Effects of Surface Viscosities on the Stability of a Draining Plane Parallel Liquid Film as a Small Bubble Approaches a Liquid-Gas Interface

When a small bubble is driven through a liquid phase to a liquid-gas interface, a thin liquid film forms between them and drains until an instability forms and coalescence occurs. Following Lin and Slattery (1982b), Chen et al. (1984) and Hahn et al. (1985) analyzed this process, neglecting the effects of electrostatic forces and of the surface viscosities. Here we extend their theory to include the effects of the surface viscosities. We employ a modification of the development by Barber and Hartland (1976; Flumerfelt et al., 1982) for a draining film bounded by parallel planes.

For a large intermediate range of the surface viscosities, the coalescence time is a strong function of these parameters. Inclusion of the surface viscosities acts to moderate or even reverse trends previously established for the dependence of the coalescence time on the bubble radius, the viscosity of the film liquid, the interfacial tension, the strength of the London-van der Waals forces, and the density difference between the two phases.

P.-S. HAHN
and
J. C. SLATTERY
Department of Chemical Engineering
Northwestern University
Evanston, IL 60201

SCOPE

The rate at which bubbles suspended in a liquid coalesce is important to the preparation and stability of foams, to the separation of minerals by froth flotation, to the displacement of an unstable foam used for mobility control in a tertiary oil recovery process, and to a broad class of operations including gas adsorption and sparging in which a gas or vapor dispersion is formed. On a smaller scale, when two bubbles are forced to approach one another in a liquid phase or when a bubble is driven through a liquid phase to a liquid-gas 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 1000 Å), the effects of the London-van der Waals forces and of any electrostatic double layer become significant. Depending on 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 and ruptures, and coalescence occurs.

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. Flumerfelt et al. (1982) extended their analysis to the latter stages of thinning by taking the effect of the London-van der Waals forces into account.

We also adopt the development of Barber and Hartland (1976; see also Flumerfelt et al., 1982), but with three important modifications.

First, we assume that the rate of thinning of the liquid film is sufficiently small that the surfactant concentration in each of the dividing surfaces bounding the film may be considered to be nearly independent of position. In order to establish the validity of this assumption, we adapt to this problem an argument presented by Giordano and Slattery (1983, their Appendix A). On this basis, we neglect the effect of the interfacial tension gradient with respect to the effect of the interfacial viscosities in the force balance at each interface. Barber and Hartland (1976) and Flumerfelt et al. (1982) combine any effects of surface tension gradients with those of the interfacial viscosities, employing an intuitive justification.

Second, 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), Chen et al. (1984), and Hahn et al. (1985) are normally larger than 120 Å, we represent the London-van der Waals forces as being retarded. Flumerfelt et al. (1982) describe these forces as nonretarded, which would normally be appropriate for a film thickness less than 120 Å.

Third, we adopt the linear stability analysis suggested by Chen et al. (1984) in order to predict the critical time or coalescence time at which the film becomes unstable and presumably begins to rupture. Flumerfelt et al. (1982) assume that the film remains stable and drains to zero thickness at their predicted coalescence times.

CONCLUSIONS AND SIGNIFICANCE

If the surface viscosities are sufficiently large and the bubble radius appropriately small, the interfaces bounding the film act as though they are immobile (incapable of lateral motion) and any effects of the surface viscosities disappear. If the surface viscosities are sufficiently small and the bubble radius large enough, these interfaces behave as though they are fully mobile (offer no resistance to lateral motion) and again any effects of the surface viscosities disappear. For a large intermediate range of the surface viscosities and of the bubble radius, the coalescence time is a strong function of these variables.

Previous analyses (Chen et al., 1984; Hahn et al., 1985) have assumed that the interfaces bounding the draining film are immobile. They have concluded that the coalescence time increases as the bubble radius increases, as the viscosities 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. Inclusion of the surface viscosities acts to moderate or even reverse each of these effects (refer to Figure 2 and Eq. 30). This may explain the wide differences in functional dependence of coalescence time on drop radius that have been observed for liquid-liquid systems (see Chen et al., 1984, for a review).

Chen et al. (1984) and Hahn et al. (1985) were relatively unsuccessful in using their theories to describe the rest times for nitrogen bubbles rising in various liquids as observed both by Allan et al. (1961) and by MacKay and Mason (1963). By regarding the phase interfaces of these systems as not being fully immobile, these observations could be explained by the present theory using plausible values of the surface viscosities for these systems.

