Effects of London-van der Waals Forces on the Thinning and Rupture of a Dimpled 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 and begins to drain. As the thickness of the draining film become sufficiently small [about 1,000 Å (100 nm)], the effects of the London-van der Waals forces and of the repulsive force of any electrostatic double layer become important. Lin and Slattery (1982b) developed a hydrodynamic theory for the first portion of the coalescence process: the drainage of the thin liquid film while it is sufficiently thick that the effects of London-van der Waals forces and of electrostatic forces can be ignored. Here the effect of the London-van der Waals forces are included. Given only the drop radius and the required physical properties, the configuration of the film as a function of time is predicted. For the case of a negative disjoining pressure, it is possible to estimate an upper bound for the coalescence time or the time during which a small drop or bubble appears to rest at a phase interface before it coalesces under the influence of London-van der Waals forces.

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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 and drains. If the disjoining pressure is positive, a stable liquid film will be formed eventually. If the disjoining pressure is negative, the liquid film will be unstable and will rupture. In this latter case, we speak of the coalescence time as the elapsed time between the formation of the film and its rupture, or the time during which a drop or bubble appears to rest at a phase interface before it coalesces under the influence of London-van der Waals forces.

Lin and Slattery (1982b) discussed only the first portion of this 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. They focused on those systems in which the interface may be assumed to be immobile.

In what follows, we extend their theory to the latter stage of the drainage process by including the effects of London-van der Waals forces. In order to simplify the problem, we consider only the case of small drops or bubbles and liquid films sufficiently thin that the Reynolds lubrication theory approximation is applicable.

Our primary attention is focused on the most common situation: a drop or bubble forced to approach its homophase. For this case, the disjoining pressure is always negative, the liquid film is unstable, and coalescence occurs.

CONCLUSIONS AND SIGNIFICANCE

The effects of London-van der Waals forces on the configuration of the dimpled liquid film are negligible when the film thickness at the rim (the thinnest portion of the film) is larger than the distance over which these forces are effective. For the cyclohexanol-water system observed by Burrill and Woods (1973b) and for the toluene-water system studied by Liem and Woods (1974), the effects of London-van der Waals forces are negligible at short times and the predictions of the present theory coincide with those given by Lin and Slattery (1982b). At longer times, the present theory is an improvement.

We are able to predict the coalescence time for a small drop or bubble approaching its homophase, given only the appropriate physical properties and its radius. The general trends

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predicted by our results agree with those derived from the more approximate theory of Chen et al. (1984): the coalescence time increases as the bubble or drop diameter increases, as the viscosity of the draining film increases, as the interfacial tension decreases, as the strength of the London-van der Waals forces decreases, and as the density difference between the two phases increases.

Our predicted coalescence time is an upper bound in the sense that it does not allow for the development of asymmetric drainage and of instabilities leading to premature rupture as observed by some experimenters. It would not necessarily give an upper bound for systems in which electrostatic double-layer forces played an important role. It should also not be expected to give an upper bound when a poor estimate of the strength of the London-van der Waals force is employed.

Our predicted upper bounds for coalescence times agree fairly well with the experimental data of MacKay and Mason (1963). These upper bounds generally give a more accurate description of the experimental data than does the approximate analysis of Chen et al. (1984).

The comparison with data from Woods and Burrill (1972) and from Burrill and Woods (1973b) is less satisfactory. They noted the development of asymmetric drainage and instabilities that would lead to premature coalescence. They also added KCl in order to minimize any potential electrostatic double layer, but no criteria are offered by which we can judge the success of this strategy.

In all of our comparisons with experimentally observed coalescence times we employed an estimated value for the strength of the London-van der Waals forces, since reliable a priori estimates were not available. We belive that this contributed to the deviation between theory and observation, particularly for the data of Allan et al. (1961).

INTRODUCTION

As a drop is forced to approach a fluid-fluid interface, the minimum film thickness is initially at the center. As thinning proceeds, the minimum film thickness moves to the rim or barrier ring (Allan et al., 1961; MacKay and Mason, 1963; Hodgson and Woods, 1969).

Princen (1963) extended the theory of Frankel and Mysels (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) for two plane parallel discs.

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 fluid-fluid interfaces 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 experimentally.

Barber and Hartland (1976) included the effects of the interfacial viscosities in considering the thinning of a liquid film bounded by partially mobile parallel planes. They limited their analysis to the initial stage of thinning in which the effects of any disjoining pressure are negligible. The force of their result is weakened by the manner in which they combined the effects of the interfacial viscosities with that of the interfacial tension gradient.

Allan et al. (1961) studied experimentally the approach of nitrogen bubbles to an air-aqueous glycerol solution interface. They observed that the rupture of the liquid film occurred over a range of film thicknesses in any given system, in many cases less than 900 Å (90 nm). They pointed out that the effect of an added surfactant was to decrease the rate of film thinning at comparable thicknesses, to increase the film rest time, and to decrease the film thickness at rupture.

Burrill and Woods (1973a,b) studied experimentally the coalescence of small oil drops at an interface between oil and an aqueous solution of sodium lauryl sulfate and KCl. They observed that nearly all of the films ruptured at the rim and that the rim thickness at which rupture occurred was between 300 and 500 Å (30–50 nm) (Burrill and Woods, 1973a).

The addition of more KCl to the aqueous solution resulted in more rapid drainage to rupture (Burrill and Woods, 1973b), which was probably attributable to diminished repulsive forces of the electrostatic double layer.

The effect of surfactant on the coalescence time has also been studied by Hodgson and Lee (1969), Hodgson and Woods (1969), Komasawa and Otake (1970), Lang and Wilke (1971), and Burrill and Woods (1973a,b). In the absence of surfactant, the coalescence time was extremely short. The addition of a small amount of surfactant dramatically increased the coalescence time.

MacKay and Mason (1963) extended the Reynolds (1886) equation for plane parallel discs to include the effect of London-van der Waals forces. They found that the film thickness can become zero in a finite time when the disjoining pressure is negative. A similar conclusion was reached by Hodgson and Woods (1969), who employed a cylindrical drop model. Neither of these developments is as complete as that provided by Buevich and Lipkina (1978) for the drainage of a thin film on a solid plane.

Flumerfelt et al. (1982) have extended the analysis of Barber and Hartland (1976) to include the effects both of London-van der Waals forces and of the interfacial viscosities in considering the thinning of a liquid film bounded by partially mobile parallel planes. As with Barber and Hartland (1976), the impact of their argument is diminished by the manner in which they combine the effects of the interfacial viscosities with that of the interfacial tension gradient.

Lin and Slattery (1982b) have considered the drainage of a thin liquid film between a small drop or bubble and a fluid-fluid interface. The film was considered to be sufficiently thick that the effects of London-van der Waals forces and of electrostatic forces could be ignored. Starting with this development and taking London-van der Waals forces into account, Chen et al. (1984) followed Buevich and Lipkina (1975, 1978) to obtain an expression for the rate of thinning at the rim as a drop approaches a fluid-fluid interface. For a bubble or drop approaching its homophase, the disjoining pressure will be negative, leading to the development of an instability, rupture, and coalescence. Motivated by the experimental observation that rupture occurs off-center (Charles and Mason, 1960; Burrill and Woods, 1973a), Chen et al. (1984) constructed a linear stability analysis of this thinning equation. They compared their predicted coalescence times with those observed experimentally by Allen et al. (1961), Mackay and Mason (1963), Woods and Burrill (1972), and Burrill and Woods (1973b).

In what follows, we extend Lin and Slattery's (1982b) development to carry out a more complete analysis leading to the prediction of the entire film profile as a function of time and to the estimation of the coalescence time or the time during which a small drop or bubble appears to rest at a phase interface before it coalesces under the influence of London-van der Waals forces.

