( F \)  Faraday constant

\( g \)  acceleration due to gravity

\( h \)  film thickness

I  light intensity

\( k \)  wavenumber; Boltzmann constant

\( K \)  Van der Waals-Hamaker constant

\( m \)  wavenumber

\( n \)  wave growth rate; number of molecules, number of immobile surfaces; refractive index.

\( P \)  pressure

\( P_\sigma \)  capillary pressure

\( Q \)  volume outflow

r  radial distance, Fresnel coefficient

\( R \)  radius of circular film; gas constant; reflectance

\( R_b \)  radius of bubble

\( S_{h,\infty} \)  entropy of a thin film and a thick film respectively

\( t \)  time

\( T \)  tension of a thin film; absolute temperature; transmittance

\( U_{h,\infty} \)  energy of a thin film and a thick plane parallel film respectively
Velocity of approach of upper film surface

volume per molecule

Volume

axial distance; valency of ion.

Greek symbols

\(\alpha\)
- electromagnetic polarisability

\(\beta\)
- London constant

\(\Gamma\)
- surface concentration of surfactant

\(\varepsilon\)
- surface elasticity; dielectric constant

\(\sigma\)
- surface tension

\(\hbar\)
- Planck's constant

\(\lambda\)
- wavelength of light

\(\lambda_L\)
- wavelength of the London wave

\(\eta\)
- wave displacement on film surface

\(\Pi\)
- disjoining pressure

\(\phi\)
- potential of the diffuse double layer

\(\rho\)
- density; volume electric charge density

\(\psi\)
- streamfunction

\(\tau\)
- viscous stress

\(\mu\)
- dynamic viscosity; dipole moment

\(\mu_{h,\infty}\)
- chemical potential of a thin film and a thick film respectively.

\(\nu\)
- kinematic viscosity; characteristic frequency of electromagnetic oscillation.

\(\Omega\)
- frequency of photon.
INTRODUCTION

Much research has been directed towards thin liquid films because their study yields valuable information on the properties of a variety of important disperse systems. Free liquid films can be considered as models for the behaviour of foams; a thin film between a substrate and a gaseous phase is analogous to the pre rupture stage in ore-flotation; a thin film of a liquid in another liquid is a model for an emulsion and a thin liquid film between solids is considered as a model for colloidal suspensions.

The coalescence of such systems involves both hydrodynamic and surface chemistry considerations. However, the hydrodynamics of the coalescence is largely determined by the forces imposed by the surface properties and intermolecular forces. The general method of approach by most researchers has been directed towards the understanding of these surface and intermolecular forces and has thus tended to become a physical chemistry problem.

Foam stability has relevance in many chemical engineering aspects. Relatively recently, a separation technique based upon the differences in surface activity of various components in a mixture has been proposed. This "adsorptive bubble separation technique" relies on detailed knowledge of the behaviour of foams and especially the stability of such systems.

The forces present in thin films can be treated as intermolecular attractions of the London-Van der Waals type, electrostatic effects which generally lead to repulsive forces and lastly the influence of the surface itself on these forces. The latter is particularly important in the case of a solid substrate and much recent work has been directed towards a better understanding of its properties.
The forces in thin films are generally represented in terms of a disjoining pressure.

The development of models for the Van der Waals attraction and electrostatic effects is outlined in the introduction to Section I. Most of the initial work on these two contributions centred on the study of wetting films on silica substrates. Derjaguin and Kussakov\(^3\) detected significant surface forces up to 1000 Å from the surface during observations of wetting films on silica. They considered that the magnitude of this force was too large to be due to electrostatic repulsion but rather to an induced water structure near the solid surface. By the time the DLVO theory (Derjaguin, Landau, Verwey and Overbeck) was developed a vast quantity of conflicting experimental results\(^4,5\) was available some showing thick films even at high electrolyte concentrations. The DLVO theory predicted thick films at low electrolyte concentrations. Derjaguin\(^6\) has consistently claimed that their results could not be explained quantitatively by the electrostatic and Van der Waals contributions alone. He proposed that surface forces modified the structure of the solvent adjacent to a solid surface to provide another positive component to the disjoining pressure which may extend 100 Å or 1000 Å from the surface. This structured water became known as "anomalous water". However, objections can be raised to most of their experiments especially with regard to surface smoothness, dust and gelatinous hydrated surface layers. In experiments where these objections do not arise, as with soap films, the evidence points strongly against the existence of thick structured water layers. Recent investigations with nuclear magnetic resonance and neutron scattering\(^7,8,9\) have suggested that the water structuring is
confined to two or three molecular layers.

The work of Read and Kitchener\textsuperscript{10} on wetting films on silica, under strict purity conditions, showed that the electrical double layer component of the disjoining pressure calculated from the DLVO theory was too small to account for the equilibrium film thicknesses observed, particularly at low electrolyte concentrations. However, they showed that the existence of a charge (10 mV) at the air-water interface could explain most of the discrepancy between theory and observation. Even with this charge accounted for, the results still indicate that the electrical double layer component of the disjoining pressure is larger than that predicted by the DLVO theory.

The possibility of long range Van der Waals forces between a film and a solid have been the subject of much recent discussion\textsuperscript{2} and their significance is as yet unclear.

A complete description of the process of coalescence is difficult due to the number of variables involved, although the process can be broken down into separate stages of development. In the case of a gas bubble-solid particle coalescence, as occurs in ore flotation, the mechanism of capture can be considered as three stages. Firstly, the bubble-particle collision; secondly, the thinning and subsequent rupture of the intermediate liquid film and, finally, the recession of the liquid film from the solid to form a stable gas solid bond. At each stage the surface exerts considerable influence on the outcome of the process.

In the first stage, the probability of a collision occurring depends upon the relative motions of the bubble and particle and upon the size and inertia of the particle. Derjaguin\textsuperscript{11} has
postulated that a diffusiophoretic effect occurs when bubbles rise through solutions of ionic surfactants. The bubbles set up ionic concentration gradients resulting in electric fields of considerable intensity and extending up to 10 μm from the surface of the bubble. Particles within the range of this force are subjected to an electrophoretic force and are attracted or repelled depending upon their charge.

Once bubble – particle collision has occurred it is necessary for the second and third stages to be completed within the contact time of the collision if flotation is to be achieved. Since the bubble – particle collision is of very short duration (approximately 10 ms) \(^{12}\) film thinning and rupture must occur rapidly for flotation to be successful.

Many investigations \(^{13}\) have shown that, with a decrease in pressure in the flotation cell, dissolved gases are precipitated as air bubbles on to minerals whose surfaces are sufficiently hydrophobic. These precipitated bubbles are themselves capable of floating the particles and can also improve the attachment of much larger air bubbles. Klassen \(^{14}\) suggested an intermediate mechanism of attachment in which a large bubble coalesces with a 'microbubble' attached to the surface of the mineral and in this way the particles are attached faster than in the absence of microbubbles. This coalescence mechanism has been confirmed by a number of investigations \(^{15,16}\) In this case the liquid film drains between two gas bubbles and the smaller the film diameter the higher is the draining rate. The large difference in capillary pressures between the bubbles is an additional force utilized in the disruption of the water film. The most notable work on the hydrodynamics of film thinning
under the influence of disjoining pressure has been conducted by Scheludko\textsuperscript{17} and Platikanov\textsuperscript{18}.

In the final stage, once rupture has occurred, the recession of the water over a hydrophobic surface takes place rapidly because of the uncompensated water–air interfacial tension. Recent experiments by Mysels\textsuperscript{19} have shown that, during the bursting of free soap films, a region of film thickening spreads ahead of the narrow rim surrounding the hole. This 'aureole' is believed to result from large surface tension gradients created by the high speed compression of the surface.

Taylor and Michael\textsuperscript{20} have, in a paper to be published, investigated the stability of holes in a sheet of liquid. The stability of such holes was obtained by considering a soap film suspended axisymmetrically on two circular rings. The equilibrium configuration is the well known catenary of revolution\textsuperscript{21}. Two solutions are obtained on either side of the critical condition. One position is stable to displacements of a general nature and the other is unstable. Experiments were performed with holes made in sheets of water on glass treated with a wax coating and in mercury under water. Holes were created by an air jet and the larger holes would remain open and within a small range of depths a large hole would increase in size. The fact that holes can remain stationary is contrary to the predictions from the theory for an invariant, contact angle and in agreement with contact angle hysteresis. If the two curves of the angle of contact for advancing and receding menisci are drawn in a film thickness–hole radius plane they were able to define a range of radii for any given liquid thickness within which a hole can be trapped.
It has been found experimentally that in many systems the contact angle can assume a range of values between certain limits without any apparent movement of the three phase boundary. This phenomenon of contact angle hysteresis is of considerable importance in flotation.

Coalescence in all systems depends upon the draining of an intervening liquid film and the subsequent instability and rupture of this film. The present research is directed towards this intermediate stage in the process of coalescence. Section 1 is concerned with the hydrodynamic instability of a thin film under given surface and intermolecular properties and Section 2 is concerned with an experimental study of the draining and rupture process of a thin film between a gas bubble and a hydrophobic surface.

Further introductions, more specific to the topic under discussion, are given at the beginning of each of the following sections.
REFERENCES


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SECTION I

HYDRODYNAMIC STUDY OF THIN FILM INSTABILITY

1.1 Intermolecular Forces

It has long been established that wetting phenomena could not be explained adequately by the simple capillarity theory. Derjaguin suggested that the properties of a thin liquid film are not independent of the form of the liquid and introduced the 'disjoining pressure' as a measure of the corresponding change in the thermodynamic properties. Hamaker had previously been able to show that on the basis of intermolecular interactions, two large condensed phases exert a pressure on a thin liquid film between them, thus showing that the energy per unit volume of the film is different to that of the surrounding material.

All forces between atoms and molecules are electrostatic in origin and are gradients of potential functions. It is often more convenient to describe the potential energies rather than the forces themselves. It is possible to distinguish the following varieties of intermolecular and interionic potential energies.

1. The coulombic energy of interaction between ions with net charges, leading to long-range attraction with $U \propto r^{-1}$.
2. The energy of interaction between permanent dipoles with $U \propto r^{-3}$.
3. The energy of interaction between an ion and a dipole induced by it in another, with $U \propto r^{-2}$.
4. The energy of interaction between a permanent dipole and a dipole induced by it in another molecule with $U \propto r^{-6}$.
5. The forces between neutral atoms or molecules, with $U \propto r^{-6}$.
6. The overlap energy arising from the interactions of positive nuclei and electron cloud of one molecule with those of another.
The overlap leads to repulsion at very close internuclear separations with \( U \propto r^{-n} \) where \( n \) lies between 9 and 12.

The Van der Waals attractions between molecules must arise from interactions belonging to classes (2), (4) & (5). Keesom\(^3\) was the first to attempt to explain them theoretically based on the interaction between permanent dipoles. Since the two dipoles are in rapid thermal motion their orientation will at some time be attractive and at others repulsive. On average they are closer together in an attractive configuration and there is a net attractive energy. Lennard-Jones\(^4\) calculated this energy to be

\[
U = -\frac{2\mu^2}{3r^6} \frac{1}{K}
\]

where \( \mu \) is the dipole moment. However the theory did not explain the attractive forces between molecules of inert gases which show no permanent dipole moments. Debye\(^5\) extended the theory to allow for the induction effect. A permanent dipole induces a dipole in another molecule and the result is an attractive force. This interaction depends upon the electromagnetic polarisability, \( \alpha \), of the molecules and leads to

\[
U = -\frac{2\alpha\mu^2}{r^6}
\]

However, the effect is usually very small and insufficient to explain the case of the inert gases.

London\(^6\) solved the problem by an application of quantum mechanics. He considered the interacting system as two spherically symmetric, three dimensional, isotropic oscillators. The fluctuating dipole in one oscillator induced a dipole in the other resulting in a net attraction. This dispersion interaction leads to a potential

\[
U = -\frac{3}{4} \frac{\hbar v_o \alpha^2}{r^6}
\]

where \( v_o \) is the characteristic frequency of oscillation of the charge distribution and \( \hbar \) is Planck's constant.
It is these London dispersion forces which are the major contribution to the Van der Waals attractions and, along with the electrical double layer forces in a thin film, is a major constituent of the disjoining pressure.

1.2. The Van der Waals Disjoining Pressure

The changes in the chemical potential of the film cause corresponding changes in the intensive parameters determining the state of the film. A thin film has to be considered as a volume and a surface phase in a thermodynamic treatment. The thermodynamic properties are considered as functions of the film's thickness $h$. Here the derivation is restricted to free liquid films since they offer a simpler interpretation.

$$
\frac{dF}{dh} = -S_h \frac{dT}{dh} - P_h \frac{dV}{dh} + T \frac{dA}{dh} + \mu_h \frac{dn}{dh} \quad (1.2.1)
$$

For an incompressible film, $dV = 0$ so that

$$
\mu_h = \frac{dF}{dn} \quad (1.2.2)
$$

$\Delta \mu(h)$ represents the increase of the chemical potential of the thin film in relation to that of a thick film so that

$$
\Delta \mu(h) = \mu_h - \mu_\infty \quad (1.2.3)
$$

Considering the pressure of the film

$$
\Delta \mu(h) = (P_h - P_\infty) v = -\Pi v \quad (1.2.4)
$$

where $\Pi$ is the disjoining pressure. Following Derjaguin's suggestion, the negative sign is inserted so that $\Pi > 0$ when $P_h < P_\infty$, so that $\Pi$ then acts towards thickening of the film.

From equation (1.2.2.) and $F = U - TS$

$$
\mu = \frac{d\mu}{dn} \quad (1.2.5)
$$

According to Lifshitz, the second term is normally negligible in comparison to the first which is determined by the Van der Waals intermolecular forces.
From equations (1.2.3.), (1.2.4.) and (1.2.5.) we get

\[ \Pi_{V} = \left[ \left( \frac{\partial U}{\partial n} \right)_A - \left( \frac{\partial U}{\partial n} \right)_A \right] \frac{1}{v} \quad (1.2.6.) \]

where \( \Pi_{V} \) is the Van der Waals component of the disjoining pressure. \( \Pi_{V} \) can be evaluated from the energies \( u_\infty \) and \( u_h \) and Scheludko determined \( \Pi_{V} \) by considering the energies of attraction of the surface molecules. The differentiation is equivalent to the reversible isothermal removal of a molecule from the surface and the subsequent regrouping of the molecules. The latter procedure is the same for thick and thin films and hence disappears when the difference between \( u_\infty \) and \( u_h \) is taken.

:: From equation (1.2.6.)

\[ \Pi_{V} = \frac{(u_\infty - u_h)}{v} \quad (1.2.7.) \]

for the disjoining pressure of a thin liquid film whose structure remains the same on thinning. \( u_\infty \) and \( u_h \) represent the energy of attraction for a molecule.

Assuming molecular interaction to be independent of the medium, Scheludko obtained using Fig 1.1
\[ u_\infty = u_h + u_{\infty} \quad (1.2.8.) \]

which leads to the expression
\[ \Pi_{\infty} = \frac{u_{\infty}}{v} \quad (1.2.9.) \]

The disjoining pressure in a film of thickness \( h \) is determined by the energy of attraction between a molecule and a semi-infinite phase separated by a distance \( h \).

Providing the distance \( h \) is large compared to the intermolecular spacings in the semi-infinite phase, the summation of the molecular interactions between the molecule at a distance \( h \) from the semi-infinite phase and this phase can be performed by integration.

\( \Pi_{\infty} \) can easily be found according to equation (1.2.9.) for London dispersion forces where interactions of \( \beta r^{-6} \) are concerned, where \( \beta \) is the London constant. The condition of additivity allows integration over the interactions of a molecule with molecules in a spherical segment, as shown in Fig 1.2.

\[
\int_{h}^{\infty} -\frac{2\pi\beta}{v} \frac{r-h}{r^5} \, dr
\]

This gives \( \Pi_{\infty} = \frac{-m\beta}{6v} \cdot \frac{1}{h^3} = \frac{-K}{h} \quad (1.2.10.) \)

where Scheludko called \( K \) the Van der Waals - Hamaker constant.
Representing the London dispersion forces as \(-\beta r^{-6}\) holds only when the atoms and molecules are separated by distances small compared with the wavelength of the characteristic frequency of oscillation of the charge distribution. When the time of propagation of the waves is of the same order as the oscillation time \(\frac{c}{v_0}\), the induced oscillation is out of phase with the original oscillator and hence the attractive force is diminished. The energy of interaction falls off more rapidly than that given by \(r^{-6}\) expression. Casimir and Polder\(^9\) showed that this effect was considerable at large separations. Their modified relationship for the energy of interaction was

\[
u = -\frac{3}{4} \frac{\hbar c}{\pi} \frac{\alpha^2}{r^6} f(p) \tag{1.2.11.}\]

where \(p = 2\pi r/\lambda_L\) and \(\lambda_L = \) wavelength of the London wave.

Overbeek\(^10\) obtained the following relationships for \(f(p)\):

\[
\begin{align*}
0 < p < 3 & \quad f(p) = 1.01 - 0.14 \frac{2.45}{p} - 2.04 \frac{2}{p^2} & \tag{1.2.12.} \\
3 < p < \infty & \quad f(p) = \frac{1.01}{p} - 0.28 \left(\frac{2\pi r}{\lambda_L}\right) + 14.3 \times 10^{-3} \left(\frac{2\pi r}{\lambda_L}\right)^3 \\
& \quad - 1.96 \times 10^{-3} \left(\frac{2\pi r}{\lambda_L}\right)^4 \tag{1.2.13.} \\
\end{align*}
\]

Thus, the integration for \(\Pi_{\nu, j}\) should be performed for the case of \(h < 3\lambda_L/2\pi\) and for \(h > 3\lambda_L/2\pi\).

The results for \(\Pi_{\nu, j}\) have the following form\(^7\):

for \(0 < h < 3\lambda_L/2\pi\)

\[
\Pi_{\nu, j} = -\frac{K}{\hbar^3} \left[1.01 - 0.28 \left(\frac{2\pi h}{\lambda_L}\right) + 14.3 \times 10^{-3} \left(\frac{2\pi h}{\lambda_L}\right)^3 \right. \\
- 1.96 \times 10^{-3} \left(\frac{2\pi h}{\lambda_L}\right)^4 \tag{1.2.13.} \\
\]

for \(3\lambda_L/2\pi < h < \infty\)

\[
\Pi_{\nu, j} = -\frac{K}{\hbar^3} \left[\frac{1.43}{(2\pi h/\lambda_L)} - 0.82 \left(\frac{2\pi h}{\lambda_L}\right)^2 \right] \tag{1.2.14.}
\]

for \(h\) small compared to \(\lambda_L\), equation (1.2.13.) asymptotes to equation (1.2.10.). For \(h\) large compared to \(\lambda_L\), equation (1.2.14.)
Hunter$^{11}$ treated the case of a thin film between two thin plates, taking into account the effect of retardation. If the effect of retardation is not accounted for, the results for the case of a plane parallel film between two different semi-infinite phases 1 and 2 can be presented as$^{12}$

$$\Pi_{V,J} = \frac{(K_{13} + K_{23} - K_{33} - K_{12})}{h^3}$$

(1.2.16.)

where $K_{ij} = \frac{\mu_{ij}^3}{6v_{ij}^3}$ and where $\beta_{ij}$ is the London constant for the interaction of a molecule $i$ with a molecule $j$.

The expressions obtained before assumed that the interaction between molecules in a medium is the same as that in a vacuum. Lifshitz$^{3}$ however, developed a theory of molecular attraction originating from a fluctuating electromagnetic field between phases. This theory is generally known as the macroscopic theory and was extended by Dzyaloshinskii, Lifshitz and Pitaevskii$^{13}$. This very complex theory has been given in greater detail in Abrikosov's$^{14}$ book. The use of the theory is at present limited since it requires data on the real and imaginary components of the dielectric constants over a wide range of electromagnetic frequencies. However, use has been made in certain limiting cases and the theory has been shown$^{15}$ to give results of similar magnitude to those obtained by the retarded Hamaker type calculations.