Burrill and Woods (1973a) pointed out that the cause of film rupture was often seen to be dust, dirt, or local asymmetries in the film thickness. Since our computation assumes symmetric drainage and parallel, plane 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 the London-van der Waals forces and assuming that electrostatic forces could be neglected. For this reason, we do not recommend that our prediction be used to interpret experimental data for coalescence times in terms of the surface viscosities of the system.

Rather, these results might be used to estimate coalescence times based upon previous measurements of the surface viscosities. By comparison of these predicted coalescence times with measured values, the role of the surface viscosities in coalescence might be qualitatively confirmed.

INTRODUCTION

Some experimental studies suggest that the rate of coalescence of bubbles in foams and therefore the stability of foams is strongly affected by the surface viscosities (Brown et al., 1953; Davies, 1957; Kanner and Glass, 1969; Bikerman, 1973, p. 232; Joly, 1972; Barber and Hartland, 1976; Sagert and Quinn, 1978a,b). These studies are not entirely convincing, either because they are not sufficiently systematic or because the technique used to measure the surface shear viscosity is open to question. There were no measurements of the surface dilatational viscosity, which is likely to be the dominant of the two (Stoodt and Slattery, 1984). A major difficulty is that, until Barber and Hartland (1976; Flumerfelt et al., 1982), there was no theory available with which to guide experiments or compare results.

Barber and Hartland (1976; Flumerfelt et al., 1982) considered the rate of thinning of a plane parallel liquid film as a small bubble approaches a liquid-gas interface. Unfortunately, we have not been able to justify the manner in which they have included the effects of the surface tension gradient in their analysis. The parameter K in their Eq. 6 has nothing to do with what is now called the surface dilatational (or dilational) viscosity. Since surface tension should be an explicit function of the surface mass density of surfactant, their Eq. 6 should result from the first two terms of a Taylor series expansion. This implies that, in their Eq. 6, the local surface mass density of surfactant has been assumed to be proportional to the local rate of expansion of the interface, an intuitive statement. By comparing their Eq. 8 with the overall jump mass balance and neglecting the effects of mass transfer with the adjacent phases (Slattery, 1980; Slattery and Flumerfelt, 1982), we can identify their local rate of expansion of the interface as being proportional to the time rate of change of area per unit total mass following a surface material particle. Why the local surface mass density of surfactant should be proportional to the time rate of change of area per unit total mass following a surface material particle is not clear. The local surface mass density of surfactant should be the result of satisfying the jump mass balance for surfactant (Slattery, 1980; Slattery and Flumerfelt, 1982), which was not mentioned.

In what follows, we modify the analyses of Barber and Hartland (1976) and of Flumerfelt et al. (1982). In contrast with their developments, we show that the effects of any interfacial tension gradient can be neglected for sufficiently small bubbles. We follow Flumerfelt et al. (1982) in including the effects of the London-van der Waals forces, although we recommend that they be treated as retarded rather than nonretarded (see assumption 13 below). Having obtained an expression for the rate of thinning of this film, we adopt the suggestion of Chen et al. (1984) to construct a linear stability analysis of this thinning equation. When the film thickness is less than a critical value, the film is unstable and rupture occurs. In this way, we are able to predict the rest time or coalescence time for the bubble as a function of system properties.

For more complete reviews, see Sheludko (1967), Buscall and Ottewill (1975), Ivanov and Jain (1979), Jain et al. (1979), Ivanov (1980), and Chen et al. (1984).

STATEMENT OF PROBLEM

We make a number of assumptions.

1. Viewed in the cylindrical coordinate system of Figure 1, the two interfaces bounding the draining film are parallel planes and therefore axisymmetric. We work in a moving frame of reference in which the position of the one interface is fixed at $z = 0$ and the position of the other interface varies as a function of time:

$$z = h = h(t) \tag{1}$$

2. The Reynolds lubrication theory approximation applies in the sense that

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

where

R = film radius.

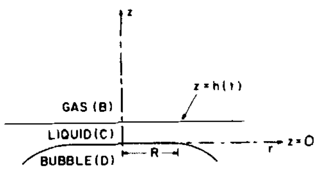

Figure 1. Film formed as a small bubble (phase *D*) rises through a continuous liquid (phase *C*) to an interface between the liquid and another gas (phase *B*). The film is observed in a frame of reference in which the interface between phases *C* and *D* is stationary.