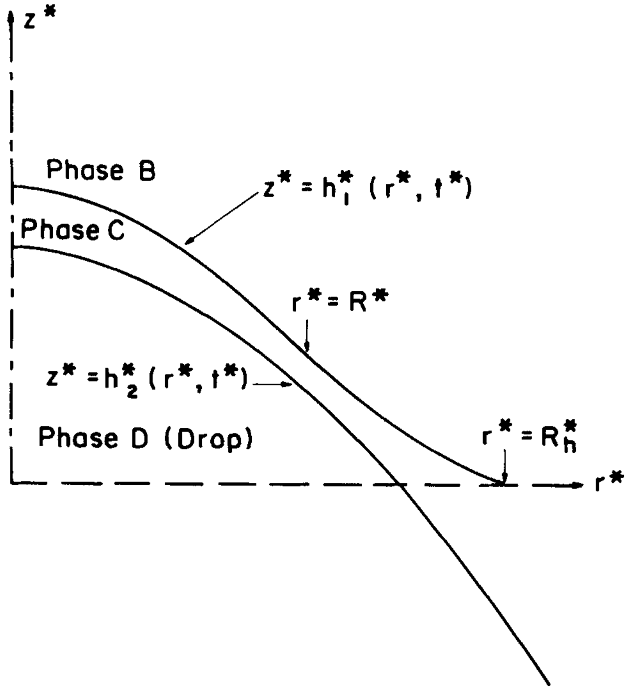

Figure 1. A symmetric drop or bubble (phase *D*) moves through a liquid (phase *C*) as it approaches a fluid-fluid interface (between phases *C* and *B*).

Configuration of drop-fluid interface: $z^* = h_2^*(r^*, t^*)$.

Configuration of fluid-fluid interface: $z^* = h_1^*(r^*, t^*)$.

STATEMENT OF PROBLEM

Figure 1 shows the draining liquid film formed as a small drop or bubble approaches a fluid-fluid interface. We will adopt many of the same assumptions made by Lin and Slattery (1982b) in their discussion of the early stages of this drainage process.

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

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

(The superscript * denotes a dimensional variable).

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

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

iii) Introducing

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

let R^* be the rim radius of the drop such that at

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

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

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

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

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

Here 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 (Sheludko, 1967; Lin and Slattery, 1982a,b; also see Appendix). 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 and of electrostatic forces are neglected within the draining liquid film. [In contrast with Lin and Slattery (1982b), we will account for the effect of London-van der Waals forces.]

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 ($r^* = R_h^*$), the two principal curvatures of the drop are constants independent of time,

$$\text{at } r^* = R_h^*: \frac{\partial h^*}{\partial r^*} = \left(\frac{\partial h^*}{\partial r^*}\right)_{t^*=0} \tag{9}$$

$$\text{at } r^* = R_h^*: \frac{\partial^2 h^*}{\partial r^{*2}} = \left(\frac{\partial^2 h^*}{\partial r^{*2}}\right)_{t^*=0} \tag{10}$$

xi) Experimental observations (Allan et al., 1961; 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, so long as the effects of any disjoining pressure are negligible.

xii) The drop is sufficiently small that it may be assumed to be spherical. This is equivalent to assuming that the Bond number

$$N_{Bo} \equiv \frac{\Delta\rho^* g^* R_d^{*2}}{\gamma^*} \ll 1 \tag{11}$$

Here $\Delta\rho^*$ is the density difference between the drop phase and the continuous phase, g^* is the magnitude of the acceleration of gravity, R_d^* is the radius of the drop, and γ^* is the interfacial tension.

In addition, we will say (Chen and Slattery, 1982):

xiii) Within the draining liquid film, the mutual force per unit mass b_m^* known as the London-van der Waals force is representable in terms of a scalar potential ϕ^*:

$$\mathbf{b}_m^* = -\nabla\phi^* \tag{12}$$

At a planar fluid-fluid interface (Sheludko et al., 1965; Ruckenstein and Jain, 1974)

$$\rho^*\phi^*(h_i^*) = \Phi_B^* + \frac{B^*}{h^{*m}} \tag{13}$$

where ρ^* is the mass density of the liquid film and $\Phi_B{}^*$ is the interaction potential per unit volume of a semiinfinite film liquid in the limit as the fluid-fluid interface is approached. When the film thickness is less than 120 Å (12 nm), $m \doteq 3$; when the film thickness is larger than 400 Å (40 nm), $m = 4$ (Churaev, 1974a,b). We speak of

$$\pi^* \equiv -\frac{B^*}{h^{*m}} \tag{14}$$

as the disjoining pressure of a flat film of thickness h^*. Note that B^* is always positive when two homophases approach each other. In this case, the interaction potential per unit volume of the continuous phase at the interface is larger than it would be if the continuous phase were semiinfinite. This corresponds to a negative disjoining pressure that acts to draw the two fluid-fluid interfaces together. A stable film of uniform thickness can never be formed in this case.

xiv) Because the dependence of h^* upon r^* is weak (assumption *ii*), we will assume that the local value of the interaction energy per unit volume of the film liquid at the fluid-fluid interface is equal to that of a flat film of the same thickness.

xv) Since the critical film thicknesses measured or predicted by Allan et al. (1961), MacKay and Mason (1963), Vrij (1966), Ivanov et al. (1970), Burrill and Woods (1973a), and Chen et al. (1984) are normally larger than 120Å (12 nm), we expect that $m = 4$ in Eq. 13 is more appropriate. Several authors (Kitchener and Prosser, 1957; Black et al., 1960; Sheludko et al., 1965; Churaev, 1974a; Derjaguin et al., 1977) reported the approximate values of B^* between two flat surfaces as

$$\text{for } m = 4{:}\,|B^*| \sim 10^{-19}\ \text{erg·cm}$$

Since we lack more detailed information, we will use this value for B^* in our analysis.

SOLUTION

The analysis of this problem is very similar to that described by Lin and Slattery (1982b). The only change is the addition of the London-van der Waals mutual force in the equation of motion for the draining liquid film. This can be accomplished simply by replacing p^* in their equation of motion (Lin and Slattery, 1982b, Eq. 12) with $(p^* + \rho^*\phi^*)$.

Following this change through their analysis, we find that the differential equation describing the thickness of the draining liquid film becomes [see Chen and Slattery (1982) for an analogous development]

$$\begin{aligned}-\frac{\partial h}{\partial t'} = {} & \frac{1}{3}h^3\left(\frac{1}{r^3}\frac{\partial h}{\partial r} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} + \frac{\partial^4 h}{\partial r^4}\right) \\ & + h^2\frac{\partial h}{\partial r}\left(-\frac{1}{r^2}\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3}\right) \\ & + \frac{2}{3}mB\left[\frac{1}{r}\frac{1}{h^{m-2}}\frac{\partial h}{\partial r} + \frac{1}{h^{m-2}}\frac{\partial^2 h}{\partial r^2} - \frac{(m-2)}{h^{m-1}}\left(\frac{\partial h}{\partial r}\right)^2\right]\end{aligned} \tag{15}$$

where

$$\begin{aligned} h &\equiv \frac{h^*}{h_0^*} & r &\equiv \frac{r^*}{R_0^*} \\ t' &\equiv \frac{t^*\mu^*}{8\rho^* R_0^{*2} N_{ca}}\left(\frac{h_0^*}{R_0^*}\right)^3 & B &\equiv \frac{R_0^{*2}B^*}{\gamma_0^* h_0^{*m+1}}\end{aligned} \tag{16}$$

and the capillary number is defined as

$$N_{ca} \equiv \frac{\mu^{*2}}{\rho^* R_0^* \gamma_0^*} \tag{17}$$

Note that, after an application of L'Hospital's rule (Lin and Slattery, 1982b, Eq. 45)

$$\text{limit } r \to 0{:}\ -\frac{\partial h}{\partial t'} = \frac{8}{9}h^3\frac{\partial^4 h}{\partial r^4} + \frac{4}{3}\frac{mB}{h^{m-2}}\frac{\partial^2 h}{\partial r^2} \tag{18}$$

Our first objective is to calculate the initial dependence of h upon radial position consistent with assumption *xi*. Recognizing that the rate of thinning is independent of radial position at the initial time, we can use Eqs. 15 and 18 to say at $t' = 0$

$$\begin{aligned}\frac{8}{3}\left(\frac{\partial^4 h}{\partial r^4}\right)_{r=0} + 4mB\left(\frac{\partial^2 h}{\partial r^2}\right)_{r=0} & \\ = h^3\left(\frac{1}{r^3}\frac{\partial h}{\partial r} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} + \frac{\partial^4 h}{\partial r^4}\right) & \\ + 3h^2\frac{\partial h}{\partial r}\left(-\frac{1}{r^2}\frac{\partial h}{\partial r} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3}\right) & \\ + 2mB\left[\frac{1}{r}\frac{1}{h^{m-2}}\frac{\partial h}{\partial r} + \frac{1}{h^{m-2}}\frac{\partial^2 h}{\partial r^2} - \frac{m-2}{h^{m-1}}\left(\frac{\partial h}{\partial r}\right)^2\right] &\end{aligned} \tag{19}$$

As discussed by Lin and Slattery (1982b), we require that the result be consistent with

$$\text{at } r = 0{:}\ \frac{\partial h}{\partial r} = 0 \tag{20}$$

$$\text{at } r = 0{:}\ \frac{\partial^3 h}{\partial r^3} = 0 \tag{21}$$

$$\text{at } r = 1{:}\ \frac{\partial h}{\partial r} = 0 \tag{22}$$

$$\text{as } r \to R_h{:}\ \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) \to \frac{2}{R_d^*}\frac{R_0^{*2}}{h_0^*} \tag{23}$$

In order to integrate a finite-difference form of Eq. 19, we replace Eq. 23 by

$$\text{at } r = 1{:}\ \frac{\partial^2 h}{\partial r^2} = C \tag{24}$$

where C, which is the difference between the sum of the principal curvatures for interface 1 and the sum of the principal curvatures for interface 2, is a free parameter, the value of which will be determined shortly.