Dzyaloshinskii, Lifshitz and Pitaevskii$^{13}$ have pointed out that the microscopic theory suffers from the assumption that interactions are in pairs and additive so that the effect of the medium is neglected. The macroscopic theory is free from this defect since it is founded upon the total fluctuation fields of the phases. Electromagnetic retardation arises naturally out of this theory. However, the
microscopic theory on the basis of London dispersion forces corrected for electromagnetic retardation offers very reasonable results at present.

1.3. Electrostatic Disjoining Pressure

Near the phase boundaries in aqueous solutions of electrolytes there exist electric double layers in which the electric charge of the phase boundary is diffused in the volume of liquid as a result of thermal motion. This double layer consists of an excess quantity of ions at the phase boundary and an equal number of ions of opposite charge distributed throughout the solution. If the film is thinner than the electric double layer, then the opposite layers emanating from the phase boundaries are deformed which causes an increase in the energy of the film and gives rise to a positive component to the disjoining pressure, \( \Pi_{el} \).

\( \Pi_{el} \) has been calculated by Verwey and Overbeek\(^{16} \) who evaluated the change in energy of the electric double layers. Derjaguin and Landau\(^{17} \) obtained the same result by calculating the pressure in the film. Landau\(^{18} \) and Fradin\(^{19} \) both considered the osmotic pressure due to the change in ion concentration between two plates. Here, the method of Scheludko\(^{20} \) is presented which uses the Gouy and Chapman\(^{21} \) model for the diffuse part of the electrical double layer. This gives a good approximation provided that simple ions are present.

For a binary electrolyte, the fall in potential \( \phi \) in a direction \( x \) normal to a plane phase boundary with potential \( \phi_0 \) is given by

\[
\frac{d^2 \phi}{dx^2} = \frac{\Delta \Pi_{el}}{\varepsilon_0} \sinh \left( \frac{zF\phi}{RT} \right)
\]

(1.3.1.)

where \( z \) is the valency of the ions, \( C \) the concentration of electrolyte in the bulk in moles per cm\(^3 \), \( \varepsilon_0 \) the dielectric constant and \( R \) and \( T \) are the gas constant and absolute temperature.
\( F \) is the Faraday constant. If \( \rho \) is the volume charge density at a point \( x \) with potential \( \phi \), then Poisson's equation can be used to relate \( \rho \), \( \phi \) and \( x \).

\[
\frac{\partial^2 \phi}{\partial x^2} = -\frac{4\pi \rho}{\varepsilon_0} \quad (1.3.2)
\]

The charge density per cm\(^2\) on the surface is

\[
e = \int_0^\infty \rho \, dx \quad (1.3.3)
\]

If the two phases are mutually charged and a potential drop of \( \phi_0 \) exists at the boundary of the two phases then from electrostatics the force per cm\(^2\) between them will be

\[
\frac{2\pi e^2}{\varepsilon_0} \quad (1.3.4)
\]

For a plane film, this depends only on the magnitude of \( e \) and not on the charge distribution. With a thinning film of aqueous electrolyte, the charge \( e_h \) in it will decrease because of the deformation of the two opposite diffuse electric layers, which leads to a reduced force with which the two semi-infinite phases act on the film. If the film remains electrically neutral overall then the corresponding change in the pressure will give \( \Pi_{el} \),

\[
\Pi_{el} = \frac{2\pi}{\varepsilon_0} \left( e_\infty^2 - e_h^2 \right) \quad (1.3.5)
\]

Using equations (1.3.2) and (1.3.3) gives \( e_\infty \) and \( e_h \) as

\[
e_\infty = \int_0^\infty \rho \, dx = \frac{\varepsilon_0}{4\pi} \left( \frac{\partial \phi}{\partial x} \right)_{0, \infty} \quad (1.3.6)
\]

\[
e_h = \int_0^{h/2} \rho \, dx = \frac{\varepsilon_0}{4\pi} \left( \frac{\partial \phi}{\partial x} \right)_{0, h}
\]

The subscripts 0 indicate that the slope \( \frac{\partial \phi}{\partial x} \) is taken at \( x = 0 \) and subscripts \( \infty \) and \( h \) that a thick film and a film of thickness \( h \) are being considered. The integration to \( h/2 \) refers to a
symmetric film. The system is shown schematically in Fig 1.3.

Integrating equation (1.3.1.) from $x = 0$, $\phi = \phi_0$ to $x = \infty$, $\phi = \phi_0$ and from $x = 0$, $\phi = \phi_0$ to $x = h/2$, $\phi = \phi_{h/2}$ gives respectively

$$\frac{d\phi}{dx}_{o, \infty}^2 = \frac{16\pi \text{CRT}}{\varepsilon_0} \left( \cosh \left( \frac{z\Phi_0}{RT} \right) - 1 \right)$$ (1.3.7.)

$$\frac{d\phi}{dx}_{o, h}^2 = \frac{16\pi \text{CRT}}{\varepsilon_0} \left( \cosh \left( \frac{z\Phi_0}{RT} \right) - \cosh \left( \frac{z\Phi_{h/2}}{RT} \right) \right)$$

Substituting these values with (1.3.5.) produces

$$\Pi_{el} = 2 \text{CRT} \left( \cosh \left( \frac{z\Phi_{h/2}}{RT} \right) - 1 \right)$$ (1.3.8.)

$\phi_{h/2}$ can be evaluated by integrating equation (1.3.1.) between the limits of $x = h/2$ and $x = \infty$ and taking the square root. Thus,

$$\frac{d\phi}{dx} = -\sqrt{\frac{16\pi \text{CRT}}{\varepsilon_0} \left( \cosh \frac{z\Phi}{RT} - \cosh \frac{z\Phi_{h/2}}{RT} \right)}$$ (1.3.9.)

Separating the variables and integrating a second time between the limits $x = 0$, $\phi = \phi_0$ to $x = h/2$, $\phi = \phi_{h/2}$ gives:

$$\frac{h}{2\sqrt{\frac{16\pi \text{CRT}}{\varepsilon_0}}} = \int_{\phi=\phi_0}^{\phi=\phi_{h/2}} \sqrt{\frac{\cosh \frac{z\Phi}{RT} - \cosh \frac{z\Phi_{h/2}}{RT}}{\text{CRT}}} d\phi$$ (1.3.10.)

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Equation (1.3.10.) can be written as

$$xh = \sqrt{2} \int_{y_{h/2}}^{y_0} \frac{dy}{\sqrt{\cosh y - \cosh y_{h/2}}} \quad (1.3.11.)$$

where

$$x = \sqrt{\frac{8 \pi \varepsilon_0 F^2 c}{\varepsilon \rho RT}}$$

$$y = \frac{Z^2 \phi}{RT}, \quad y_0 = \frac{Z^2 \phi_0}{RT} \quad \text{etc.}$$

Scheludko has tabulated the elliptical integrals from (1.3.10.) and (1.3.11.). Thus, $$\Pi_{el} = f(h)$$ can be obtained by combining (1.3.3.) with (1.3.11.).

An approximate solution is obtained providing there is only a small deformation of the diffuse double layer when the potential $$\phi_{h/2}$$ can be considered as twice the potential at a distance $$h/2$$ from the phase boundary in an undeformed diffuse layer. Verwey and Overbeek obtained, after the second integration of equation 1.3.1. with boundary conditions $$x = \infty, \phi = 0$$, and $$x = 0, \phi = \phi_0$$,

$$\tanh \left( \frac{Z^2 \phi}{4RT} \right) \tanh \left( \frac{Z^2 \phi}{4RT} \right) = e^{ax} \quad (1.3.12.)$$

For large $$x$$, when $$\phi$$ is small, the numerator can be replaced by

$$\frac{Z^2 \phi}{RT}$$

Thus,

$$\phi = \frac{4RT}{Z^2} \tanh \left( \frac{Z^2 \phi_0}{4RT} \right) e^{-axx} \quad (1.3.13.)$$

$$\phi_{h/2}$$ is then obtained by doubling $$\phi$$ at $$x = h/2$$.

Expanding the $$\cosh$$ term of (1.3.8.) as far as the quadratic term gives $$\Pi_{el} = CRT \left( \frac{Z^2 \phi_{h/2}}{RT} \right)^2 \quad (1.3.14.)$$

Substituting for $$\phi_{h/2}$$ the final result becomes

$$\Pi_{el} = 64 CRT \tanh^2 \left( \frac{Z^2 \phi_0}{4RT} \right) e^{-axh} \quad (1.3.15.)$$
Following Scheludko's method it is relatively easy to deal with non-symmetrical electrolytes but it is more difficult to handle when the potentials of the two interfaces are different, as with water films on substrates.

The diffuse electric layers can be suppressed by high electrolyte concentrations. However, this action tends to give the thin film a marked layer structure which could lead to difficulties in calculating $\Pi_{WJ}$ due to the film's multicomponent nature.

A more accurate theory of the electric double layer would have to account for the Stern layer and the effect of electric reflection, both of which effects are important at high electrolyte concentrations.

The total disjoining pressure is given by the sum of $\Pi_{WJ}$ and $\Pi_{el}$ since they have been assumed to be independent. Throughout this project $\Pi_{WJ}$ is the predominant term in the disjoining pressure since the electric double layers will be, or assumed to be, suppressed by a sufficient quantity of electrolyte in aqueous solutions.

1.4. The Thinning of Thin Liquid Films

$\Pi_{el}$ is always positive and for free liquid films, with which section I is concerned, $\Pi_{WJ}$ is always negative. Thin liquid films are invariably contacted by bulk liquid which means that there is a change in curvature of the surface at the area of contact. The film is thus subjected to a capillary pressure which together with the Van der Waals component of the disjoining pressure creates a pressure difference directed from the film to the bulk liquid. The chemical potential of the film is higher than that of the bulk so that film material is transferred from the film to the bulk and the film becomes thinner.

Providing that neither the volatility nor the viscosity of the film is too high, this transport of material occurs by fluid flow.
It is possible, because of double layer interaction, for the sum of $\Pi_V$ and $\Pi_{el}$ to equal the outside capillary or hydrostatic pressure imposed on the film. In this case an equilibrium film is formed. In the case of a free film with the double layers suppressed, the thinning continues until either the film ruptures or attains a stable state at a very much smaller thickness (by black spot formation) by first reaching an unstable state.

In the analysis to follow, microscopic circular films will be discussed where the radius of the film is of order $10^{-2}$ cm. These films arise in all disperse systems and their study is important for knowledge of the behaviour of these systems. In larger films the draining is not as easily defined, when it may be split up into smaller areas separated by thicker channels. The draining and profile of the microscopic circular films will be discussed in greater detail in Section III.

The viscosity of the film is taken as that of the bulk liquid. The surface conditions on the film have to be specified as to whether the surface is mobile or immobile. In the latter case, the surface flow can be retarded and even prevented if an adsorption layer is present. The liquid flow to the periphery of the film stretches the adsorbed layer and a concentration gradient is set up to oppose the viscous stress. Only very small quantities (of order $10^{-3}$ molar) of surface active agent are needed to meet this condition.

For a plane parallel circular film the thinning can be described by a Reynolds type flow:

$$\frac{a(1/n^2)}{dt} = \frac{16}{3\mu r_o n^2} (\Pi \sigma - \Pi(n)) \quad (1.4.1.)$$

where $r_o =$ film radius
$n =$ no. of immobile surfaces
$\Pi \sigma =$ capillary pressure.
1.5. Instability and Rupture of Thin Liquid Films

Apart from two particular cases, thin liquid films rupture on attaining a critical thickness. The two exceptions are when the film reaches an equilibrium thickness before the critical thickness or when a jump transition occurs at the critical thickness to form a stable much thinner film. This latter process is known as black spot formation.

The thinning of a thin liquid film shows that the film is in a thermodynamically unstable state. This fact shows that the condition of thermodynamic instability, although necessary, is not sufficient.

De Vries\textsuperscript{24} considered a mechanism similar to that occurring in cavitation. He considered a kinetic step with a corresponding energy barrier which ensured relative stability for thicker films. The film would rupture if a hole of critical dimensions could be formed in it as a result of local fluctuations and grow with a gain of energy. However, De Vries calculated the critical thickness on this model and obtained values much smaller than were observed so that this mechanism is energetically unfavourable. Scheludko\textsuperscript{25} proposed a mechanism whereby a concavity was produced as a result of local thinning and the forces in the thinned region would promote further thinning if the film became critical. The film would then either rupture or form a thinner thermodynamically stable film. This mechanism is much more energetically favourable. The critical condition was given by

\[
\left( \frac{\partial h}{\partial h} \right)_{\text{hcr}} + \left( \frac{\partial \sigma}{\partial h} \right)_{\text{hcr}} = 0 \quad (1.5.1.1)
\]

Representing the concavity as a part of a sphere and assigning a surface wavelength, the radius of the sphere is given by

\[
R = \frac{\lambda^2}{32Ah} \quad \text{where } Ah \text{ is the depth of the thinned region relative to the rest of the film.}
\]
Representing $\Pi$ as $2\sigma/R$ and $\Pi$ as $-K/h^3$ leads to

$$\text{hor} = \left( \frac{2K}{4\sigma} \right)^{1/3} \lambda^{1/3} \quad (1.5.2.)$$

This mechanism shows that the critical thickness is reached by a jumpwise formation of thinner regions manifested by black spots and not by gradual thinning. However, the surface wavelength, $\lambda$, remains an unknown parameter.

Vrij, as a result of his light scattering studies on thermal waves on the surface of a thin liquid film developed a much more detailed theory based upon a concavity formed by local thinning. Using the theory of thermal surface waves he was able to eliminate $\lambda$ and obtained an expression similar to (1.5.2.). For $\Pi_{\text{v'}}$ given by $-K/h^3$ and which is greater than $\Pi$, he obtained

$$\text{hor} = 0.222 \left( \frac{Ar_o^2}{\Pi_o} \right)^{1/3}$$

and for $\Pi > \Pi_{\text{v''}}$,

$$\text{hor} = 0.263 \left( \frac{A^2}{r_o^2/\Pi_o} \right)^{1/7} \quad (1.5.3.)$$

where $f$ is a factor estimated at 6.5 and $A = 6\pi K$.

The mechanism of rupture discussed refers to polymeric films. This mechanism is not applicable to the thinnest black films which probably have liquid crystal like structures composed of two adsorption layers with a minimum of water between them. The cavitation hole mechanism of rupturing of the thinnest black films was considered by Derjaguin and Gutop, and, as far as is known, has not been experimentally verified. More recently, on the basis of the Navier-Stokes equations, Scheludko considered the instability of a thin liquid film by taking into account the influence of the surfactant on the hydrodynamics of the film. He found reasonable agreement with films with low surfactant concentration but at higher concentrations the discrepancy was much more marked.
In the next subsection, the stability of a wave on a plane circular film is studied following the method of Basset and Bellman and Pennington. The wave is assumed to arise naturally from external vibrations and thermal motion of the molecules near the surface and there will be, in general, a whole spectrum of wavelengths present.

1.6. Instability of Waves on a Circular Liquid Film

Consider a circular free film of radius $R$ and of uniform thickness $h$. A wave of wave number $k$ is assumed to be present on each surface and the deviation from the undisturbed film is denoted by $\eta$. The waves on the upper and lower surfaces of the film are assumed to be symmetrical so that the thickness at any point is $h + 2\eta$. If the surface deforms at a particular point on one surface, then under the influence of the disjoining pressure the opposite surface will deform similarly. The system under consideration is shown diagrammatically in Fig 1.4.

![Diagram of a circular liquid film](image)

*The free film is in air which is assumed to behave as a vacuum.*
The amplitude of the surface wave is assumed to be infinitesimal compared to the undisturbed film thickness and the wavelength. The film is assumed also to maintain its mean thickness $h$ although in fact the film is thinning due to its thermodynamically unstable state. This assumption allows us to consider the movement in the film as a result of the surface wave only.

The liquid motion is considered to be in the $r$ and $z$ directions only. The film is thin relative to its radius so that $h \ll R$ and the flow is a low Reynolds Number flow so that the squares and products of the velocities in the equation of motion can be neglected. With this simplification, the streamfunction $\psi$ satisfies the biharmonic equation which in cylindrical coordinates for viscous flow in the $r$ and $z$ directions only is:

$$
E^2 \left( E^2 - \frac{1}{\nu} \frac{\partial^2}{\partial t^2} \right) \psi = 0 \quad (1.5.1.)
$$

where $E^2 = \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \right)$

The solution of which can be shown (see Appendix I) to be

$$
\psi = (A \cosh k z + B \sinh k z + C \cosh m z + D \sinh m z) \exp \left( \frac{ik}{\nu} r \right) \quad (1.6.2.)
$$

where $A$, $B$, $C$, $D$ are constants and $J_1(kr)$ is a Bessel function of the first kind of order unity. $n$ is the wave amplification factor. The solution for $\psi$ yields $m^2 = k^2 + n/\nu$.

The boundary conditions to be satisfied are

1) $z = -h/2$, \( \frac{\partial \psi}{\partial r} = 0 \)

2) $z = -h/2$, \( v_z = 0 \)

3) $z = 0$, normal stress on surface = 0

4) $z = 0$, tangential stress on surface = 0.

Using the streamfunction in the conventional way, the velocities are defined by

$$
\nu_r = \frac{1}{r} \frac{\partial \psi}{\partial z} \quad \text{and} \quad \nu_z = -\frac{1}{r} \frac{\partial \psi}{\partial r}.
$$
This gives
\[ v_x = k \left( k^2 \sinh(kz) + k^2 \cosh(kz) + m^2 \sinh(mz) + m^2 \cosh(mz) \right) J_1(kr) e^{nt} \]
\[ v_z = -k^2 \left( A \cosh(kz) + B \sinh(kz) + C \cosh(mz) + D \sinh(mz) \right) J_0(kr) e^{nt} \quad (1.6.3) \]

Using boundary condition (1) and (1.6.3), substituting \( z = -h/2 \)
\[ \frac{\partial v_z}{\partial z} = 0 \quad \text{at} \quad z = -h/2 \]
\[ k \left( k^2 \cosh\left(-\frac{kh}{2}\right) + k^2 \sinh\left(-\frac{kh}{2}\right) + m^2 \cosh\left(-\frac{mh}{2}\right) + m^2 \sinh\left(-\frac{mh}{2}\right) \right) \]
\[ \times J_1(kr) e^{nt} = 0. \]

Let \( L = \cosh \frac{kh}{2}, \quad M = \sinh \frac{kh}{2} \]
\[ P = \cosh \frac{mh}{2}, \quad Q = \sinh \frac{mh}{2} \]

If \( J_1(kr) e^{nt} \neq 0 \), then
\[ k^2 AL - k^2 BL + m^2 CP - m^2 DQ = 0 \quad (1.6.4) \]

Similarly treating boundary condition (2) at \( z = -h/2, v_z = 0 \)
if \( J_1(kr) e^{nt} \neq 0 \),
\[ A \cosh\left(-\frac{kh}{2}\right) + B \sinh\left(-\frac{kh}{2}\right) + C \cosh\left(-\frac{mh}{2}\right) + D \sinh\left(-\frac{mh}{2}\right) = 0 \]
\[ \text{i.e. } AL - BL + CP - DQ = 0 \quad (1.6.5) \]

With boundary condition 3, at \( z = 0 \), the normal stress = 0.
\( \eta \) is the wave elevation and can be obtained from the relationship
\[ \frac{\partial \eta}{\partial t} = \frac{v_z}{z = 0} = -\frac{1}{r} \left( \frac{\partial \psi}{\partial r} \right) \quad z = 0 \]

which on integration gives
\[ \eta = -\frac{k^2}{n} (A + 0) J_0(kr) e^{nt}. \quad (1.6.6) \]

For the normal stress condition,
\[ -P + 2 \mu \frac{d v_z}{d z} = 0 \]

where \( P \) is the total perturbation pressure. In dealing with
Thus, the normal stress condition is given by

\[ P = p - \rho g \eta + \sigma \left( \frac{\partial^2 \eta}{\partial r^2} + \frac{1}{r} \frac{\partial \eta}{\partial r} \right) + 2 \frac{\partial h}{\partial h} \cdot \eta \quad (1.6.7) \]

where \( p \) is the flow pressure in the film caused by the wave.