3. Because the film is assumed to be bounded by parallel planes, R will be identified both with the rim radius and the radial position at which the pressure in the film approaches the local hydrostatic pressure in the liquid outside the film (Lin and Slattery, 1982b).

4. The liquid-gas interfacial stress-deformation behavior can be represented by the linear Boussinesq surface fluid model (Boussinesq, 1913; Scriven, 1960):

$$\begin{aligned} \boldsymbol{S}^{(\sigma)} &\equiv \boldsymbol{T}^{(\sigma)} - \gamma \boldsymbol{P} \\ &= [(\kappa - \epsilon)\mathrm{div}_{(\sigma)}\mathbf{v}^{(\sigma)}]\boldsymbol{P} + 2\epsilon \boldsymbol{D}^{(\sigma)} \end{aligned} \tag{3}$$

where

$\boldsymbol{S}^{(\sigma)}$ = viscous portion of the surface stress tensor
$\boldsymbol{T}^{(\sigma)}$ = surface stress tensor
γ = surface tension
$\boldsymbol{P}$ = projection tensor that transforms vectors defined on the dividing surface into their tangential components
κ = surface dilatational viscosity
ϵ = surface shear viscosity
$\mathbf{v}^{(\sigma)}$ = surface velocity vector

$$\boldsymbol{D}^{(\sigma)} \equiv \frac{1}{2}[\boldsymbol{P} \cdot \nabla_{(\sigma)}\mathbf{v}^{(\sigma)} + (\nabla_{(\sigma)}\mathbf{v}^{(\sigma)})^T \cdot \boldsymbol{P}] \tag{4}$$

surface rate of deformation tensor

$\nabla_{(\sigma)}$ = surface gradient operator
$div_{(\sigma)}$ = corresponding surface divergence operation (Wei et al., 1974; Briley et al., 1976).

5. The rate of thinning of the liquid film is sufficiently small that the surfactant concentration in each of the dividing surfaces bounding the film may be considered to be nearly independent of position. Since the surface tension and the two surface viscosities are determined by the local surfactant concentration, they may be treated as being independent of position as well. In order to establish the validity of this assumption, we repeat the argument that Giordano and Slattery (1983, their Appendix A) developed for displacement in a capillary. In following their discussion, take a film radius $R = 10^{-2}$ cm as your characteristic length and a rate of thinning

$$-\frac{dh}{dt} = \frac{1\ \mu\text{m}}{10\ \text{s}} = 10^{-5}\text{cm/s}$$

as your characteristic speed. It is because we assume that the surfactant concentration in each of the dividing surfaces is independent of position that we neglect the effect of the interfacial tension gradient with respect to the effect of the interfacial viscosities in the jump momentum balance or the force balance at each of the interfaces.

6. We expect that a freshly formed bubble will have a different surfactant concentration than the older interface that it is approaching and that this surfactant concentration is changing rapidly as a function of time as the result of adsorption. For simplicity, we will assume that both interfaces have the same surfactant concentrations, surface tension, and surface viscosities and that all of these properties are independent of time.

7. Viscous effects in the gas phase are neglected with respect to those of the liquid phase in the jump momentum balance at each of the interfaces.

8. The pressure within the bubble is independent of time and position. The pressure within phase B in Figure 1 is equal to the local hydrostatic pressure.

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

10. All inertial effects are neglected.

11. The effects of gravity and of electrostatic forces are neglected within the draining liquid film; London-van der Waals forces are taken into account. Even for ionic surfactant systems, the effects of electrostatic forces can be neglected, when there are sufficient electrolytes in the solution (Davies and Rideal, 1963; Sheludko, 1967; Burrill and Woods, 1973b).

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

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

where

$\Delta\rho$ = density difference between the liquid and the gas
g = magnitude of the acceleration of gravity
R_b = radius of the bubble.