For each value of C we can determine for a given value of B a tentative initial configuration of the film by integrating Eq. 19 consistent with Eq. 20–22 and 24. 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 15 can be integrated consistent with each of these tentative initial configurations, Eq. 20, 21, 9, and 10, the latter two boundary conditions first having been made dimensionless. Equation 22 permits us to identify R as a function of time; R_f is the value of R as $t' \to \infty$, which can be obtained from our numerical computation. We employed the Crank-Nicolson technique (Myers, 1971); accuracy was checked by decreasing the time and space intervals. We used $\Delta r = 0.02$ and $\Delta t' = 0.02 - 0.05$.

In addition to requiring that at time $t' = 0$ the thinning rate is

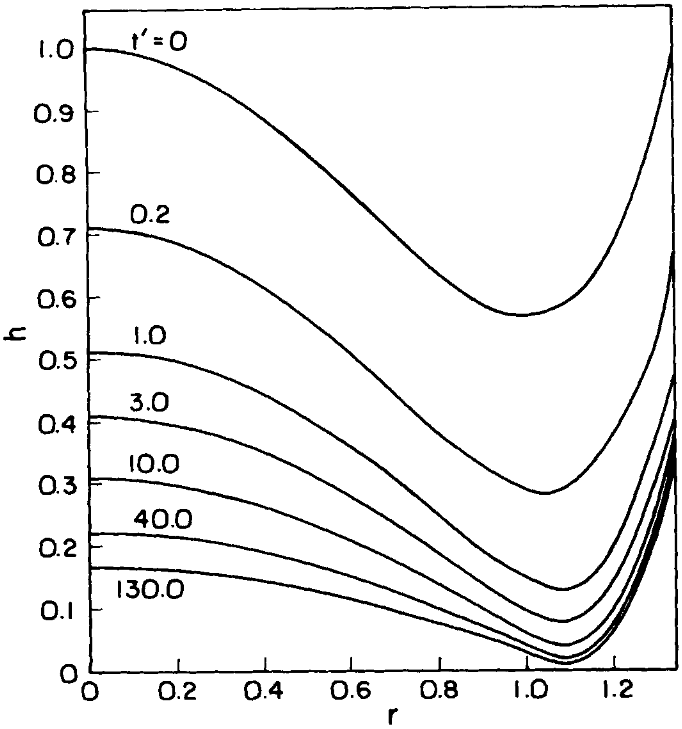

Figure 2. Dimensionless film thickness, *h*, as a function of dimensionless radial position and dimensionless time.
$R_h = 1.69$, $B = 0$, $m = 4$, $C = 5.05$.

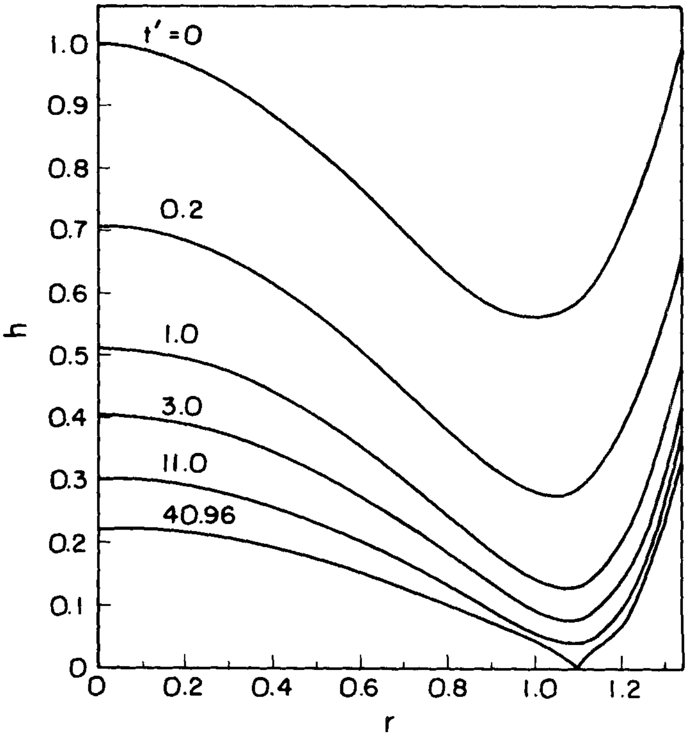

Figure 4. Dimensionless film thickness, *h*, as a function of dimensionless radial position and dimensionless time.
$R_h = 1.69$, $B = 10^{-8}$, $m = 4$, $C = 5.05$.

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, so long as the effects of any disjoining pressure are negligible. Our numerical computations indicate that, for sufficiently small $B > 0$, there is a minimum value of C such that the thinning rate at the center is always greater than the thinning rate at the rim in the early stage of the thinning process

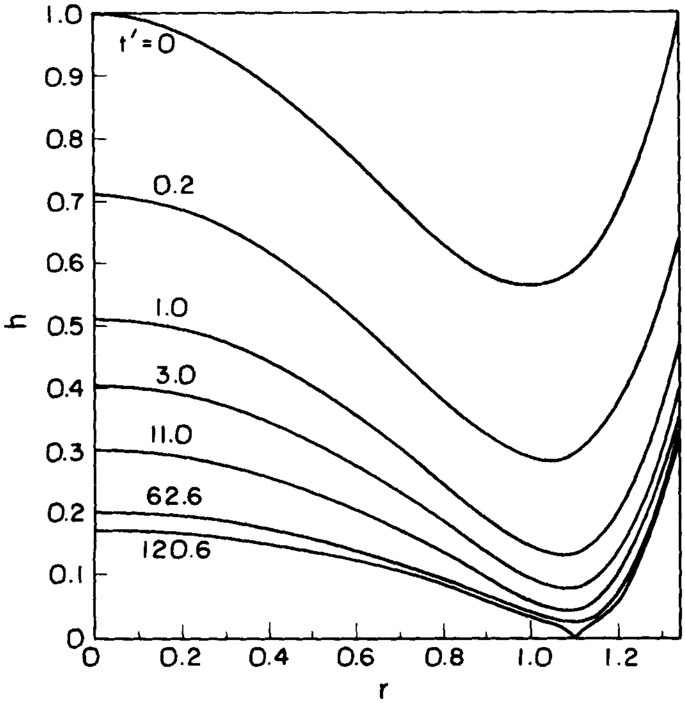

Figure 3. Dimensionless film thickness, *h*, as a function of dimensionless radial position and dimensionless time.
$R_h = 1.69$, $B = 10^{-7}$, $m = 4$, $C = 5.05$.

