Effects of Electrostatic Double-Layer Forces on Coalescence

Jing-Den Chen
Schlumberger-Doll Research Center
Old Quarry Road
Ridgefield, CT 06877

Pil-Soo Hahn, J. C. Slattery
Department of Chemical Engineering
Northwestern University
Evanston, IL 60201

As buoyancy forces a drop or bubble to approach a fluid-fluid interface, a film of the continuous phase is formed. The minimum film thickness, several microns, is initially at the center. As thinning proceeds, the minimum film thickness moves to the rim (or barrier ring) and the film becomes dimpled (Allan et al., 1961; MacKay and Mason, 1963; Hodgson and Woods, 1969).

In a series of papers, we have discussed the approach of a bubble or drop to a solid plane (Lin and Slattery, 1982a; Chen and Slattery, 1982; Chen, 1984), to a fluid-fluid interface (Lin and Slattery, 1982b; Chen et al., 1984; Hahn et al., 1985; Hahn and Slattery, 1985, 1986), and to another bubble or drop (Chen, 1985), summarizing the prior literature. In particular, Hahn et al. (1985) analyzed the effects of London-van der Waals forces upon the drainage and stability of the film formed as a drop or bubble approaches a fluid-fluid interface.

Our objective in what follows is to extend the analysis of Hahn et al. by also including the effects of electrostatic forces. We know that London-van der Waals forces always create a negative contribution to the disjoining pressure as a bubble or drop approaches its homophase, which tends to destabilize the film and accelerate coalescence. Electrostatic forces always create a positive contribution to the disjoining pressure, which tends to stabilize the film and retard coalescence. There have been no systematic studies of the effects upon the drainage and stability of these films, when both London-van der Waals forces and electrostatic forces are active.

Statement of Problem

We will adopt the first twelve assumptions made by Hahn et al. (1985) with two minor qualifications. First, we recognize that an immobile interface can be created not only by very small interfacial tension gradients (Sheludko, 1967; Lin and Slattery, 1982a, b; Hahn et al., 1985) but also by very large interfacial viscous forces (Hahn and Slattery, 1985, 1986). Second and most important, although we continue to neglect the effects of gravity within the draining liquid film, we will account for the effects both of electrostatic forces and of London-van der Waals forces.

In addition, we will say (Chen, 1984):

(xiii) Within the draining liquid film, the mutual force per unit mass b_m^* is representable in terms of the sum of a London-van der Waals scalar potential ϕ_v^* and an electrostatic double-layer potential ϕ_e^*:

$$b_m^* = -\nabla(\phi_v^* + \phi_e^*) \tag{1}$$

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

$$\rho^*\phi_v^* = \Phi_B^* + \frac{B^*}{h^{*m}} \tag{2}$$

where ρ^* is the 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. When the film thickness h^* is less than 120 Å, $m \approx 3$ and $|B| \approx 10^{-14}$ erg; when the film thickness is larger than 400 Å, $m = 4$ and $|B| \approx 10^{-19}$ erg · cm (Kitchener and Prosser, 1957; Black et al., 1960; Sheludko et al., 1965; Gregory, 1969; Churaev, 1974a, b; Derjaguin et al., 1977). We speak of

$$\pi_v^* \equiv -\frac{B^*}{h^{*m}} \tag{3}$$

Pil-Soo Hahn is currently with the Chemical Engineering Division, Advanced Energy Research Institute, Daejun, South Korea.

as the disjoining pressure attributable to London-van der Waals forces 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. In the absence of electrostatic double-layer forces, a stable film of uniform thickness can never be formed in this case.

At planar fluid-fluid interfaces separated by a layer of a symmetric electrolyte (which dissociates into two ions, the valances of which are equal in magnitude) sufficiently thick that the potential profiles associated with the two double layers do not interact or $\kappa^* h^* > 4$ (Verwey and Overbeek, 1948)

$$\rho^* \phi_e^* = - D^* \exp(-\kappa^* h^*) \tag{4}$$

Here

$$\kappa^* \equiv \left(\frac{8 \pi n^* z^2 e^{*2}}{\epsilon k^* T^*} \right)^{1/2} \tag{5}$$

is the inverse of the Debye length,

$$D^* \equiv 64 n^* k^* T^* \tanh^2 \left(\frac{z e^* \psi^*}{4 k^* T^*} \right) \tag{6}$$

e^* is the elementary charge, ϵ is the dielectric constant of the medium, k^* is the Boltzmann constant, T^* is the absolute temperature, n^* is the number density of either ionic species, z is the magnitude of the valence of either ionic species, and ψ^* is the electrostatic surface potential of the interfaces. We speak of

$$\pi_e^* \equiv D^* \exp(-\kappa^* h^*) \tag{7}$$

as the disjoining pressure attributable to the electrostatic double layer of a flat film of thickness h^*. When the electrostatic surface potentials have the same sign as in the case that we are discussing here, there is a positive disjoining pressure attributable to the electrostatic double layer that acts to repel the fluid-fluid interfaces from each other.