\( \rho g \eta \) is the gravity term.

\( \sigma \left( \frac{\partial^2 \eta}{\partial r^2} + \frac{1}{r} \frac{\partial \eta}{\partial r} \right) \) is the capillary pressure change due to deformation.

2. \( \frac{\partial h}{\partial h} \cdot \eta \) represents the change in the disjoining pressure.

Thus, the normal stress condition is given by

\[ - \left( p - \rho g \eta + \sigma \frac{\partial^2 \eta}{\partial r^2} + \sigma \frac{\partial \eta}{r \partial r} + 2 \frac{\partial h}{\partial h} \right) + 2 \mu \frac{\partial^2 \eta}{\partial z \partial z} = 0 \quad (1.6.8) \]

The pressure caused by the wave motion can be evaluated from the equation of motion and is represented by

\[ p = [(\rho n + \mu k^2) (kB + mD) - \mu (k^3 B + Dn^3)] \text{ Jo} (kr) \text{ e}^{nt} \quad (1.6.9) \]

The derivation is presented in full in Appendix II.

From equation 1.6.6.

\[ \frac{\partial \eta}{\partial r} = \frac{k^3}{n} (A + C) \text{ Jo} (kr) \text{ e}^{nt} \]

\[ \frac{\partial^2 \eta}{\partial r^2} = \frac{k^3}{n} (A + C) \text{ Jo} (kr) - \frac{k^3}{nr} (A + C) \text{ Jo} (kr) \text{ e}^{nt} \]

So that

\[ \frac{\partial^2 \eta}{\partial r^2} + \frac{1}{r} \frac{\partial \eta}{\partial r} = \frac{k^3}{n} (A + C) \text{ Jo} (kr) \text{ e}^{nt} \]

Substituting for \( p, \eta \) and \( \frac{\partial \eta}{\partial z} \) into (1.6.8) gives

\[ \left[ - (\mu k^2 + \rho n)(kB + mD) + \mu (k^3 B + Dn^3) \right] \text{ Jo} (kr) \text{ e}^{nt} \]

\[ - \frac{\rho k^2}{n} (A + C) \text{ Jo} (kr) \text{ e}^{nt} - \frac{\sigma k^2}{n} (A + C) \text{ Jo} (kr) \text{ e}^{nt} \]

\[ + 2 \mu \frac{k^2}{n} (A + C) \text{ Jo} (kr) \text{ e}^{nt} - 2 \mu k^2 (Bk + Dn) \text{ Jo} (kr) \text{ e}^{nt} = 0 \quad (1.6.10) \]
Rearranging and dividing produces
\[
A \left( \frac{2\pi n}{k} - \frac{\sigma k}{n} - \rho k \right) + B \left( -\rho n - 2\mu k^2 \right) + C \left( \frac{2\pi n}{k} - \frac{\sigma k}{n} - \rho k \right) + D \left( -\frac{\rho n a}{k} + \frac{\mu m^3}{k} - 3\mu k m \right) = 0 \quad (1.6.11)
\]

**Boundary condition**

At \( z = 0 \), the tangential stress equals zero.

The tangential stress due to the fluid motion is represented by
\[
\tau_{rz} = -\mu \left( \frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right)
\]

Substituting for \( v_r \) and \( v_z \) from equation (1.6.7) gives
\[
\tau_{rz} = -\mu (2k^3 \cosh k z + 2k^3 \sinh k z + C (k^3 + n^3) \cosh k z + D (k^3 + n^3) \sinh k z) J_1 (kr) e^{nt} \quad (1.6.12)
\]

For the surface flow to be equal to zero, the surface tension gradient has to balance the viscous force at the surface.

\[\text{i.e. } \mu \left( \frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right) - \frac{\partial \sigma}{\partial r} = 0 \quad (1.6.13)\]

This can only be achieved if surface active agent is present.

Following the method of Levich,\(^{33}\)
\[
\frac{\partial \sigma}{\partial r} = \frac{\partial \Gamma}{\partial t} \cdot \frac{\partial r}{\partial r}
\]

where \( \Gamma \) is the surface concentration of the surfactant.

Let \( \Gamma = \Gamma_0 + \Gamma' \) where \( \Gamma_0 \) is the constant concentration on the surface and \( \Gamma' \) is the perturbation.

It is now necessary to express the surface concentration \( \Gamma \) in terms of the liquid velocity. The conservation equation for mass flow on a surface which is almost planar is
\[
\frac{\partial \Gamma}{\partial t} + \frac{1}{r} \left( v_r \Gamma - D_s \frac{\partial \Gamma}{\partial r} \right) + \frac{v_r \Gamma}{r} - \frac{D_s}{r} \frac{\partial \Gamma}{\partial r} = 0 \quad (1.6.14)
\]

where \( D_s \) is the surface diffusivity. Substituting for \( \Gamma \) and neglecting second order differential terms which are infinitesimal gives
\[
\frac{\partial \Gamma'}{\partial t} + \Gamma_0 \frac{\partial \Gamma'}{\partial r} + \frac{v_r \Gamma}{r} = D_s \frac{\partial^2 \Gamma'}{\partial r^2} + \frac{D_s}{r} \frac{\partial \Gamma'}{\partial r} \quad (1.6.15)
\]

The surfactant is assumed to be insoluble so that diffusion from the bulk to the surface does not occur. This condition is approximately valid for soluble materials when volume count is low.
Since $\tau_{\alpha z}$ in (1.6.12.) carries to $J_1(kr) e^{int}$ term
let $\Gamma' = \gamma J_1(kr) e^{int}$

Substituting for $\Gamma'$ and $\nu_{\alpha z}$ in 1.6.15. produces

$$\gamma n J_1(kr) + \Gamma_0 k^2 (k^2 \cosh k\alpha \ldots \ldots) J_0(kr) = D_s \gamma J_1(kr) \left( \frac{1}{x^2} - k^2 \right)$$

Rearranging gives

$$\gamma = \frac{-\Gamma_0 k^2 J_0(kr) (k^2 \cosh k\alpha \ldots \ldots)}{J_1(kr) \left( n - D_s \left( \frac{1}{x^2} - k^2 \right) \right)} \quad (1.6.16.)$$

$$\therefore \Gamma' = \frac{-\Gamma_0 k^2 J_0(kr) (k^2 \cosh k\alpha \ldots \ldots) e^{int}}{\left( n - D_s \left( \frac{1}{x^2} - k^2 \right) \right)} \quad (1.6.17.)$$

But $\frac{\partial \sigma}{\partial r} = \frac{\partial \sigma}{\partial r'} + \frac{\partial \Gamma'}{\partial r}$

$$\frac{\partial \Gamma'}{\partial r} = \frac{\Gamma_0 k^2 (k^2 \cosh k\alpha \ldots \ldots) J_1(kr)}{n - D_s \left( \frac{1}{x^2} - k^2 \right)} + \frac{2\Gamma_0 k^2 D_s (k^2 \ldots \ldots) J_0(kr)}{x^3 \left( n - D_s \left( \frac{1}{x^2} - k^2 \right) \right)^2} \quad (1.6.18.)$$

Equation (1.6.18.) is too complex to obtain a simple solution with easily interpretable results. However if $kr$, the argument of the Bessel function, is assumed to be $> 1$ (ie. corresponding to large radial distances compared with the wavelength) then we obtain

$$\frac{\partial \Gamma'}{\partial r} = \frac{\Gamma_0 k^2 J_1(kr) (k^2 \cosh k\alpha \ldots \ldots) e^{int}}{n + D_s k^2} \quad (1.6.19.)$$

In Appendix III an edited treatment of the whole instability problem is presented in cartesian coordinates. The corresponding results for $\gamma$ and $\frac{\partial \Gamma'}{\partial x}$ are

$$\gamma = \frac{i k \Gamma_0 (\text{Aksinhky} \ldots \ldots)}{n + D_s k^2} \quad (1.5.26.)$$

$$\frac{\partial \Gamma'}{\partial x} = \frac{\Gamma_0 k^2 (\text{Aksinhky} \ldots \ldots) e^{ikx+nt}}{n + D_s k^2} \quad (1.6.21.)$$
It can be seen that there is a great similarity between equations (1.6.19.) and (1.6.21.). It will also be noticed that the expressions obtained in the cartesian coordinate system for the other three boundary conditions are identical to those given by equations (1.6.14.), (1.6.5.) and (1.6.11.) for the cylindrical polar system.

The equation for the tangential stress at the surface to be equal to zero on the cartesian system is

\[
A \left[ 2\mu k^2 \right] + B \left[ \frac{k^3 \varepsilon}{(n+D_s k^2)} \right] + C \mu \left[ k^2 + n^2 \right] + D \left[ \frac{k^2 \varepsilon m e}{(n+D_s k^2)} \right] = 0
\]  

(1.6.22.)

where \( \varepsilon = -\Gamma_0 \left( \frac{\partial \sigma}{\partial t} \right) \) and is called the surface elasticity.

The solution to the instability of a wave on a circular film has been obtained using the equation (1.6.22.) as the expression for the tangential stress boundary condition. In fact, the solution obtained is that for the cartesian system but since the other three boundary conditions yield the same expressions and equations (1.6.19.) and (1.6.21.) have a close resemblance it is felt that the final result will not depart too much from the cylindrical polar system.

In Section III the results obtained in the derivation for the surface tension gradient in cylindrical polar coordinates (ie equations (1.6.16.), (1.6.17.), and (1.6.18.)) will be discussed in greater detail.

The four equations to be solved are:

1. \( k^2 AL - k^2 B \varepsilon + n^2 CP - m^2 D_2 = 0 \)
2. \( AL - B \varepsilon + CP - D_2 = 0 \)
3. \( A \left[ -\frac{B}{\mu n} \right] + \left[ n^2 + k^2 \right] B + C \left[ -\frac{B}{\mu n} \right] + D \left[ \frac{m_2}{\mu n} + 3m_2 - \frac{B}{\mu n} \right] = 0 \)
4. \( A \left[ 2\mu k^2 \right] + B \left[ \frac{k^3 \varepsilon}{(n+D_s k^2)} \right] + C \mu \left[ k^2 + m^2 \right] + D \left[ \frac{k^2 \varepsilon m e}{(n+D_s k^2)} \right] = 0 \)
where B.C. 3 has been rearranged and where

\[ \beta = (2k\mu - \sigma k^3 - \rho k) \]

The solution for \( n \) can be obtained by solving the following determinant.

\[
\begin{bmatrix}
A & k^2 L & 2\mu k^2 & -\frac{\beta}{\mu n} \\
B & -k^2 M & \frac{k^3 e}{(n+D_s k^2)} & (m^2 + k^2) \\
C & m^2 P & \mu(k^2 + m^2) & -\frac{\beta}{\mu n} \\
D & -2 & -n P & \frac{k^2 e}{(n+D_s k^2)} & \left[ \frac{mn}{\nu k} - \frac{3\kappa a}{k} \right] \\
\end{bmatrix}
\]

\[ = 0 \quad (1.6.23.) \]

the solution yields

\[
n^2 + n \left[ \frac{4k^2 v + 2k^3 e}{\rho h(n+D_s k^2)} \right] - \frac{2\chi}{2\rho} = 0 \quad (1.6.24.)
\]

Rearranging into the cubic form and dividing by \( \rho h \) leads to

\[
n^3 + n^2 \left[ D_s k^2 + 4k^2 v \right] + n \left[ 4D_s k^4 v + \frac{2k^3 e}{\rho h} - \frac{8\chi}{2\rho} \right] - \frac{D_s k^3 h \beta}{2\rho} = 0 \quad (1.6.25.)
\]

For an unstable wave, \( n \) must be > 0. This can only occur if the corresponding value of \( \beta \) is > 0 since all the other variables are positive.

If \( \epsilon \) is large or if for any wavenumber the amplification factor \( n \) is small (i.e. \( n < < D_s k^2 \)) then (1.6.24.) can be rewritten in the quadratic form

\[
n^2 + n \left( 4k^2 v + \frac{2\epsilon}{\rho h D_s} \right) - \frac{2\chi}{2\rho} = 0 \quad (1.6.26.)
\]

whose solution is

\[
n = -\left( 2k^2 v + \frac{\epsilon}{\rho h D_s} \right) + \sqrt{\left( 2k^2 v + \frac{\epsilon}{\rho h D_s} \right)^2 + \frac{2\chi}{2\rho}} \quad (1.6.27.)
\]
1.7. The Growth Rate and Instability Criterion

Equation (1.6.24.) represents the growth rate in terms of viscous, surface elastic and disjoining pressure effects. If the surface elasticity term is ignored, which corresponds to the case of a completely mobile interface, then the growth rate expression becomes

$$n^2 + n \left(4k^2 v \right) - \frac{8kh}{2\rho} = 0$$  
(1.7.1*)

(This is the same result as that obtained in cylindrical coordinates if the surface elasticity is ignored in boundary condition 4).

The solution is

$$n = -2k^2 v + \sqrt{4k^2 v^2 + \frac{8kh}{2\rho}}$$  
(1.7.2)

If no surfactant is present and the fluid is considered inviscid then (1.6.24.) will reduce to

$$n = \sqrt{\frac{8kh}{2\rho}}$$  
(1.7.3)

which is the same result as that obtained by Scheludko30 under ideal fluid conditions.

From (1.6.25.) it has been pointed out that for an unstable wave to grow $\beta$ has to be $> 0$. An important feature of (1.6.25.) is that the surface elasticity term is expected to act like viscosity in that it does not affect the onset of instability but will affect the rate of growth of an unstable wave.

$$\beta = \left(2k^2 n^4 - k^3 \sigma - \rho \rho c \right) > 0$$  
(1.7.4)

The instability criterion presented here is the same as that derived by both Vrij27 and Scheludko30 in their studies, although all three derivations were obtained in a different manner. $\frac{\partial n}{\partial t}$ is always positive for free liquid films and is the destabilizing term in the expression for $\beta$. This is to be expected since a small decrease in thickness will increase the local disjoining pressure and promote
further thinning. \(-k^3 \sigma\) represents the stabilizing effect of surface tension resisting deformation on the liquid surface. \(-\rho g k\) represents the stabilizing effect of gravity when a deformation occurs.

Since we are concerned only with microscopic plane parallel circular films whose thickness is less than 1000\(\AA\), the gravity term can be ignored since \(\rho g\) is going to be negligible in comparison to \(\frac{\partial \Pi}{\partial h}\) and \(k^3 \sigma\). Hereafter, \(\beta\) is to be written as

\[
\beta = (2k \Pi' - k^3 \sigma) \tag{1.7.5.}
\]

1.8. Effect of Surface Tension being a Function of Thickness

As was pointed out in subsection 1.2, the parameters describing a thin film are different to those describing a thick film. In a thin film parameters such as chemical potential and pressure were shown to be a function of the size of the phase. Strictly, it is not correct to consider the film as 'surface' and 'volume' phases in the Gibbs sense. This is true for the surface tension or, more correctly, the tension of the film. That the tension of the film is less than the bulk value is obvious when considering the equilibrium around the contact angle between the film and the bulk.

In the derivation of the growth rate the tension of the film was assumed independent of \(h\) and the bulk value of \(2\sigma\) was used.

It has been shown that \(T\) (which will denote the tension of the thin film) is related to \(\Pi\) and \(h\) by

\[
\frac{dT}{d\Pi} = h \tag{1.0.1.}
\]

Integrating from \(h_1\) to \(h_2\) produces

\[
T(h_1) - T(h_2) = \int_{h_1}^{h_2} \Pi dh + \Pi(h_1)h_1 - \Pi(h_2)h_2 \tag{1.3.2.}
\]

As \(h_2 \to \infty, \Pi \to 0\) and \(T(h_2)' \to 2\sigma\),

\[
T = 2\sigma + \int_{h_1}^{\infty} \Pi dh + \Pi h \tag{1.3.3.}
\]

If \(\Pi = \frac{-1}{h^3}\)
Then \( T = 2\sigma - \frac{3k}{2h^2} \) \( \quad (1.6.4.) \)

\[ \frac{dT}{dh} = \frac{3k}{h^3} \] \( \quad (1.6.5.) \)

Therefore, the change in tension due to a disturbance is

\[ \eta \cdot \frac{dT}{dh} = 3\eta \Pi \] \( \quad (1.6.6.) \)

Providing the disturbance is infinitesimal compared to \( h \) the error in \( T \) is negligible. If \( k \) is of order \( 10^{-13} \) (average value for many liquids) then from equation (1.6.4.) \( h \) has to be about \( 100\text{Å} \) before any significant change from the bulk value occurs. At these thicknesses we approximate to the black film region whose nature and structure would probably render the other assumptions invalid. In the discussion later, films of thicknesses around \( 400\text{Å} \) will be of concern. However, if a non-linear study of the wave amplification was made involving disturbances which were no longer infinitesimal, then the effect discussed and given by (1.6.6.) would have to be included.

For pure liquids (\( \varepsilon = 0 \)) which merge into the bulk via a contact angle, there will be a small surface tension gradient directed towards the bulk. Since no surfactant is present to oppose the stretching of the surface by the viscous stress, this surface tension gradient actually enhances the surface movement and assists in film drainage. In this case it would be expected that the wave growth rate given by (1.7.2.) to be higher than that for when surface active agent is present.

1.9. Results from the Growth Rate Equations

The data used in obtaining results from the growth rate equations are based upon Scheludko's\(^{34,35} \) work on chlorobenzene and aniline films. From experiments involving the thinning of free liquid films formed from a biconcave drop, he obtained an accurate isotherm for \( \Pi(h) \) by
relating the rate of thinning to equation (1.4.1.1). He has also obtained critical thicknesses of rupture for films of various radii for these systems. The chlorobenzene films were stabilized by the addition of $2 \times 10^{-4}$ gm per cc of Aerosol MA to ensure surface immobility. All the following results have been calculated for the chlorobenzene system and can ultimately be compared with Scheludko's critical thicknesses of rupture.

The data used for the solution of equation (1.6.25.) is as follows

$$\Pi = -\frac{\frac{1}{2}47\pi}{(2\pi/\lambda_L)^2} + \frac{0.62K}{(2\pi/\lambda_L)^2 h^2}$$

where $\lambda_L$ = wavelength of the London wave = $3.1 \times 10^{-6}$ cm and

$\chi = 3.1 \times 10^{-13}$ dyne cm.

$\nu = 0.073$ cm$^2$ sec$^{-1}$

$\sigma = 32.6$ dyne cm$^{-1}$

$D_s = 10^{-5}$ cm$^2$ sec$^{-1}$

In the following graphs where the surface elasticity is varied, the concentration changes necessary to cause the variation are assumed not to affect the values of the other variables in the growth rate equation.

Fig 1.5. shows $n$ plotted against $k$ for various values of $\varepsilon$ at $h = 500\AA$. With very small quantities of surfactant present to ensure immobile interfaces the values of $\varepsilon$ are likely to be low, approximately of order 1, and as can be seen from Fig 1.5, only small values of $\varepsilon$ cause significant changes in the growth rate. It can be seen that $\varepsilon$ in no way affects the criterion of instability. The upper curve with $\varepsilon = 0$ represents the case of a pure viscous liquid. For $\varepsilon > 10$, equation 1.6.26., which assumes $n << D_s^{1/2}$, can be further simplified by neglecting $k^2\nu$ in relation to

$$\frac{\varepsilon}{\rho D_s}.$$ Since $\left(\frac{kh_0}{2\rho}\right)$ is small compared to $\left(\frac{\varepsilon}{\rho D_s}\right)^2$
FIG. 1.5
THE EFFECT OF SURFACE ELASTICITY ON THE WAVE GROWTH RATE FOR CHLOROBENZENE
it is also permissible to evaluate the square root by the binomial theorem. This leads to the final result

\[ n = \frac{k h^2 D_s \beta}{4\varepsilon} \]  

(1.9.2.)