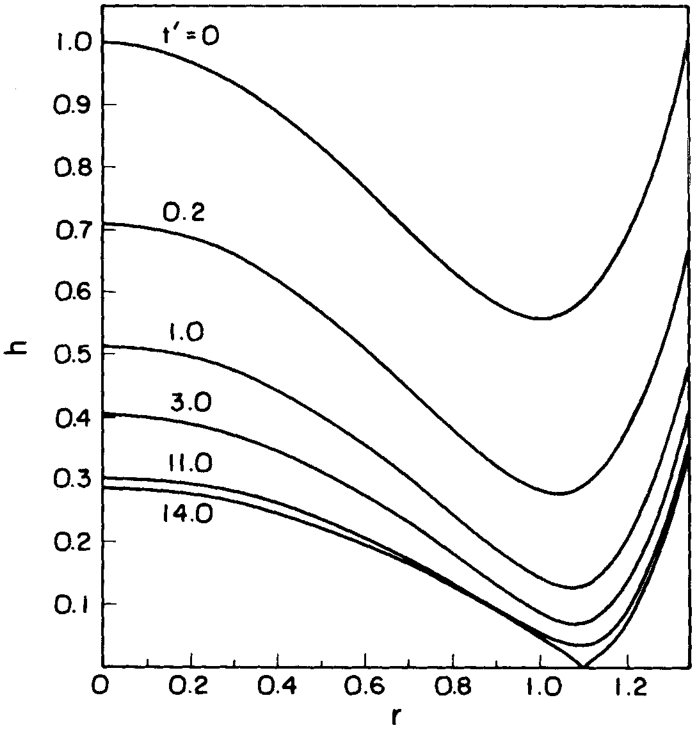

Figure 5. Dimensionless film thickness, *h*, as a function of dimensionless radial position and dimensionless time.
$R_h = 1.69$, $B = 10^{-6}$, $m = 4$, $C = 5.05$.

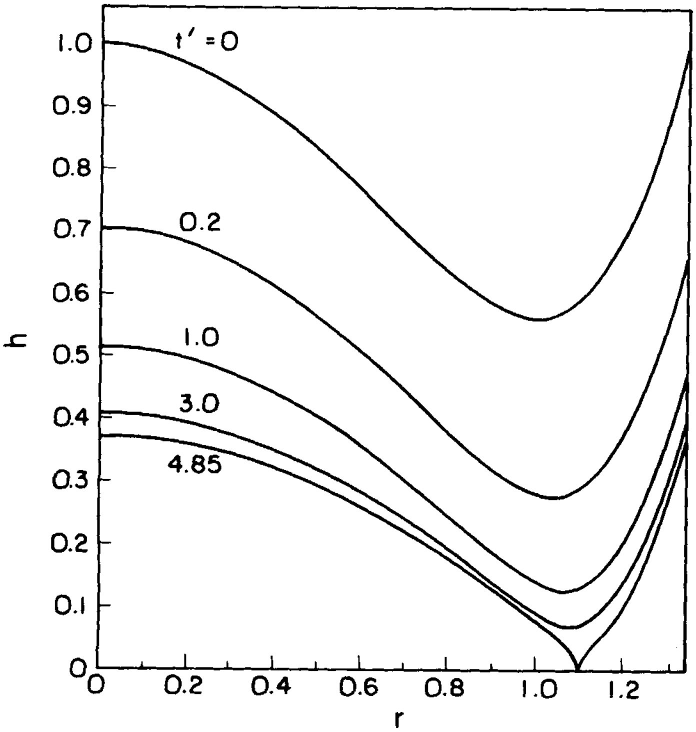

Figure 6. Dimensionless film thickness, *h*, as a function of dimensionless radial position and dimensionless time.
$R_h = 1.69$, $B = 10^{-5}$, $m = 4$, $C = 5.05$.

where the effects of the disjoining pressure can be neglected. 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.

For a drop freely approaching a liquid-liquid interface under the influence of gravity and of a disjoining pressure that is greater than or equal to zero, R_d^* is measured and R_f^* is determined by (Chappelear, 1961; Princen, 1963; Lin and Slattery, 1982b)

$$\text{as } t' \to \infty:\ R^* \to R_f^* = \left(\frac{4}{3}\,\frac{\Delta\rho^* g^*}{\gamma_0^*}\right)^{1/2} (R_d^*)^2 \qquad (25)$$

From Figures 2 through 7, as well as Figures 2 through 5 of Chen and Slattery (1982), we see that R_f is independent of the magnitude and sign of the disjoining pressure. There is no reason to believe that the initial film radius R_0^* should be dependent upon the magnitude or sign of the disjoining pressure. It follows that R_f^* must also be independent of the magnitude and sign of the disjoining pressure. This implies that Eq. 25 is valid for the case of a negative disjoining pressure as well, in the limit as the time at which the film ruptures is approached.

Having determined R_f^* from Eq. 25 and R_f from our numerical computation, we can identify $R_0^* = R_f^*/R_f$. From our numerical computation, we obtain $\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) = 12.58$ which allows us to determine h_0^* from Eq. 23.

We must now check whether assumption *ii* is satisfied at R_h; if it is satisfied here, it will be satisfied everywhere. It is desirable 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. If assumption *ii* cannot be satisfied by reducing R_h, C must be increased. For this reason, $h(r,t')$ is weakly dependent upon the bubble radius and the other physical parameters that enter Eq. 25.

RESULTS: FILM PROFILES

Figures 2 through 7 show the dimensionless film thickness h as a function of r and t' for $m = 4$ and varying values of $B \geq 0$. In each case the initial profiles are identical, suggesting that for sufficiently small values of B the effects of the disjoining pressure can be neglected during the early stage of the thinning process. Figure 8 also shows that the London-van der Waals forces are ineffective in the early stages of drainage, effective in the intermediate stages, and dominant in the latter stages. For relatively small values of B ($= 10^{-7}$ to 10^{-8}) the increase in the thinning rate that leads to film rupture is much smaller than that for larger values of B ($= 10^{-4}$ to 10^{-5}). For very small values of B, the film becomes very thin at the rim before the effect of the London-van der Waals forces is noticed.

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 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, since we have assumed symmetric profiles (assumption *i*). We have carried out our computations for only two of their systems.

Since insufficient data were given to identify our $t' = 0$ (see assumption *xi* and Eq. 19), we related our time scale to the experimental time scales by matching in each case the initial

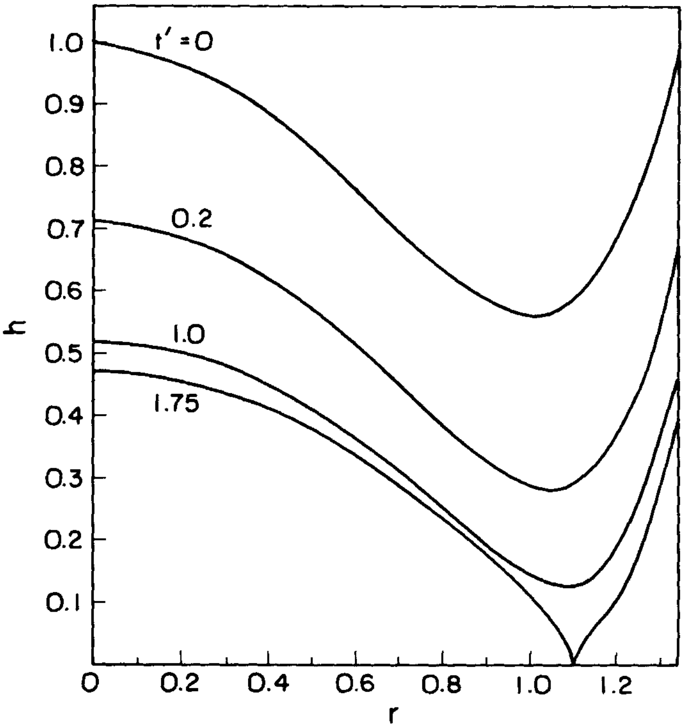

Figure 7. Dimensionless film thickness, *h*, as a function of dimensionless radial position and dimensionless time.
$R_h = 1.69$, $B = 10^{-4}$, $m = 4$, $c = 5.05$.