13. 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:

$$\boldsymbol{b}_m = -\nabla\phi \tag{6}$$

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

$$\rho\phi = \rho\phi_0 = \Phi_B + \frac{B}{h^m} \tag{7}$$

where

ρ = mass density of the liquid film
Φ_B = interaction potential per unit volume of a semi-infinite film liquid in the limit as the fluid-fluid interface is approached

When the film thickness is larger than 400 Å, the London-van der Waals forces are retarded and $m = 4$; when the film thickness is less than 120 Å, they are nonretarded and $m = 3$ (Black et al., 1960; Churaev, 1974a,b). We speak of

$$\pi = -\frac{B}{h^m} \tag{8}$$

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 semi-infinite. This corresponds to a negative disjoining pressure that acts to draw the two fluid-fluid interfaces together.

14. 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), Chen et al. (1984), and Hahn et al. (1985) are normally larger than 120 Å, we expect that $m = 4$ in Eq. 7 is more appropriate. Several authors (Kitchener and Prosser, 1957; Black et al., 1960; Sheludko et al., 1965, Churaev, 1974a; Derjaguin et al., 1977) report approximate values of B between two flat surfaces as

$$\text{for } m = 4\text{: } B \sim 10^{-19}\text{erg}\cdot\text{cm}$$

Lacking more detailed information, we recommend that this value for B be used in example computations.

SOLUTION

With two modifications, we can follow the analysis of Barber and Hartland (1976; see also Flumerfelt et al., 1982) to determine that the rate at which the film thins is described by

$$-\frac{dh}{dt} = \frac{M}{12\pi\mu R^4}\left(F_g h^3 + \pi R^2 \frac{B}{h}\right) \tag{9}$$

where

$$M \equiv -X^3\left[\frac{I_0(X)}{2I_1(X) - xI_0(X)}\right] \tag{10}$$

$$X \equiv \left[\frac{6\mu}{(\kappa + \epsilon)h}\right]^{1/2} R \tag{11}$$

$$F_g \equiv \frac{4}{3}\pi R_b^3 \Delta\rho g \tag{12}$$

t = time
μ = viscosity of the liquid
$I_0(X)$ and $I_1(X)$ = modified Bessel functions of the first kind, zeroth and first orders, respectively.

The first modification is that we have neglected the effects of any surface tension gradient as described in assumption 5. This requires only that the dilational surface viscosity η_d of Barber and Hartland (1976) be replaced by our κ.

The second modification in the analysis of Barber and Hartland (1976) is that we have included the effects of the London-van der Waals forces. This requires only that pressure p in their equation of motion (their Eq. 2) be replaced by $p + \rho\phi$. (Flumerfelt et al. [1982] included the effects of nonretarded London-van der Waals forces corresponding to $m = 3$ in our Eq. 7. As explained in assumption 14, we prefer to regard the London-van der Waals forces as being retarded with $m = 4$.)

In considering the same film configuration, MacKay and Mason (1963) assumed that their interfaces were immobile and in this way neglected the effects of the interfacial viscosities. An immobile interface is one in which the tangential component of velocity is zero. An immobile interface may be the result of very small surface tension gradients (Lin and Slattery, 1982a,b; Hahn et al., 1985). In this analysis, immobile interfaces result when the surface viscosities are very large:

$$\text{limit } X \to 0\text{: } M \to 8 \tag{13}$$

In this limit, Eq. 9 correctly reduces to the result of MacKay and Mason (1963) (see also Chen et al., 1984, their Eq. 48).

It is convenient to rewrite Eq. 9 as

$$\frac{dX}{dY} = (1 + \alpha X^8)\left[\frac{I_0(X)}{XI_0(X) - 2I_1(X)}\right] \tag{14}$$

in which

$$\alpha \equiv \frac{\pi B}{F_g R^6}\left(\frac{\kappa + \epsilon}{6\mu}\right)^4 \tag{15}$$

and

$$Y \equiv \frac{3\mu F_g}{2\pi(\kappa + \epsilon)^2} t \tag{16}$$

with the observation that

$$\text{at } Y = 0\text{: } X \to 0 \tag{17}$$

Equation 14 can be integrated to find

$$Y = \int_0^X \frac{[X'I_0(X') - 2I_1(X')]}{(1 + \alpha X'^8)\, I_0(X')}\, dX' \tag{18}$$

Equation 18 describes film thickness h ($\sim X^{-1}$) as a function of time t ($\sim Y$) up to the point where the film finally disappears ($X \to \infty$). This implies that the film remains intact and does not rupture during the entire drainage process.

