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Coalescence Time for a Small Drop or Bubble at a Fluid-Fluid Interface

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When a small drop or bubble is driven through a liquid phase to a fluid-fluid interface, a thin liquid film which forms between them drains, until an instability forms and coalescence occurs. Lin and Slattery (1982b) developed a hydrodynamic theory for the first portion of this coalescence process: the drainage of the thin liquid film which occurs while it is sufficiently thick that the effects of London-van der Waals forces and electrostatic forces can be ignored. Here we extend their theory to include the effects of the London-van der Waals forces. To simplify the analysis, we follow the suggestion of Buevich and Lipkina (1975, 1978) in developing an expression for the rate of thinning at the rim or barrier ring of the draining film. A linear stability analysis permits us to determine the coalescence time or the elapsed time between the formation of a dimpled film and its rupture at the rim.

For comparison, this same linear stability analysis is applied to the thinning equations developed by MacKay and Mason (1963) for the plane parallel disc model and by Hodgson and Woods (1969) for the cylindrical drop model.

For all three models, our linear stability estimate for the coalescence time t_c is in better agreement with the available experimental data than is the elapsed time t_∞ between the formation of a dimpled film and its drainage to zero thickness at the rim in the absence of instabilities.

SCOPE

The rate at which drops or bubbles suspended in a liquid coalesce is important to the preparation and stability of emulsions, of foams and of dispersions, to liquid-liquid extraction, to the formation of an oil bank during the displacement of oil from a reservoir rock, and to the displacement of an unstable foam used for mobility control in a tertiary oil recovery process.

On a smaller scale, when two drops (or bubbles) are forced to approach one another in a liquid phase or when a drop is driven through a liquid phase to a fluid-fluid interface, a thin liquid film forms between the two interfaces and begins to drain. As the thickness of the draining film becomes sufficiently small (about 1,000 Å), the effects of the London-van der Waals forces and of any electrostatic double layer become significant. Depending upon the sign and the magnitude of the disjoining pressure attributable to the London-van der Waals forces and the repulsive force of any electrostatic double layer, there may be a critical thickness at which the film becomes unstable, ruptures and coalescence occurs.

Lin and Slattery (1982b) considered the early stage of this coalescence process, when the draining film is sufficiently thick that the effects of the London-van der Waals forces and of any electrostatic double layer can be neglected. To simplify the

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problem, they considered only the case of small drops or bubbles and they assumed that the liquid films are so thin that the Reynolds lubrication theory approximation could be applied.

We extend their theory to include the effects of London-van der Waals forces on the drainage process. To simplify the problem, we follow the suggestion of Buevich and Lipkina (1975, 1978) in developing an expression for the rate of thinning at the rim or barrier ring of the draining film. A linear stability analysis of this relationship permits us to determine the critical rim thickness at which an instability develops. In this way, we estimate t_c, the coalescence time or the elapsed time between the formation of the dimpled film and its rupture at the rim.

For comparison, this same linear stability analysis is applied to the thinning equations of MacKay and Mason (1963) for the plane parallel disc model and of Hodgson and Woods (1969) for the cylindrical drop model.

The results for our model, for the plane parallel disc model and for the cylindrical drop model, are compared with the experimental data of MacKay and Mason (1963), of Woods and Burrill (1972, 1973b), and of Allan et al. (1961).

CONCLUSIONS AND SIGNIFICANCE

For all three models, our linear stability estimate t_c for the coalescence time is generally in better agreement with the experimental data of MacKay and Mason (1963), of Woods and Burrill (1972, 1973b), and of Allan et al. (1961) than is t_∞, the elapsed time between the formation of a dimpled film and its drainage to zero thickness at the rim in the absence of instabilities.

The coalescence time increases as: the bubble or drop diameter increases; the viscosity of the drainage film increases; the interfacial tension decreases; the strength of the London-van der Waals forces decreases; and the density difference between the two phases increases.

The available experimental data do not permit a definitive conclusion concerning the relative merit of our model, the plane parallel disc model of MacKay and Mason (1963), and the cylindrical drop model of Hodgson and Woods (1969). The comparison is hampered by the absence of a sufficiently accurate *a priori* estimate of the strength of the London-van der Waals forces.

INTRODUCTION

In examining prior studies, it is helpful to consider separately those pertinent to the early stage of thinning in which the effects of any disjoining pressure are negligible, those describing the latter stage of thinning in which the disjoining pressure may be controlling, and those concerned with the stability of the film. [Interesting reviews are also given by Sheludko (1967), Buscall and Ottewill (1975), Ivanov and Jain (1979), Jain et al. (1979), and Ivanov (1980).]

INITIAL STAGE OF THINNING

In the initial stage of thinning, the effects of London-van der Waals forces and of electrostatic forces can be neglected.

As a drop (or bubble) 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) and a dimpled film is formed. Allan et al. (1961) found that the dimpling developed when the film was 0.3 to 1.2 μm thick. The rim radius is a function of time (Allan et al., 1961; MacKay and Mason, 1963; Hodgson and Woods, 1969).

Princen (1963) extended 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). But, just as in the Frankel and Mysels (1962) theory, there is an adjustable parameter (an initial time) that has no physical significance.

Hartland (1970) developed a more detailed analysis to predict film thickness as a function 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.

Lin and Slattery (1982b) developed a more complete hydrodyanmic theory for the thinning of a liquid film between a small, nearly spherical drop and a fluid-fluid interface. Their theory is in reasonable agreement with data of Woods and Burrill (1972), Burrill and Woods (1973b), and Liem and Woods (1974) for the early stage of thinning in which any effects of London-van der Waals forces and of electrostatic forces generally can be neglected. [Because their theory assumes that the drop is small and nearly spherical, it could not be compared with Hartland's (1967, 1968, 1969) data for larger drops.]