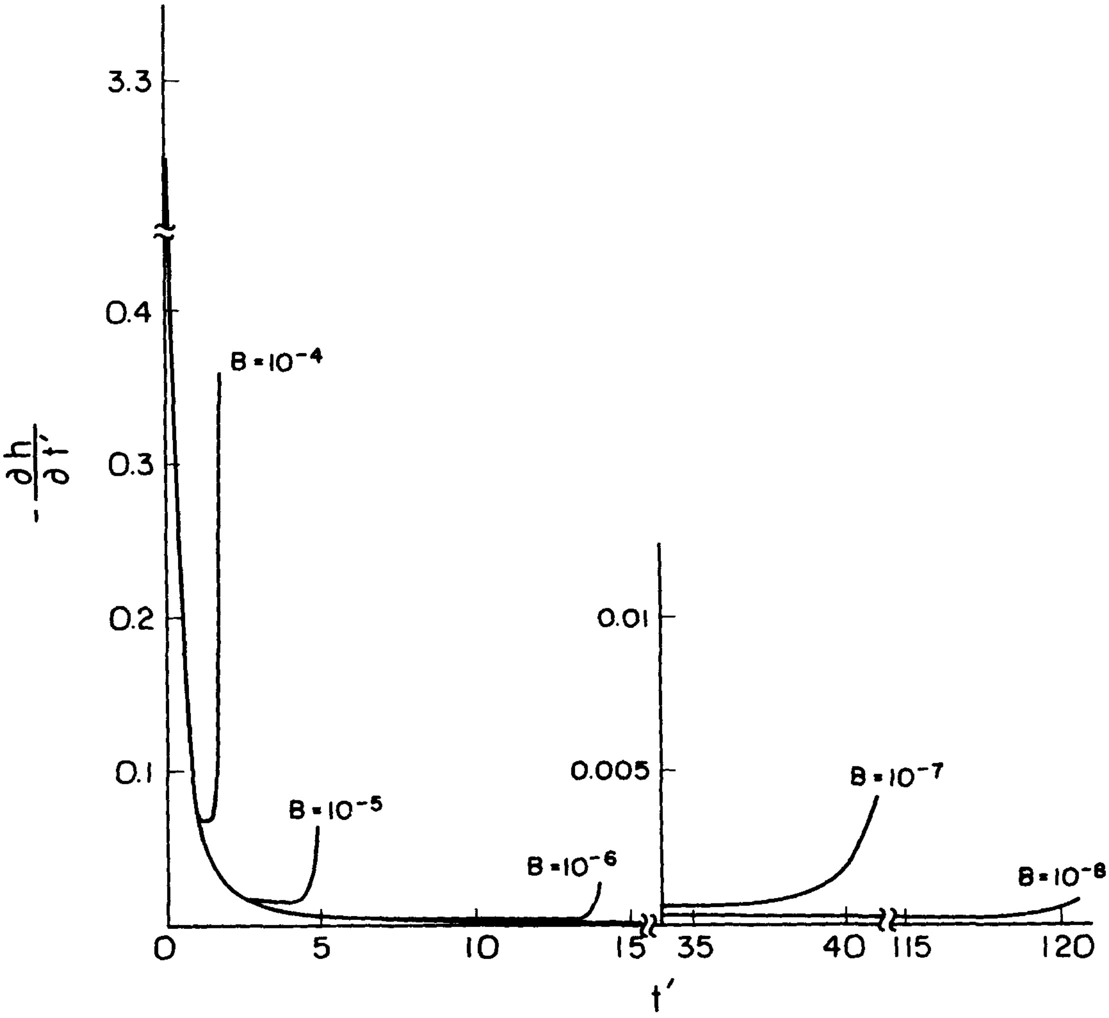

Figure 8. Dimensionless thinning rate $\partial h/\partial t'$ at the rim as a function of dimensionless time for different values of B.

measurement of the film thickness at the rim. As we shall demonstrate, we found it satisfactory to identify $R_h = 1.69$ for both systems. (Remember that R_h should be sufficiently large for the pressure gradient to be negligible and yet sufficiently small for assumption *ii* to remain valid.) Since the film thickness at the rim is generally larger than 120 Å (12 nm), we used $m = 4$ to describe the fully retarded London-van der Waals interaction potential in the film (Black et al., 1960; Churaev, 1974a). Because no values of B^* are available for these systems, in both cases we chose $B^* = 10^{-19}$ erg·cm (assumption *xv*) as an order of magnitude approximation.

Cyclohexanol-Water

Burrill and Woods (1973b) report observations for a cyclohexanol drop approaching a water-cyclohexanol interface: $R_d^* = 0.62$ mm, $\gamma_0^* = 3.93$ mN/m, $\mu^* = 1.0$ mPa·s, $\Delta\rho^* = 5.1 \times 10^{-2}$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

$$R_0^* = R_F^*/1.1 = 1.44 \times 10^{-2} \text{ cm}$$

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

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.

Burrill and Woods (1973b) measured film thickness as a function of time only at the center and at the rim. Figure 9 compares our computations ($R_h = 1.69$, $B = 1.26 \times 10^{-7}$, $m = 4$, $C = 5.05$), Lin and Slattery's (1982b) computations ($R_h = 1.69$, $B = 0$, $C = 5.05$), Burrill and Woods' (1973b) data, and Princen's (1963) estimation. [For a discussion of the limitations of Princen's approximation, see Lin and Slattery (1982b).] Both our time scale and Princen's time scale were adjusted by matching the theoretical predictions to the first experimental measurement at the rim. At shorter times ($t^* < 100$ s) when the film thickness is larger than the distance over which the London-van der Waals forces are effective, our predictions are identical with those of Lin and

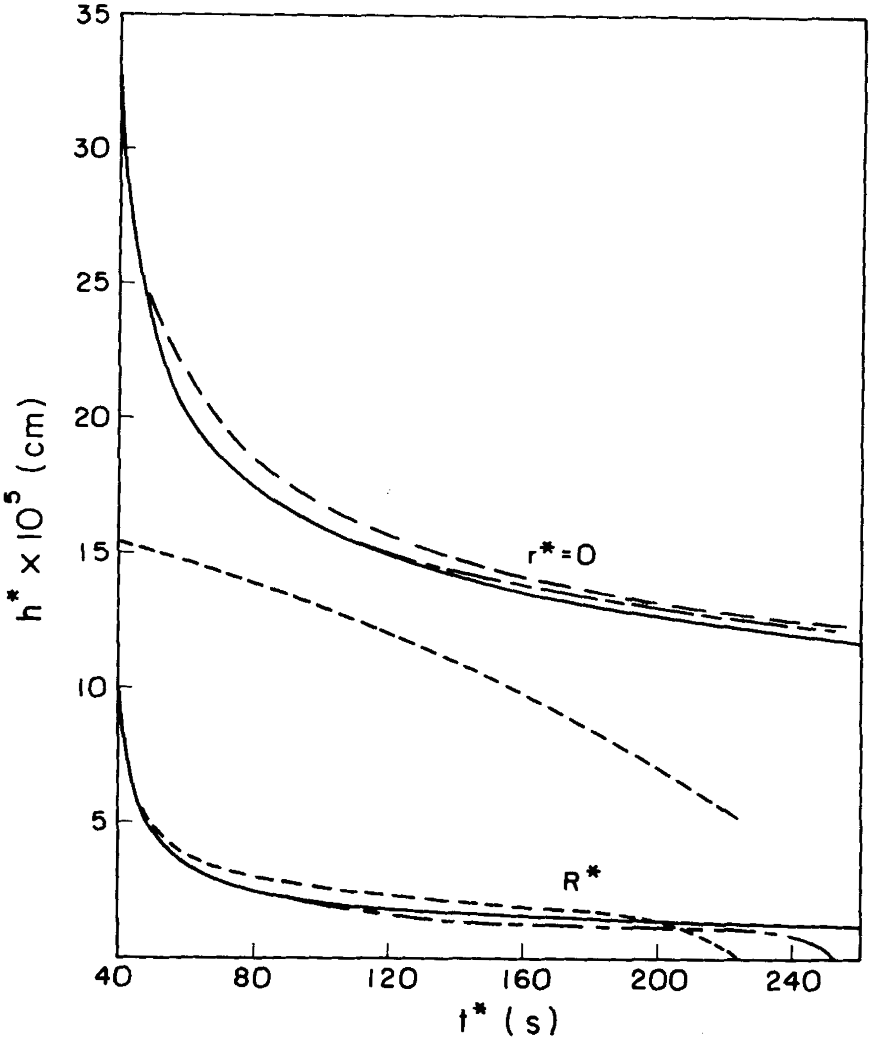

Figure 9. Comparisons of film thickness at center and at rim for a cyclohexanol-water system; t^* represents experimental time scale of Burrill and Woods (1973b).

— · — · — Present theory; $R_h = 1.69$, $B = 1.26 \times 10^{-7}$, $m = 4$, $C = 5.05$.

——— Lin and Slattery (1982b) theory; $R_h = 1.69$, $B = 0$, $C = 5.05$.

— — — Princen (1963) estimation; $n = 2$.

- - - - - - Burrill and Woods (1973b) measurements.

Slattery (1982b). But at longer times ($t^* > 120$ s), our theory predicts smaller rim thicknesses, larger center thicknesses, and slower draining than that of Lin and Slattery (1982b). This is attributable to the London-van der Waals component of the negative disjoining pressure, the effect of which is more pronounced at longer times when the film thickness at the rim is smaller.