LINEAR STABILITY ANALYSIS

In reality, as a bubble approaches an interface, the thin film is subject to small disturbances or perturbations. Here we follow Chen et al. (1984) in determining the critical time t_c ($\sim Y_c$) and corresponding critical film thickness h_c ($\sim X_C^{-1}$) at which the film becomes unstable and presumably begins to rupture.

With respect to any small, dimensionless parameter characterizing these perturbations, let h_0 ($\sim X_0^{-1}$) represent the zeroth order solution of Eq. 9, Eq. 14, or

$$\begin{aligned} -\frac{dh}{dt} &= \frac{k}{X^3}\frac{dX}{dY} \\ &= k\left(\frac{1}{X^3} + \alpha X^5\right)\left[\frac{I_0(X)}{XI_0(X) - 2I_1(X)}\right] \end{aligned} \tag{19}$$

subject to the boundary conditions Eq. 17. Here we have introduced

$$k \equiv \left(\frac{12\mu R^2}{\kappa + \epsilon}\right)\left[\frac{3\mu F_g}{2\pi(\kappa + \epsilon)^2}\right] \tag{20}$$

This zeroth-order solution is consequently fixed as a function of Y by Eq. 18.

From Eq. 19, we see that the first-order perturbation h_1 must satisfy

$$\frac{dh_1}{dt} = -\beta X_1 \tag{21}$$

in which

$$\beta = \beta(X_0) \tag{22}$$

Any disturbance will grow with time and the film will be unstable at a particular value of X_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. Consequently, β will be negative and the film will be unstable when X_0 is greater than X_c, where X_c is the solution of

$$\beta(X_c) = 0 \tag{23}$$

or

$$\begin{aligned} \alpha X_c^8 = {}& \{2X_c[I_0(X_c)]^2 - 4I_0(X_c)I_1(X_c) + 2X_c[I_1(X_c)]^2\} \\ & \times \{6X_c[I_0(x_c)]^2 - 12I_0(X_c)I_1(X_c) - 2X_c[I_1(X_c)]^2\}^{-1} \end{aligned} \tag{24}$$

From Eq. 16, we see that the coalescence time or time at which the film becomes unstable is

$$t_c = \frac{2\mu(\kappa + \epsilon)^2}{3\pi F_g} \tag{25}$$

in which Y_c is the value of Y corresponding to X_c from Eq. 18. Let us estimate (Chappelear, 1961; Princen, 1963; Lin and Slattery, 1982b) that

$$R = R_b^2\left(\frac{4\Delta\rho g}{3\gamma}\right)^{1/2} \tag{26}$$

which describes the rim radius of a stable film formed at a fluid-fluid interface as equilibrium is approached (see assumption 3).

Table 1. Dimensionless Coalescence Time t_c^* and Critical Film Thickness h_c^* as a Function of α

α	X_c	Y_c	h_c^*	t_c^*
2.993×10^8	0.1	1.891×10^{-6}	1.001	0.999
1.162×10^6	0.2	3.023×10^{-5}	1.002	0.997
4.484×10^4	0.3	1.528×10^{-4}	1.005	0.989
4.423×10^3	0.4	4.817×10^{-4}	1.008	0.980
1.659×10^2	0.6	2.420×10^{-3}	1.018	0.953
2.504	1.0	1.816×10^{-2}	1.046	0.879
8.409×10^{-2}	1.5	8.638×10^{-2}	1.086	0.766
2.350×10^{-4}	3.0	1.002	1.181	0.470
3.265×10^{-6}	5.0	4.708	1.238	0.260
2.046×10^{-7}	7.0	11.68	1.263	0.162
1.117×10^{-8}	10.0	28.48	1.280	9.209×10^{-2}
2.546×10^{-9}	12.0	43.95	1.286	7.629×10^{-2}
2.489×10^{-10}	16.0	85.16	1.294	4.111×10^{-2}
4.117×10^{-11}	20.0	1.401×10^2	1.299	1.769×10^{-2}
1.578×10^{-12}	30.0	3.377×10^2	1.305	1.298×10^{-2}
2.613×10^{-14}	50.0	9.927×10^2	1.309	4.909×10^{-3}
1.010×10^{-16}	100.0	4.417×10^2	1.313	1.275×10^{-3}

