Thinning of a Liquid Film As a Small Drop or Bubble Approaches a Fluid–Fluid Interface

When a small drop or bubble approaches a fluid–fluid interface, a thin liquid film forms between them, drains, until an instability forms and coalescence occurs. A hydrodynamic theory is developed for the first portion of this coalescence process: the drainage of the thin liquid film while it is still sufficiently thick that the effects of London-van der Waals forces and electrostatic forces can be ignored. The time rate of change of the film profile is predicted, given only the drop radius and the required physical properties. Comparisons are offered with the limited experimental data available.

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SCOPE

As a drop or bubble moving through a liquid phase under the influence of buoyancy forces approaches an interface, a liquid film forms. The interfaces deform due to the development of a pressure gradient in the film (Allan et al., 1961; Hodgson and Woods, 1969). With time, the film drains, becomes unstable, ruptures, and coalescence occurs.

In order to simplify the problem, we discuss only the first portion of the coalescence process: the drainage of the liquid film while it is still sufficiently thick that the effects of London-van der Waals forces and electrostatic forces can be ignored. We have previously considered the drainage of a liquid film as a drop or bubble approaches a solid plane (Lin and Slattery, 1982). Here we analyze the thinning of a liquid film as a drop approaches a fluid–fluid interface. We do not consider the development and growth of instabilities in these thin films that would lead to coalescence.

We focus only on those systems in which the interfaces may be assumed to be immobile. An immobile interface is one in which the interfacial tension gradients developed are sufficiently large so as to eliminate all lateral motion.

The analysis is limited to small drops and to liquid films so thin that the Reynolds lubrication theory approximation is applicable.

CONCLUSIONS AND SIGNIFICANCE

This analysis of the drainage of a liquid film between a drop and a fluid–fluid interface can predict the time rate of change of the film configuration, given only the drop radius and the required physical properties. It is more complete than the estimates offered by Princen (1962), who extended the Frankel and Mysels (1963) theory to estimate the thinning rate only at the center and at the rim (or barrier ring). His theory includes one free parameter; ours, none.

Our prediction for the limiting value of the rim radius approached as time becomes large agrees with that suggested by Chappelear (1961). The rim radius is the radius at which the thickness of the liquid film is a minimum.

In agreement with our previous work (Lin and Slattery, 1982), we find that very small interfacial tension gradients are sufficient to immobilize the fluid–fluid interfaces. This suggests that the interfacial viscosities (Slattery, 1980; Slattery and Flumerfelt, 1981) will usually have little effect upon the rate at which a film thins prior to the development of an instability leading to coalescence. This is consistent with the conclusions of Whitaker (1966).

The theory developed here is the best available representation of reported data, but the available data for small drops are too limited for definitive conclusions to be drawn.

INTRODUCTION

Woods and Burrill (1972) have summarized the several approximate developments that have been proposed for the thinning rate at the rim radius, the radius at which the thickness of the liquid film is a minimum. The most important of these is due to Princen (1963), who extended the Frankel and Mysels theory (1962) to estimate the thinning rate both at the center and at the rim as a small drop approaches a fluid–fluid interface. His prediction for the thinning rate at the rim is nearly equal to that given by the simple analysis of Reynolds (1886), who assumed a uniform film thickness.

Hartland (1970) developed a more detailed analysis to predict film thickness as a function both of time and of radial position. He assumed that both the drop-fluid interface and the fluid–fluid interface are equidistant from a spherical "equilibrium" surface at all times and that the film shape immediately outside the rim is independent of time. The initial film profile had to be given a priori from experimental data. No detailed comparison with experimental data was shown.

Jones and Wilson (1978) have made an attempt to account for the partial mobility of the drop-fluid and fluid–fluid interfaces, but they were not able to solve their governing integro-differential equation numerically. No prediction of the thinning rate was given.

In what follows, we develop a more complete hydrodynamic theory for the thinning of a liquid film between a drop and a fluid–fluid interface. Since we have previously demonstrated that

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an interface can be immobile in the presence of a very small interfacial tension gradient (Lin and Slattery, 1982), we consider only immobile drop-fluid and fluid–fluid interfaces. For this limiting case, our analysis applies equally well to a liquid drop approaching a liquid–liquid interface or to a gas bubble approaching a liquid–gas interface.

STATEMENT OF PROBLEM

A drop (or bubble) is shown in Figure 1 approaching a fluid–fluid interface. The objective of the following analysis is to determine the rate at which the thin liquid film separating the drop from the fluid–fluid interface drains as a function of time.

A number of assumptions are required in this computation.

i) Viewed in the cylindrical coordinate system of Figure 1, the two interfaces bounding the draining liquid film are axisymmetric ($i = 1,2$):

$$z^* = h_i^*(r^*,t^*) \tag{1}$$

ii) The dependence of h_i^* ($i = 1,2$) upon r^* is sufficiently weak that

$$\left(\frac{\partial h_i^*}{\partial r^*}\right)^2 \ll 1 \tag{2}$$

iii) Introducing

$$h^* \equiv h_1^* - h_2^* \tag{3}$$

let R^* be the rim (or barrier ring) radius of the drop such that

$$\text{at } r^* = R^* = R^*(t^*)\text{: } \frac{\partial h^*}{\partial r^*} = 0 \tag{4}$$