Toluene-Water

Liem and Woods (1974) studied a toluene drop approaching a water-toluene interface: $R_d{}^* = 0.842$ mm, $\gamma_0{}^* = 33.5$ mN/m, $\mu^* = 1.0$ mPa·s, $\Delta\rho^* = 1.33 \times 10^{-1}$ g/cm^3. The water contained 10^{-4}M palmitic acid.

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

$$R_0^* = R_f^*/1.1 = 1.47 \times 10^{-2} \text{ cm}$$

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

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 10 compares our computations ($R_h = 1.69$, B = 5.80×10^{-8}, $m = 4$, C = 5.05), Lin and Slattery's (1982b) computations ($R_h = 1.69$, $B = 0$, $C = 5.05$), Liem and Woods' (1974) data, and Princen's (1963) estimation.

Discussion

There are several possible explanations for the difference be-

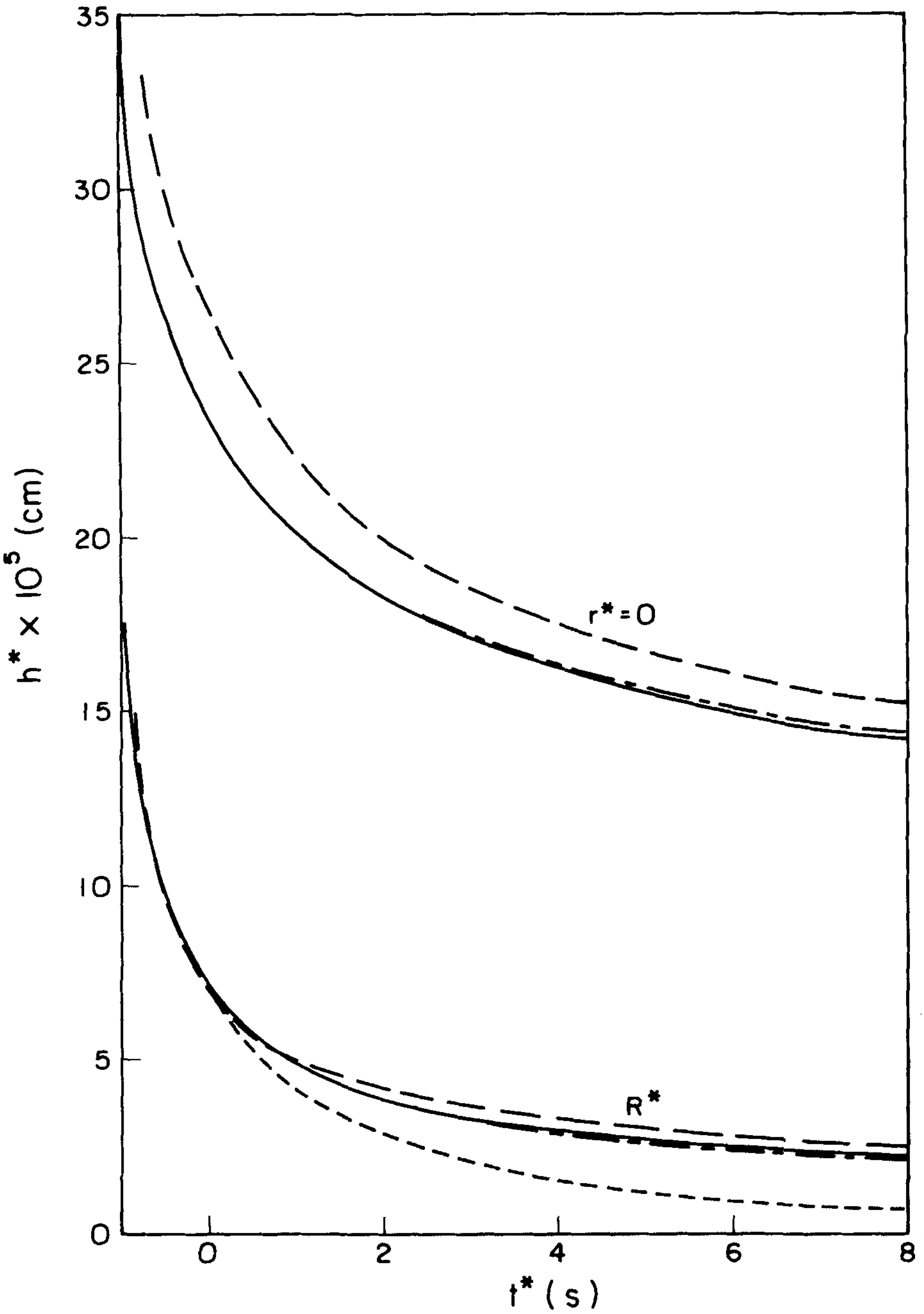

Figure 10. Comparisons of film thickness at center and at rim for a toluene-water system; t^* represents experimental time scale of Liem and Woods (1974).

— - — - — Present theory; $R_h = 1.69$, $B = 5.80 \times 10^{-8}$, $m = 4$, $C = 5.05$.

——— Lin and Slattery (1982b) theory; $R_h = 1.69$, $B = 0$, $C = 5.05$.

— — — Princen (1963) estimation; $n = 2$.

- - - - - - - Liem and Woods (1974) measurements.

tween our computations and the experimental data shown in Figures 9 and 10.

In most of the experimental data of Burrill and Woods (1973b) and Liem and Woods (1974), there is evidence of asymmetric drainage patterns, indicating instabilities. To the extent that this was true also for the data discussed here, we could not expect good agreement between our theory and the experimental data, since our theory assumes symmetric profiles (assumption *i*). For more about the development of asymmetric instabilities, see the next section.

Since the experimental film thickness at the rim is substantially less than 400 Å (40 nm) at long times, it may not be justified to assume $m = 4$ (assumption *xv*).

We know that the value for B^* we have assumed is only an approximation (assumption *xv*).

The interfaces may not have been entirely immobile as presumed both in our theory (assumption *iv*) and in the estimation of Princen (1963).

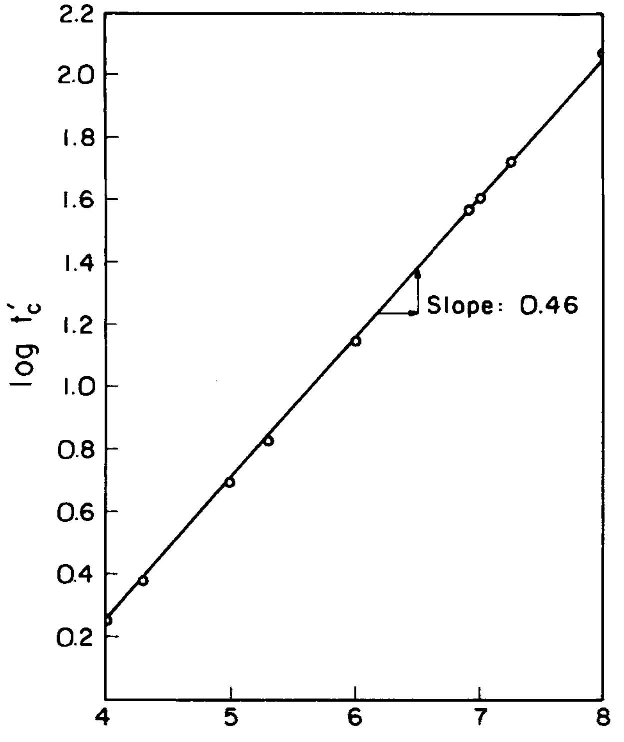

Figure 11. Dependence of t_c' on B.

RESULTS: COALESCENCE TIMES

Let us define t_c' as the dimensionless time at which the film thickness at the rim goes to zero or the dimensionless time at which the film ruptures. We will refer to this as our dimensionless coalescence time.