If we eliminate $\kappa + \epsilon$ using Eq. 15, F_g using Eq. 12, and R using Eq. 26, Eq. 25 may be rearranged as

$$\begin{aligned} t_c^* &\equiv \frac{t_c}{t_c(M)} \\ &= 30.6\,\alpha^{1/2} Y_c \end{aligned} \tag{27}$$

Here

$$t_{c(M)} \equiv 1.046 \frac{\mu R_b^{9/2}}{\gamma^{3/2} B^{1/2}} (\Delta\rho g) \tag{28}$$

is the corresponding coalescence time calculated by Chen et al. (1984) starting from the thinning rate equation derived by MacKay and Mason (1963) for a film bounded by immobile, parallel planes (see Eqs. 9 and 13 above). Observe that Y_c is a function only of α from Eqs. 18 and 24. As a result, t_c^* is a function only of α, as shown in Table 1 and Figure 2. A least-square error fit of this relationship gives

$$\log_{10} \alpha^{1/4} = \tanh^{-1}(2t_c^{*0.9566} - 1) - 0.8902 \tag{29}$$

In considering the implications of this result, it may be helpful to observe that, as an alternative to Eq. 15, we can write

$$\alpha^{1/2} = \frac{B^{1/4}\gamma^{3/4}(\kappa + \epsilon)}{8\mu\, \Delta\rho g R_b^{15/4}} \tag{30}$$

Rearranging Eq. 11, we see that the critical thickness at which the film becomes unstable is

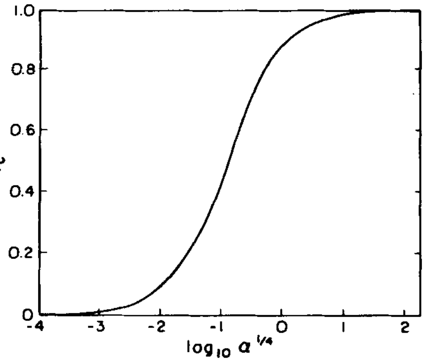

Figure 2. The dimensionless coalescence time t_c^* as a function of α.

$$h_c = \frac{R^2}{X_c^2}\left(\frac{6\mu}{\kappa + \epsilon}\right) \tag{31}$$

Eliminating $\kappa + \epsilon$ by Eq. 15 and R by Eq. 26, Eq. 31 may be more conveniently written as

$$\begin{aligned} h_c^* &= \frac{h_c}{h_{c(M)}} \\ &= 1.32\,\alpha^{-1/4} X_c^{-2} \end{aligned} \tag{32}$$

By

$$h_{c(M)} \equiv 0.760 \left(\frac{\pi R^2 B}{F_g}\right)^{1/4} \tag{33}$$

we mean the corresponding critical film thickness calculated by Chen et al. (1984) starting from the thinning rate equation derived by MacKay and Mason (1963) for a film bounded by immobile, parallel planes (see Eqs. 9 and 13 above). Like t_c^* above, h_c^* is a function only of α.

DISCUSSION

There are several interesting aspects of our prediction for the rest time or coalescence time t_c shown in Table 1, Figure 2, and Eqs. 29 and 30.

In the limit as the sum of the interfacial viscosities $\kappa + \epsilon \rightarrow \infty$, $t_c \rightarrow t_{c(M)}$, $t_{c(M)}$ is the corresponding coalescence time calculated by Chen et al. (1984) starting from the thinning rate equation derived by MacKay and Mason (1963) for a film bounded by immobile, parallel planes (see Eqs. 9 and 13 above). An immobile interface is one in which the tangential component of velocity is zero. An immobile interface may be the result of very small surface tension gradients (Lin and Slattery, 1982a,b; Hahn et al., 1985). In this analysis, immobile interfaces result when the surface viscosities are very large.

In the limit as $\alpha^{1/4} \rightarrow 0$ in Eq. 29 or as the surface viscosities $(\kappa + \epsilon) \rightarrow 0$, $t_c \rightarrow 0$, this is a physically incorrect result, outside the range of validity for our computation for several reasons. As $t_c \rightarrow 0$, inertial effects become important, but these are neglected in our computation. Our argument assumes that the motion is sufficiently slow that the surface concentration of surfactant is nearly independent of position in the phase interfaces. This would certainly not be true as $t_c \rightarrow 0$. Finally, as $(\kappa + \epsilon) \rightarrow 0$, it would no longer be reasonable to neglect the effects of the surface tension gradient in the jump momentum balance.