The Reynolds lubrication theory approximation applies in the sense that, if

$$h_0^* \equiv h^*(0,0) \tag{5}$$

and

$$R_0^* \equiv R^*(0) \tag{6}$$

we will require

$$\left(\frac{h_0^*}{R_0^*}\right)^2 \ll 1 \tag{7}$$

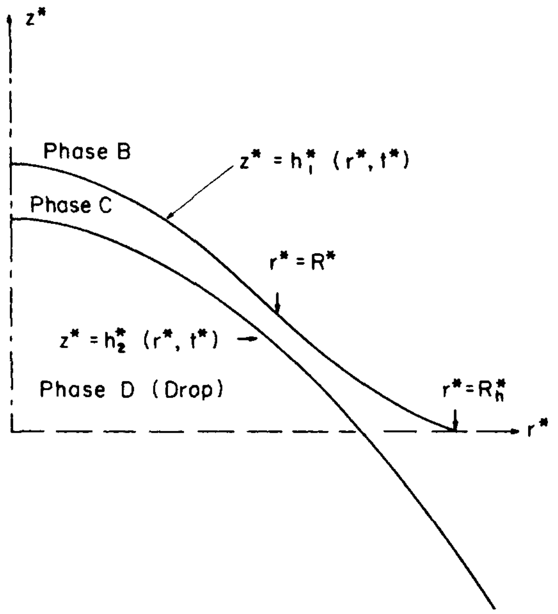

Figure 1. A symmetric drop or bubble (phase D) moves through a liquid (phase C) as it approaches a fluid–fluid interface (between phases C and B). The configuration of the drop–fluid interface is given by $z^* = h_2^*(r^*,t^*)$; that of the fluid–fluid interface by $z^* = h_1(r^*,t^*)$.

iv) There is surfactant present in both interfaces. The resulting interfacial tension gradients are sufficiently large that the tangential components of velocity $\underset{\sim}{v}^*$ are zero ($i = 1,2$)

$$\text{at } z^* = h_i^*\text{: } \underset{\sim}{P} \cdot \underset{\sim}{v}^* = \underset{\sim}{0} \tag{8}$$

Here $\underset{\sim}{P}$ is the projection tensor that transforms every vector on an interface into its tangential components. The interfacial tension gradient required to create such an *immobile* interface is very small (Lin and Slattery, 1982). We will consequently assume that at the same radial positions the interfacial tensions in the two interfaces are equal. In this limit, the results developed will apply both to a liquid drop approaching a liquid–liquid interface and to a gas bubble approaching a gas–liquid interface, since all circulation within phases B and D in Figure 1 is suppressed.

v) The effect of mass transfer on the velocity distribution is neglected.

vi) The pressure p_o^* within the drop is independent of time and position. The pressure within phase B is equal to the local hydrostatic pressure p_h^*.

vii) The liquid is an incompressible, Newtonian fluid, the viscosity of which is a constant.

viii) All inertial effects are neglected.

ix) The effects of gravity, of London-van der Waals forces, and of electrostatic forces are neglected within the draining liquid film.

x) The pressure within the draining film approaches its local hydrostatic value beyond the rim, where the Reynolds lubrication theory approximation (assumption iii) is still valid. At this point, the first and second derivatives of h^* with respect to r^* are constants independent of time. We will assume that at this point $h_1^* = 0$ independent of time.

xi) Experimental observations (Hodgson and Woods, 1969) suggest that there is a time at which the thinning rate at the rim is equal to the thinning rate at the center. At time $t^* = 0$ in our computations, the thinning rate is independent of radial position. We will also assume that for $t^* > 0$ the thinning rate at the center is always greater than the thinning rate at the rim.

xii) The drop is sufficiently small that it may be assumed to be spherical.

In constructing this development, we will find it convenient to work in terms of the dimensionless variables

$$\begin{aligned}
&r \equiv \frac{r^*}{R_0^*} \qquad z \equiv \frac{R_0^* z^*}{h_0^* R_0^*} \\
&h_i \equiv \frac{R_0^* h_i^*}{h_0^* R_0^*} \qquad H_i \equiv H_i^* R_0^* \qquad (i = 1,2) \\
&h \equiv h_1 - h_2 \qquad p \equiv \frac{p^* - p_0^*}{\rho^*(v_0^*)^2} \\
&v_r \equiv \frac{v_r^*}{v_0^*} \qquad v_z \equiv \frac{R_0^* v_z^*}{h_0^* v_0^*} \\
&t \equiv \frac{t^* v_0^*}{R_0^*} \qquad \gamma \equiv \frac{\gamma^*}{\gamma_0^*}
\end{aligned} \tag{9}$$

and dimensionless Reynolds, Weber, and capillary numbers

$$\begin{aligned}
N_{Re} &\equiv \frac{\rho^* v_0^* R_0^*}{\mu^*} \\
N_{We} &\equiv \frac{\rho^*(v_0^*)^2 R_0^*}{\gamma_0^*} \\
N_{ca} &\equiv \frac{\mu^* v_0^*}{\gamma_0^*}
\end{aligned} \tag{10}$$

Here H_i^* ($i = 1,2$) are the mean curvatures of the interfaces, γ^* the interfacial tension and γ_0^* the equilibrium interfacial tension. The characteristic speed v_0^* will be defined later.