Our numerical computations give the graphical relationship between t_c' and B shown in Figure 11. Alternatively, we can express this relationship as

$$t_c' = 2.5 \times 10^{-2} B^{-0.46} \tag{26}$$

In using this relationship, we recommend that Eq. 25 be employed to identify

$$R_0^* = \frac{R_f^*}{1.1} = 1.05 \left(\frac{\Delta\rho^* g^*}{\gamma_0^*} \right)^{1/2} (R_d^*)^2 \tag{27}$$

The dimensionless mean curvature at $r = R_h$ was generated in our computation to be 12.58. This together with Eq. 23 and 27 fixes the initial film thickness at the center:

$$h_0^* = 0.175 \frac{\Delta\rho^* g^* (R_d^*)^3}{\gamma_0^*} \tag{28}$$

In view of Eqs. 16, 27, and 28, Eq. 26 may be rearranged as

$$t_c^* = 0.79 \frac{\mu^* (R_d^*)^{4.06} (\Delta\rho^* g^*)^{0.84}}{\gamma_0^{*1.38} B^{*0.46}} \tag{29}$$

Allan et al. (1961) report that, instead of Eq. 25, their experimental measurements of R_f^* were better described as though the drop were approaching an immobile, plane interface. This implies as an alternative to Eq. 27 (Derjaguin and Kussakov, 1939; Lin and Slattery, 1982a)

$$R_0^* = \frac{R_f^*}{1.1} = 0.742 \left(\frac{\Delta\rho^* g^*}{\gamma_0^*} \right)^{1/2} (R_d^*)^2 \tag{30}$$

The corresponding initial film thickness at the center is

$$\bar{h}_0^* = 8.75 \times 10^{-2} \frac{\Delta\rho^* g^* (R_d^*)^3}{\gamma_0^*} \tag{31}$$

Using Eqs. 16, 30, and 31, we find that Eq. 26 gives

$$\bar{t}_c^* = 0.44 \frac{\mu^* (R_d^*)^{4.06} (\Delta\rho^* g^*)^{0.84}}{\gamma_0^{*1.38} B^{*0.46}} \tag{32}$$

(We use the overbar here to remind ourselves that Eq. 30 is being employed rather than Eq. 27.)

Table 1 lists the theoretical expressions for the coalescence time developed by Chen et al. (1984) for their model, for the plane parallel disc model, and for the cylindrical drop model.

The experimentally observed rest time or coalescence time is the elapsed time during which an experimentalist perceives a drop to be resting on an interface before coalescence occurs. It does not begin at what we have defined to be $t^* = 0$ in our computations, but the difference must be very small. Marrucci (1969) describes coalescence as occurring in two stages. During the first stage, the dimpled film is formed very rapidly; during the second, the film drains until it ruptures and coalescence occurs. Our computations, as well as those described by Chen et al. (1984), are intended to approximate this second stage, neglecting the very small additional time required to execute the first stage.

For lack of better information, we again choose $B^* = 10^{-19}$ erg·cm and $m = 4$ (assumption *xv*) in comparing these various theoretical results with the available experimental data.

Comparing our results in the forms of Eq. 29 and 32 with those developed by Chen et al. (1984) in Table 1, we see that the general trends are similar. The functional dependence of coalescence time upon system properties such as drop diameter, viscosity of the draining film, interfacial tension, and the London-van der Waals constant B^* was discussed by Chen et al. (1984). The cylindrical drop model predicts that the coalescence time is independent of the density difference in contrast with the other models, but the available experimental data do not permit discrimination on this basis.

TABLE 1. OTHER EXPRESSIONS FOR COALESCENCE TIME FROM A LINEAR STABILITY ANALYSIS OF CHEN ET AL. (1984)

Coalescence Time	Remarks
$t_{c(4)}^* = 1.070 \frac{\mu^* R_d^{*3.4}}{\gamma^{*1.2} B^{*0.4}} (\Delta\rho^* g^*)^{0.6}$	Rim of dimpled film
$\bar{t}_{c(4)}^{*\dagger} = 0.705 \frac{\mu^* R_d^{*3.4}}{\gamma^{*1.2} B^{*0.4}} (\Delta\rho^* g^*)^{0.6}$	
$t_{c(M)}^* = 1.046 \frac{\mu^* R_d^{*4.5}}{\gamma^{*1.5} B^{*0.5}} (\Delta\rho^* g^*)$	Plane parallel disc model (MacKay and Mason, 1963)
$\bar{t}_{c(M)}^{*\dagger} = 0.370 \frac{\mu^* R_d^{*4.5}}{\gamma^{*1.5} B^{*0.5}} (\Delta\rho^* g^*)$	
$t_{c(H)}^* = 5.202 \frac{\mu^* R_d^{*1.75}}{\gamma^{*0.75} B^{*0.25}}$	Cylindrical drop model (Hodgson and Woods, 1969)

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† Overbar indicates that Eq. 30 was used rather than Eq. 27.

TABLE 2. COMPARISONS WITH EXPERIMENTAL DATA OF MACKAY AND MASON (1963)

	System				
	1	2	3	4	5
γ^*, mN/m	14.0	34.1	19.1	34.1	19.1
$\Delta\rho^*$, gm/cm^3	0.0538	0.1145	0.0483	0.1145	0.0483
μ^*, mN·s/m$^2 \times 10^{-2}$	0.0522	0.0463	0.192	0.01	0.01
R_d^*, cm	0.0325	0.0425	0.0425	0.0425	0.0425
N_{Bo}	0.0040	0.0059	0.0045	0.0059	0.0045
t^*_{exp}, s	8.1	17.6	>90	<4	<4
$t^*_{c(4)}$, s[$\bar{t}^*_{c(4)}$, s]	8.8 [5.8]	10.5 [6.9]	51.6 [34]	2.3 [1.5]	2.7 [1.8]
$t^*_{c(M)}$, s[$\bar{t}^*_{c(M)}$, s]	34.8 [12.3]	58.0 [20.5]	242 [85.7]	12.4 [4.4]	12.7 [4.5]
$t^*_{c(H)}$, s	5.2	3.8	24.5	0.8	1.3
t^*_c, [$\bar{t}^*_c$, s]	15.0 [8.4]	21.8 [12.2]	97.7 [54.4]	4.7 [2.6]	5.1 [2.8]

Sys.	Drop-Bulk Phase
1	H_2O-cinnamaldehyde
2	H_2O-diphenyl sulphide
3	H_2O-dibutyl phthalate
4	Diphenyl sulphide-H_2O
5	Dibutyl phthalate-H_2O

Equations 29 and 32 are in good agreement with the experimental data of MacKay and Mason (1963), as shown in Table 2. Since they used all of their materials in the condition in which they were received, and since it is very difficult to produce and maintain uncontaminated aqueous solutions, we follow the suggestion of Platikanov (1964) in assuming that some surface-active material was present and that both interfaces are immobile.

The comparison with the experimental data of Woods and Burrill (1972; Burrill and Woods, 1973b) in Table 3 is mixed. Going from left to right in Table 3, they experienced increasing difficulties with asymmetric instabilities, which are not taken into account in our analysis. Our computations also neglect the effect of any electrostatic double layer (assumpiton *ix*). They added KCl in an attempt to minimize this effect, but clearly there was some difference between the two cyclohexanol-water systems shown that was not taken into account here. Burrill and Woods (1973a) pointed out that the cause of film rupture was often seen to be dust, dirt, or local depressions in film thickness. Since our computation assumes sysmmetric drainage and fully immobile interfaces free of dust, our estiamte of the coalescence time could be expected at best to be only an upper bound, given the proper magnitude of B^* and assuming that electrostatic forces could be neglected.

All theories other than the cylindrical drop model overestimate the coalescence times observed by Allan et al. (1961) in Table 4. We do not attach any significance to the fact that the cylindrical drop model gives a better representation of the experimental data. The analysis of Hodgson and Woods (1969) was unrealistic (Chen et al., 1984). Perhaps our estimate of B^* was too small for this system (assumption *xv*) or the interfaces are partially mobile.