(xiv) Because the dependence of h^* upon r^* is weak (Hahn et al., 1985; see their assumption ii), we will assume that the local value of the interaction potential per unit volume of the liquid at the fluid-fluid interfaces 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 (1973), and Chen et al. (1984) are normally larger than 400 Å, we expect that $m = 4$ in Eq. 2 is more appropriate. Several authors (Kitchener and Prosser, 1957; Black et al., 1960; Sheludko et al., 1965; Churaev, 1974a; Derjaguin et al., 1977) reported approximate values of B^* between two flat surfaces as:

$$\text{for } m = 4: |B^*| \approx 10^{-19} \text{ erg} \cdot \text{cm} \tag{8}$$

Solution

The analysis of this problem is very similar to that described by Hahn et al. (1985). The only change is the addition of the electrostatic mutual force in the equation of motion for the draining liquid film.

Following this change through their analysis, we find that the differential equation describing the thickness of the draining liquid film becomes

$$\begin{aligned} -\frac{\partial h}{\partial t'} = {} & \frac{1}{3} h^3 \left(\frac{1}{r^3} \frac{\partial h}{\partial r} - \frac{1}{r^2} \frac{\partial^2 h}{\partial r^2} + \frac{2}{r} \frac{\partial^3 h}{\partial r^3} + \frac{\partial^4 h}{\partial r^4} \right) \\ & + h^2 \frac{\partial h}{\partial r} \left(- \frac{1}{r^2} \frac{\partial h}{\partial r} + \frac{1}{r} \frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3} \right) \\ & + \frac{2}{3} m B \left[\frac{1}{r} \frac{1}{h^{m-2}} \frac{\partial h}{\partial r} + \frac{1}{h^{m-2}} \frac{\partial^2 h}{\partial r^2} - \frac{m-2}{h^{m-1}} \left(\frac{\partial h}{\partial r} \right)^2 \right] \\ & - \frac{2}{3} D \kappa e^{-\kappa h} \left[\frac{1}{r} h^3 \frac{\partial h}{\partial r} + h^3 \frac{\partial^2 h}{\partial r^2} - \kappa h^3 \left(\frac{\partial h}{\partial r} \right)^2 + 3 h^2 \left(\frac{\partial h}{\partial r} \right)^2 \right] \end{aligned} \tag{9}$$

where

$$\begin{aligned} h &\equiv \frac{h}{h_o^*} & r &\equiv \frac{r^*}{R_o^*} \\ t' &\equiv \frac{t^* \mu^*}{8 \rho^* R_o^{*2} N_{ca}} \left(\frac{h_o^*}{R_o^*} \right)^3 & B &\equiv \frac{R_o^{*2} B^*}{\gamma^* h_o^{*m+1}} \\ D &\equiv \frac{R_o^{*2} D^*}{\gamma^* h_o^*} & \kappa &\equiv \kappa^* h_o^* \end{aligned} \tag{10}$$

γ^* is the interfacial tension, μ^* is the viscosity of the liquid film, and

$$N_{ca} \equiv \frac{\mu^{*2}}{\rho^* R_0^* \gamma^*} \tag{11}$$

is the capillary number. The corresponding equation describing the initial film profile is