LATER STAGE OF THINNING

For a drop or bubble forced to approach its homophase, the contribution of the London-van der Waals forces to the disjoining pressure is always negative. The effect is to enhance the rate of thinning at the rim and destabilize the film. This effect becomes significant, when the film thickness is of the order of 1,000 Å and increases with decreasing film thickness. When the film thickness at the rim is reduced to a few hundred angstroms, the London-van der Waals forces become sufficiently strong that the film ruptures at the rim.

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 (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 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.

The effect of drop size on the coalescence time has been studied by Gillespie and Rideal (1956), Charles and Mason (1960), Jeffreys and Hawksley (1965), Hodgson and Lee (1969), Komasawa and Otake (1970), Lang and Wilke (1971), Woods and Burrill (1972), and Burrill and Woods (1973b). All the researchers, with the exceptions of Hodgson and Lee (1969) and of Lange and Wilke (1971), found that the rest time increased with drop size.

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.

STABILITY OF THIN FILMS

Because of its simple geometry, plane parallel thinning films, both radially unbounded and radially bounded, have received the most attention (Vrij, 1966; Vrij and Overbeek, 1968; Scheludko and Manev, 1968; Ivanov et al., 1970; Ivanov and Dimitrov, 1974; Manev et al., 1974; Gumerman and Homsy, 1975; Jain et al., 1979; Ivanov et al., 1979; Ivanov, 1980).

The critical thickness of a free, circular, plane parallel, thinning film decreases with increasing surfactant concentration (Scheludko and Manev, 1968; Ivanov et al., 1970; Manev et al., 1974; Ivanov, 1980) and decreasing radius (Scheludko and Manev, 1968; Ivanov et al., 1970; Manev et al., 1974; Gumerman and Homsy, 1975; Ivanov, 1980). This means that smaller films containing more concentrated surfactant are more stable than larger films containing less concentrated surfactant.

We can expect that the stability of a thinning film formed between a drop (or bubble) and a fluid-fluid interface is somewhat different from that predicted for a plane parallel film. For example, Gumerman and Homsy (1975) predict that a free, circular, plane parallel, thinning film will rupture at its center, where the minimum thickness occurs during a fluctuation according to their analysis. But as a drop or bubble approaches a fluid-fluid interface, the minimum thickness is at the rim, and rupture occurs off-center (Charles and Mason, 1960; Burrill and Woods, 1973a).

ANALYSIS OF PROBLEM

Motivated by the experimental observations and by the analysis of Buevich and Lipkina (1978), we obtain an expression for the rate of thinning at the rim and we construct a linear stability analysis of this thinning equation. When the film thickness at the rim is less than a critical value, the film is unstable and rupture occurs. In this way, we are able to predict the coalescence time.

We make a number of assumptions.

i) Viewed in the cylindrical coordinate system for Figure 1, the two interfaces bounding the draining 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 radius of the film and h_0 the characteristic thickness of the film. The Reynolds lubrication theory approximation applies in the sense that

$$\left(\frac{h_0}{R}\right)^2 \ll 1 \tag{4}$$

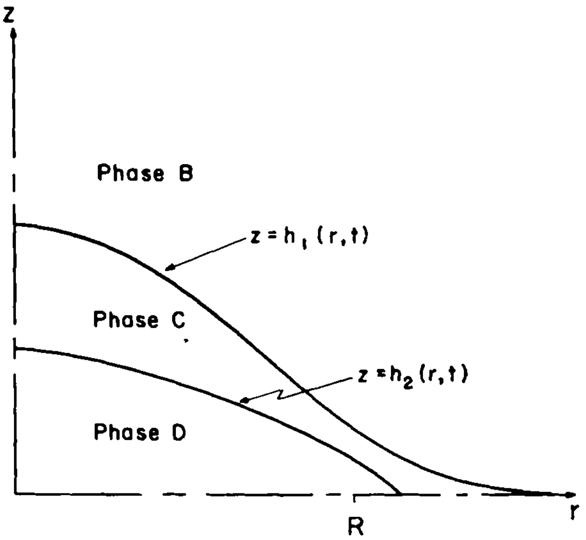

Figure 1. A symmetric drop or bubble (phase D) moves through a liquid (phase C) as it approaches a fluid-fluid interface (between phases C and B). The configuration of the drop-fluid interface is given by $z = h_2(r,t)$; that of the fluid-fluid interface by $z = h_1(r,t)$. The rim or barrier ring of the draining liquid film of phase C is located at $r = R$.

iv) If there is a surfactant present, the tangential components of velocity **v** at the fluid-fluid interface are zero and the interfacial tension gradient required to achieve this condition is very small, which has been verified for drops or bubbles approaching a solid plane by Lin and Slattery (1982a). These interfaces will be termed *immobile*.

v) Mass transfer at the fluid-fluid interface is neglected.

vi) Viscous effects are neglected within the bubble or drop phase. Since the fluid-fluid interface is immobile, the analysis applies to both a gas bubble and a liquid drop, since it is reasonable to assume that all circulation within a liquid drop would be suppressed.

vii) The pressure p_o within the bubble or drop is independent of time and position. The pressure within phase B is equal to the local hydrostatic pressure.

viii) Phase C, of which the draining liquid film is composed, is an incompressible, Newtonian fluid, the viscosity of which is a constant.

ix) All inertial effects are neglected.

x) The effects of gravity and of electrostatic forces are neglected within the draining liquid film. The effect of London-van der Waals forces is taken into account.