Notice in Tables 2 through 4 that our estimate t_c^* for the coalescence time is always two to three times larger than the comparable estimate $t_{c(4)}^*$ by Chen et al. (1984). This might suggest that Chen et al. have more accurately accounted for the development of instabilities in their analysis. We do not believe that this is the case. We follow Neitzel and Davis (1981) in

TABLE 3. COMPARISONS WITH DATA OF WOODS AND BURRILL (1972; BURRILL AND WOODS, 1973b)

	System				
	1		2	3	4
Conc. SLS*, gm/L	10^{-4}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
Normality KCl	0.05	0.01	0.01	0.01	0.01
γ^*, mN/m	3.93		20.5(25)**	28.9	35(33.5)**
$\Delta\rho$,* gm/cm^3	0.051		0.0097	0.053	0.133
μ, mN·s/m$^2 \times 10^{-2}$	0.01		0.01	0.01	0.01
R_d^*, cm	0.062		0.1061	0.1061	0.1061
N_{Bo}	0.049		0.0052	0.020	0.042
t^*_{exp}, s	~204	<110	<15	<16	<12
$t^*_{c(4)}$, s[$\bar{t}^*_{c(4)}$, s]	67.5 [44.5]		21.3 [14.1]	39.2 <25.8]	54.1 [35.6]
$t^*_{c(M)}$, s[$\bar{t}^*_{c(M)}$, s]	780 [276]		141.3 [50.0]	455.2 [161.5]	859.4 [304.0]
$t^*_{c(H)}$, s	8.1		6.0	4.6	4.0
t^*_c, s[$\bar{t}^*_c$, s]	219 [122]		49.2 [27.4]	127 [71.0]	212 [118]
Remarks	Composite of even and uneven drainage		Uneven drainage at $t^* = 1$ s	Uneven drainage from $t^* = 4$ s	Uneven drainage at $t^* = 8$ s

Sys.	Drop-Bulk Phase
1	Cyclohexanol-water
2	Anisol-water
3	CA-water (CA = mixture of 0.84 mole fraction anisole with 0.16 mole fraction cyclohexane)
4	Toluene-water

* Sodium lauryl sulfate

** Liem and Woods (1974) report different values from those given by Woods and Burrill (1972; Burrill and Woods, 1973a). Here we use only the first values.

TABLE 4. COMPARISONS WITH DATA OF ALLAN ET AL. (1961) FOR RISING NITROGEN BUBBLES AT 20°C

	System							
	1	2	3	4	5	6	7	8
γ^*, mN/m	63.6	64.1	64.5	61.5	52.0	35.3	34.5	32.0
ρ^*, gm/cm^3	1.2535	1.2367	1.2221	1.2371	1.2362	1.0447	1.0378	1.0295
μ,* mN·s/m^2 × 10^{-2}	8.05	2.65	1.15	2.75	2.61	8.02	2.63	1.13
R_d^*, cm	0.0285	0.0285	0.0285	0.0285	0.0285	0.0275	0.0275	0.0275
N_{Bo}	0.016	0.015	0.015	0.016	0.019	0.022	0.022	0.024
t^*_{exp}, s	340	18.1	14.9	28.0	>360	>360	69.1	40.0
$t^*_{c(4)}$, s[$\bar{t}^*_{c(4)}$, s]	938 [618]	302 [199]	131 [86]	329 [217]	382 [252]	1,507 [993]	442 [291]	247 [163]
$t^*_{c(M)}$, s[$\bar{t}^*_{c(M)}$, s]	7,186 [2,542]	2,307 [816]	981 [347]	2,547 [901]	3,109 [1,100]	12,289 [4,347]	4,144 [1,466]	1,976 [699]
$t^*_{c(H)}$, s	207	68	29	73	78	301	101	46
t^*_c, s [$\bar{t}^*_c$, s]	2,370 [1,320]	763 [425]	325 [181]	839 [467]	1,003 [558]	3,949 [2,199]	1,329 [740]	629 [350]

Sys.	Aqueous Glycerol
1	97% (no emulsifier)
2	91% (no emulsifier)
3	85% (no emulsifier)
4	91% (with 0.0025% Tween 20)
5	91% (with 0.0050% Tween 20)
UNICON Oil Mixture	
6	(1)
7	(2)
8	(3)

believing that the small truncation errors inherent in our computations are sufficient to constitute small disturbances. This suggests that our resulting numerical solution follows the mathematically most stable path as a function of time and consequently allows for the development of all physical instabilities consistent with axisymmetric profiles. In contrast, Chen et al. examine the consequence of a small perturbation in the thickness of the film at the rim without explicit assurance that the perturbation develops in a manner consistent with their assumption of axisymmetry.

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NOTATION

b_m^* = mutual force per unit mass
B^* = London-van der Waals constant
B = dimensionless London-van der Waals constant defined by Eq. 16
C = parameter in Eq. 24
g^* = magnitude of acceleration of gravity
h^* = film thickness
h = dimensionless film thickness defined by Eq. 16
h_0^* = film thickness at $t^* = 0$ and $r^* = 0$
h_1^* = configuration of the fluid-fluid interface
h_2^* = configuration of the drop-fluid interface
k = perturbation parameter defined as h_0^*/R_0^*
m = parameter in Eq. 14
N_{Bo} = Bond number defined by Eq. 11
N_{ca} = capillary number defined by Eq. 17
p^* = pressure in liquid film
p = dimensionless pressure defined as $(p^* - p_o^*)\ \rho^* R_0^2/\mu^{*2}$
$\mathbf{P}$ = projection tensor that transforms any vector on the interface into its tangential component
p_h^* = hydrostatic pressure
p_o^* = pressure within the drop
r^* = cylindrical coordinate
r = dimensionless cylindrical coordinate defined by Eq. 16
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 $t \rightarrow \infty$ or just prior to the development of an instability and coalescence
R_f = defined as R_f^*/R_0^*
R_h^* = radial position where the pressure p^* within the draining film approaches the local hydrostatic pressure in the neighborhood of the bubble
R_0^* = rim radius of the drop at $t^* = 0$
R_h = defined as R_h^*/R_0^*
t^* = time
t' = dimensionless time defined by Eq. 16
t_c' = dimensionless time at which the film ruptures
$\underline{t}_c^*$ = predicted coalescence time defined by Eq. 29
$\bar{t}_c^*$ = predicted coalescence time defined by Eq. 32
$\underline{t}_c(4)^*$ = predicted coalescence time defined in Table 1
$\bar{t}_c(4)^*$ = predicted coalescence time defined in Table 1
t_{exp}^* = experimentally observed coalescence time
$t_{c(\mathrm{H})}^*$ = predicted coalescence time defined in Table 1
$\underline{t}^*_{c(\mathrm{M})}$ = predicted coalescence time defined in Table 1
$\bar{t}^*_{c(\mathrm{M})}$ = predicted coalescence time defined in Table 1
$\mathbf{v}^*$ = velocity vector
z^* = cylindrical coordinate

Greek Letters

α = order of dimensionless velocity assumed by Eq. A3
β = order of N_{ca} assumed by Eq. A4
γ^* = interfacial tension
γ_0^* = equilibrium interfacial tension
μ^* = bulk viscosity of the liquid film
π^* = disjoining pressure defined by Eq. 14
ρ^* = density of the liquid film
$\Delta\rho^*$ = density difference between liquid film and the drop
ϕ^* = potential energy per unit mass of the liquid film
ϕ_0^* = ϕ^* evaluated in the limit as the fluid-fluid interface is approached
Φ_B^* = interaction potential energy per unit volume of the semiinfinite film liquid in the limit as the interface is approached.

APPENDIX: MAGNITUDE OF THE INTERFACIAL TENSION GRADIENT

We have simplified our analysis by adopting the lubrication theory approximation (assumption *iii*). Alternatively, we could say that we have carried out a first-order perturbation analysis with

$$k \equiv h_0^*/R_0^* \tag{A1}$$

as the perturbation parameter. One advantage of this latter point of view is that we can more easily make a statement about the magnitude of the interfacial tension gradient required to achieve an immobile interface, when the effects of surface viscosities are neglected.

After the introduction of dimensionless variables (Lin and Slattery, 1982b, Eq. 9), we assume

$$\frac{\partial}{\partial r}, \frac{\partial}{\partial z} = 0(1) \text{ as } k \to 0 \tag{A2}$$

$$v_r, v_z = 0(k^{\alpha}) \text{ as } k \to 0 \tag{A3}$$

$$N_{ca} = 0(k^{\beta}) \text{ as } k \to 0 \tag{A4}$$

Let us begin by examining the r component of the Navier-Stokes equation (Lin and Slattery, 1982b, Eq. 12), keeping in mind that pressure p^* must be replaced by the modified pressure $p^* + \rho^*\phi^*$. This implies that

$$p = 0(k^{\alpha-2}) \text{ as } k \to 0 \tag{A5}$$

From the z component of the jump momentum balance, we observe that

$$\alpha + \beta = 3 \tag{A6}$$

We conclude from the r component of the jump momentum balance (Lin and Slattery, 1982b, Eqs, 15 and 17)

$$\frac{\partial \gamma}{\partial r} = 0(k^2) \tag{A7}$$

which can be safely neglected in our lubrication theory or first-order perturbation analysis.

This is consistent with the analysis of Lin and Slattery (1982b) and assumption *iv*.

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