By analogy with our discussion of the drainage of a thin film between a drop and a solid wall (Lin and Slattery, 1982), the equation of continuity reduces to

$$\frac{1}{r}\frac{\partial}{\partial r}(r\, v_r) + \frac{\partial v_z}{\partial z} = 0 \tag{11}$$

the Navier-Stokes equation requires

$$\frac{\partial p}{\partial r} = \frac{1}{N_{\mathrm{Re}}}\left(\frac{R_0^*}{h_0^*}\right)^2 \frac{\partial^2 v_r}{\partial z^2} \tag{12}$$

$$\frac{\partial p}{\partial \theta} = 0 \tag{13}$$

$$\frac{\partial p}{\partial z} \ll \frac{\partial p}{\partial r} \tag{14}$$

and the jump momentum balances for the two interfaces (the requirements of Euler's first law or Newton's second law) demand

$$\text{at } z = h_1\text{: } \frac{\partial \gamma}{\partial r} - N_{\mathrm{ca}}\frac{R_0^*}{h_0^*}\frac{\partial v_r}{\partial z} = 0 \tag{15}$$

$$\text{at } z = h_1\text{: } 2H_1\gamma + N_{\mathrm{We}}(p - p_h) = 0 \tag{16}$$

$$\text{at } z = h_2\text{: } \frac{\partial \gamma}{\partial r} + N_{\mathrm{ca}}\frac{R_0^*}{h_0^*}\frac{\partial v_r}{\partial z} = 0 \tag{17}$$

$$\text{at } z = h_2\text{: } 2H_2\gamma - N_{\mathrm{We}}\, p = 0 \tag{18}$$

We will recognize assumptions (iii) and (iv) to say

$$\text{at } z = h_i\text{: } v_r = 0 \ (i = 1,2) \tag{19}$$

and we will employ Eqs. 15 and 17 to calculate the interfacial tension gradient required to create the immobile interfaces assumed here.

Since we neglect the effect of mass transfer on the velocity distribution (assumption v),

$$\text{at } z = h_i\text{: } v_z = \frac{\partial h_i}{\partial t} + \frac{\partial h_i}{\partial r} v_r \ (i = 1,2) \tag{20}$$

We will note that

$$\text{at } r = R\text{: } \frac{\partial h}{\partial r} = 0 \tag{21}$$

$$\text{at } r = 0\text{: } \frac{\partial h}{\partial r} = \frac{\partial h_1}{\partial r} = 0 \tag{22}$$

and

$$\text{at } r = 0\text{: } \frac{\partial p}{\partial r} = 0 \tag{23}$$

With Eqs. 14, 16, and 18 together with assumptions ii and iv, Eq. 23 implies

$$\text{at } r = 0\text{: } \frac{\partial (H_1 - H_2)}{\partial r} = \frac{1}{2}\frac{h_0^*}{R_0^*}\left(-\frac{1}{r^2}\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3}\right) = 0 \tag{24}$$

An application of L'Hospital's rule shows us that

$$\text{at } r = 0\text{: } \frac{\partial^2 h}{\partial r^2} = \frac{1}{r}\frac{\partial h}{\partial r} \tag{25}$$

and Eq. 24 reduces to

$$\text{at } r = 0\text{: } \frac{\partial^3 h}{\partial r^3} = 0 \tag{26}$$

According to assumption x, there is a point $r = R_h > R$ where the pressure p within the draining film approaches the local hydrostatic pressure in the neighborhood of the drop.

$$\text{at } r \to R_h\text{: } p \to p_h,\ h_1 \to 0 \tag{27}$$

Assumption x also requires that

$$\text{at } r = R_h\text{: } \frac{\partial h}{\partial r} = \left(\frac{\partial h}{\partial r}\right)_{t=0} \tag{28}$$

$$\text{at } r = R_h\text{: } \frac{\partial^2 h}{\partial r^2} = \left(\frac{\partial^2 h}{\partial r^2}\right)_{t=0} \tag{29}$$

The initial time is to be chosen by requiring (assumption xi)

$$\text{at } t = 0\text{: } \frac{\partial h}{\partial t} = \text{constant} \tag{30}$$

Since the drop is sufficiently small to be assumed spherical (assumption xii)

$$p_h = -\frac{2}{N_{\mathrm{We}} R_d} \tag{31}$$

where R_d^* is the radius of the drop.

An integral momentum balance for the drop requires [for more details, see Lin and Slattery (1982)]

$$N_{\mathrm{ca}} \int_0^{R_h} (p - p_h) r\, dr = \frac{(R_0^*)^2 \Delta\rho^* g^*}{\gamma_0^*}\frac{2}{3}(R_d)^3 \tag{32}$$

If R_f^* denotes the value of the dimple radius as time becomes large, we would expect from Eqs. 16 and 18 that

$$\text{as } t \to \infty\text{: } p \to \frac{1}{2} p_h \qquad \text{for } 0 \le r \le R_f \tag{33}$$

and from Eq. 27 that

$$\text{as } t \to \infty\text{: } p \to p_h \qquad \text{for } r > R_f \tag{34}$$

Recognizing Eqs. 31, 33, and 34, we find that Eq. 32 gives (Chappelear, 1961)

$$\text{as } t \to \infty\text{: } R \to R_f = \left[\frac{4}{3}\frac{\Delta\rho^* g^* (R_0^*)^2}{\gamma_0^*}\right]^{1/2} (R_d)^2 \tag{35}$$

Given R_d^*, we determine R_f^* by requiring Eq. 35 to be satisfied; we identify $R_0^* = R_f^*/R_f$.

For the sake of simplicity, let us define our characteristic speed

$$v_0^* = \frac{\mu^*}{\rho^* R_0^*} \tag{36}$$

which means

$$N_{\mathrm{Re}} = 1,\ N_{\mathrm{We}} = N_{\mathrm{ca}} = \frac{\mu^{*2}}{\rho^* R_0^* \gamma_0^*} \tag{37}$$

Note that we have not used this definition for v_0^* or this definition for N_{Re} in scaling the Navier-Stokes equation to neglect inertial effects (assumption viii). The scaling argument required to suggest a priori under what circumstances inertial effects can be ignored would be different, based perhaps on the initial value of the speed of displacement of one of the fluid–fluid interfaces calculated at the center of the film.