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

$$N_{Bo} \equiv \frac{\Delta\rho g R_d^2}{\gamma} \ll 1 \tag{5}$$

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

xii) The rim radius R is independent of time. If the effect of any London-van der Waals forces is neglected, there is a 10% change in R (Lin and Slattery, 1982b).

xiii) The pressure drop in the film from the center to the rim will be approximated by

$$p_c - p_r \doteq \frac{\gamma}{R_d} \tag{6}$$

where p_c and p_r are the pressure in the film at the center and that immediately outside the rim respectively. The assumption here is that p_c and p_r can be approximated by the values appropriate to a stable draining film as $t \to \infty$ (Chappelear, 1961; Princen, 1963; Lin and Slattery, 1982b, Eqs. 33 and 34):

$$p_c - p_o \doteq -\frac{\gamma}{R_d} \tag{7}$$

$$p_r - p_o \doteq -\frac{2\gamma}{R_d} \tag{8}$$

xiv) The pressure gradient reaches a maximum at the rim. This appears to be correct in the early portion of the drainage process before the effect of any London-van der Waals forces becomes important (Lin and Slattery, 1982b).

xv) The film thickness h immediately outside the rim can be approximated by the first two terms in a Taylor series expansion

$$h \doteq h_r + \frac{(r-R)^2}{R_d} \tag{9}$$

where h_r is the film thickness at the rim. We recognize here that $\partial h/\partial r = 0$ by definition at the rim. The second derivative is approximated by noticing that just beyond the rim in agreement with Eq. 8.

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) \to \frac{2}{R_d} \tag{10}$$

xvi) Within the draining liquid film, the mutual force per unit mass $\boldsymbol{b}_m$ known as the London-van der Waals force is representable in terms of a scalar potential φ:

$$\boldsymbol{b}_m = -\nabla\varphi \tag{11}$$

At a planar fluid-fluid interface (Ruckenstein and Jain, 1974)

$$\rho\varphi = \rho\varphi_0 = \Phi_B + \frac{B}{h^m} \tag{12}$$

where ρ is the mass density of the liquid film and Φ_B is the interaction potential per unit volume of a semiinfinite film liquid in the limit as the fluid-fluid interface is approached. We define

$$\pi_v \equiv -\frac{B}{h^m} \tag{13}$$

as the disjoining pressure of a flat film of thickness h. When B is positive, the interaction potential per unit volume of the continuous phase C at the interface is larger than it would be, if this phase where semiinfinite. This corresponds to a negative disjoining pressure that acts to attract the two fluid-fluid interfaces. When the film thickness is less than 120 Å, $m = 3$ and $|B| \sim 10^{-14}$ erg; when the film thickness is larger than 400 Å, $m = 4$ and $|B| \sim 10^{-19}$ erg·cm (Black et al., 1960; Sheludko et al., 1965; Gregory, 1969; Churaev, 1974a,b). Because the dependence of h upon r is weak (assumption ii), we will assume that the local value of interaction energy per unit volume of the continuous phase C at the fluid-fluid interfaces is equal to that of a flat film of the same thickness.

RATE OF THINNING AT RIM

Lin and Slattery (1982b) analyzed the thinning of a liquid film as a small drop or bubble approached a fluid-fluid interface during the early stage of the coalescence process, when the effects of any disjoining pressure could be neglected. When we revise their discussion by including the mutual force attributable to London-van der Waals forces in their equation of motion, we find (Lin and Slattery, 1982b, Eqs. 38 and 41)

$$v_r = \frac{1}{2\mu}\frac{\partial\mathscr{P}}{\partial r}\left[z^2 - (h_1 + h_2)z + h_1h_2\right] \tag{14}$$

and

$$\frac{\partial h}{\partial t} = \frac{1}{12\mu}\frac{1}{r}\frac{\partial}{\partial r}\left(h^3 r\frac{\partial\mathscr{P}}{\partial r}\right) \tag{15}$$

where

$$\mathscr{P} \equiv p + \rho\varphi \tag{16}$$

Their finding that (Lin and Slattery, 1982b, Eq. 42)

$$p + \frac{\gamma}{R_d} = -\frac{\gamma}{2}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) \tag{17}$$

remains unchanged.

In view of Eq. 14, we can define

$$\begin{aligned} Q &\equiv \int_{h_2}^{h_1} v_r\,dz \\ &= -\frac{1}{12\mu}\frac{\partial\mathscr{P}}{\partial r}h^3 \end{aligned} \tag{18}$$

and rewrite Eq. 15 as

$$\frac{\partial h}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}(rQ) \tag{19}$$

Using Eqs. 12, 16 and 18, we can express the derivative of Eq. 17 as

$$\begin{aligned} \frac{\gamma}{2}\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right] - \frac{d(\rho\varphi_0)}{dh}\frac{\partial h}{\partial r} &= -\frac{\partial\mathscr{P}}{\partial r} \\ &= \frac{12\mu}{h^3}Q \end{aligned} \tag{20}$$

When $h \gg 1{,}000$ Å, the effect of the London-van der Waals forces can be neglected with respect to the effect of the interfacial tension in Eq. 20 to find

$$\frac{\gamma}{2}\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right] = \frac{12\mu}{h^3}Q = -\frac{\partial\mathscr{P}}{\partial r} \tag{21}$$

Starting with Eqs. 19 and 21 and recognizing assumptions (xi–xiv), we can follow Buevich and Lipkina (1975; for corrections, see Buevich and Lipkina, 1978) to estimate that at the rim

$$\frac{dh_r}{dt} = -0.406\frac{\gamma}{\mu R_d R^2}h_r^3 \tag{22}$$

in which h_r is the film thickness at the rim.