From Fig 1.5, the value of \( \varepsilon = 10^{-3} \) approximately corresponds to that for \( \varepsilon = 0 \). Both the treatment of Scheludko and Vrij excluded the effect of surface elasticity as a parameter even though surface immobility was assumed. For \( \varepsilon = 1 \), the results obtained with (1.6.25.) are of similar order to those predicted by Scheludko and Vrij.

The wave growth rate for \( \varepsilon = 0 \) is of order \( 10^4 \). A high value for the pure liquid was predicted in the discussion in the previous subsection due to surface tension gradients assisting the surface flow. The extremely high value of \( n \) indicates that the pure liquid film is likely to rupture immediately after it becomes unstable. This is borne out experimentally by the fact that pure liquids do not form a foam and that they do not form plane parallel microscopic films.

The growth rate with a surface elasticity value of 1 dyne/cm is of order \( 10^{-4} \) lower than that for the pure liquid. Thus, it can be seen that the surface elasticity plays a major role in the damping of wave amplification. The importance of this is discussed in subsection 1.11 with respect to the stability of foams.

The peak of each curve in Fig 1.5 changes with the value of surface elasticity. On increasing the surface elasticity the most unstable wave occurs at a higher wavenumber (i.e. a shorter wavelength).

It is important to relate the wavenumber to the size of the film under consideration. At the periphery of the film another boundary condition can be introduced.

i.e. At \( r = R \), \( v \) \( _r \) = 0.

From equation (1.6.3.) this condition is met when \( J_1(kR) = 0 \).

This is equivalent to saying that the roots of \( J_1(kR) = 0 \) will
give the wavenumbers of those waves which will fit exactly on to the film of radius $R$.

The first root, other than that corresponding to an infinite wavelength, is at $kr = 3.332$, so that $k = \frac{3.332}{R}$.

Combining this with the instability criterion gives a relationship for $R$ and $h$ under which conditions a free film becomes unstable.

ie. $\frac{dh}{dn} = \frac{(3.332)^2}{2R^2}$  \hspace{1cm} (1.9.3.)

The other roots of $J_1(kr) = 0$ also give similar relationships to that expressed by (1.9.3.) and the value of $kr$ determines how many crests and troughs are displayed over the film's radius. Fig 1.6 shows the onset of instability curves for various roots of $J_1(kr)$.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$kr$</th>
<th>No. Root of $J_1(kr)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.332</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>7.015</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>13.32</td>
<td>4</td>
</tr>
<tr>
<td>D</td>
<td>25.90</td>
<td>6</td>
</tr>
<tr>
<td>E</td>
<td>51.04</td>
<td>16</td>
</tr>
<tr>
<td>F</td>
<td>76.10</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 1.1

Table 1.1 shows the values taken in Fig 1.6.

The higher the value of $kr$ the shorter is the wavelength relative to the film's radius. It is obvious from the instability criterion that for smaller wavelengths the higher is the value of $\frac{dh}{dn}$ needed to cause instability and hence is stable to a thinner film.

Curve G. on Fig 1.6. shows the critical thicknesses of rupture for microscopical circular chlorobenzene films obtained by Scheludko. Fig 1.6. shows that the film ruptures at a considerably thinner film than that at which instability occurs. In that time the film thickens and as it does so, shorter waves become unstable and in turn grow on.
FIG 1.6 ONSET OF INSTABILITY AS A FUNCTION OF WAVENUMBER AND FILM RADIUS
FIG. 1.7
WAVE GROWTH RATE DEPENDENCE UPON THICKNESS FOR DIFFERENT WAVENUMBERS.
Fig 1.7 shows the growth rate curves of particular waves as the film thins. The wavenumbers chosen correspond to the same \( \lambda (kr) \) root numbers considered in Fig 1.6 and are for a film of radius \( 10^{-2} \text{cm} \).

<table>
<thead>
<tr>
<th>Curve</th>
<th>Wavenumber</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>383.2</td>
</tr>
<tr>
<td>B</td>
<td>701.5</td>
</tr>
<tr>
<td>C</td>
<td>1332</td>
</tr>
<tr>
<td>D</td>
<td>2590</td>
</tr>
<tr>
<td>E</td>
<td>5104</td>
</tr>
<tr>
<td>F</td>
<td>7613</td>
</tr>
</tbody>
</table>

Table 1.2

A surface elasticity value of 5 dyne/cm. was used to calculate the growth rate in Fig 1.7.

Fig 1.7 illustrates that as successive wavenumbers become unstable their growth rates rise rapidly to overtake the previously unstable waves, so that at the rupture thickness the most significant wavenumbers will be those most recently unstable. Figs 1.6 and 1.7 show that for any particular film radius, a large number of waves with different wavelengths will amplify on the liquid surface before the film ruptures.

1.10. The Initial Disturbance

For a theoretical prediction of the critical thickness of rupture it is necessary to know, firstly, when an unstable wave occurs and, secondly, how that wave amplifies on the liquid surface. The simplest model for rupture assumes that the film will break when the disturbance amplifies to a value equal to half the film's thickness.

The previous section has been concerned with the instability and growth rate of waves on a film. The main factor involved in a study on the second part of the problem is to evaluate the amplitude of the
initial disturbance. From equation (1.6.6.), \( \eta \) was represented by

\[
\eta = - \frac{k^2}{n} (A+C) \text{Jo}(kr) e^{nt}
\]

However, the constants A and C were eliminated when the determinant was solved for the wave amplification factor. It is not possible to obtain any information on the value of the initial disturbance from the theory derived.

Both Vrij\textsuperscript{27} and Scheludko\textsuperscript{30} were faced with the same problem and both resorted to the principle of equipartition. This states that the free energy of a fluctuation mode should be equal to \( kT/2 \), where \( k \) is the Boltzmann constant. By applying this theorem of Einstein\textsuperscript{36}, they obtained a value for the initial disturbance. However, for a real fluid this implies that all the energy \( kT/2 \) is used up forming the wave which would result in a surface temperature of absolute zero. Thus, if this approach is valid, only a small fraction of the energy represented by \( kT/2 \) can be used to produce an initial wave.

More recently Katyl and Ingard\textsuperscript{37} studying light scattering from thermal fluctuations on a liquid surface considered the incident light as photons hitting the surface and interacting with surface waves or ripplons. They obtained a momentum equation (see (1.10.1.)) for the interaction of the photon with the ripplon of wave number \( k \). The effect is illustrated schematically in Fig 1.8.

\[
\left( \frac{k}{K} \right)^2 = \sin^2 \theta + \sin^2 \theta_0 - 2 \sin \theta \sin \theta_0 \cos \phi \quad (1.10.1.)
\]

![Diagram of light scattering](image)
The ripplon is specified as a quasi-particle with momentum $\mathbf{q}$
along the surface and an energy $\hbar \omega$ where $\hbar = \text{Planck's constant}$
and $\omega$ is the frequency of oscillation. $\theta$ and $\phi$ are the
scattering angles and $K = 2\pi / \lambda$ is the wavenumber of the photon.

Energy conservation requires that the frequencies of the
scattered light are related by

$$\Omega' = \Omega + \omega$$
corresponding to absorption by or creation
of a ripplon.

Compared to the frequencies of light waves, the frequencies of
ripplons relevant to any subsequent instability will be very small
indeed. Thus, the light energy involved in creating a ripplon would
be very small. By a similar analogy it seems likely that the thermal
energy involved in creating a thermal wave is also very small if the
surface conditions are not to change drastically. At $25^\circ C$ and for
visible light, the value of $\hbar \Omega$ denoting the incident light energy
is very much greater than $h \Omega / 2$. 

Approximately, $\frac{\hbar \Omega}{h \Omega / 2} \approx 100$

The purpose of this has been to show that both effects can produce
short surface waves. In general there will be a whole range of short
waves on the surface caused by these two effects and by external
vibrations.

The treatment of Vrij and Scheludko seems to be based upon a
rather tenuous argument. As was shown in subsection 1.9 it is likely
that a number of wavelengths will be unstable and grow on the surface
before rupture occurs. This will lead to energy interaction between
the waves especially when harmonics are concerned.

A reasonable solution to this problem seems likely only by a
hydrodynamic study of the growth and interaction of waves on a liquid
surface. Yuen$^{38}$, who studied the non-linear capillary instability of
a liquid jet, showed that the development of an initially sinusoidal
wave is a non-linear effect with generation of higher harmonics as well as feedback into the fundamental wave. Rutland and Jameson\textsuperscript{39}, following Yuen's treatment, showed that the theoretical prediction of drop sizes resulting from breakup of a liquid jet were only a slight function of the guessed initial disturbance. A similar analysis for waves on a circular film, when disjoining pressure cannot be ignored, would be complicated by the fact that the stability of the higher harmonics depend upon a smaller film thickness and hence there would be interaction between stable and unstable waves.

1.11. The Relevance of the Results to Foam Stability

The study of the draining and rupture characteristics of a single thin liquid film can easily be extended to yield information on foam drainage and foam collapse. The lifetime of the foam can be related to the lifetime of a thin film. According to the previous discussion there are two effects occurring in a thin liquid film. The first involves the film becoming unstable to particular waves which subsequently amplify and secondly, the film drains to cause higher growth rates and cause more waves to become unstable. Thus, the lifetime of the film is dependent primarily upon the wave growth rate and the film drainage rate.

Miles\textsuperscript{40} et al noticed that small quantities of polar organic compounds such as lauryl alcohol markedly lowered the drainage rates in films. The draining rate in the film was reduced by the viscous drag of the adsorbed film on the neighbouring molecules. The coefficient of viscosity is thus different at the surface in the presence of such a film and has been called the 'surface viscosity'.

Brown\textsuperscript{41} et al obtained surface viscosity data which confirmed that foams of greater stability were produced from solutions having an appreciable surface viscosity. Similar results were also obtained
by Davies\textsuperscript{42} with aqueous films with 0.1\% sodium laurate at pH10 with added lauryl alcohol. Schelud\textsuperscript{ko}\textsuperscript{30} found that the critical thickness of rupture of free aniline films reduced from 540\AA\ with 10\textsuperscript{-6} molar C\textsubscript{12}H\textsubscript{25} OH to about 400\AA\ with 6 \times 10\textsuperscript{-6} molar C\textsubscript{12}H\textsubscript{25} OH using a film radius of 1.25 \times 10\textsuperscript{-2} cm. Unfortunately the surface elasticity was not measured.

The addition of surface active agents increases the surface elasticity and from the previous subsections it has been shown to exert a considerable damping effect on the growth rate of unstable waves. In aqueous films, surface elasticity measurements\textsuperscript{43} have given $\varepsilon$ values of up to 100 dynes/cm. With these values of $\varepsilon$, equation (1.9.2) is appropriate to predict the growth rate since this would be expected to be of the order 10\textsuperscript{-3} or 10\textsuperscript{-4} sec\textsuperscript{-1}.

Thus, taking Hiles' results on film drainage and the effect of surface elasticity discussed here, it can be seen that addition of certain surface active agents profoundly effects the two factors determining foam stability.

With films having high values of $\varepsilon$ the surface elasticity effect on the wave growth rate is probably the controlling factor even though high values of 'surface viscosity' are also likely to be exhibited. It is crucial that as the film drains, the damping effect of the surface elasticity is sufficient to cause a low wave growth rate. A slow drainage rate would allow a longer time for the wave to grow and in this respect make things worse.

Since surface elasticity and 'surface viscosity' are to some degree related, it is possible that Brown, Davies and Schelud\textsuperscript{ko}'s results can be explained on the basis of surface elasticity influencing the lifetime of the film rather than the surface viscosity.
In aqueous films, an additional factor will be the presence of dilute electrolyte. If the electric double layers are not suppressed by high electrolyte concentrations then the equilibrium thickness may be reached without rupture. High values of surface elasticity would increase the probability of this occurring by damping the wave growth rate.

Scheludko has also pointed out that the influence of the adsorbed layers may be more marked as the film thins by modifying the Van der Waals disjoining pressure and by increasing the effective viscosity of the film. The former will probably have little significance until the black film region or at very high concentrations of surfactant. If the surface layer exerts a greater drag on the neighbouring molecules as the film thins, causing a reduced drainage rate, then on the same argument, the surface elasticity is also likely to be affected on thinning and cause a greater wave damping than that predicted by assuming \( \varepsilon \) is constant. Thus, if the monolayer does act in this way as the film thins, then the increased draining time is approximately compensated by the increase in time necessary to cause wave growth, so that the final rupture thickness would be roughly the same as that obtained by neglecting the change in viscosity and surface elasticity with thickness.

1.12. Summary of Conclusions

1. The theory derived to describe the instability of a plane parallel circular film incorporating the effect of surface elasticity predicts values for the growth rate of an unstable wave which are in good agreement with values obtained by other workers and of order of magnitude necessary to explain the stability of foams.

2. The surface elasticity exerts a considerable damping effect on the growth rate and it has been shown to be a major factor influencing the stability of foams.
3. If the addition of surfactant produces a greater effect in reducing the growth rate than in reducing the draining rate, then the critical thickness of rupture will be reduced.

4. Before a prediction of the final rupture thickness can be made, a theory describing the growth of waves on the surface, taking into account the interaction between harmonics, has to be developed.

Recommended Experimental Work

The importance of surface elasticity could be determined by measuring the critical thickness of rupture of free films under varying concentrations of surfactant whose surface elasticity dependence with concentration would also be measured. From the previous argument, increasing the surface elasticity should produce increased wave damping and hence a longer life time and reduced critical thickness for the film. The relative effect of the surfactant on the surface viscosity could be found from the changes in the drainage rate up to the critical thickness.

Also, at surfactant concentrations corresponding to black spot formation it has been suggested that the adsorbed monolayer is saturated. If the surface elasticity remained approximately constant above this concentration (but still lower than the c.m.c.), then the critical thickness would also be expected to remain constant (provided that the drainage rate remained similar).
REFERENCES


37. Katyl R.H. and Ingard U., 'In Honour of Philip M. Morse',
Investigation of the Rupture of Aqueous Films on a Hydrophobic Surface

The object of this experimental work is to investigate the mechanism of rupture of an aqueous film on a hydrophobic surface and to obtain values for the critical thickness of rupture.

Padday, in recent experiments, found that a number of pure liquids ruptured spontaneously at very large thicknesses of order 100 - 500 \( \mu \text{m} \) on low energy surfaces such as polytetrafluoroethylene. The area of the film in Padday's work was not mentioned, although it is evident from his apparatus that they were large (of order 10 sq. cm). In this study microscopic circular films with radii of order 10\(^{-2}\) cm are considered.

2.1 Hydrophobicity

The Van Der Waals disjoining pressure of a film, 2, on a substrate, 1, can be represented by

\[
\Pi_{vw} = \frac{(A_{12} - A_{22})}{6\pi h^3}
\]  

(2.1.1)

where \( A \) = London - Hamaker constant

If \( A_{12} \) (referring to the solid - liquid interactions) is greater than \( A_{22} \) (for interactions between molecules in the liquid), the solid is said to be hydrophilic since \( \Pi_{vw} \) is positive.

\( A_{12} \) can be represented approximately by

\[
A_{12} \propto \sqrt{A_{11}A_{22}}
\]  

(2.1.2)

so that \( \Pi_{vw} \) is positive if \( A_{11} > A_{22} \)

According to London's\(^2\) theory of dispersion forces

\[
A_{12} = 2 \sqrt{\frac{\nu_1 \nu_2}{\nu_1 + \nu_2}} \cdot \sqrt{A_{11} + A_{22}} = \sqrt{A_{11}A_{22}}
\]  

(2.1.3)

where \( \nu_1 \) and \( \nu_2 \) are the characteristic frequencies of the electron charge distribution. A maximum value of \( \alpha = 1 \) is obtained when \( \nu_1 = \nu_2 \). When \( \nu_1 \neq \nu_2 \) the attraction is less because the
oscillations of each species are out of resonance. Thus, with materials of very different electronic properties it is possible for $A_{11} > A_{22} > A_{12}$ and the solid would exhibit hydrophobic properties.

Also, if the electronic properties are different, the retardation effect would become significant at different distances for different components of the London Force and the $A_{12}$ interaction could change with thickness in a different manner to the $A_{22}$ term. It is therefore possible for $\Pi_{\text{adm}}$ to change sign with film thickness.

All systems that exhibit a finite contact angle at the solid - liquid - gas boundary must have a negative value of disjoining pressure over a certain range of film thickness. As the liquid drains from the solid, if at a certain thickness a negative disjoining pressure occurs and the film becomes unstable, it will separate into thicker and thinner regions, i.e., macroscopic drops and an adsorbed multilayer.

Scheludko and Platikanov\(^3\) considered the Lyophobic case of benzene on mercury experimentally and obtained negative values for $\Pi$ in the thickness range 240 - 1200 Å and positive values below 240 Å. If $\Pi$ is positive at all thicknesses an equilibrium film will eventually be formed.

The Born repulsive forces and the permanent dipole interactions cannot be neglected, as is usual, when calculating the disjoining pressure from intermolecular theory in two cases\(^4\). Firstly, where dipolar molecules are strongly orientated on the solid substrate leading to autohydrophobic and secondly, with highly associated liquids like water which may be structurally incompatible with various solids.

Laskowski and Kitchener\(^5\) investigated the hydrophobic-hydrophobic transition on silica using aqueous solutions and vitreous
silica which had been methylated with trimethylchlorosilane. The contact angle was found to be dependent upon the pH of the solution and the time of contact. The surface eventually became hydrophilic at all pH values, the process being more marked at high pH values. The rehydration of the silica was not due to loss of methyl groups as the surface could be rendered hydrophobic by heating to $110^\circ\text{C}$, showing that only physically adsorbed water is involved.

On the classical thermodynamic treatment, the work of adhesion of liquid to solid, $W_a$, and the work of cohesion of the liquid, $W_c$, can be defined by

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{st}$$  \hspace{1cm} (2.1.4)

$$W_c = 2\gamma_l$$  \hspace{1cm} (2.1.5)

where the subscripts refer to the solid - vapour, the liquid - vapour and solid-liquid interfaces and where $\gamma$ is the surface energy. $W_a$ and $W_c$ can be related to intermolecular forces and Laskowski and Kitchener divided the work of adhesion of water to a solid into three independent terms

$$W_a = W^d + W^h + W^i$$ \hspace{1cm} (2.1.6)

where $W^d$ is the contribution from London dispersion forces, $W^h$ is the contribution from the hydration of polar sites and $W^i$ is the contribution from ionic sites.

For an ideal non-polar solid such as pure graphite $W^i$ and $W^h$ are both zero, so that $W_a$ involves only $W^d$. The dispersion force contribution to the surface energy for water has been calculated to be $21.3$ erg cm$^{-2}$. Other values given by Laskowski and Kitchener show that for no substance is $W^d$ as large as the work of cohesion of water and so all solids would be hydrophobic if they did not carry polar or ionic groups. According to Bowkes, on dispersion energies alone, water should spread on paraffin wax, but the
Cohesive energy of water is mainly due to hydrogen bonding. Ionization of surface sites contributes a $W_i$ term which increases with pH. For pure hydrated silica $\gamma^h$ would be expected to be of similar order to the work of adsorption of saturated water vapour ($244 \text{ erg cm}^{-2}$). A value of this order would be needed to cause methylated silica to become hydrophilic at low pH values after long immersion. On the disjoining pressure analysis, the hydration of polar and ionic sites would cause a positive contribution to $\Pi$.