$$\begin{aligned} & \frac{8}{3} \left(\frac{\partial^4 h}{\partial r^4} \right)_{r=0} + 4 m B \left(\frac{\partial^2 h}{\partial r^2} \right)_{r=0} - 4 D \kappa e^{-\kappa} \left(\frac{\partial^2 h}{\partial r^2} \right)_{r=0} \\ & = h^3 \left(\frac{1}{r^3} \frac{\partial h}{\partial r} - \frac{1}{r^2} \frac{\partial^2 h}{\partial r^2} + \frac{2}{r} \frac{\partial^3 h}{\partial r^3} + \frac{\partial^4 h}{\partial r^4} \right) \\ & + 3 h^2 \frac{\partial h}{\partial r} \left(- \frac{1}{r^2} \frac{\partial h}{\partial r} + \frac{1}{r} \frac{\partial^2 h}{\partial r^2} + \frac{\partial^3 h}{\partial r^3} \right) \\ & + 2 m B \left[\frac{1}{r} \frac{1}{h^{m-2}} \frac{\partial h}{\partial r} + \frac{1}{h^{m-2}} \frac{\partial^2 h}{\partial r^2} - \frac{m-2}{h^{m-1}} \left(\frac{\partial h}{\partial r} \right)^2 \right] \\ & - 2 D \kappa e^{-\kappa h} \left[\frac{1}{r} h^3 \frac{\partial h}{\partial r} + h^3 \frac{\partial^2 h}{\partial r^2} - \kappa h^3 \left(\frac{\partial h}{\partial r} \right)^2 + 3 h^2 \left(\frac{\partial h}{\partial r} \right)^2 \right] \end{aligned} \tag{12}$$

The boundary conditions and method of solution remain unchanged from those given by Hahn et al. One minor difference from the computations of Hahn et al. is that they used $\Delta r = 0.02$ and $\Delta t' = 0.02$ to 0.05 in their finite-difference computations; here we used $\Delta r = 0.02$ and $\Delta t' = 0.01$.

Results and Discussion

In order to estimate appropriate ranges of the values for B, D, and κ, we assumed $T^* = 298$ K, $\gamma^* \approx 10^{-2}$ to 30 mN/m, $B^* = 10^{-19}$ erg · cm, $\psi^* = 0$ (Hahn et al.) to 200 mv, the ion concen-

Table 1. Dimensionless Time t'_f, at which an Equilibrium Film of Uniform Thickness h_f Is Formed or Ruptures*

	B (Eq. 10)									
	10^{-4}		10^{-5}		10^{-6}		10^{-7}		10^{-8}	
κ	t'_f	h_f	t'_f	h_f	t'_f	h_f	t'_f	h_f	t'_f	h_f
For $D = 10^2$										
10^2	1.79	0	6.28	0	601	0.0235	316	0.0273	307	0.0276
10^3	1.78	0	4.93	0	14.0	0	40.9	0	121	0
10^4	1.78	0	4.93	0	14.0	0	40.9	0	121	0
For $D = 10^4$										
10^2	32.7	0.0678	27.8	0.0729	27.5	0.0734	27.4	0.0734	27.4	0.0734
10^3	1.78	0	4.93	0	14.0	0	40.9	0	1732	0.0045
10^4	1.78	0	4.93	0	14.0	0	40.9	0	121	0
For $D = 10^6$										
10^2	7.92	0.118	7.84	0.119	7.84	0.119	7.84	0.119	7.84	0.119
10^3	1.78	0	4.93	0	14.0	0	41.4	0	90.2	0
10^4	1.78	0	4.93	0	14.0	0	40.9	0	121	0
For $D = 10^8$										
10^2	3.60	0.165	3.60	0.165	3.60	0.165	3.60	0.165	3.60	0.165
10^3	1.78	0	4.93	0	14.0	0	37.2	0	47.2	0
10^4	1.78	0	4.93	0	14.0	0	40.9	0	121	0
For $D = 10^{10}$										
10^2	1.85	0.211	1.85	0.211	1.85	0.211	1.85	0.211	1.85	0.211
10^3	1.78	0	4.93	0	13.8	0	27.5	0	30.3	0
10^4	1.78	0	4.93	0	14.0	0	40.9	0	121	0

*$h_f = 0$: film ruptures and coalescence occurs

tration from 10^{-5} to 10^{-1} N, $\epsilon = 80$ (for water), $h_0^* = 5.30 \times 10^{-4}$ cm (Hahn et al.), and $R_0^* = 1.44 \times 10^{-2}$ cm (Hahn et al.).

Qualitatively, the film profiles are similar to those presented previously (Lin and Slattery, 1982b; Hahn et al., 1985). Like Hahn et al., we find that the initial profiles are independent of the parameters (B, D, κ) used to describe the London-van der Waals forces and electrostatic forces. This suggests that for sufficiently small disjoining pressures, the initial film profile is independent of the disjoining pressure.

Although there are no experimental data available with which to compare our calculated film profiles, we can gain some insight with respect to the relative effects of the London-van der Waals forces and the electrostatic double-layer forces. Consider the dimensionless time t'_f and dimensionless film thickness h_f at which the dimpled film becomes flat (or ruptures), which are shown as functions of B, D, and κ in Table 1. We can draw several conclusions.