When h is sufficiently small that the effect of the London-van der Waals forces dominate the effect of the interfacial tension in Eq. 20, we have

$$-\frac{d(\rho\varphi_0)}{dh}\frac{\partial h}{\partial r} = \frac{12\mu}{h^3}Q \tag{23}$$

Beginning with Eqs. 19 and 23 and employing assumptions (xv) and (xvi), we can use the same approach as Buevich and Lipkina (1978) to estimate that at the rim

$$\frac{dh_r}{dt} = -\frac{B}{2\mu R_d}\frac{1}{h_r} \qquad \text{for } m = 3 \tag{24}$$

and

$$\frac{dh_r}{dt} = -\frac{2B}{3\mu R_d}\frac{1}{h_r^2} \qquad \text{for } m = 4 \tag{25}$$

From Eqs. 12, 19 and 20, we find that h as a function of r and t is governed by

$$\begin{aligned} -\frac{\partial h}{\partial t} = \frac{h^3}{12\mu}\Bigg\{\frac{\gamma}{2}\Bigg[&\frac{\partial^4 h}{\partial r^4} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2} + \frac{1}{r^3}\frac{\partial h}{\partial r} \\ &+ \frac{3}{h}\frac{\partial h}{\partial r}\left(\frac{\partial^3 h}{\partial r^3} + \frac{1}{r}\frac{\partial^2 h}{\partial r^2} - \frac{1}{r^2}\frac{\partial h}{\partial r}\right)\Bigg] \\ &+ mB\left[\frac{1}{h^{m+1}}\frac{\partial^2 h}{\partial r^2} + \frac{1}{h^{m+1}}\frac{1}{r}\frac{\partial h}{\partial r} - \frac{(m-2)}{h^{m+2}}\left(\frac{\partial h}{\partial r}\right)^2\right]\Bigg\} \end{aligned} \tag{26}$$

In the limit as $r \to R$, this reduces to

$$-\frac{\partial h}{\partial t} = \frac{h^3}{12\mu}\left[\frac{\gamma}{2}\left(\frac{\partial^4 h}{\partial r^4} + \frac{2}{r}\frac{\partial^3 h}{\partial r^3} - \frac{1}{r^2}\frac{\partial^2 h}{\partial r^2}\right) + \frac{mB}{h^{m+1}}\frac{\partial^2 h}{\partial r^2}\right] \tag{27}$$

This suggests that, in the intermediate range of h_r when the effects of both London-van der Waals forces and of interfacial tension are both important, the rate of thinning at the rim may be estimated by a simple addition of Eqs. 22 and 24 (Buevich and Lipkina, 1978).

$$-\frac{dh_r}{dt} \doteq \frac{1}{\mu R_d}\left(\frac{0.406\gamma}{R^2}h_r^3 + \frac{B}{2h_r}\right) \qquad \text{for } m = 3 \tag{28}$$

or of Eqs. 22 and 25

$$-\frac{dh_r}{dt} = \frac{1}{\mu R_d}\left(\frac{0.406\gamma}{R^2} h_r^3 + \frac{2B}{3h_r^2}\right) \qquad \text{for } m = 4 \tag{29}$$

For the case $m = 3$, Eq. 28 can be expressed more simply as

$$\frac{dZ}{dY} = Z^3 + Z^{-1} \tag{30}$$

with the change of variables

$$Z \equiv h_r/\alpha \tag{31}$$

and

$$Y \equiv (t_f - t)/\tau \tag{32}$$

where

$$\alpha = \alpha_{(3)} \equiv 1.055\left(\frac{BR^2}{\gamma}\right)^{1/4} \tag{33}$$

$$\tau = \tau_{(3)} \equiv 2.22\,\mu R_d R(\gamma B)^{-1/2} \tag{34}$$

Here t_f denotes the time when the film thickness at the rim is reduced to zero. Equation 30 can be solved consistent with the condition

$$\text{at } Y = 0: \quad Z = 0 \tag{35}$$

to learn

$$Y = \frac{1}{2}\tan^{-1}(Z^2) \tag{36}$$

Similarly, for the case $m = 4$, Eq. 29 is transformed into

$$\frac{dZ}{dY} = Z^3 + Z^{-2} \tag{37}$$

with the understanding that now

$$\alpha = \alpha_{(4)} \equiv 1.104\left(\frac{BR^2}{\gamma}\right)^{1/5} \tag{38}$$

$$\tau = \tau_{(4)} \equiv 2.02\,\mu R_d B^{-2/5}\left(\frac{R^2}{\gamma}\right)^{3/5} \tag{39}$$

The solution to Eq. 37 consistent with Eq. 35 is (Gradshteyn and Ryzhik, 1980)

$$\begin{aligned} Y &= \int_0^Z \frac{w^2}{1 + w^5}\,dw \\ &= \frac{1}{5} ln(1 + Z) \\ &- \frac{1}{5}\sum_{k=1}^{2} \cos\left[\frac{3\pi}{5}(2k - 1)\right] ln\left\{1 - 2Z\cos\left[\frac{\pi}{5}(2k - 1)\right] + Z^2\right\} \\ &= \frac{2}{5}\sum_{k=1}^{2} \sin\left[\frac{3\pi}{5}(2k - 1)\right] \tan^{-1}\left\{\frac{Z - \cos\left[\frac{\pi}{5}(2k - 1)\right]}{\sin\left[\frac{\pi}{5}(2k - 1)\right]}\right\} \\ &+ \frac{2}{5}\sum_{k=1}^{2} \sin\left[\frac{3\pi}{5}(2k - 1)\right] \tan^{-1}\left\{\cot\left[\frac{\pi}{5}(2k - 1)\right]\right\} \end{aligned} \tag{40}$$