Our objective in what follows is to obtain a solution to Eqs. 11 and 12 consistent with Eqs. 16, 18 through 22, 25 through 30, and the second portion of assumption xi. Given R_d^*, we determine R_f^* by requiring that as $t \to \infty$ or just prior to the development of an instability and coalescence Eq. 35 be satisfied; we identify $R_0^* = R_f^*/R_f$. Note that, in addition to physical properties, only one parameter is required: R_d^*.

SOLUTION

Integrating Eq. 12 twice consistent with Eq. 19, we find in view of Eq. 37

$$v_r = \frac{1}{2}\left(\frac{h_0^*}{R_0^*}\right)^2 \frac{\partial p}{\partial r}\,[z^2 - (h_1 + h_2)z + h_1 h_2] \tag{38}$$

Substituting Eq. 38 into Eq. 11 and integrating once, we have

$$v_z = -\frac{1}{2}\left(\frac{h_0^*}{R_0^*}\right)^2 \left\{\left[\frac{\partial^2 p}{\partial r^2} + \frac{1}{r}\frac{\partial p}{\partial r}\right]\left[\frac{z^3}{3} - \frac{1}{2}(h_1 + h_2)z^2 + h_1 h_2 z\right] + \frac{\partial p}{\partial r}\left[-\left(\frac{\partial h_1}{\partial r} + \frac{\partial h_2}{\partial r}\right)\frac{z^2}{2} + \left(\frac{\partial h_1}{\partial r} h_2 + h_1 \frac{\partial h_2}{\partial r}\right) z\right]\right\} + C(r) \tag{39}$$

in which $C(r)$ is an as yet undetermined function of r.

With Eqs. 38 and 39, 20 tells us ($i = 1,2$)

$$-\frac{\partial h_i}{\partial t} = \frac{1}{2}\left(\frac{h_0^*}{R_0^*}\right)^2 \left\{\left[\frac{\partial^2 p}{\partial r^2} + \frac{1}{r}\frac{\partial p}{\partial r}\right]\left[\frac{1}{3}h_i^3 - \frac{1}{2}(h_1 + h_2)h_i^2 + h_1 h_2 h_i\right] + \frac{\partial p}{\partial r}\left[-\left(\frac{\partial h_1}{\partial r} + \frac{\partial h_2}{\partial r}\right)\frac{h_i^2}{2} + \left(\frac{\partial h_1}{\partial r}h_2 + h_1\frac{\partial h_2}{\partial r}\right)h_i\right]\right\} - C(r) \quad (40)$$

and the difference of these two expressions gives

$$\frac{\partial h}{\partial t} = \left(\frac{h_0^*}{R_0^*}\right)^2\left[\frac{1}{12}\left(\frac{\partial^2 p}{\partial r^2} + \frac{1}{r}\frac{\partial p}{\partial r}\right)h^3 + \frac{1}{4}h^2\frac{\partial h}{\partial r}\frac{\partial p}{\partial r}\right] \quad (41)$$

Taking the difference between Eqs. 16 and 18, recognizing Eq. 31, and applying the appropriate expressions for the dimensionless mean curvatures H_i ($i = 1,2$), we see

$$N_{ca}p + \frac{1}{R_d} = -\frac{1}{2}\frac{h_0^*}{R_0^*}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) \quad (42)$$

In writing this, we have taken $\gamma = 1$ by assumption iv.

Inserting Eq. 42 into 41, we discover

$$-\frac{\partial h}{\partial t'} = \frac{h^3}{3}\left(\frac{\partial^4 h}{\partial r^4} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{1}{r^3}\frac{\partial h}{\partial r}\right) + h^2\frac{\partial h}{\partial r}\left(\frac{\partial^3 h}{\partial r^3} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} - \frac{1}{r^2}\frac{\partial h}{\partial r}\right) \quad (43)$$

in which

$$t' \equiv \frac{t}{8N_{ca}}\left(\frac{h_0^*}{R_0^*}\right)^3 \quad (44)$$

Note that, after an application of L'Hospital's rule with full recognition of Eqs. 22, 25, and 26, we obtain

$$\text{limit } r \to 0: -\frac{\partial h}{\partial t'} = \frac{8}{9}h^3\frac{\partial^4 h}{\partial r^4} \quad (45)$$

Equations 43 and 45 have the same form as the governing equations describing a bubble approaching a solid plane (Lin and Slattery, 1982), except that the thinning rate for the present case is only half as large. This is consistent with the difference between the Frankel and Mysels (1962) theory and Princen's (1963) result.

Having been given N_{ca} in the form of the physical properties, we can carry out the integration of Eq. 43 in a manner similar to that used previously in the context of a bubble approaching a solid surface (Lin and Slattery, 1982).