Since the hydrophobicity arises from the exceptionally large cohesive energy of water, of which about 70% is due to hydrogen bonding, Laskowski and Kitchener concluded that the instability of water films of a certain thickness on hydrophobic solids is fundamentally due to a deficiency of hydrogen bonding in the films as compared to liquid water, i.e., the proximity to any non-polar surface imposes a diminished mean hydrogen bonding compared with bulk water.

### 2.2 Film Thickness Measurement Techniques

(a) Interferometry

Interferometric methods to determine the thickness of liquid films have been widely used since Wells employed this technique earlier in the century. Much literature has been published on the subject notably by Tolansky and Françon.

![Interferometric Diagram](image)

Fig 2.1
The intensity of the reflected beam is dependent upon the optical path difference between successive rays.

Consider unit amplitude of the incident wave and assume normal incidence. The reflected amplitude, \( r_1 \), at the interface between medium 0 and the thin film and the reflected amplitude, \( r_2 \), at the interface of the thin film and medium 2 are given by the Fresnel formulae:

\[
\begin{align*}
    r_1 &= \frac{n_0 - n_1}{n_0 + n_1} \\
    r_2 &= \frac{n_1 - n_2}{n_1 + n_2}
\end{align*}
\] (2.2.1)

Let \( \phi = \frac{2\pi n_1 h}{\lambda} \)

where \( h \) = thickness of the film

\( \lambda \) = wavelength of the incident light

The reflectance is defined as the ratio of the reflected flux to the incident flux. Taking into account the total of the multiple reflections gives

\[
R = \frac{r_1^2 + r_2^2 + 2r_1r_2 \cos 2\phi}{1 + r_1^2r_2^2 + 2r_1r_2 \cos 2\phi}
\] (2.2.2)

The transmittance is the ratio of transmitted flux to the incident flux

\[
T = \frac{(1 - r_1^2) (1 - r_2^2)}{1 + r_1^2r_2^2 + 2r_1r_2 \cos 2\phi}
\] (2.2.3)

The conditions should be that \( R + T = 1 \) which assumes that there is no energy absorbed in the film.

Equation (2.2.2) strictly refers to normal incidence. However, this relationship, by which the thickness of the film is related to the reflected intensity, is valid for small angles of incidence since the Fresnel coefficients do not change for incident angles less than 30°.

When \( n_0 = n_2 \), as \( h \to 0 \) the reflected intensity \( \to 0 \) so that
there is no lower limit to the values of \( h \) that can be measured providing the detecting system is sufficiently sensitive. If \( n_0 \neq n_2 \), then as \( h \to 0 \) the reflected intensity tends to a fixed value and when very thin films are considered (\( h < \lambda/20 \)) the measurement depends upon the small difference between two large values.

This experimental technique is useful for the study of non-equilibrium films and permits the study of the instantaneous values of critical thicknesses of rupture. Derjaguin\(^{10}\) eliminated the necessity for quantitative photometry by varying the wavelength to obtain a minimum in the intensity of the reflected light.

(b) **Ellipsometry**

This technique utilizes the change in polarisation of a light beam upon reflections. Circularly polarised incident light on a transparent medium produces a plane polarised beam on reflection. If a thin film of liquid is present on the surface, the reflected beam is elliptically polarised. The ellipticity and the phase changes of the normal and parallel components are related to the optical properties of the film.

To relate the film thickness to the properties of the reflected beam is somewhat complex and usually relies on particular angles of incidence. For small film diameters the experimental optical system has to be carefully designed since the alignment and axis of rotation of the incident and reflected light are critical.

However, ellipsometry is a very much more sensitive method of film measurement than interferometry and thicknesses below 100 \( \AA \) can be measured. The method is not suitable for unstable thinning films but is widely used in the equilibrium black film region.
(c) Conductometric Method

With this technique the thickness of the film is computed from the longitudinal electrical resistance of the liquid film. Using a galvanometer to measure the current flowing between suitably positioned electrodes the resistance of the film is obtained, from which it is relatively easy to relate, via the specific conductance of the liquid, the film's thickness.

It is possible to measure thinning films and the critical thickness of rupture with this method. However, relatively large film areas have to be employed (of order 1 cm²) and the method cannot detect irregularities in the film's profile. It is also difficult to measure with accuracy the capillary suction pressure caused by the thicker regions around the electrodes. Another drawback is the uncertainty of the specific conductivity of very thin films in relation to the bulk value. The conductance method is therefore used more for determining the kinetics of thinning of thick films.

(d) Capacitance Method

This technique is suitable for the measurement of the thickness of films of non-conducting liquids between 2 drops of a conducting liquid and hence is employed in the study of emulsion films. The capacitance is measured using an alternating current of known frequency.

The method can be used for thinning films as well as equilibrium films. Like the conductometric method, it cannot detect small irregularities in the profile. Neither can the results be interpreted accurately since the dielectric constant of the film and the adsorption layers can vary widely and the value for the adsorption layer is not known. The influence of
the adsorption layer is much more marked in this method than in interferometric measurements.

However, if the technique is combined with an interferometer more information can be obtained concerning the effect of the dielectric constant of the adsorbed layer and provide a check on the results.

For this project an interferometric technique was chosen mainly because detailed information of the film could easily be obtained. The conductance and capacitance methods were not suitable for the system under consideration and ellipsometry would involve tedious calculations and is not suited for rapidly changing films. However, if a film thickness of 250 Å were to be seen then ellipsometry would have to be used.

2.3 The Optical System

The optical system used is shown schematically in Fig 2.2. The light source used was a 55 watt quartz-halogen lamp fed from a stabilized 12 volt D.C. supply. The light was focused on to a pinhole by a condensing lens and collimated into a parallel beam by a triplet lens. A Wratten No 24 filter produced red monochromatic light with a mean wavelength of 6600 Å. All these optical components were mounted on an optical bench. The parallel beam was directed on to a beam splitting prism which gave 50% reflection and 50% transmission at this wavelength and the reflected portion was then focused by the objective on to the film in the glass cell, the base of which formed the substrate. The transmitted part of the parallel beam was directed via a neutral density filter (N.D.4.0) to photomultiplier 1.

A watching eyepiece fitted over the microscope eyepiece enabled the reflected interference pattern to be observed and
Objective

Cell

Monochromatic

Pi

Pinhole

Neutral

Density

Filter

Beam splitting

Prism

Triplet

Collimating Lens

Source

Condensing Lens

Photomultiplier 1

Objective

Neutral

Density Filter

Beam splitting Prism

Triplet Collimating Lens

Source

Measuring Scale

Rotating Beam Splitting unit

Watching Eyepiece

Photomultiplier 2

Fig 2.2
recorded simultaneously. The watching eyepiece consisted of
two interchangeable beam splitting prisms (95% transmission -
5% reflection or 50% transmission - 50% reflection) on a rotating
arm. The transmitted light was directed towards photomultiplier
2 via 2 convex lenses situated in a 9" length tube. By adjusting
or changing these convex lenses the film area to be photometered
could be altered.

The microscope eyepiece employed was a Ramsden 15x unit and
either a 2½" working distance, 12x objective or a 1" working distance
6x objective was used depending upon the size of the film under study.

The base of the cell and the faces of the beam splitting prism
situated in the path of the original parallel beam were coated with
an antireflecting layer for use in red light. This work was
carried out by Optical and Electrical Coatings Ltd, of Howard Road,
Reigate, Surrey. Without these coatings the interference pattern
produced by the liquid film would have been swamped by the
unwanted reflections on these surfaces.

2.4 Electronic Equipment

Two EMI type 9731R side window photomultiplier tubes were
used which exhibited a guaranteed red response. The two tubes were
positioned as shown in Fig 2.2 and were each fed from a 750 volt
d.c. supply. By using the tubes in a balance circuit it was not
necessary to completely eliminate all stray light, so that if the
output was balanced for no film on the substrate, the variable
output produced corresponded to changes in the thickness of the
film. This balance system also compensated for fluctuations in
the intensity from the light source.

The photomultiplier output is linearly related to the light
intensity provided that the output current does not exceed 10 μA.
The maximum mean current allowed for these photomultipliers is 500 μA.

![Diagram of balance circuit](image)

**Fig 2.3**

The balance circuit is shown diagrammatically in Fig 2.3. When the balance was set to 50 kΩ (i.e., as indicated '500' on the adjusting dial) the voltage of either photomultiplier with respect to zero volts should not be greater than 600 mV for the linearity limit not to be exceeded. The balanced output from the photomultipliers was wired up to a chart recorder.

For the intensities observed in the optical system the photomultipliers were found to be too sensitive and a neutral density filter (ND2.0) had to be introduced into the light path to photomultiplier 2 to meet the linearity requirement.

### 2.5 Apparatus

The cell used was a fused, rectangular, open topped, fluorimeter cell made in high quality optical glass. The 45 mm high by 12.5 mm square base was supplied by Thermal Syndicate Ltd, of Maxwell Road, Stevenage, Hertfordshire. The base and each side was polished to a standard flatness of one wavelength (5.89 nm) per cm.
A bubble was produced downwards onto the base of the cell by using a microsyringe to which a glass nozzle of diameter 1.10 mm was attached by a machined Teflon tube. The micrometer controlled piston was also machined out of Teflon so that the capillary to the nozzle could, filled with liquid leaving only a small volume of air necessary to form the bubble. In this way, the volume of air needed in the capillary was minimised which reduced the sensitivity of the gas to slight temperature variations. The nozzle was fitted with a glass shield which fitted over the cell so that particulate matter was prevented from entering the system.

The cell was cemented by Araldite to a $\frac{3}{8}$ in metal arm which in turn was bracketed to the moving sleeve on the post of a travelling microscope. By using two such posts fixed perpendicularly together and the base of a travelling microscope it was possible to obtain movement of the cell in three dimensions. It was relatively easy to remove the cell for washing by unscrewing the retaining bolt in the bracket. The microsyringe and nozzle unit was fixed to a platform in the framework supporting the apparatus.

The microscope was mounted vertically on a travelling microscope stand and post and together with the focusing adjuster on the microscope body it was possible to move the objective in three dimensions.

The light source was kept at a distance of at least 6 feet from the test cell so that the cell was unaffected by thermal currents arising from the source. A perspex screen was also placed in front of the microscope so that the space around the cell was protected from the warmth of the experimenter.

2.6 Cell Treatment for Hydrophobicity

Several methods on various optical glass test pieces were tried
to discover the best technique to be used. It was necessary for the treatment to produce a highly hydrophobic surface without distorting the optical characteristics of the polished cell.

(A) A 2% molar solution of a low viscosity silicone fluid in Analar Benzene was poured on to the optical test piece and the solution allowed to evaporate for half an hour. Due to the deposition of silicone fluid on to the surface, it was found to be highly hydrophobic. However, when the surface was studied under the 180x magnification needed for the study of microcircular films, the deposition had occurred dropwise so that the surface was unevenly covered. It was also obvious from this visual observation that the surface would not allow an interference pattern to be seen without distortions.

(B) A thin graphite film, approximately 500 Å was vacuum deposited on to the surface of another test piece that had previously been cleaned with chromic sulphuric acid. The surface obtained was hydrophobic but after several immersions in water the film began to detach from the glass surface. Apart from this, the graphite film was found to absorb too much light, even at this thickness.

(C) A layer of silicone fluid with an S.G. of 1.1 and kinematic viscosity of 500 cs was introduced into a test cell and, after a planar surface had been formed, water was carefully poured on to it. The silicone layer thus became the hydrophobic substrate, but, unfortunately, it was not possible to obtain a planar water - silicone interface which did not cause distortion and light scattering.

(D) The method finally chosen was the methylation of the glass surface with trimethylchlorosilane. By changing the properties of
the surface chemically, the optical properties of the glass were unaffected. Freshly treated glass test pieces were found to be highly hydrophobic. The properties of this methylated surface have been discussed briefly in subsection 2.1.

A disadvantage of this method involved the slow physical adsorption of water molecules on to the methylated surface. Since with the cell to be used, it would be difficult to measure contact angles or zeta potentials, it would be necessary to standardize the surface before each set of tests. The physically adsorbed water would have to be removed by heating to 110°C for several hours so that the hydrophobicity could be regenerated. From Laskowski and Kitchener's results, this would yield a contact angle in water of 60°, slightly less than the value for freshly methylated silica.

Methylation of the cell was performed with a 0.04 molar solution of trimethylchlorosilane in 'Analar' Benzene. Before treatment, the inside of the cell was cleaned with a chromic sulphuric cleaning mixture and then thoroughly rinsed with high quality distilled water and dried by heating to 110°C. The cell was then coated by standing the solution in the cell for 15 minutes, followed by rinsing with Analar Benzene and drying for 24 hours at 110°C. During this treatment, it was imperative that no organic solvent was allowed to come into contact with the antireflecting layer on the base of the cell since this layer could easily be damaged by such reagents.

2.7 Procedure

The materials used in these experiments were high quality distilled water prepared by deionization and double distillation and 'Analar' glycerol as supplied by Hopkin and Williams Ltd.
The purity of the water was checked by surface tension measurements and by shaking. Before and after each set of tests the cell was thoroughly rinsed with the distilled water. Also, before each set of tests the nozzle and microsyringe unit was dismantled and cleaned in chromic acid followed by thorough rinsing in distilled water. Since it was not possible to clean the cell in a similar manner because of the antireflecting layer and the chemical properties of the treated surface, the cell was heated to 175°C for 20 hours after each test. This had the effect of removing any surfactant still present as well as removing the adsorbed water on the surface.

Five mls of the distilled water containing 0.1 molar 'Analar' KCl and 0.01 molar 'Analar' isoamyl alcohol were poured into the cell. The KCl was used to suppress the electrostatic double layer and the isoamyl alcohol was used to ensure zero surface flow at the air - water interface. The microsyringe and nozzle unit was filled with distilled water and enough air for 4 or 5 bubbles drawn into it. The unit was lowered into the cell and then fixed to its support. The cell was raised so that the glass surface and the tip of the nozzle were approximately 1 nozzle diameter's distance apart. By slowly turning the micrometer, a bubble was produced and allowed to contact the surface. The area of contact could be adjusted by the micrometer.

The microscope was then focused on to the area of contact and the bubble withdrawn. (Because of the strongly hydrophobic nature of the surface a small bubble was retained by the surface). The cell was moved horizontally so that a fresh surface area was viewed by the microscope. In this way the alignment of the nozzle and microscope and the focusing on to the treated glass surface were accomplished.
For the experimental tests the bubble was produced again by careful manipulation of the micrometer until spontaneous thinning occurred and the subsequent action observed. By moving the cell horizontally in either direction, it was possible to perform 4 such tests with a different part of the cell surface each time.

2.8 Observations

With the water - KCl - isoamyl alcohol solution, as the bubble was slowly expanded towards the treated glass surface, a barrier ring was initially formed followed soon after by the formation of a secondary smaller ring on a part of this barrier ring. A Newton fringe pattern developed in this secondary ring and the pattern changed rapidly with the formation of more rings emanating from the centre. The rapid production of these rings signified that rapid thinning was occurring at this point. The remainder of the barrier ring did not appear to change as this localized thinning took place. Within seconds of the formation of this secondary ring, rupture occurred and was seen to be initiated in the centre of the secondary ring. The rupture time after the formation of the secondary ring depended upon the size of the secondary ring; the smaller the ring the faster the rupture.

This process was seen to occur in about 50% of the observations with this water system. At other times, rupture occurred soon after the formation of the barrier ring without any fringes being seen at all, occasionally, before a barrier ring was fully developed. The secondary ring occasionally appeared as a very small circle, like a very small hole in which the fringe orders changed very quickly. It appeared microscopic in comparison with the diameter of the barrier ring which was of order $10^{-2}$ cm.

*The ambient temperature during these experiments was $22^\circ C \pm 1^\circ C$. 

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The rest of the fringe pattern in this case was probably outside the limit of the microscope. All these observations were made with 180x magnification.

That the film was rupturing at the barrier ring if no secondary ring pattern was formed was confirmed by the fact that after rupture small droplets of water were left in the central area previously surrounded by the barrier ring. During the coalescence of the bubble with the glass, rupture had occurred preferentially around the barrier ring and had not allowed all the water under the dimple formed to escape. It seemed logical to expect the film to collapse at the barrier ring at this stage in the thinning since this corresponded to the minimum thickness of the water film. At no time did a plane parallel wetting type film form before rupture occurred.

Observations were also made on a glycerol film since the draining rate and rupture would occur at a much slower rate than in aqueous films. The fringe pattern with the glycerol was much less distinct than for aqueous films due to the similarities in the refractive index for the glycerol and the glass. (i.e. 1.472 and 1.522 respectively). However, the fringes did indicate that a large dimple had formed inside the barrier ring. Against a wetting surface the glycerol would drain and eventually, at very small thicknesses, the dimple would drain to form a plane parallel film. However, the high viscosity and the highly hydrophobic nature of the surface made this impossible and as with aqueous films, rupture was triggered at the barrier ring.

The observations seen in the water system were surprising since a film similar to that obtained in free film or wetting systems was expected to form by draining after the initial

*The refractive index for the aqueous solution was \( 1.340 \pm 0.002 \) at 20°C.
appearance of the barrier ring. The observations showed that a long range force existed which did not allow the expected film structure to form.

Since these observations showed a totally different process of rupture, it was obvious that the measurement of the rupture thicknesses of aqueous films by photometry would be impossible for two reasons. Firstly, the size of the secondary ring pattern necessitated a much higher magnification and meant that the area to be photometered was exceedingly small; and secondly, the secondary ring did not occur in a fixed position on the barrier ring so that it would not be possible to align the photometer accordingly in advance, even if such a small area could be effectively photometered.

For these reasons the photomultipliers were withdrawn and a Bolex 16 mm cine camera was inserted in place of photomultiplier 2 below the watching eyepiece. The focusing of the camera was arranged so that visual observation with the watching eyepiece and the camera were focused simultaneously.

Since a very small area was being considered and it was necessary to use a high magnification, a framing speed of 3 f.p.s. at full aperture, f.1.4, was used to ensure sufficient light necessary to photograph the process. Also, the watching eyepiece was arranged to give 95% transmission to the camera and 5% reflection to the observer. Kodak 4X film was used which had an ASA rating of 400 in artificial light. By developing in D19 for 4 minutes the ASA rating was effectively increased to 1000.

2.9 Results

The photographs of the process of rupture for an aqueous film are shown in Plate 1. The size of the secondary ring formed
in this case was one of the largest seen and has been presented to show the interference pattern with greater clarity. The size of the secondary ring most often seen was approximately half the size of that shown in Plate 1.

Photo 1 shows the initial stages of the formation of the secondary ring just after the appearance of the barrier ring. The barrier ring when fully developed was $10^{-2}$ cm in diameter. The number of frames between the photographs are as follows. (Framing speed = 3 f.p.s.)

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<th>Photograph Number</th>
<th>Frames from Photo 1</th>
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Photos 2-4 show the expansion of the central area in the secondary ring and the Newton ring pattern. Photos 5-7 show the formation of two smaller rings inside this secondary ring until this is fully established by photo 11. Photograph 14 shows rupture having occurred and the area of contact has expanded further in photo 15. Although it is not clear, rupture probably occurs between photo 12 and 13. With smaller secondary ring structures, the formation of two smaller rings inside it was not seen. This latter formation appears to be dependent upon the size of the secondary ring and only forms at sizes similar to that shown.

During this process the remaining part of the barrier ring has been largely unaffected. The diameter has remained constant.
Plate 2. Rupture of a glycerol film on methylated silica.
after photo 3. By counting back the number of fringes from
the contact position it is evident that the secondary ring
initially forms at a thickness of approximately \( \frac{20.00}{8} \) \( \mu \)m. (and electric)

The formation of the secondary ring was not due to the
nozzle not being perpendicular to the glass surface (which could
have caused a preferential local thinning) because in the same
set of tests on different parts of the cell surface, the secondary
ring appeared in different angular positions around the barrier
ring.