A simple estimate of the coalescence time is the elapsed time required for a dimpled film to drain to zero thickness at the rim,

$$\begin{aligned} t_\infty &\equiv Y_\infty \tau \\ &= \begin{cases} t_{\infty(3)} \equiv \dfrac{\pi}{4}\tau_{(3)} & \text{for } m = 3 \\ t_{\infty(4)} \equiv 0.660\,\tau_{(4)} & \text{for } m = 4 \end{cases} \end{aligned} \tag{41}$$

in which

$$Y_\infty \equiv \lim_{Z \to \infty} Y \tag{42}$$

LINEAR STABILITY ANALYSIS

In reality, as a drop or bubble approaches an interface, the thin film is subject to small disturbances or perturbations. Let ϵ be a dimensionless parameter characterizing these perturbations at the rim of the film and let Z_0 represent the solution, Eq. 36 or 40, to Eq. 30 or 37 describing the rate of thinning at the rim. The first perturbation Z_1 to Eq. 30 or 37 must satisfy an equation of the form

$$\frac{dZ_1}{dY} = \beta Z_1 \tag{43}$$

where $\beta = \beta(Z_0)$. Note that boundary condition Eq. 35 assumes $\epsilon = 0$ and consequently does not apply to Eq. 43. Since Y, defined by Eq. 32, decreases with time, any disturbance will grow with time and the film will be unstable at a particular value of Z_0, if the corresponding value of β is negative. When β is positive, any disturbance will die out with time and the film will be stable. The limit of stability corresponds to $\beta = 0$.

In particular, we find that β is negative and the film will be unstable at the rim, when Z_0 is less than a critical value Z_c:

$$Z_c = \begin{cases} 3^{-1/4} & \text{for } m = 3 \\ (2/3)^{1/5} & \text{for } m = 4 \end{cases} \tag{44}$$

The corresponding value of dimensionless time is

$$Y_c = \begin{cases} \dfrac{1}{2}\tan^{-1}(3^{-1/2}) & \text{for } m = 3 \\ 0.214 & \text{for } m = 4 \end{cases} \tag{45}$$

Equation 45 permits us to predict the coalescence time t_c for a small drop or bubble approaching a fluid-fluid interface as

$$\begin{aligned} t_c &\equiv (Y_\infty - Y_c)\tau \\ &= \begin{cases} t_{c(3)} \equiv 0.523\,\tau_{(3)} & \text{for } m = 3 \\ t_{c(4)} \equiv 0.446\,\tau_{(4)} & \text{for } m = 4 \end{cases} \end{aligned} \tag{46}$$

The corresponding critical thickness of the film at the rim becomes

$$\begin{aligned} h_c &\equiv Z_c\alpha \\ &= \begin{cases} h_{c(3)} \equiv 0.760\,\alpha_{(3)} & \text{for } m = 3 \\ h_{c(4)} \equiv 0.922\,\alpha_{(4)} & \text{for } m = 4 \end{cases} \end{aligned} \tag{47}$$

PLANE PARALLEL DISC MODEL

MacKay and Mason (1963) extended the Reynolds (1886) equation for plane parallel discs to include the effects of London-van der Waals forces. They found that the rate of thinning of a film of uniform thickness is described by

$$-\frac{dh_r}{dt} = \frac{2}{3\pi\mu R^4}\left(F_g h_r^3 + \pi R^2\frac{B}{h_r}\right) \tag{48}$$

for $m = 4$, where

$$F_g \equiv \frac{4}{3}\pi R_d^3 \Delta\rho g \tag{49}$$

Equation 48 can be rearranged as Eq. 30 through the change of variables Eqs. 31 and 32 with

$$\alpha = \alpha_{(M)} \equiv \left(\frac{\pi R^2 B}{F_g}\right)^{1/4} \tag{50}$$

and

$$\tau = \tau_{(M)} \equiv \frac{3}{2}\pi\mu R^3(\pi B F_g)^{-1/2} \tag{51}$$

By analogy with Eq. 41, the elapsed time for a film to drain to zero thickness is

TABLE 1. COMPARISONS WITH 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
$\Delta\rho$ (g/cm^3)	0.0538	0.1145	0.0483	0.1145	0.0483
μ (mN·s/m^2) × 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) [$t_{\infty(4)}$ (s)]	8.8 [13.0]	10.5 [15.5]	51.6 [76.3]	2.3 [3.4]	2.7 [4.0]
$h_{c(4)}$ (Å)	847	855	908	855	908
$t_{c(M)}$ (s) [$t_{\infty(M)}$ (s)]	34.8 [52.3]	58.0 [87.1]	242 [363]	12.4 [18.6]	12.7 [19.1]
$t_{c(H)}$ (s) [$t_{\infty(H)}$ (s)]	5.2 [6.7]	3.8 [4.9]	24.5 [31.4]	0.8 [1.0]	1.3 [1.7]

drop − bulk
System 1: H_2O − cinnamaldehyde
2: H_2O − diphenyl sulphide
3: H_2O − dibutyl phthalate
4: diphenyl sulphide − H_2O
5: dibutyl phthalate − H_2O