Our first objective is to calculate the initial dependence of h upon radial position consistent with assumption xi. Recognizing Eq. 30, we can use Eq. 45 to write Eq. 43 as

$$\left(\frac{\partial^4 h}{\partial r^4}\right)_{r=0} = \frac{3}{8}h^3\left(\frac{\partial^4 h}{\partial r^4} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{1}{r^3}\frac{\partial h}{\partial r}\right) + \frac{9}{8}h^2\frac{\partial h}{\partial r}\left(\frac{\partial^3 h}{\partial r^3} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} - \frac{1}{r^2}\frac{\partial h}{\partial r}\right) \quad (46)$$

We require that the result be consistent with Eqs. 22, 26 and 21 in the form

$$\text{at } r = 1: \frac{\partial h}{\partial r} = 0 \quad (47)$$

and Eq. 27 expressed as

$$\text{as } r \to R_h: \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) \to \frac{2}{R_d^*}\frac{(R_0^*)^2}{h_0^*} \quad (48)$$

where p_h has been determined by Eq. 31 and p by Eq. 42.

In order to integrate a finite-difference form of Eq. 46, we replace Eq. 48 by

$$\text{at } r = 1: \frac{\partial^2 h}{\partial r^2} = C \quad (49)$$

where C is a free parameter, the value of which will be determined shortly.

For each value of C, we can determine a tentative initial configuration of the film by integrating Eq. 46 consistent with Eqs. 22, 26, 47 and 49. The dimensionless radial position at which the pressure gradient becomes negligible is tentatively identified as R_h, subject to later verification that assumption ii is still satisfied at this point.

Equation 43 can be integrated consistent with each of these tentative initial configurations, Eqs. 22, 26, 28, and 29. Equation 21 permits us to identify R as a function of time; R_f is the value of R as $t' \to \infty$. We employed the Crank-Nicolson technique (Myers, 1971); accuracy was checked by decreasing the time and space intervals.

In addition to requiring that at time $t^* = 0$ the thinning rate is independent of radial position, assumption xi demands that for $t^* > 0$ the thinning rate at the center is always greater than the thinning rate at the rim. Our numerical computations indicate that there is a minimum value of the parameter C for which this condition is satisfied. This also corresponds to the maximum value of h_0^* for which the thinning rate at the center is always greater than the thinning rate at the rim for $t^* > 0$. We will choose this maximum value of h_0^* as our initial film thickness at the center.

From Eq. 35, we can determine R_f^*. This permits us to identify $R_0^* = R_f^*/R_f$. The initial film thickness at the center, h_0^*, is fixed by Eq. 48.

We must now check whether assumption ii is satisfied at R_h; if it is satisfied here, it will be satisfied everywhere. We wish to choose R_h as large as possible, in order to make the pressure gradient at this point clearly negligible. But if R_h is assigned too large a value, assumption ii will be violated.

We have from Eqs. 16, 31 and 42,

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h_1}{\partial r}\right) = \frac{1}{2}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) - \left(\frac{R_0^*}{h_0^*}\right)\frac{1}{R_d} \quad (50)$$

This can be integrated consistent with Eqs. 22 and 27 to determine h_1, the configuration of the interface between phases B and C in Figure 1.

Finally, we can examine assumption iv that the interfacial tension gradient required to achieve an immobile interface is very small. Given Eqs. 15, 17, 38, and 42, we can reason

$$\frac{\partial \gamma}{\partial r} = -\frac{1}{4}\left(\frac{h_0^*}{R_0^*}\right)^2 h\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right] \quad (51)$$

This can be integrated with the observation that, since the surface tension gradient is proportional to the pressure gradient from Eqs. 15, 17 and 38,

$$\text{at } r = R_h: \gamma = 1. \quad (52)$$

RESULTS

For $R_h = 1.69$, we conclude

$$C = 5.05$$

$$R_f = 1.10$$

$$\text{at } r = R_h: \frac{\partial h}{\partial r} = 6.08$$

$$\text{at } r = R_h: \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) = 12.61$$

Figure 2 gives h as a function of r and t'. In Figure 3, we see the variation of dimensionless pressure as a function of time and position within the draining film; the results are consistent with Eqs. 33 and 34.

There have been very few experimental studies of the film configuration as a function of time.

Hartland (1967, 1968) observed large drops for which the analysis developed here is not applicable (assumption xii).

Hodgson and Woods (1969), Woods and Burrill (1972), Burrill

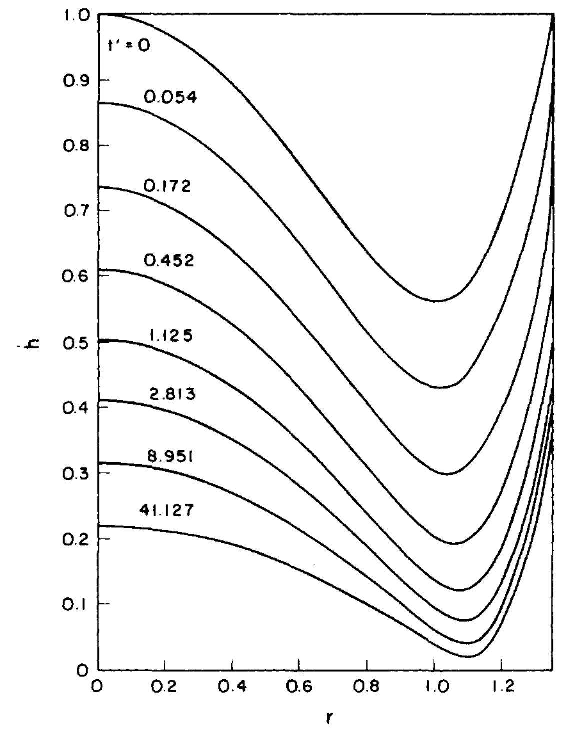

Figure 2. Dimensionless film thickness h as a function of dimensionless radial position and dimensionless time for R_h = 1.69.

and Woods (1973a,b), and Liem and Woods (1974) found five distinct drainage patterns with small drops. Most of their results show asymmetric patterns, indicating instabilities. We could not expect good agreement between this portion of their data and the theory developed here. We have carried out our computations for only three of their systems.