For $\kappa = 10^4$, the film ruptures at the rim in a finite time t'_f and the effect of electrostatic double-layer forces is negligible. The coalescence time (rest time) t'_f increases as B decreases, in agreement with the prediction of Hahn et al. (1985, their Eq. 29).

For $\kappa = 10^3$, the film is also unstable, except for $D = 10^4$ and $B = 10^{-8}$. The coalescence time t'_f increases as B decreases, but the effect of the electrostatic forces is evident only for $D \geq 10^4$. For $B = 10^{-7}$, t'_f increases and then decreases as D increases from 10^2 to 10^{10}. This contradicts our naive intuition, which suggests that the coalescence time should increase as D increases. The answer is that it is the gradient of the disjoining pressure, which appears in the last two terms of Eq. 10, and that as a result the curvature of the dimpled film modifies the impact of the disjoining pressure upon the rate of thinning.

For $\kappa = 10^2$, the effects of electrostatic repulsion are stronger. For a strong electrostatic repulsion ($D > 10^4$), the effects of London-van der Waals attraction are negligible and the time t'_f required to reach the final equilibrium film thickness is essentially independent of B. For weaker electrostatic repulsion ($D < 10^4$), the film ruptures when the London-van der Waals attraction is strong ($B > 10^{-6}$), but it drains to an equilibrium film of uniform thickness when the attraction is weaker ($B \leq 10^{-6}$). The time t'_f to reach equilibrium is shorter and the final film thickness h_f larger for weaker London-van der Waals attraction (smaller B).

In summary, this theory describes the evolution of the film as a function of time given only the radius of the drop or bubble and all of the required physical properties. We follow Neitzel and Davis (1981) in 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. When coalescence occurs, our predicted coalescence time is an upper bound in the sense that it does not allow for the development of asymmetric drainage and of asymmetric instabilities leading to premature rupture as observed by some experimenters.

Acknowledgment

This work was sponsored in part by Grant No. CBT-8511207 from the National Science Foundation. Pil-Soo Hahn thanks the Korean Government for financial support during a portion of this work.

Notation

b_m^* = mutual force per unit mass
B = defined by Eq. 10
B^* = London-van der Waals parameter, Eq. 2
D = defined by Eq. 10
D^* = electrostatic double-layer parameter, Eq. 4
e^* = elementary charge
h = defined by Eq. 10

h^* = film thickness
h_0^* = film thickness at $t^* = 0$ and $r^* = 0$
k^* = Boltzmann constant
m = London-van der Waals parameter, Eq. 2
n^* = number density of either ionic species
N_{ca} = capillary number, Eq. 11
r = defined by Eq. 10
r^* = cylindrical coordinate
R_o^* = rim radius of film at $t^* = 0$
t^* = time
t' = defined by Eq. 10
T^* = absolute temperature
z = Magnitude of the valence of either ionic species

Greek letters

γ^* = interfacial tension
ϵ = dielectric constant of medium
κ = defined by Eq. 10
κ^* = inverse of Debye length, Eq. 5
μ^* = viscosity of liquid film
π_e = disjoining pressure attributable to electrostatic double-layer forces, Eq. 7
π_v = disjoining pressure attributable to London-van der Waals forces, Eq. 3
ρ^* = density of liquid film
ϕ_e^* = scalar potential for electrostatic double-layer force per unit mass
ϕ_v^* = scalar potential for London-van der Waals force per unit mass
Φ_B^* = interaction potential per unit volume of a semiinfinite film liquid in the limit as the fluid-fluid interface is approached
ψ^* = electrostatic surface potential of interfaces

Literature Cited

Allan, R. S., G. E. Charles, and S. G. Mason, "The Approach of Gas Bubbles to a Gas/Liquid Interface," *J. Colloid Sci.*, **16,** 150 (1961).

Black, W., J. G. V. de Jongh, J. Th. G. Overbeek, and M. J. Sparnaay, "Measurements of Retarded van der Waals Forces," *Trans. Faraday Soc.*, **56,** 1597 (1960).

Burrill, K. A., and D. R. Woods, "Film Shapes for Deformable Drops at Liquid-Liquid Interfaces. II: The Mechanism of Film Drainage," *J. Colloid Interface Sci.*, **42,** 15 (1973).