$$t_{\infty(M)} = \frac{\pi}{4}\,\tau_{(M)} \tag{52}$$

Recognizing that there is a critical film thickness at the rim below which the film is unstable, we can estimate the coalescence time by analogy with Eq. 46 as

$$t_{c(M)} = 0.523\,\tau_{(M)} \tag{53}$$

Referring to Eq. 47, we see that the critical film thickness at the rim is

$$h_{c(M)} = 0.760\,\alpha_{(M)} \tag{54}$$

CYLINDRICAL DROP MODEL

Hodgson and Woods (1969) included the effects of London-van der Waals forces to find that the rate of thinning at the rim of the film is

$$-\frac{dh_r}{dt} = \frac{\gamma}{6\mu R_d^2}\left(h_r^2 + \frac{BR_d}{\gamma}\frac{1}{h_r^2}\right) \tag{55}$$

for $m = 4$. Their analysis is unrealistic in two respects. They model the drop as a two-dimensional cylinder. Their relation between Q and $\partial h/\partial t$ is not clearly justified; compare their Eq. 4 with our Eq. 19. In arriving at their Eq. 5, they assume $\partial h/\partial t$ is independent of position. But we include their results for completeness.

Equation 55 can be rewritten as

$$\frac{dZ}{dY} = Z^2 + Z^{-2} \tag{56}$$

through the change of variables Eqs. 31 and 32 with

$$\alpha = \alpha_{(H)} \equiv \left(\frac{BR_d}{\gamma}\right)^{1/4} \tag{57}$$

and

$$\tau = \tau_{(H)} \equiv \frac{6\mu R_d}{B}\left(\frac{BR_d}{\gamma}\right)^{3/4} \tag{58}$$

The solution to Eq. 56 consistent with Eq. 35 is

$$Y = -\frac{1}{4\sqrt{2}}\,ln\left(\frac{Z^2+\sqrt{2}\,Z+1}{Z^2-\sqrt{2}\,Z+1}\right) + \frac{1}{2\sqrt{2}}\tan^{-1}\left(\frac{\sqrt{2}\,Z}{1-Z^2}\right) \tag{59}$$

for $0 < Z < 1$ and

$$Y = \frac{\pi}{2\sqrt{2}} - \frac{1}{4\sqrt{2}}\,ln\left(\frac{Z^2+\sqrt{2}\,Z+1}{Z^2-\sqrt{2}\,Z+1}\right) + \frac{1}{2\sqrt{2}}\tan^{-1}\left(\frac{\sqrt{2}\,Z}{1-Z^2}\right) \tag{60}$$

for $Z > 1$.

The elapsed time for a film to drain to zero thickness can be computed in a manner similar to that used to arrive at Eq. 41:

$$t_{\infty(H)} = \frac{\pi}{2\sqrt{2}}\,\tau_{(H)} \tag{61}$$

This result was also reported by Hodgson and Woods (1969).

There is a critical film thickness at the rim below which the film is unstable. Following the derivation of Eq. 46, we can estimate the coalescence time as

$$\begin{aligned} t_{c(H)} &= \left\{\frac{\pi}{2\sqrt{2}} - \frac{1}{4\sqrt{2}}\left[\pi - ln\left(\frac{2+\sqrt{2}}{2-\sqrt{2}}\right)\right]\right\}\tau_{(H)} \\ &= 0.867\,\tau_{(H)} \end{aligned} \tag{62}$$

The corresponding film thickness at the rim is

$$h_{c(H)} = \alpha_{(H)} \tag{63}$$

COMPARISONS WITH EXPERIMENTAL DATA

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.

Tables 1 through 3 compare the mean values of coalescence times $t_{\exp}$ observed experimentally by MacKay and Mason (1963), by Woods and Burrill (1972; Burrill and Woods, 1973b), and by Allen et al. (1961) with the various theoretical estimates developed here. We take the elapsed time t_∞ for a film to drain to zero thickness from Eqs. 41, 52 and 61. The elapsed time t_c for a film to reach the critical film thickness at which an instability develops is taken from Eqs. 46, 53 and 61. The corresponding critical film thickness h_c at the rim is determined by Eqs. 47, 54 and 63.

In making our predictions in Tables 1 and 2, we estimate that (Chappelear, 1961; Princen, 1963; Lin and Slattery, 1982b)

$$R = R_d^2\left(\frac{4\Delta\rho g}{3\gamma}\right)^{1/2} \tag{64}$$

which describes the rim radius of a stable film formed at a fluid-fluid interface as equilibrium is approached. MacKay and Mason (1963) find that their experimental measurements of R scatter between Eq. 64 and (Derjaguin and Kussakov, 1939; Lin and Slattery, 1982a)

$$R = R_d^2\left(\frac{2\Delta\rho g}{3\gamma}\right)^{1/2} \tag{65}$$

which describes the rim radius of a stable film formed at a plane interface as equilibrium is approached. Except for their cyclohexanol-water system, Burrill and Woods (1973b) find that Eq. 64 describes their experimental measurements of R better than Eq. 65 does. Given Eq. 64, Eqs. 34, 39, and 51 become

$$\tau_{(3)} = 2.56\,\frac{\mu R_d^3}{\gamma}\left(\frac{\Delta\rho g}{B}\right)^{1/2} \tag{66}$$

$$\tau_{(4)} = 2.40\,\frac{\mu R_d^{17/5}}{\gamma^{6/5}B^{2/5}}\,(\Delta\rho g)^{3/5} \tag{67}$$

TABLE 2. COMPARISONS WITH DATA OF WOODS AND BURRILL (1972, 1973b)