Since insufficient data were given to identify our t =0 (Eq. 30), we related our time scale to the experimental time scales by matching in each case the initial measurement of the film thickness at the rim. As we shall demonstrate, we found it satisfactory to identify R_h = 1.69 for all three systems.

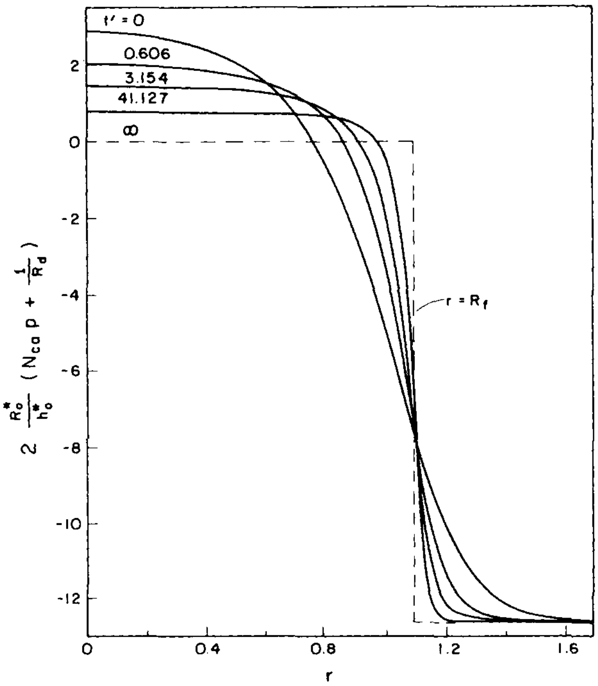

Figure 3. Dimensionless film pressure as a function of dimensionless radial position and dimensionless time for R_h = 1.69.

For comparison, we also show the predictions of Princen (1963):

$$\text{at } r^* = 0\text{: } h^* = \left[\frac{0.0192\, n^2\, \mu^* R^{*6}}{\gamma^* R_d^*}\right]^{1/4} [t^* - t_0^*]^{-1/4} \qquad (53)$$

$$\text{at } r^* = R^*\text{: } h^* = \left[\frac{0.180\, n^2\, \mu^* R^{*2} R_d^*}{\gamma^*}\right]^{1/2} [t^* - t_0^*]^{-1/2} \qquad (54)$$

In these relationships, the rim radius R^* is assumed to be a constant and t_0^* is an adjustable parameter. For immobile interfaces, n = 2. Our comparisons assume that both interfaces are immobile.

Water-Cyclohexanol

Burrill and Woods (1973b) report observations for a cyclohexanol drop approaching a water-cyclohexanol interface: R_d^* = 0.62mm, γ_0^* = 3.93 mN/m, μ^* = 1.0 mPa s, $\Delta\rho^*$ = 5.1 × 10^{-2} g/cm^3. The water contained 10^{-4} g/L sodium lauryl sulfate and 0.05 N KCl. During the first 60 s of elapsed time, the film alternately drained symmetrically and asymmetrically. Thereafter, it drained symmetrically, until it ruptured.

We find that at our t=0 [Burrill and Woods (1973b) t^* = 38 s] when the thinning rate is independent of position

$$h_0^* \equiv h^*(0,0) = 5.30 \times 10^{-4} \text{ cm}$$

and

$$\left(\frac{h_0^*}{R_0^*}\right)^2 = 1.36 \times 10^{-3}$$

which means that the Reynolds lubrication theory approximation (assumption iii) is applicable. At $r = R_h$ = 1.69,

$$\left(\frac{\partial h^*}{\partial r^*}\right)^2 = 5.03 \times 10^{-2}$$

and assumption ii is still satisfied at this point. From Eqs. 51 and 52, the calculated difference between the interfacial tension at the center and the equilibrium interfacial tension is only 1.43 × 10^{-5}

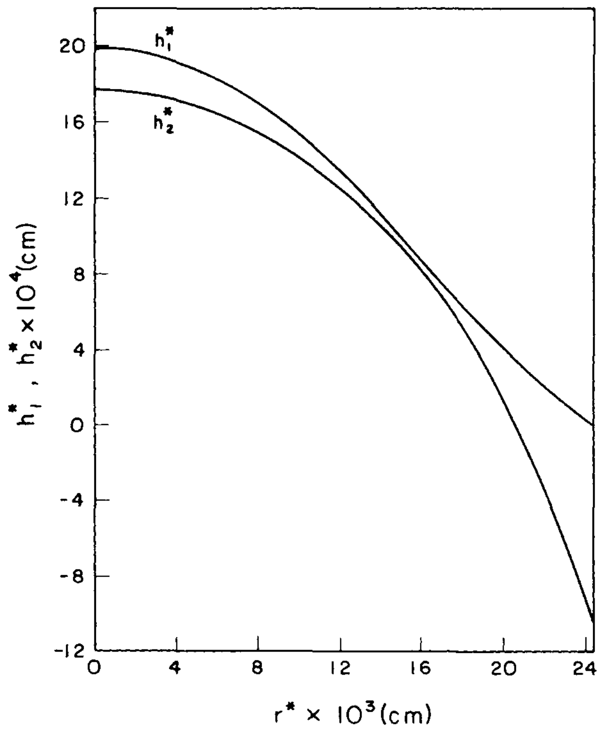

Figure 4. Calculated configurations of fluid-fluid interface ($z^* = h_1^*$) and of drop-fluid interface ($z^* = h_2^*$) at our time t^* = 19.0 s for water-cyclohexanol system.