For $-2 < \log_{10} \alpha_{1/4} < 0.5$, t_c^* is sensitive to small changes in $\kappa + \epsilon$ and R_b. In agreement with this result, Hodgson and Lee (1969) observed a sharp increase in the drop rest time, when sufficient surfactant was added to the system. Nielsen et al. (1958), Picknett (1967), and Hodgson and Lee (1969) reported an increase in the apparent mobility of interfaces as the bubble diameter decreased while maintaining the chemical composition of the system constant.

Chen et al. (1984) and Hahn et al. (1985) have assumed in their analyses that the interfaces bounding the draining film are immobile, or $t_c^* = 1$ in Figure 2. They have concluded that the coalescence time increases as the bubble radius 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. Figure 2 indicates that for $-2 < \log_{10} \alpha^{1/4} < 0.5$, the effect of α is to moderate or even reverse each of these trends. This may explain the wide difference in functional dependence of coalescence time on drop radius that have been observed for liquid-liquid systems (see Chen et al., 1984, for a review).

Chen et al. (1984) and Hahn et al. (1985) were relatively unsuccessful in using their theories to describe the rest times for nitrogen bubbles rising in various liquids as observed by Allan et al. (1961) and by MacKay and Mason (1963). By regarding the phase interfaces of these systems as not being fully immobile, these observations could be explained by the present theory using plausible values of the surface viscosities for these systems ($\epsilon \sim 10^{-3}$ to 10^{-2} mN·s/m and $\kappa \sim 10^{-1}$ to 1 mN·s/m. Although the surface shear viscosity ϵ is often relatively small, the surface dilatational viscosity κ may be relatively large, if the observation that $\kappa \sim 10^2\epsilon$ [Stoodt and Slattery, 1984] proves to be generally true.)

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NOTATION

b_m = mutual force per unit mass
B = London-van der Waals constant in Eq. 7
$\mathbf{D}^{(\sigma)}$ = surface rate of deformation tensor defined by Eq. 4
F_g = defined by Eq. 12
g = magnitude of the acceleration of gravity
h = film thickness defined by Eq. 1
h_1 = first-order perturbation of h
h_c = critical film thickness
$h_{c(M)}$ = defined by Eq. 33
h_c^* = dimensionless critical film thickness defined by Eq. 32
I_0, I_1 = modified Bessel functions of the first kind, zeroth and first orders, respectively
k = defined by Eq. 20
m = parameter in Eq. 7
M = defined by Eq. 10
N_{Bo} = Bond number defined by Eq. 5
p = pressure in the film
$\mathbf{P}$ = projection tensor that transforms any vector on an interface into its tangential component
r = cylindrical coordinate
R = film radius
R_b = radius of bubble
$\mathbf{S}^{(\sigma)}$ = viscous portion of the surface stress tensor defined by Eq. 3
t = time
t_c = critical time or coalescence time at which the film becomes unstable
$t_{c(M)}$ = defined by Eq. 28
t_c^* = dimensionless coalescence time defined by Eq. 27
$\mathbf{T}^{(\sigma)}$ = surface stress tensor
$\mathbf{v}^{(\sigma)}$ = surface velocity vector
X = defined by Eq. 11
X_0 = solution to Eq. 14
X_1 = first-order perturbation to Eq. 14
X_c = critical value of X
Y = dimensionless time defined by Eq. 16
Y_c = critical dimensionless time
z = cylindrical coordinate

Greek Letters

α = defined by Eq. 15
β = growth coefficient of disturbance in Eq. 21
γ = surface tension
ϵ = surface shear viscosity
κ = surface dilatational viscosity
μ = viscosity of liquid
π = Van der Waals disjoining pressure defined by Eq. 8
ρ = density of liquid
ϕ = scalar potential in terms of which b_m is represented by Eq. 6
ϕ_0 = ϕ evaluated in the limit as the interface described by Eq. 1 is approached
Φ_B = interaction potential per unit volume of a semi-infinite film liquid in the limit as the interface is approached; see Eq. 7

Other

$div_{(\sigma)}$ = surface divergence operation (Wei et al., 1974; Briley et al., 1976)
$\nabla_{(\sigma)}$ = surface gradient operator (Wei et al., 1974; Briley et al., 1976)
$\ldots T$ = superscript denoting transpose operation

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