System	1	2	3	4
Conc. SLS[a] (g/L)	10^{-6}	10^{-6}	10^{-6}	10^{-6}
Normality KCl	0.01	0.01	0.01	0.01
γ (mN/m)	3.93	20.5 (25)[c]	28.9	35 (33.5)[c]
$\Delta\rho$ (g/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)	<110	<15	<16	<12
$t_{c(4)}$ (s) [$t_{\infty(4)}$ (s)]	67.5 [102.4]	21.3 [32.3]	39.2 [59.5]	54.1 [82.1]
$h_{c(4)}$ (Å)	2336	1330	1629	1814
$t_{c(M)}$ (s) [$t_{\infty(M)}$ (s)]	780 [1171]	141.3 [212.2]	455.2 [683.6]	859.4 [1502]
$t_{c(H)}$ (s) [$t_{\infty(H)}$ (s)]	8.1 [10.4]	6.0 [7.7]	4.6 [5.9]	4.0 [5.1]
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)

	Drop	– Bulk
System 1:	cyclohexanol	– H_2O
2:	anisol	– H_2O
3:	CA[b]	– H_2O
4:	toluene	– H_2O

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[a] Sodium lauryl sulfate.

[b] Mixture of 0.84 mole fraction anisole with 0.16 mole fraction cyclohexane.

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

and

$$\tau_{(M)} = 2.00\,\frac{\mu R_d^{9/2} \Delta\rho g}{\gamma^{3/2} B^{1/2}} \tag{68}$$

In contrast, Allan et al. (1961) find that Eq. 65 describes their experimental measurements of R immediately prior to coalescence very well. For this reason, we use Eq. 65 in making the comparisons shown in Table 3 and we employ an overbar $\overline{\ldots}$ there to remind the reader of this change. The expressions corresponding to Eqs. 66 through 68 may be obtained by dividing by $\sqrt{2}$, $2^{3/5}$, and $2\sqrt{2}$ respectively.

For lack of better information, we choose $B = 10^{-14}$ erg for $m = 3$ and $B = 10^{-19}$ erg·cm for $m = 4$ (Black et al., 1960; Sheludko et al., 1965; Gregory, 1969; Churaev, 1974a,b). In reality, we recognize that B is a function of the system studied.

We do not show the comparisons for $m = 3$ in Tables 1 through 3, since in all cases $h_{c(3)} > h_{c(4)} > 400$ Å, indicating that $m = 4$ is more appropriate. (See assumption xvi.)

Equation 46 with Eq. 67 is in good agreement with the experimental data of MacKay and Mason (1963) in Table 1. Since they used all of their materials in the conditions 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 were immobile.

The comparison with the experimental data of Woods and Burrill (1972; Burrill and Woods, 1973b) in Table 2 is mixed. In going from left to right in Table 2, 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 (assumption x); they added KCl in an attempt to minimize this effect. 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 symmetric drainage and fully immobile interfaces free of dust, our estimate 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 over-estimate the coalescence times observed by Allen et al. (1961) in Table 3. 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) is unrealistic as discussed in the previous section.

We have also compared these three models with the experimental measurements of MacKay and Mason (1963) for N_2–86% glycerol and N_2-dibutyl phthalate systems. Since these systems are similar to those used by Allen et al. (1961) and since the comparisons show the same trend, we do not show the results here.

TABLE 3. COMPARISONS WITH DATA OF ALLEN ET AL. (1961)[d] 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 (g/cm^3)	1.2535	1.2367	1.2221	1.2371	1.2362	1.0447	1.0378	1.0295
μ (mN·s/m^2) $\times 10^{-2}$	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
$\bar{t}_{c(4)}$ (s)	618	199	86	217	252	993	291	163
[$t_{\infty(4)}$ (s)]	[913]	[296]	[127]	[321]	[373]	[1,474]	[431]	[241]
$\bar{h}_{c(4)}$ (Å)	681	677	674	687	735	809	779	850
$\bar{t}_{c(M)}$ (s)	2,542	816	347	901	1,100	4,347	1,466	699
[$\bar{t}_{\infty(M)}$ (s)]	[3,813]	[1,224]	[520]	[1,352]	[1,650]	[6,521]	[2,199]	[1,049]
$\bar{t}_{c(H)}$ (s)	207	68	29	73	78	301	101	46
[$t_{\infty(H)}$ (s)]	[265]	[87]	[37]	[93]	[100]	[385]	[129]	[59]

System 1: 97% aqueous glycerol (no emulsifier)
2: 91% aqueous glycerol (no emulsifier)
3: 85% aqueous glycerol (no emulsifier)
4: 91% aqueous glycerol (with 0.0025% Tween 20)
5: 91% aqueous glycerol (with 0.025% Tween 20)
6: UCON oil mixture (1)
7: UCON oil mixture (2)
8: UCON oil mixture (3)

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[d] Overbar indicates that Eq. 65 was used rather than Eq. 64.

Several conclusions can be drawn.

1. In all cases, t_c generally gives a better estimate of the experimental coalescence time than does t_∞.

2. Coalescence time increases with increasing bubble or drop diameter.

There have been several studies of the effect of drop size on the coalescence time (Gillespie and Rideal, 1956; Elton and Picknett, 1957; Charles and Mason, 1960; MacKay and Mason, 1963; Jeffreys and Hawksley, 1965; Hodgson and Lee, 1969; Hodgson and Woods, 1969; Komasawa and Otake, 1970; Lang and Wilke, 1971; Woods and Burrill, 1972; Burrill and Woods, 1973b). All workers, except Hodgson and Lee (1969) and Lang and Wilke (1971), found that the coalescence time increased with drop size. In view of Eq. 58 and Eqs. 66–68, this is consistent with our theory Eq. 46 as well as the plane parallel disc model, Eq. 53, and the cylindrical drop model, Eq. 62.