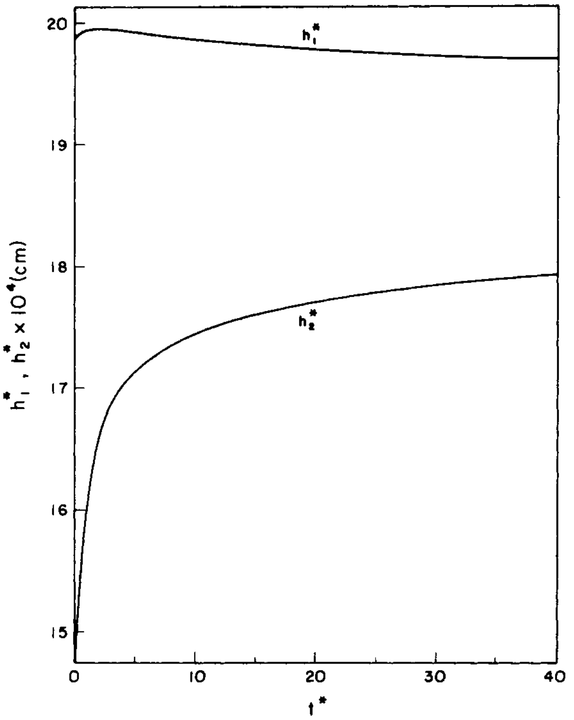

Figure 5. Comparison of h_1^* and h_2^* at $r^* = 0$ as functions of our time for water-cyclohexanol system.

N/m at our t=0 and 6.56 × 10^{-7} N/m at our t^* = 143 s, which suggests assumption iv is reasonable.

Figure 4 presents the calculated profiles h_1^* and h_2^* at our t^* = 19.0 s. According to our computations, h_2^* increases monotonically with time, but the variation of h_1^* with time is more complicated. Initially, h_1^* increases with time from our t^* = 0 to 2.4 s. Thereafter, h_1^* decreases near the center, while continuing to increase elsewhere. As time increases, the region in which h_1^* decreases becomes broader. Overall, h_1^* changes more slowly with time than does h_2^*.

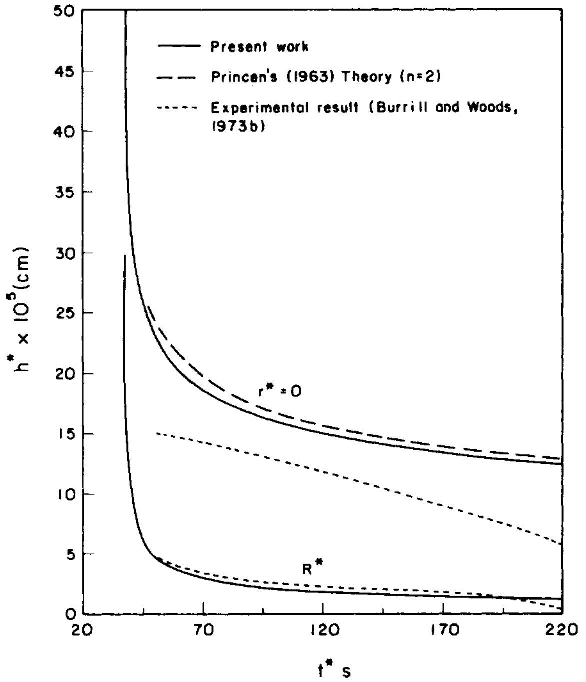

Figure 6. Comparisons of theories with experimental measurements at center ($r^* = 0$) and at rim ($r^* = R^*$) for water-cyclohexanol system. Here t^* represents the experimental time scale of Burrill and Woods (1973b). Princen's (1963) estimate for the rim coincides with our own.

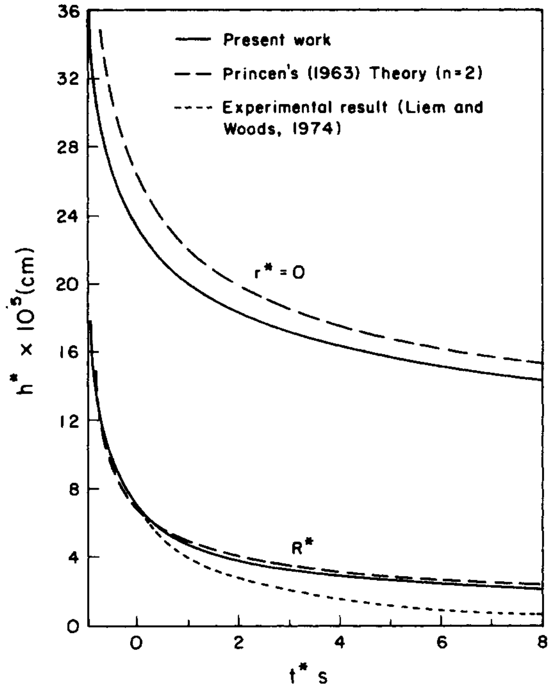

Figure 7. Comparisons of theories with experimental measurements for water-toluene system. Here t^* represents the experimental time scale of Liem and Woods (1974).

This is illustrated in Figure 5, which compares h_1^* and h_2^* at the center with time.