The thinning profiles of the secondary ring are shown in
Fig 2.4. The figures on the right of each curve correspond
to the number of frames since photo 1 in Plate 1. The abscissa
is the angular position around the barrier ring with 90°
arbitrarily fixed at the centre of the secondary ring in photo 2.

Plate 2 shows the rupture of a glycerol film on slow expansion
of the bubble towards the glass surface. The number of frames
from photo 1 are as follows

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The rupture can clearly be seen to initiate from the periphery
of the film in photo 2. (ie at the barrier ring). Subsequent
photos show the expansion of the area of contact radially from
this point. Six scale divisions shown in the photographs are
equivalent to \( 10^{-2} \) cm so that the barrier ring diameter is
\( 3.1 \times 10^{-2} \) cm. The microscope objective used in this case gave
90x magnification.

Rupture is likely to occur at the barrier ring for such
FIG 2.4 PROFILES OF THE DRAINING FILM IN THE SECONDARY RING

FILM THICKNESS (Å)

ANGLE AROUND BARRIER RING (DEGREES)
films because of the persistence of a pronounced dimple in a draining glycerol film. It is not possible to see whether the mechanism of local thinning also occurs with glycerol because of the similarity of the refractive indices.

The process of rupture was also studied for the case of a bubble blown against a bubble previously attached to the surface. This would be analogous to the capture of an ore particle by a bubble when a microbubble exists on the surface of the mineral. This mechanism has been suggested as a means of particle capture.

For an attached surface 'microbubble' in the water system, rupture always occurred in the film separating the two gas phases. On blowing the bubble against this microbubble, a barrier ring formed around the microbubble and axisymmetric interference patterns were seen between the top of the attached bubble and the expanding bubble. Rupture always occurred in this film and the area of contact expanded radially from its centre. The formation of a barrier ring depended upon the relative sizes of the bubbles and the approach velocity of the blown bubble. The slower the velocity of approach the less likely was barrier ring formation. For a barrier ring to be seen, the expanding bubble had to be at least twice the size of the microbubble. Due to the small diameter of the film between the 2 gas phases, the coalescence time was very short and occurred almost immediately after the first interference patterns were seen.

However, with glycerol two processes of rupture were seen with equal regularity. Plate 3 shows rupture occurring at the barrier ring and then expanding around the microbubble. The number of frames from the first photograph for each photograph in Plate 3 is given as follows:
Plate 3. Coalescence of a bubble with a microbubble – rupture initiating at the barrier ring.
Plate 4. Coalescence of a bubble with a microbubble - rupture initiating with the microbubble.
From Plate 3, it can be seen that the barrier ring is not fully formed around the microbubble but is tilted on one side. Rupture is triggered from a very small section of the barrier ring and expands in such a way as to envelope the microbubble. In this sequence, the bubble coalesces with the microbubble and leaves a crescent shaped area of trapped water. In many cases where rupture followed a similar procedure, the area of contact of the microbubble was left with a halo of trapped water surrounding it.

In Plate 4, a perfectly developed barrier ring is formed around the microbubble. The photograph numbers and frames correspond as follows:

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In the time interval between photo 1 and 2 the barrier ring has apparently tipped over and rupture has commenced at the centre with the microbubble. The area of contact expands radially outwards to meet the barrier ring. Since rupture occurs on the opposite side of the microbubble to direction of tilt it seems likely that the bubble tilts before coalescence begins. By tilting, a faster draining rate is obtained on the opposite side of the bubble.
2.10 Discussion

The process of rupture of an aqueous film, as illustrated by Plate 1, has relevance in the capture of an ore particle by a bubble in ore flotation. For capture to occur, it is necessary for the intermediate film of liquid to drain so that surface forces can aid the final rupture of the film and give strong adhesion of particle to bubble. In the aqueous films investigated the film exhibited a local thinning on a secondary area of considerably smaller diameter than that of the barrier ring. If the film had to thin uniformly through the whole of the barrier ring the time required could exceed the contact time of the gas - particle collision.

Since the thinning rate at a given separation and pressure drop for a liquid between two flat circular plates pressed together is inversely proportional to the square of the radius, it would be highly advantageous for the film to thin over as small a radius as possible. In the observations made, the process of rupture involves local thinning on a radius equivalent to $10^{-3}$ cm and less, i.e. the rate of thinning is of order 100 times that for the uniform thinning of the whole film. Thus, this localized thinning is far more favourable for gas - particle contact.

In practice, when the particles are not perfect geometrical shapes, local thinning would be preferential on the protruding points of the particle. The secondary ring was also seen to split into two further rings if its size was large. This would promote more rapid thinning than if a single large ring remained.

Padday\(^1\) found that pure water on Teflon ruptured at a thickness of $5 \times 10^{-2}$ cm, i.e. considerably thicker than the films here. It is difficult to obtain an actual value for the critical thickness.
of rupture but from Plate 1 the film had not ruptured until photo 12 at the earliest when the minimum thickness of the film was of order 1000 Å. For rupture to occur a negative disjoining pressure at the rupture thickness is required. It is quite possible that Padday's large values of rupture thicknesses could be explained by a similar mechanism as that shown here.

The fact that rupture occurred occasionally before the barrier ring became noticeable gives evidence of the action of a long range force (as compared to the shorter acting Van der Waals component of the disjoining pressure). This force apparently is able to extend to distances of at least 20,000 Å from the surface. The draining of an aqueous film on a hydrophilic surface showed no secondary ring and drainage occurred over the whole of the barrier ring. Therefore, this long range force seems to be a property of a hydrophobic surface. The local thinning observed could be due to certain areas on the surface being more hydrophobic than others. This long range force probably increases the draining pressure rate in a manner similar to that of a negative disjoining in films of thickness around 1000 Å. The change in curvature around the concavity produced would cause a higher capillary pressure which would also increase the thinning rate.

The origin of the long range force is unclear. It could be produced as a result of the surface influence on the state of hydrogen bonding in the water, although this itself seems unlikely to extend to such distances. Padday's results with pure water might eliminate the possibility of a 'diffusio-phoretic' effect although the presence of a positive charge on the Teflon surface could give a long range coulombic force. Padday found that approximately 10⁻³ molar sodium dioctyl sulphosuccinate on
Teflon was stable at all measurable thicknesses (i.e., greater than $3 \times 10^{-3}$ cm). He concluded that solutions of anionic surfactant rendered the surface negative so that the electrical effects produce a positive disjoining pressure. This may be analogous to the addition of anionic surfactant to methylated silica which renders the surface hydrophilic, as has been discussed in subsection 2.1 with high values of pH.

Whichever mechanism produces the long range force, from the experiments performed here the rupture of the film is shown to be based upon a localized thinning mechanism which is highly favourable for rapid film rupture.

If quantitative information on the long range force can be obtained then the instability of a liquid film on a hydrophobic surface to surface waves could be studied in a similar way to that given in Section I. In this case, the long range destabilizing force would be analogous to the negative disjoining pressure term.

In a paper to be published, Taylor and Michael have performed experiments in which holes in water films on mercury or wax coated surfaces were produced by an air jet. They found that for certain film thicknesses and hole diameters the hole remained stationary after the air jet was cut off. This suggests that the contact angle depends upon whether the meniscus is advancing or retreating. When the curves of these two angles of contact were drawn in the $(h,R)$ plane they define a range of hole radii for a given value of film thickness within which a hole can be trapped, it would seem likely that the sequence shown in Plate 1 corresponds to the process of formation of such a hole.

With bubbles blown against a microbubble a rapid thinning rate between the two bubbles occurs because a very small diameter film is produced between them. The smaller the microbubble then
the faster is the film likely to thin so that coalescence will occur. This case is also one of localized thinning where the microbubble acts as a catalyst.

With the water system, no pronounced dimple was formed during draining so that coalescence always occurred via rupture of the intervening liquid film between the two gas phases. With glycerol, the dimple, produced as a result of the pressure gradient in the draining film, is much more pronounced and is evidently sufficiently thick in the centre to fit over the microbubble so that rupture could be initiated at the barrier ring.

2.11 Summary of conclusions

1). The experiments have produced evidence to show that a long range force may extend to distances at least 20,000 Å from a hydrophobic surface, although the exact origin of this force is unclear.

2). The mechanism of rupture of an aqueous film on methylated silica has been shown to consist of a very localized thinning on a part of the barrier ring followed by rupture of the liquid film at a thickness less than 1000 Å. This process would be favourable for ore flotation in the absence of surface microbubbles.

3). It is likely that the long range force on a hydrophobic surface acts in a similar way to a negative disjoining pressure ($\Pi_{vn}$) in thin films.

4). The formation of the secondary rings may be due to irregularities in the surface properties of the methylated silica.

5). When no interference pattern is seen it is possible that very small holes are produced which were visually unnoticeable.

6). The rupture of a glycerol film also initiates from the barrier ring but this is to be expected because of the persistence of a
very marked central dimple until very small thicknesses. It was not possible to see whether a localized thinning occurred with glycerol as with aqueous films since the refractive indices of the glycerol and the glass were of similar value and caused an indistinct fringe pattern.

7). For the coalescence of a bubble with a microbubble in glycerol systems, two different mechanisms were seen both of which depend upon a non-axisymmetric bubble displacement.

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SECTION III

THE PROFILE OF A DRAINING FILM

3.1. Introduction

This section is concerned with the theoretical prediction of the profile of a draining microscopic film. When a bubble or drop approaches an interface, the film obtained between the latter and the flattened part of the bubble exhibits a dimple trapped by a thinner barrier ring. Platikanov's experiments on the dimpling of thin aqueous films showed, for a bubble blown against a plane interface, that the dimple has a regular central form. Thinning occurred more rapidly at the periphery. After prolonged thinning and because of the influence of a positive disjoining pressure, the dimple decreased to give a circular plane parallel equilibrium film with a thickness of order 500Å for a film radius of $1.5 \times 10^{-2}$ cm. It was generally found that the larger the radius of film, the larger the dimple that was produced. When the film radius was less than $5 \times 10^{-3}$ cm, practically no dimple was observed. With more viscous liquid films, the initial stages of the formation of the dimple are visible.

Dimples were observed in free aqueous foam films with a radius of about $10^{-3}$ cm. Their form was generally irregular and asymmetric with respect to the centre. During the thinning process the dimple moves to the periphery and rapidly flows out to the bulk liquid. For larger free films dimples are not usually seen, but instead irregular thickened parts like 'channels' are formed directed towards the periphery. The liquid flows rapidly through these channels to the periphery of the film. If the free circular film has a central thickness greater than 1000Å, it always has a convexity in the centre but upon further thinning this convexity disappears and below 1000Å the film appears completely plane parallel in reflected light.
Frankel and Kysels developed a hydrodynamic theory for the profile and draining of the dimple taking only the capillary pressure into account and neglecting disjoining pressure. Their equation for the maximum thickness \( h \) in the centre of the film is given by

\[
h = \left[ \frac{0.0096 n \mu R_b}{\sigma (t-t_o)} \right]^{\frac{1}{4}} \frac{1}{(t-t_o)^{\frac{3}{4}}} (3.1.1)
\]

and the minimum thickness at the barrier ring by

\[
z_o = \left[ \frac{0.0090 \mu R_b}{\sigma (t-t_o)} \right]^{\frac{3}{2}} \frac{1}{(t-t_o)^{\frac{3}{2}}} (3.1.2)
\]

where \( t_o \) is the time of formation of the hypothetical dimple with infinite thickness,

\[
z = \frac{3.066 R}{h} \text{ and } n = \text{number of immobile surfaces.}
\]

\[
\mu = \text{viscosity.}
\]

\[
R_b = \text{Radius of the bubble.}
\]

\[
R = \text{radius of the circular film.}
\]

\[
\sigma = \text{surface tension.}
\]

From equations (3.1.1) and (3.1.2) we obtain

\[
\frac{z_o}{h} = 3.066 \frac{R_b}{R^2} (3.1.3)
\]

which predicts that the dimple should become more pronounced as the film thins.

Platikanov's experimental results with films on substrates showed that over thickness ranges where disjoining pressure effects are negligible the dimple was less pronounced than that predicted by this theory. For high viscosity liquid films, the initial stages of formation of the dimple were considerably less pronounced.

Free liquid films with dimples do not allow a useful comparison because of the asymmetric flow with respect to the centre of the film. The Frankel and Kysels theory does not allow the formation of...
plane parallel films of small diameter observed by Platikanov. His results, however, do confirm the assumptions made by Scheludko that small films are plane parallel below 1000° and that the liquid flows from them as if between two approaching parallel discs.

Reynold's equation below can thus be used for the draining rate of the film and Scheludko has used this as a basis for the determination of the disjoining pressure.

\[ \frac{d(h^{-2})}{dt} = \frac{16}{3\pi^2} \Delta P^2 \]  
(3.1.4.)

where \( \Delta P \) is the total pressure difference between the film and the bulk and in this case is represented by the sum of the capillary and disjoining pressures

i.e. \( \Delta P = P_T - \Pi \).

Fig. 3.1. shows the draining rate and thickness as a function of time calculated by equation (3.1.4.) based on \( h = 2000\AA \) at \( t = 0 \). The curves refer to a chlorobenzene free film of radius \( 10^{-2} \) cm.

More recently, Hartland has obtained partial differential equations to represent the profile of a draining film under various boundary conditions on the interfaces. Starting with the simplified Navier-Stokes equation for low Reynolds number flow, he equated the excess pressure in the film above that in the surrounding phases to the surface stress created by the deformation of the film interface. Like Frankel and Kysela, the disjoining pressure terms were not included and so only thick films were considered.

His experiments were conducted with very viscous liquids such as glycerol and, using an early experimental profile as his theoretical starting point, he was able to compare the draining profiles obtained experimentally and theoretically. For the case of a film between a rigid sphere and a deformable fluid-liquid interface, he found that the experimental profiles usually lay
FIG. 3.1

THE DRAINING CHARACTERISTICS OF A CHLOROBENZENE FILM (RADIUS $10^{-2}$ CM)
between those predicted assuming a fully mobile and an immobile interface. The experimental and theoretical profiles also suggested an increase in mobility with time.

Lysela et al have suggested that the profile at the periphery of the film could be useful in the investigation of equilibrium films and secondary black films by using the contact angle formed at the border of the plane parallel film and the bulk. This method could find increasing favour since the contact angle is determined by the free surface energy of the film which in turn is related to the disjoining pressure. Schaludko has shown that the contact angle can easily be calculated from the Newton ring pattern surrounding the plane parallel film.

As has been seen, the film thickness range in which disjoining pressure effects are insignificant has received attention from various workers. In this section the film thickness is assumed to be less than 1000Å and the diameter sufficiently small so that the flow is symmetric from the film centre. Observations have shown that draining films under these conditions are plane parallel even though a pressure gradient exists in the film. The object of the study in this section is to predict the plane parallel profile of these films theoretically using data obtained experimentally from these films.

3.2. Derivation of the equations representing the film profile
Consider a thin circular film formed between two gas bubbles as shown in Fig. 3.2. The radial axis is taken along the mid-plane of the film with \( r = 0 \) at the centre. The thickness is denoted by \( h(r) \). Let the hydrostatic pressure in the film at \( z = 0 \) and \( r = 0 \) be denoted by \( P_L \).

A pressure balance at a radial distance \( r \) from the centre across the liquid-gas interface yields

\[
P_G = P_L + \sigma \cdot (\text{curvature})_r - \Pi(r) + P_{\text{flow}} + 2\mu \frac{\partial v_z}{\partial z} \quad \text{at } z = h(r)
\]

where \( \sigma \) = surface tension

\( \Pi(r) \) = disjoining pressure

\( P_{\text{flow}} \) = flow pressure in the film.

The curvature is given by \( \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right) \)

Therefore, equation (3.2.1.) becomes on rearranging

\[
\sigma \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right) = (P_G - P_L) + \Pi(r) - P_{\text{flow}} - 2\mu \frac{\partial v_z}{\partial z} \quad \text{at } z = h
\]

In the following analysis, the profile at a particular instant in time is considered so that although the film is thinning the thickness at the centre will be fixed. Over this infinitesimal time interval, \( P_G \) and \( P_L \) can be assumed constant so that (3.2.2.) becomes

\[
\frac{\partial^2 h}{\partial r^2} = \text{constant} - \frac{1}{r} \frac{\partial h}{\partial r} + \frac{\Pi(r)}{\sigma} - \frac{P_{\text{flow}}}{\sigma} - \frac{2\mu}{\sigma} \frac{\partial v_z}{\partial z} \quad \text{at } z = h
\]

The solution of this equation for \( h(r) \) gives the surface profile.

The flow pressure depends upon the rate of thinning and the film thickness. Consider a film element at a radius \( r \) of length \( dr \) and thickness \( h \). Let the lower surface be considered stationary and be represented by \( z = 0 \) as shown in Fig. 3.3.
At \( z = h \), let the velocity of approach of the upper surface be \( U = -\frac{dh}{dt} \). Assuming low Reynolds number flow, the Navier-Stokes equation in the radial direction in cylindrical polar coordinates simplifies to

\[
\frac{\partial \eta}{\partial r} = \mu \frac{\partial^2 v_r}{\partial r^2} \tag{3.2.4.}
\]

The boundary conditions applicable are:

- \( z = 0 \): \( v_r = v_z = 0 \)
- \( z = h \): \( v_r = 0 \), \( v_z = -U \)

Integrating Equation (3.2.4.) and substituting these boundary conditions gives:

\[
v_r = \frac{1}{2\mu} \left( \frac{\partial \eta}{\partial r} \right) (z^2 - h^2) \tag{3.2.5.}
\]

The volumetric outflow at any radial position is

\[
Q = 2\pi r \int_0^h v_r \, dz \tag{3.2.6.}
\]

Using (3.2.5.), this gives on integration

\[
Q = -\frac{m h^3}{6\mu} \left( \frac{\partial P}{\partial r} \right) \tag{3.2.7.}
\]

\[
\frac{dQ}{dr} = -\frac{m h}{6\mu} \left( \frac{\partial P}{\partial r^2} + h \frac{\partial P}{\partial r} + 3r \left( \frac{\partial h}{\partial r} \right) \left( \frac{\partial P}{\partial r} \right) \right) \tag{3.2.8.}
\]

The rate of reduction of volume of the film within the element described due to the approach of the upper surface with velocity \( U(z) \)
\[ \frac{dQ}{dr} = 2\pi r U(r) \quad (3.2.9.\text{)} \]

Equating (3.2.3.) and (3.2.9.) gives

\[ \frac{\partial^2 P}{\partial r^2} + \frac{1}{r} \frac{\partial P}{\partial r} + \frac{2}{h} \left( \frac{\partial h}{\partial r} \right) \left( \frac{\partial P}{\partial r} \right) = -\frac{12\mu U(r)}{h^3} \quad (3.2.10.\text{)} \]

The solution of (3.2.10.) gives \( P(r) \). However, \( P \) represented here consists of \( P_{\text{flow}} \) and also \( \Pi(r) \), since a change in thickness will cause a pressure gradient due to the change in the local disjoining pressure.

i.e. \( P(r) = P_{\text{flow}}(r) - \Pi(r) \quad (3.2.11.\text{)} \)

To obtain the profile \( h(r) \), equations (3.2.3.) and (3.2.10.) must be solved simultaneously.

3.3. Simplification of the Equations and Method of Solution.

The centre of the film is taken as the starting point for the solution to the film profile and thus the starting conditions at \( r = 0 \) must be specified. A chlorobenzene film stabilized with a sufficient quantity of surface active agent is considered. As has been stated previously in Section I, the data for the disjoining pressure isotherm of chlorobenzene have been accurately determined by Scheludko\(^9\) using the technique based upon the thinning of plane parallel films (equation 3.1.4.). Thus, the data are consistent for this particular case and in effect the object is to reproduce theoretically the plane parallel condition on which these data are based.