Previous workers disagree on the functional relation between coalescence time and drop size. For a water drop approaching a water-benzene interface, Charles and Mason (1960) report $t_c \sim R_d^{3.15}(0.124 \leqq N_{Bo} \leqq 0.306)$; Jeffreys and Hawksley (1965) $t_c \sim R_d$ $(0.140 \leqq N_{Bo} \leqq 0.430)$; Lang and Wilke (1971) say t_c is independent of R_d $(0.153 \leqq N_{Bo} \leqq 0.604)$. For a benzene drop approaching a water-benzene interface, Komasawa and Otake (1970) report $t_c \sim R_d^{2.1}$ $(0.158 \leqq N_{Bo} \leqq 0.455)$. But note that none of these experimental studies satisfies the requirement of assumption xi of this analysis that $N_{Bo} \ll 1$. For comparison, we predict for $N_{Bo} \ll 1$ that $t_c \sim R_d^3$ for $m = 3$ and $t_c \sim R_d^{3.4}$ for $m = 4$ from Eqs. 46, 66, and 67. The plane parallel disc model, Eqs. 51 and 68, gives $t_c \sim R_d^{4.5}$; the cylindrical drop model, Eqs. 58 and 62, $t_c \sim R_d^{1.75}$.

3. The coalescence time increases as the viscosity of the draining film increases, as the interfacial tension decreases, and as the strength of the London-van der Waals forces (denoted by B) decreases.

Our model agrees with the plane parallel disc model and the cylindrical drop model as far as the general trends are concerned. The available experimental data do not permit discrimination between the models on the basis of this conclusion.

All of the data in Table 3 support the coalescence time being proportional to the viscosity of the draining film. The data for aqueous glycerol solutions with Tween 20 is consistent with the coalescence time increasing as the interfacial tension decreases, although none of the models can explain the large difference without permitting B to change. There are no experimental data that would allow us to directly check the dependence of coalescence time upon B.

4. The coalescence time increases as the density difference between the two phases increases.

Our model and the plane parallel disc model are in agreement on this point. The cylindrical drop model predicts the coalescence time is independent of the density difference.

There are no experimental data that would allow this conclusion to be tested.

Similar conclusions regarding the functional dependence of the critical film thickness at the rim of the film can be developed in a similar manner. The data available do not permit discrimination among the models.

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NOTATION

B = parameter in Eq. 13
F_g = buoyancy force
g = magnitude of gravitational acceleration
h = film thickness
h_c = film thickness at the rim and t_c, defined by Eq. 47
$h_{c(H)}$ = film thickness at the rim and $t_{c(H)}$, defined by Eq. 63
$h_{c(M)}$ = film thickness at $t_{c(M)}$, defined by Eq. 54
h_r = film thickness at the rim
h_0 = characteristic film thickness
h_1 = configuration of fluid-fluid interface, Figure 1
h_2 = configuration of drop-fluid interface, Figure 1
m = parameter in Eq. 13
N_{Bo} = bond number defined by Eq. 5
p = pressure in the film
p_c = pressure in the film at the center
p_o = pressure in the drop phase
p_r = pressure in the film immediately outside the rim
$\mathcal{P}$ = modified pressure defined by Eq. 16
Q = volume flow rate of liquid per unit length of periphery defined by Eq. 18
r = cylindrical coordinate
R = rim radius
R_d = drop or bubble radius
t = time
t_c = predicted coalescence time defined by Eq. 46
$t_{\exp}$ = experimental mean coalescence time
t_f = time at which the film thickness at the rim h_r reduces to zero
$t_{c(H)}$ = predicted coalescence time defined by Eq. 62
$t_{\infty(H)}$ = predicted coalescence time defined by Eq. 61
$t_{c(M)}$ = predicted coalescence time defined by Eq. 53
$t_{\infty(M)}$ = predicted coalescence time defined by Eq. 52
t_∞ = predicted coalescence time defined by Eq. 41
$\mathbf{v}$ = velocity vector in the film
v_r = r-component of velocity vector $\mathbf{v}$
Y = dimensionless time defined by Eq. 32
Y_c = defined by Eq. 45
Y_∞ = defined by Eq. 42
z = cylindrical coordinate
Z = dimensionless film thickness at the rim defined by Eq. 31
Z_c = defined by Eq. 44

Greek Letters

$\alpha_{(3)}, \alpha_{(14)}$ = defined by Eqs. 33 and 38
$\alpha_{(H)}$ = defined by Eq. 57
$\alpha_{(M)}$ = defined by Eq. 50
β = negative of the growth coefficient of disturbance
γ = interfacial tension between phases C and D (or B); phases B and D are the same fluid
μ = bulk viscosity of the liquid film
π_v = van der Waals disjoining pressure
$\Delta\rho$ = density difference between phases C and D (or B); phases B and D are the same fluid
$\tau_{(3)}, \tau_{(4)}$ = defined by Eqs. 34 and 39
$\tau_{(H)}$ = defined by Eq. 58
$\tau_{(M)}$ = defined by Eq. 51
φ = interaction potential energy per unit mass of the liquid in the film
φ_0 = φ evaluated in the limit as the interface is approached
Φ_B = interaction potential energy per unit volume of the semiinfinite film liquid in the limit as the interface is approached

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