Chen, J. D., "Effects of London-van der Waals and Electric Double Layer Forces on the Thinning of a Dimpled Film between a Small Drop or Bubble and a Horizontal Plane," *J. Colloid Interface Sci.*, **98,** 329 (1984).

———, "A Model of Coalescence between Two Equal-Sized Spherical Drops or Bubbles," *J. Colloid Interface Sci.*, **107,** 209 (1985).

Chen, J. D., P. S. Hahn, and J. C. Slattery, "Coalescence Time for a Small Drop or Bubble at a Fluid-Fluid Interface," *AIChE J.*, **30,** 622 (1984).

Chen, J. D., and J. C. Slattery, "Effects of London-van der Waals Forces on the Thinning of a Dimpled Liquid Film as a Small Drop or Bubble Approaches a Horizontal Solid Plane," *AIChE J.*, **28,** 955 (1982); *ibid.*, **29,** 174, 526 (1983).

Churaev, N. V., "Molecular Forces in Wetting Films of Nonpolar Liquids. 1: Thick Films," *Colloid J. USSR* (Engl. Transl.), **36**(2), 283 (1974a).

———, "Molecular Forces in Wetting Films of Nonpolar Liquids. 2: Thim Films," *Colloid J. USSR* (Engl. Transl.), **36**(2), 287 (1974b).

Derjaguin, B. V., Y. I. Rabinovich, and N. V. Churaev, "Measurement of Forces of Molecular Attraction of Crossed Fibres as a Function of Width of Air Gap," *Nature (London)*, **265,** 520 (1977).

Gregory, J., "The Calculation of Hamaker Constants," *Adv. Colloid Interface Sci.*, **2,** 396 (1969).

Hahn, P. S., J. D. Chen, and J. C. Slattery, "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," *AIChE J.*, **31,** 2026 (1985).

Hahn, P. S., and J. C. Slattery, "Effects of Surface Viscosities on the Stability of a Draining Plane Parallel Liquid Film as a Small Bubble Approaches a Liquid-Gas Interface," *AIChE J.*, **31,** 950 (1985).

———, "Effects of Surface Viscosities on the Thinning and Rupture of a Dimpled Liquid Film as a Small Bubble Approaches a Liquid-Gas Interface," *AIChE Symp. Ser.*, **82**(252), 100 (1986).

Hodgson, T. D., and D. R. Woods, "The Effect of Surfactant on the Coalescence of a Drop at an Interface. II," *J. Colloid Interface Sci.*, **30,** 429 (1969).

Ivanov, I. B., B. Radoev, E. Manev, and A. Sheludko, "Theory of the Critical Thickness of Rupture of Thin Liquid Films," *Trans. Faraday Soc.*, **66,** 1262 (1970).

Kitchener, J. A., and A. P. Prosser, "Direct Measurement of the Long-Range van der Waals Forces," *Proc. Royal Soc. Ser. A.*, **242,** 403 (1957).

Lin, C. Y., and J. C. Slattery, "Thinning of a Liquid Film as a Small Drop or Bubble Approaches a Solid Plane," *AIChE J.*, **28,** 147 (1982a).

———, "Thinning of a Liquid Film as a Drop or Bubble Coalesces at a Fluid-Fluid Interface," *AIChE J.*, **28,** 786 (1982b).

MacKay, G. D. M., and S. G. Mason, "The Gravity Approach and Coalescence of Fluid Drops at Liquid Interfaces," *Can. J. Chem. Eng.*, **41,** 203 (1963).

Neitzel, G. P., and S. M. Davis, "Centrifugal Instabilities during Spin-Down to Rest in Finite Cylinders. Numerical Experiments," *J. Fluid Mech.*, **102,** 329 (1981).

Ruckenstein, E., and R. K. Jain, "Spontaneous Rupture of Thin Liquid Films," *J. Chem. Soc., Faraday Trans. II*, **70,** 132 (1974).

Sheludko, A., "Thin Liquid Films," *Adv. Colloid Interface Sci.*, **1,** 391 (1967).

Sheludko, A., D. Platikanov, and E. Manev, "Disjoining Pressure in Thin Liquid Films and the Electromagnetic Retardation Effect of the Molecule Dispersion Interactions," *Discuss. Faraday Soc.*, **40,** 253 (1965).

Verwey, E. J. W., and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, New York (1948).

Vrij, A., "Possible Mechanism for the Spontaneous Rupture of Thin, Free Liquid Films," *Discuss. Faraday Soc.*, **42,** 23 (1966).

Manuscript received Aug. 14, 1986, and revision received May 30, 1987.