The thickness at the film centre, \( h_0 \), is taken as 300\(\AA\). The film is assumed, also, to be formed in a biconcave drop holder of radius 1 mm and that the thinning rate of the film is \( 3.2 \times 10^{-7} \text{ cm/sec} \). As can be seen from Fig. 3.1, this corresponds to the conditions given above for a plane parallel film of radius \( 10^{-2} \text{ cm} \).
Since the experimental observations show a plane parallel film and that the film remains plane parallel during the thinning process, \( U(r) \) must be constant over the film radius so that \( U \) can be assumed equal to \( U(0) \).

From film symmetry, the gradient of the profile at the centre must be zero. Similarly, the pressure gradient at the centre must also be zero. The pressure, \( P_{\text{flow}} \), at the centre must be specified as must the constant in equation (3.2.3). However, these two variables are inter-related in that together they define, along with the known values of the other variables, the initial curvature at the centre. Thus, say, by keeping \( (P_0 - P_L) \) constant and varying the initial value of \( P_{\text{flow}} \) we effectively set the starting curvature and vice versa.

As has been pointed out, \( P \) in equation (3.2.10) represents the combination of \( P_{\text{flow}} \) and \( \Pi(x) \). The overall pressure difference required for a film of radius 10 cm and of uniform thickness 800 \( \AA \) to thin at a rate of 3.2 \( \times \) \( 10^{-5} \) cm/sec (32 \( \AA \)/sec) can be calculated assuming the approach of two flat plates under similar conditions. The overall pressure difference in this latter case is represented by \( P_0 - P_R = \frac{3\mu U R^2}{h^3} \) (3.3.1).

This can easily be obtained by integrating equation (3.2.10) with \[ \frac{dh}{dr} = 0 \] and with boundary conditions \[ r = R, \quad P = P_R \]
\[ r = 0, \quad \frac{dP}{dr} = 0 \]

Using the values given above and taking \( \mu \) as \( 10^{-2} \) poise approximately,
\[ \Delta P = P_0 - P_R \approx 1900 \text{ dynes/cm}^2 \]
The disjoining pressure at 800 Å calculated from the isotherm given in section 1.9 is 129 dynes cm⁻². Thus, even if the film thickness at the periphery of the film was so large that the disjoining pressure was negligible, the pressure difference due to a disjoining pressure gradient is more than an order of magnitude lower than that necessary. On this basis the pressure difference is due almost entirely to the flow pressure and \( P \) can be replaced by \( P_{\text{flow}} \) in equation (3.2.10).

The final term in equation (3.2.3), \( 2\mu \frac{\partial v_z}{\partial z} \), is found to be negligible in comparison with the other terms as is shown below.

\[
\frac{\partial v_z}{\partial z} = -\frac{1}{r} \frac{\partial}{\partial r} (rv_r) \quad \text{(from continuity)}
\]

Substituting for \( v_z \) from equation (3.2.5) and using

\[
P = \frac{3\mu U (R^2 - r^2)}{h^3}
\]

obtained in the same manner as (3.3.1). The result for \( \frac{\partial v_z}{\partial z} \) gives

\[
\left( \frac{\partial v_z}{\partial z} \right)_{z=h} = \frac{3V}{2h}
\]

Therefore, the final term becomes \( 6 \mu V/2h \) and for the case under consideration this term is of order \( 10^{-3} \), i.e., negligible in comparison to terms such as \( P_{\text{flow}} \) and \( \Pi \). The equations to be solved simultaneously thus become, if \( h \) and \( P \) are functions of \( r \) only

\[
\frac{d^2 h}{dr^2} = \frac{P_G - P_r}{\sigma} + \frac{\Pi(r)}{\sigma} - \frac{P_{\text{flow}}}{\sigma} - \frac{1}{r} \frac{dh}{dr} \quad (3.3.2)
\]

\[
\frac{d^2 P_{\text{flow}}}{dr^2} = -\frac{12\mu V}{h^3} - \frac{3}{h} \left( \frac{dh}{dr} \right) \left( \frac{dP_{\text{flow}}}{dr} \right) - \frac{1}{r} \frac{dP_{\text{flow}}}{dr} \quad (3.3.3)
\]

The two second order differential equations can be solved by splitting them up into four first order equations.
\[
\frac{dh}{dr} = H \quad (3.3.4.)
\]

and \[
\frac{dP_{\text{flow}}}{dr} = G \quad (3.3.5.)
\]

so that (3.3.2.) and (3.3.3.) become

\[
\frac{dh}{dr} = \frac{(P_G - P_L)}{\sigma} + \frac{H(r)}{\sigma} - \frac{P_{\text{flow}}}{\sigma} - \frac{H}{r} \quad (3.3.6.)
\]

\[
\frac{dG}{dr} = -\frac{12\mu H}{h^3} - \frac{3}{h} \frac{H^2 - G}{r} \quad (3.3.7.)
\]

Thus, equations (3.3.4. - 7.) must be solved simultaneously with initial conditions

\[
h = 800 \AA
\]

\[
H = 0
\]

\[
G = 0
\]

\((P_G - P_L)\) is assumed constant over the film and can be taken approximately as \(2\sigma/\lambda_b\). Its value does not have to be specified exactly since \(P_{\text{flow}}\) at \(r = 0\) is the outstanding initial condition and these two values in conjunction with the other initial values in (3.3.6.) define the initial curvature.

3.4. Results

Equations (3.3.4.) - (3.3.7.) were solved simultaneously on a digital computer using a Runge-Kutta integration technique with a step length equivalent to \(10^{-6}\) cm. The initial value of \(P_{\text{flow}}\) was varied to obtain profiles with different central curvatures.

Fig. 3.4. shows the profiles for initial curvatures of 0, -0.05, -0.75 and -0.875 cm\(^{-1}\) with the data given above. With zero curvature the plane parallel region extends to about \(2.2 \times 10^{-3}\) cm, but with more negative values the 'plane parallel' structure lengthens to about \(5 \times 10^{-3}\) cm for an initial curvature of -0.75 cm\(^{-1}\). It can be seen that the plane parallel regions fall far short of the
FIG 3.4
PREDICTED PROFILES OF A CHLOROBENZENE FILM

Draining Rate = 32 Å/sec
radii of order $10^{-2}$ cm on which the data were based. Positive initial curvatures led to smaller parallel sections as would be expected. For more negative values of curvature than -0.75, the steeper gradient from the centre causes a pronounced minimum as is illustrated by the curve representing an initial curvature of -0.875 cm$^{-1}$. Beyond the minimum, the profile rises steeply to produce, overall, a dimple and barrier ring form. Thus, the maximum plane parallel section is illustrated in this particular case, by the curve with a central curvature of -0.75 cm$^{-1}$.

It is obvious that there appears to be a large discrepancy between the predicted and experimental profiles. Although it is possible that the film is not as plane parallel as it appears under visual observation, the experimental results involve very small errors.

The profile equations were also solved using an initial curvature of -0.25 cm$^{-1}$ and with various thinning rates. In Fig. 3.4, a thinning rate of $3.2 \times 10^{-7}$ cm.sec$^{-1}$ corresponding to the experimentally determined value was assumed. In Fig. 3.5, curves for thinning rates of 3.2, 2.4, 1.6 and 0.8 cm.sec$^{-1}$ are shown. For more negative values of curvature than -0.25 cm$^{-1}$, the profile with a thinning rate of $3 \times 10^{-8}$ cm.sec$^{-1}$ exhibited a sharp minimum similar to that shown in Fig. 3.4.

Even when the thinning rate is only half that of the experimental value, the profile is still not significantly more plane parallel. Only when the thinning rate is a quarter of this value does the profile begin to show parallelism to the dimensions seen in practice.

The equations were also solved with the initial conditions based upon a central film thickness of 500Å. The results yielded exactly similar forms as those presented here for a thickness of 300Å.
FIG 3.5
PREDICTED PROFILES OF A CHLOROBENZENE FILM

Initial Curvature $-0.25\text{cm}^{-1}$

FILM THICKNESS (Å) vs. RADIUS (CM*10^{-4})

Various lines indicating different film thicknesses.
In Hartland's calculations on very viscous liquid films the barrier ring persisted over the range of film thicknesses considered. Under these conditions the boundary conditions at the boundary yields \( \frac{dh}{dr} = 0 \). However, in the cases considered here, the barrier ring has long since disappeared and no such boundary condition can be specified. In fact it is difficult to define the film's radius exactly although the usual method is to base it on the radius of the first interference ring and subtract a correcting factor. In the neighbourhood of this interference ring the surface slopes gradually from the plane parallel form.

It has been experimentally determined by Scheludko and others that a film under the conditions stated in section 3.3. thins with a velocity of \( 3.2 \times 10^{-7} \) cm/sec, and this film appears to be of uniform thickness to a radius of \( 10^{-2} \) cm. The calculated pressure gradient has been shown to be approximately \( 1500 \) dyne-cm and since the surfaces are deformable and the disjoining pressure gradient in practice does not contribute significantly to the pressure gradient, the change in pressure must be balanced by the curvature. This is seen in the profiles obtained here, but is not in the experimental observations.

In the following sections, possible contributions to the discrepancies between theory and experiment are outlined.

3.5. Effect of a Surface Tension Gradient.

With reference to the discrepancy between the experimental observations and the Frankel and Kyuels theory of dimpling of liquid films, Scheludko proposed that a surface tension gradient may be responsible for the disagreement. In this analysis the surface tension was assumed constant over the film surface.
This is not true in practice for two reasons. Firstly, since the surfaces were assumed immobile a surface tension gradient is necessary to balance the viscous shear stress at the surface. The adsorbed surfactant concentration gradient is such that the tension decreases with radial distance to fulfil this condition. In practice with films of the type under consideration here only small quantities of surfactant are required.

From equations (3.2.5.) and (3.3.1.)

$$\nu_r = \frac{3\pi \nu}{h^3} (z^2 - hz)$$  \hspace{1cm} (3.5.1.)

The viscous shear stress for an area $2\pi r \, dr$ on the surface of the film $z = h$ is therefore

$$d\Gamma = 2\pi \mu r \, dr \left( \frac{\partial \nu_r}{\partial z} \right)_{z=h} = \frac{6\pi \mu U r^2}{h^4} \, dr$$  \hspace{1cm} (3.5.2.)

This force is balanced by the gradient of surface tension which is

$$\frac{\partial \sigma}{\partial r} = 2\pi \nu \, dr$$  \hspace{1cm} (3.5.3.)

Equating these latter two expressions and using equation (3.1.4.) gives

$$\frac{\partial \sigma}{\partial r} = \frac{2\pi h}{\mu} \Delta P$$  \hspace{1cm} (3.5.4.)

Thus, the total variation of $\Gamma$ between the centre of the film and at a radius $R$ with surfactant present is

$$\int_{r=0}^{R} \, dr = h \Delta P$$  \hspace{1cm} (3.5.5.)

This assumes that no diffusion of surfactant occurs from the volume to the surface and is applicable for adsorbed layers of strong surfactants which show small volume concentrations. Equation (3.5.5.) shows that with the typical values of $h$ and $\Delta P$ used here the change in tension is very small in order to satisfy the surface condition.
The second reason for a non constant value of surface tension is due to the dependence of the tension on the film's thickness as was demonstrated in section 1.3.

\[ T = 2\sigma + \int_{h}^{\infty} \eta dh + \frac{\eta h}{h^3} \quad (1.3.3) \]

and if \( \eta h \approx -\frac{K}{h^3} \)

\[ T = 2\sigma - \frac{K}{2h^3} \quad (1.3.4) \]

The tension is greater at the periphery of the film than at the centre if the profile shows an increasing thickness towards the periphery. This is in the opposite direction to the gradient caused by a surfactant concentration gradient.

Using \( h = 800\AA \) and \( K = 3.1 \times 10^{-13} \) for chlorobenzene the change in the tension from the bulk value of 32.6 dynes/cm is 7.4 \( \times 10^{-3} \) dynes/cm.

Again it is plain that the departure from the bulk value is very small and the bulk value can be used with only a very small error involved. The two effects mentioned are in some way compensatory.

Associated directly with a surface tension gradient is the question of surface mobility. As has been shown here the film surfaces can be considered immobile. However, with very viscous films considered by Hartland it is possible that such films require a much higher surfactant concentration before surface immobility is achieved. His results for a draining film between a rigid sphere and a deformable fluid-liquid interface showed good theoretical agreement if \( n \) was given a value between 1 and 2 (\( n \) is the number of immobile surfaces).
3.6. Effect of a Surface Wave on the Local Disjoining Pressure

Experimental observations show that a microscopic film surface appears plane parallel at thicknesses less than 1000Å and it has been shown in Section I that for films of radii of order $10^{-2}$ cm, the film becomes unstable to surface fluctuations at approximately the same thickness. It was therefore thought that the two effects could be connected and the plane parallelism due to a surface wave.

Let the time average film thickness be denoted by $h_0$ and let a wave of amplitude $A$ progress along the surface. Then the disjoining pressure effects are important the disjoining pressure at a wave trough is $\Pi(h-A)$ and at a wave crest is $\Pi(h+A)$. The time average value of the disjoining pressure is therefore

$$\frac{\Pi(h+A) + \Pi(h-A)}{2} = \Pi_{\text{wave}} \quad (3.6.1.)$$

Since $\Pi \propto h^{-1}$ at 800Å it is obvious that the time average value of $\Pi_{\text{wave}}$ is greater than $\Pi(h_0)$ (i.e., more negative). The magnitude of the difference between these two values depends upon the wave amplitude and the time average thickness.

The surface wave on a circular film has a Bessel function form which exhibits a decreasing amplitude with increasing radial distance. Thus, the presence of such a wave would create a favourable disjoining pressure gradient.

The magnitude of this pressure gradient can be estimated by considering the time average value of the disjoining pressure at the centre of the film with various values of wave amplitude relative to the disjoining pressure of an undisturbed surface. This effect is shown in Table 3.1. below for a time average thickness of 300Å.
Table 3.1.

<table>
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<th>Wave Amplitude $A$</th>
<th>Mean Disjoining Press. $\Pi$ wave dynes/cm</th>
<th>$\Pi(h_0)$ $^2$ dynes/cm</th>
<th>$\Delta P=\Pi_{wave}-\Pi(h_0)$$^2$ dynes/cm</th>
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</tbody>
</table>

The high amplitudes necessary to cause any significant disjoining pressure gradient would be equivalent to relatively high values of curvature and this would cause film instability and rupture. This analysis assumes that the waveform remains symmetric about the time average thickness. If the wave became distorted because of the changes in disjoining pressure then the time average pressure due to the curvature coupled with the time average disjoining pressure would yield the same result as that given in Table 3.1, assuming no changes in curvature.

The results of this section show that the neglect of a disjoining pressure gradient due to changes in thickness which led to the simplification of the pressure equation in section 3.3 is justified. However, its inclusion would lead to a slight reduction in the predicted slope of the profile.

3.7. Effect of a surface wave on the surfactant concentration

In section 1.6, boundary condition (4) required that the tangential stress at the surface to be equal to zero. For the surface flow to be zero, the surface tension has to balance the viscous force at the surface.

$$\text{ie. } \mu \left( \frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial z} \right) + \frac{\partial \gamma}{\partial r} = 0 \quad (1.6.13.)$$
Setting \( \frac{\partial \sigma}{\partial r} = \frac{\partial \sigma}{\partial r} - \frac{\partial P}{\partial r} \)

and \( \Gamma = \Gamma_0 + \Gamma' \) as defined in section 1.6

and using \( \Gamma' = \gamma J_1(\kappa r)e^{i\omega t} \) in the conservation equation for mass flow on a surface, the following result for \( \Gamma' \) was obtained.

\[
\Gamma' = -\Gamma_0 k^2 J_0(kr)(\kappa \cosh kZ) \quad \frac{1}{(n-D_s \left( \frac{1}{r^2} - \frac{k^2}{r^2} \right))} \quad (1.6.17)
\]

\( \frac{\partial P}{\partial r} \) is required for substitution in equation (1.6.13.) and this differential represented by (1.6.13.) on page 38 is too complex and unmanageable to use directly. The cartesian coordinate result was used instead although it was shown that for large values of \( kr \) the two results were basically identical.

Rewriting (1.6.17.) as

\[
\Gamma' = -\Gamma_0 k^2 J_0(kr)(\kappa \cosh kZ \ldots \ldots) \quad (3.7.1)
\]

\( \Gamma' \) can be separated into 3 regimes.

1) For \( kr \ll 1 \), Equation 3.7.1. gives

\[
\Gamma' = -\Gamma_0 k^2 J_0(kr)(\kappa \cosh kZ \ldots \ldots) \quad (3.7.2)
\]

This case would correspond to very long waves or to short radial distances compared to the wavelength.

2) For \( kr \gg 1 \), Equation (3.7.1.) gives

\[
\Gamma' = -\Gamma_0 k^2 J_0(kr)(\kappa \cosh kZ \ldots \ldots) \quad (3.7.3)
\]

This case corresponds to large radial distances compared to the wavelength.
3) kr ≈ 1, this gives for $r'$

$$r' = -\frac{\Gamma D_s \hat{\mathbf{k}}^2 J_n(kr)(k\cosh k_2z, \ldots)}{n}$$  \hspace{1cm} (3.7.4.)

For the thicknesses under consideration at least one unstable wave exists so that $n$ is real and positive. Case (2) represents the situation over most of the microscopic film radius when more than one unstable wave exists. The denominator will always be positive and $r'$ will change sign according to the $J_n(kr)$ term.

Case (1) corresponds to the situation at the central core of the film and equation (3.7.2.) shows that the denominator can become equal to zero if $n$ refers to an unstable wave. This predicts a discontinuity in $r'$ and although the analysis is restricted to small values of $r'$ the equation predicts large changes (and hence surface tension) over a narrow radial distance.

From equation (3.7.1.) the denominator is given by

$$n = \frac{D_s}{r^2} \left(1 - k^2 r^2 \right)$$

and this becomes equal to zero when

$$r = \left(\frac{D_s}{n + D_s k^2} \right)^{1/2}$$  \hspace{1cm} (3.7.5.)

From Fig 1.7 with a surface elasticity value of 5 dyne/cm. and, referring to a film radius of $10^{-2}$ cm, there are four unstable waves that can fit onto this film, three of which are shown. It is difficult to say which wavenumber will have amplified most at 300\textsuperscript{o} but since wavenumbers 333 and 701 have been unstable for a longer time than 1332, and 701 exhibits a higher growth rate, it would seem that a wave with a wavenumber of 701 might have the strongest influence on the surface. Thus, taking the case of $k = 701$ (curve B in Fig. 1.7) the wave growth rate at 300\textsuperscript{o} is $8.5 \times 10^{-3}$ sec\textsuperscript{-1}.
FIG 3.6
THE RADIAL DEPENDENCE OF $\Gamma'$ DUE TO A SURFACE WAVE
Equation (3.7.1.) can be written as

$$f' = f(z) g(r)$$  \hspace{1cm} (3.7.6.)

where

$$g(r) = \frac{1}{1 - \frac{1}{r^2}} \left( \frac{n-D}{\frac{1}{r^2} - k^2} \right)$$  \hspace{1cm} (3.7.7.)

In Fig 3.6. the radial dependence, $g(r)$, is shown graphically for the case considered above. From equation (3.7.5.), the discontinuity is calculated to occur at a radial distance of $1.425 \times 10^{-3}$ cm.

The position of the discontinuity can be approximated by $r = 1/k$, which means that case 3 effectively represents the region of the discontinuity. The radial position estimated thus is $1.423 \times 10^{-3}$ cm. This approximation is valid provided that the surface elasticity is of sufficient value to cause a low growth rate so that $F'$ predicted by (3.7.4.) is large. When $n$ is real and negative, referring to a stable wave at thicknesses where the disjoining pressure is negligible, then equation (3.7.3.) predicts a discontinuity in a region where $kr > 1$.