Burrill and Woods (1973b) measured film thickness as a function of time only at the center and at the rim. Figure 6 compares their data with our predictions and with the estimates of Princen (1963), Eqs. 53 and 54. Our time scale and t_0^* in Eqs. 53 and 54 were adjusted by matching the theoretical predictions to the first experimental measurement at the rim. The interfaces may not have been entirely immobile as presumed both by our theory and by the estimated of Princen (1963) shown or the film may have been draining asymmetrically as the result of an instability.

Water-Toluene

Liem and Woods (1974) studied a toluene drop approaching a water-toluene interface: $R_d^* = 0.842$ mm, $\gamma_0^* = 33.5$ mN/m, μ^* = 1.0 mPa·s, $\Delta\rho^* = 1.33 \times 10^{-1}$ g/cm³. The water contained 10^{-4}M palmitic acid.

At our t=0 [Liem and Woods (1974) t^* = −0.99 s],

$$h_0^* = 4.06 \times 10^{-4} \text{ cm}$$

and

$$\left(\frac{h_0^*}{R_0^*}\right)^2 = 7.64 \times 10^{-4}$$

consistent with the Reynolds lubrication theory approximation (assumption iii). At $r = R_h = 1.69$,

$$\left(\frac{\partial h^*}{\partial r^*}\right)^2 = 2.83 \times 10^{-2}$$

which indicates that assumption ii was not violated.

Figure 7 compares the data of Liem and Woods (1974) with our theory and with the estimates of Princen (1963), Eqs. 53 and 54. Liem and Woods (1974) measured the thickness of the film as a function of time only at the rim. In the absence of more complete experimental data, we must add the same caveats listed for Figure 6.

Water-Anisole

Woods and Burrill (1972) observed an anisole drop approaching a water-anisole interface: $R_d^* = 0.168$mm, $\gamma_0^* = 20.5$ mN/m, μ^*

$= 1.0$ mPa·s, $\Delta\rho^* = 9.7 \times 10^{-3}$ g/cm^2. The water contained 10^{-4} g/L sodium lauryl sulfate.

The comparison with our theory and with the estimates of Princen (1963), Eqs. 53 and 54, is very similar to that shown for the water-toluene system in Figure 7.

DISCUSSION

The comparisons shown in Figures 6 and 7 suggest that the present work is a relatively minor improvement over the simple result of Princen (1963) shown in Eqs. 53 and 54. In fact, there are two important improvements. First, the Princen (1963) result contains an adjustable parameter t_0^* that has no physical significance. In the present theory, there is no adjustable parameter and time is measured relative to the time at which the thinning rate is independent of radial position during the formation of the thin film. Second, the present theory is more complete in the sense that the entire configuration of the draining film can be described as a function of time, not just the thickness of the film at the center and at the rim.

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NOTATION

C = parameter in Eq. 49
$C(r)$ = undetermined function of r in Eq. 40
g^* = acceleration of gravity
h^* = film thickness
h = dimensionless film thickness defined by Eq. 9
h_0^* = film thickness at $t^* = 0$ and $r^* = 0$
h_1^* = configuration of the fluid–fluid interface
h_1 = defined by Eq. 9
h_2^* = configuration of the drop-fluid interface
h_2 = defined by Eq. 9
H_1^* = mean curvature of the fluid–fluid interface
H_1 = dimensionless mean curvature of the fluid–fluid interface defined by Eq. 9
H_2^* = mean curvature of the drop-fluid interface
H_2 = dimensionless mean curvature of the drop-fluid interface defined by Eq. 9
n = parameter in Eqs. 53 and 54
N_{ca} = capillary number defined by Eq. 10
N_{Re} = Reynolds number defined by Eq. 10
N_{We} = Weber number defined by Eq. 10
p^* = pressure in liquid film
p = dimensionless pressure in liquid film, defined by Eq. 9
$\underset{\sim}{P}$ = projection tensor that transforms any vector on the interface into its tangential component
p_h^* = hydrostatic pressure
p_h = dimensionless hydrostatic pressure defined by Eq. 9
p_o^* = pressure within the drop
r^* = cylindrical coordinate
r = dimensionless cylindrical coordinate defined by Eq. 9
R^* = rim radius of the drop
R = dimensionless rim radius defined as R^*/R_0^*
R_d^* = radius of the drop
R_d = dimensionless radius of the drop defined as R_d^*/R_0^*
R_f^* = dimple radius as $t \to \infty$ or just prior to the development of an instability and coalescence
R_f = defined as R_f^*/R_0^*
R_h = dimensionless radial position where the pressure p within the draining film approaches the local hydrostatic pressure in the neighborhood of the drop
R_0^* = rim radius of the drop at $t^* = 0$
t^* = time
t = dimensionless time defined by Eq. 9
t' = dimensionless time defined by Eq. 44
t_0^* = adjustable parameter in Eqs. 50 and 54
$\underset{\sim}{v}^*$ = velocity vector
v_r^* = r^* component of velocity vector $\underset{\sim}{v}^*$
v_r = defined by Eq. 9
v_z^* = z^* component of velocity vector $\underset{\sim}{v}^*$
v_z = defined by Eq. 9
v_0^* = characteristic speed defined by Eq. 36
z^* = cylindrical coordinate
z = dimensionless cylindrical coordinate defined by Eq. 9

Greek Letters

γ^* = interfacial tension
γ = dimensionless interfacial tension defined by Eq. 9
γ_0^* = equilibrium interfacial tension
μ^* = bulk viscosity of the liquid film
ρ^* = density of the liquid film
$\Delta\rho^*$ = density difference between liquid film and the drop
θ = cylindrical coordinate

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