If a discontinuity exists then this could cause important surfactant concentration changes at a particular radial distance. It must be reiterated that the analysis refers only to small changes in $F'$ relative to $F_0$ and the effect of wave interaction, and which is the most important wave at any given thickness cannot be predicted easily.

3.3. Summary of Conclusions

1) The equations derived to represent the film profile have been found to produce results which predict plane parallel films of a much smaller diameter than those seen experimentally, even though the experimental conditions have been simulated with the input data. The theory developed has been unable to provide an answer as to why a draining microscopic film with a radial pressure gradient appears...
plane parallel to the diameters observed.

2). Only when assuming a thinning rate equal to one quarter that of the known experimental value does the plane parallel section approach the experimental observation for the cases considered.

3). Films with initial conditions pertinent to a central thickness of 500Å yielded similar results.

4). It has been shown that the presence of a surface wave creates a radial pressure gradient. Although assisting in reducing the slope, it is insufficient to account for the discrepancy.

5). The effect of a surface tension gradient, as suggested by other workers, has been shown to have little significance in this case.

6). The effect of an unstable wave on the surfactant concentration on a circular film has been shown, to a first approximation, to predict a discontinuity in the surface concentration at a particular radial distance, which is short compared to the wavelength. This radial distance depends upon the wavenumber and the surface diffusivity. The presence of such a discontinuity could lead to significant changes in the local film properties.
Note on Section III

In thick draining films, where the barrier ring persists, the pressure drop over the barrier ring due to the minimum in thickness accounts for most of the pressure drop necessary for film drainage.

The discrepancy could thus be explained in terms of a small barrier ring exhibiting a shallow minimum at the periphery. However, such a minimum would be likely to be seen in experimental observation unless it was very shallow, in which case its effect would be small.

This would impose the boundary condition

$$\frac{dh}{dr} = 0 \quad \text{at} \quad r = R$$

An alternative explanation may question the assumption of complete immobility over the whole surface. The $\Delta \sigma$ required for immobility (assuming an insoluble surfactant) is only twice that which would give complete mobility (if surface diffusion is small). Since these changes are small, the film may not be completely immobile. This would result in a lower pressure gradient for a given drainage rate and cast doubt upon the data obtained by Scheludko from draining films. The discontinuity shown in $\Gamma'$ could affect the flow in such a way since the surface concentration determines the hydrodynamics of the film. The flow may not be strictly symmetric from the centre as was assumed, so that $v_0 \neq 0$ and swirling motions occur.

In Section III the difference in tension necessary to ensure surface immobility was approximately given by
\[ \Delta \sigma = h \Delta P \]

Assuming that \( \Delta P \) is given by Scheludko's expression

\[ \Delta P = P_\sigma - \Pi = P_\sigma - \frac{K'}{h^4} \]  (if retardation apparent)

then \( \frac{d\Delta \sigma}{dh} = \Delta P + h \frac{d\Delta P}{dh} \)

Assuming that \( P_\sigma \) remains constant, as is highly likely, and that changes in \( \Delta P \) are produced by changes in disjoining pressure

\[ \frac{d\Delta \sigma}{dh} = P_\sigma + \frac{K'}{h^4} - \frac{4K'}{h^4} = P_\sigma - \frac{3K'}{h^4} \]

\[ d\Delta \sigma = \left( P_\sigma - \frac{3K'}{h^4} \right) dh \]

i.e. if \( \frac{3K'}{h^4} > P_\sigma \), then as the film thins the required \( \Delta \sigma \) for immobility increases. This can only be achieved by expansion of the surface and by surface movement. Thus, as the film drains, there will be a continual surface movement so that the surface will be partially mobile.

If \( K' = \frac{K \lambda_L}{2\pi} \) where \( \lambda_L \) = wavelength of London wave

\[ K = 3.1 \times 10^{-13} \]  as before

then the thickness at which the surface becomes partially mobile will be

\[ h = \left( \frac{3K'}{P_\sigma} \right)^\frac{1}{4} = \left( \frac{3K'}{2\sigma} R_b \right)^\frac{1}{4} \]

Taking \( R_b = 0.1 \text{ cm} \) and \( \sigma = 32.6 \text{ dynes/cm} \), the appropriate value of \( h \) is 650 Å. i.e. below thickness of 650 Å the surface would be expected to be partially mobile. However considering the approximations used it can be seen that this thickness is of similar order to those considered in Section III so that the surfaces may not be completely immobile. Hence, this would
result in a smaller radial pressure gradient in the film.

It can also be noted from experimental observations that the film becomes plane parallel when the disjoining pressure becomes important. If the film is not completely immobile, then from Section I, a higher wave growth rate than that predicted would also result.

In the case of a soluble surfactant whose volume concentration is not too small, the diffusion towards the surface would relax the surface and hence increase the mobility.
REFERENCES

   1339.
APPENDIX I

Evaluation of the Streamfunction \( \psi \)

In Section 1.6, the relationship for \( \psi \) was given by

\[
E^2 \left( \frac{\partial^2}{\partial z^2} - \frac{1}{\nu} \frac{\partial}{\partial t} \right) \psi = 0
\]

which is equivalent to the equation of motion in cylindrical polar coordinates for viscous flow in the \( r \) and \( z \) directions only.

Let \( \psi = \psi_1 + \psi_2 \)

where \( \psi_1 \) and \( \psi_2 \) satisfy the individual equations

\[
E^2 \psi_1 = 0 \tag{A.1.1.}
\]

\[
\left( E^2 - \frac{1}{\nu} \frac{\partial}{\partial z} \right) \psi_2 = 0 \tag{A.1.2.}
\]

where \( E^2 = \left( \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \right) \)

Let \( \psi_1 = R(r)Z(z) \)

From (A.1.1.) by substitution

\[
Z \frac{\partial^2 R}{\partial r^2} - Z \frac{\partial R}{\partial r} + R \frac{\partial^2 Z}{\partial z^2} = 0
\]

which becomes

\[
\frac{1}{R} \frac{\partial^2 R}{\partial r^2} - \frac{1}{2r} \frac{\partial R}{\partial r} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = 0 \tag{A.1.3.}
\]

Taking the \( z \) dependence

\[
\frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = k^2
\]

Solution yields \( Z = \cosh kz, \sinh kz \tag{A.1.4.} \)

Using this result in (A.1.3.) and rearranging, produces

\[
\frac{\partial^2 R}{\partial r^2} - \frac{1}{r} \frac{\partial R}{\partial r} + k^2 R = 0 \tag{A.1.5.}
\]
The solution for the radial dependence is a Bessel function of the first kind. If we denote \( kr = \alpha \), (A.1.5.) becomes

\[
\frac{d^2 \psi}{d\alpha^2} - \frac{1}{\alpha} \frac{d\psi}{d\alpha} + \psi = 0 \quad (A.1.6.)
\]

The solution to

\[
\frac{d^2 \psi}{dx^2} - \frac{(2\nu - 1)}{x} \frac{d\psi}{dx} + \psi = 0
\]

is \( x^\nu J_\nu(x) \)

Thus the solution to (A.1.6.) is obtained with \( \nu = 1 \)

\[
R = kr J_1(kr)
\]

\[
\therefore \psi_1 = (\text{cosh \( kr \) + sinh \( kr \)})kr J_1(kr)
\]

In a similar fashion, let \( \psi_2 = R'(x)T'(z)T(t) \).

Thus (A.1.2.) becomes

\[
\frac{1}{R'} \frac{d^2 R'}{dr^2} - \frac{1}{R' r} \frac{dR'}{dr} + \frac{1}{Z'} \frac{d^2 Z'}{dz^2} - \frac{1}{\nu T} \frac{dT}{dt} = 0 \quad (A.1.7.)
\]

For the \( t \) dependence,

let \( \frac{1}{\nu T} \frac{dT}{dt} = c^2 \)

\[
\therefore \text{solution for } T \text{ is given simply by}
\]

\[
T = e^{c^2 \nu t} = e^{nt} \quad (A.1.8.)
\]

where \( n \) is defined equal to \( c^2 \nu \).

For the \( z \) dependence,

let \( \frac{1}{Z'} \frac{d^2 Z'}{dz^2} = n^2 \) \quad (A.1.9.)

As before, \( Z' = \cosh \pi z \)
\( \sinh \pi z \)

With these two latter results in (A.1.7.),
\[ \frac{\partial^2 \psi}{\partial r^2} - \frac{1}{r} \frac{\partial \psi}{\partial r} + (n^2 - c^2) \psi = 0 \quad (A.1.10) \]

Let \( s^2 = (n^2 - c^2) \), then by analogy to (A.1.5) the solution to (A.1.10) is

\[ R' = sr J_1 (sr) \]

The combination of \( \psi_1 \) and \( \psi_2 \) is easier if we relate \( m \) and \( k \) by

\[ m^2 = k^2 + c^2 = k^2 + \frac{a}{v} \]

\[ s^2 = n^2 - c^2 = k^2 \]

So that \( \psi_2 = (C \cosh nZ + D \sinh nZ) kr J_1 (kr)e^{nt} \).

\[ \psi = (A \cosh nZ + B \sinh nZ + C \cosh nZ + D \sinh nZ) kr J_1 (kr)e^{nt}. \]

with \( m^2 = k^2 + \frac{a}{v} \).


Evaluation of the Pressure due to a Surface Wave

In boundary condition 3 for the derivation of the growth rate of a surface wave, the pressure due to a surface wave is given by equation (1.6.9). This equation is obtained from the equation of motion with, in this case, the inertial terms, except the time dependence, neglected.

The equation of motion in the $r$ direction is

$$
\rho \frac{\partial v_r}{\partial t} = -\frac{\partial p}{\partial r} + \mu \left( \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial (rv_r)}{\partial r} \right) + \frac{\partial^2 v_r}{\partial z^2} \right)
$$

$$
\therefore \quad \frac{\partial p}{\partial r} = -\rho \frac{\partial v_r}{\partial t} + \mu \left( \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial (rv_r)}{\partial r} \right) + \frac{\partial^2 v_r}{\partial z^2} \right) \quad (A.2.1)
$$

From equation (1.6.3),

$$
v_r = k (k \sinh k z + k \cosh k z) J_1 (kr) e^{nt}
$$

$$
\therefore \quad -\rho \frac{\partial v_r}{\partial t} = - \rho \mu (k \sinh k z + k \cosh k z) J_1 (kr) e^{nt} \quad (A.2.2)
$$

$$
rv_r = kr (k \sinh k z + k \cosh k z) J_1 (kr) e^{nt}
$$

$$
\frac{\partial}{\partial r} (rv_r) = k^2 r J_1 (kr) (k \sinh k z + k \cosh k z) e^{nt}.
$$

$$
\therefore \quad \frac{1}{r} \frac{\partial}{\partial r} (rv_r) = k^2 (k \sinh k z + k \cosh k z) J_1 (kr) e^{nt}.
$$

$$
\therefore \quad \mu \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} (rv_r) \right) = -\mu k^3 J_1 (kr) (k \sinh k z + k \cosh k z) \quad (A.2.3)
$$

$$
\mu \frac{\partial^2 v_r}{\partial z^2} = \mu k \left[ k^3 \sinh k z + k^3 \cosh k z + m \sinh m z + m \cosh m z \right] J_1 (kr) e^{nt}.
$$

$$
\therefore \quad p = -\rho \mu (k \sinh k z + k \cosh k z + m \sinh m z + m \cosh m z) J_1 (kr) e^{nt}
$$

- $\mu k^3 (k \sinh k z + k \cosh k z + m \sinh m z + m \cosh m z) J_1 (kr) e^{nt}$
Collecting terms

\[ \frac{\partial n}{\partial r} = \left[ \left( -\rho n - \mu k^3 \right) \left( k \sinh kz + \cdots \right) + \mu k \left( k^3 \sinh kz + k^3 \cosh kz + Cn^3 \sinh mz \right) + Dm^3 \cosh mz \right] J_1 (kr)e^{nt} \]

\[ \frac{\partial n}{\partial r} = f(z) J_1 (kr)e^{nt} \]

\[ p = -f(z) J_0 (kr)e^{nt} \]

Also, at \( z = 0 \), \( \sinh kz, \sinh mz = 0 \)

\( \cosh kz, \cosh mz = 1 \)

so that the final expression for \( p \) becomes

\[ p = \left[ (\rho n - \mu k^2) (kB + nD) - \mu (k^3 B + Dm^3) \right] J_0 (kr)e^{nt} \]
Instability of a Thin Liquid Film to Surface Waves.

The same problem is treated here as in Section 1.6. but in cartesian coordinates.

The equation to be satisfied by the streamfunction is

$$ \nabla^2 \left( \frac{\nabla^2 - 1}{v} \frac{\partial}{\partial t} \right) \psi = 0 $$

Following a method similar to that shown in Appendix I the solution for $\psi$ is

$$ \psi = (A \cosh k z + B \sinh k z + C \cosh m z + D \sinh m z)e^{ikx+nt} \quad (A.3.1) $$

where $m^2 = k^2 + \frac{n}{v}$, as before.

The velocity components are given by

$$ u = -\frac{\partial \psi}{\partial z} = -(A \sinh k z \ldots \ldots \ldots) e^{ikx+nt} \quad (A.3.2) $$

$$ v = \frac{\partial \psi}{\partial x} = ik(A \cosh k z \ldots \ldots \ldots) e^{ikx+nt} \quad (A.3.3) $$

Boundary conditions:

at $z = -\frac{h}{2}$ (i) $v = 0$ (ii) $\frac{\partial u}{\partial x} = 0$

at $z = 0$ (i) Tangential Stress = 0 (ii) Normal Stress = 0.

B.C. (i) at $z = -h/2$, $v = 0$

$$ v = ik \left( \frac{A \cosh k h}{2} - \frac{B \sinh k h}{2} + \frac{C \cosh m h}{2} - \frac{D \sinh m h}{2} \right) e^{ikx+nt} = 0. $$

if the exponential term $\neq 0$ and $k \neq 0$,

then $(AL - BM + CP - DQ) = 0 \quad (A.3.3)$

where $L = \cosh \frac{k h}{2}$, $M = \sinh \frac{k h}{2}$

$$ P = \cosh \frac{m h}{2}, \quad Q = \sinh \frac{m h}{2} $$

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B.C. (ii) at $z = \frac{-h}{2}$, $\frac{\partial u}{\partial z} = 0$.

$$\frac{\partial u}{\partial z} = -(A_k^2 \cosh uz + B_k^2 \sinh uz + C_m^2 \cosh uz + D_m^2 \sinh uz).$$

This leads to

$$A_k^2 u - B_k^2 u + C_m^2 u - D_m^2 u = 0$$  \hspace{1cm} (A.3.4.)

B.C. (iii) tangential stress at $z = 0$ equals 0.

Tangential stress at the surface is given by

$$\mu \left( \frac{\partial u}{\partial z} + \frac{\partial v}{\partial x} \right) = \frac{\partial \gamma}{\partial x} = 0$$  \hspace{1cm} (A.3.5.)

and where $\frac{\partial \gamma}{\partial x} = \frac{\partial \gamma}{\partial r} \frac{\partial r}{\partial x}$ = surface tension gradient

Let $\gamma = \gamma_o + \gamma'$ where $\gamma_o$ = average conc$^\circ$.

$\gamma'$ = fluctuation.

The conservation of mass flow on a surface in cartesian coordinates is given by (if second order infinitesimals are ignored)

$$\frac{\partial \gamma'}{\partial t} + \gamma_o \frac{\partial u}{\partial x} = D_s \frac{\partial^2 \gamma'}{\partial x^2}$$  \hspace{1cm} (A.3.6.)

where $D_s$ = surface diffusivity.

Let $\gamma' = \gamma e^{ikx+nt}$

Then substituting for $\gamma'$ and $u$ in (A.3.6.) yields

$$\gamma_n - ik\gamma_o (A_k \sinh kz \ldots \ldots \ldots) = -k^2 D_s \gamma.$$  \hspace{1cm} (A.3.7.)

$$\gamma = \frac{ik\gamma_o (A_k \sinh kz \ldots \ldots \ldots)}{k^2 D_s + n}$$

$$\gamma = \gamma_o + \frac{ik\gamma_o (A_k \sinh kz \ldots \ldots \ldots) e^{ikx+nt}}{n + k^2 D_s}$$  \hspace{1cm} (A.3.7.)
\[(\frac{\partial \sigma}{\partial t})(\frac{\partial \Gamma}{\partial x}) = -\left(\frac{\partial \sigma}{\partial t}\right) k^2 \Gamma_0 (\cosh kz \cdots \cdots )e^{ikx + nt}\]
\[
= -k^2 \varepsilon (\cosh kz \cdots \cdots )e^{ikx + nt}
\]
where \(\varepsilon = -\Gamma_0 \left(\frac{\partial \sigma}{\partial t}\right)\) and is termed the surface elasticity.

Substituting for the terms in (A.3.5) gives
\[- \mu (\Delta k^2 \cosh kz + Bk^2 \sinh kz \cdots \cdots )e^{ikx + nt}\]
\[- \mu k^2 (\Lambda \cosh kz + Dk \sinh kz \cdots \cdots )e^{ikx + nt}\]
\[- \frac{k^2 \varepsilon (\Lambda \cosh kz + Dk \cosh kz \cdots \cdots )e^{ikx + nt}}{n + Dk^2} = 0\]

At \(z = 0\), \( \sinh kz \), \( \sinh mz = 0 \)
\( \cosh kz \), \( \cosh mz = 1 \)
\[\therefore - \mu (\Delta k^2 + Cn^2) - \mu k^2 (A + C)\]
\[= 0 \quad (A.3.9.)\]

Collecting terms:
\[A \left[ 2\mu k^2 \right] + B \left[ \frac{k^3 \varepsilon}{(n+Dk^2)} \right] + C \left[ \mu(k^2 + n^2) \right]\]
\[+ D \left[ \frac{k^2 m \varepsilon}{(n+Dk^2)} \right] = 0 \quad (A.3.10.)\]

B.C. (iv):
\[\text{at } z = 0, \text{ normal stress } = 0.\]

The equation expressing the normal stress is very similar to that given in section 1.6 and after substituting all the terms the resulting boundary condition equation is the same as equation (1.6.11). In view of its lengthy derivation and similarity the result will be stated here.
Thus, equations (A.3.3.), (A.3.4.), (A.3.10.) and (A.3.11.) are the four equations to be solved for \( n \) by eliminating the constants \( A, B, C \) and \( D \).

The Determinant to solve is

\[
\begin{vmatrix}
L & -1 & P & -Q \\
K^2L & -k^2 & n_2P & -m_2Q \\
2\mu k^2 & \frac{k^3e}{(n+D_s k^2)} & \mu(k+n)^2 & \frac{k^2n_2 e}{(n+D_s k^2)} \\
-\frac{\beta}{\mu n} & (n+k^2) & -\frac{\beta}{\mu n} & \frac{\rho_m + 3k m - \frac{n^3}{k}}{\mu k}
\end{vmatrix}
\]

The solution to this determinant yields

\[
n^2 + n \left[ 4k^2 v + \frac{2k^2 e}{\rho D_s k^2} \right] - \frac{\beta k h}{2p} = 0 \quad (A.3.12.)
\]

for \( n > 0 \); \( \beta > 0 \)

where \( \beta = (2k n' - \delta k^3 - \rho k g) \)

if \( n \) is small compared to \( D_s k^2 \)

then (A.3.12.) reduces to a quadratic and \( n \) is easily obtained.

i.e. \( n = -\left( 2k^2 v + \frac{e}{\rho D_s} \right) \left[ \left( 2k^2 v + \frac{e}{\rho D_s} \right) + \frac{\beta k h}{2p} \right]^\frac{1}{2} \)

(A.3.13.)