Effect of Film Size on Drainage of Foam and Emulsion Films

All available theoretical analyses for the drainage of thin plane-parallel liquid films, such as those existing between two approaching liquid droplets or bubbles in the coalescence process, predict essentially the same dependence of rate of thinning of the intervening film on its size as is described by the Reynolds equation—that is, drainage time increases with the square of the film radius. Recently, we have reported experimental data for both foam and emulsion films which showed that the measured drainage times increase with about a 0.8 power of the film radius, a value much smaller than the theoretically predicted value of 2.0. Here we present a hydrodynamic analysis to predict the experimentally observed effect of film size on the kinetics of thinning of emulsion and foam films. We extend the applicability of the Reynolds model by accounting for the flow in the Plateau borders as well as the London-van der Waals forces in the thin film phase. Our theoretical predictions are in good agreement with the experimental data on the dependence of drainage time of both foam and emulsion films on their radii.

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Introduction

When two drops or bubbles approach each other in a liquid dispersion or emulsion, a thin film of the continuous-phase liquid is formed. This film drains under the combined action of suction at the Plateau borders and disjoining pressure. The latter consists of the van der Waals dispersion forces and the electrostatic forces. The drainage of the thin film is the rate-limiting step of the coalescence process. A number of mathematical models have been developed to address various features of the problem (Woods and Burrill, 1972; Liem and Woods, 1974; Reed et al., 1974a,b; Ivanov and Traykov, 1976; Jain and Ruckenstein, 1976; Traykov and Ivanov, 1977; Ivanov and Jain, 1979; Ivanov, 1980; Maldarelli and coworkers, 1980, 1982a,b, Hahn and Slattery, 1985). For more recent reviews of the theoretical models for the thinning of films between fluid particles (bubbles or drops), the reader is referred to the work of Oppenheim (1983), Zapryanov et al., (1983), Malhotra (1984), and Ivanov et al. (1985).

Results of the available theoretical analyses, most of which are based on the Reynolds lubrication approximation, indicate the effects of many factors on the draining of thin liquid films. These factors include surface or interfacial tension and its gradient (or the Marangoni-Gibbs effect), surface viscosities, drop and film phase viscosities, surface mobilities, surfactant transfer onto the interface, surfactant adsorption-desorption kinetics, dispersion forces, interfacial curvature, dimple formation, and film size. All the theoretical expressions for the drainage of thin plane-parallel liquid films between two approaching liquid droplets or bubbles essentially predict the same dependence of rate of thinning on film radius as is described by the Reynolds equation—that is, the rate of thinning varies inversely with the square of the film radius.

Recently, Manev et al. (1984a) have determined experimentally the dependence of drainage times of foam and emulsion films on film radii, using the interferometric technique, and have compared the measured values to those calculated from the Reynolds equation, as well as the other theoretical expressions involving the model of a plane-parallel film. They plotted the experimental drainage times for a constant range of film thickness from 200 to 50 nm on a log-log scale as a function of film radius. Their plot yielded a linear dependence with a slope of about 0.8, a value much smaller than the slope of 2.0 predicted by the available theoretical models. It should be pointed out that in the range of the film radii reported by them ($\leq 5 \times 10^{-4}$ m), the thin liquid films were observed to be nearly plane-parallel in all their experiments (for film thicknesses less than 200 nm). Their experiments for foam and emulsion films were conducted with aqueous solutions of sodium dodecyl sulfate (an anionic surfactant) and octanoic acid (a nonionic surfactant) containing sodium chloride.

The objective of the present work is to develop a hydrody-

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namic model to predict the experimentally observed dependence of film size on drainage time of the intervening thin liquid films between small droplets or bubbles. The present analysis, which takes into account the flow in the thin film as well as in the thicker regions (Plateau borders), is applicable only to plane-parallel film surfaces that are rendered tangentially immobile due to the presence of surfactants. The London-van der Waals forces are also accounted for in this analysis.

Formulation of the Problem

Figure 1 shows two drops or bubbles pressed against each other and separated by a thin film and thicker regions (Plateau borders). Due to the concave shape of the Plateau borders, a capillary pressure exists that tends to drain the liquid from the film into thicker portions. This results in thinning of the film. As the thickness of the film becomes sufficiently small (<100 nm), the effects of van der Waals and electrostatic forces become significant.

Reynolds (1886) considered the flow between two rigid discs in an attempt to arrive at the film thinning velocity. Several other analyses have also considered the film to be plane-parallel but deformable. Previous studies have neglected the flow in the Plateau borders, and to arrive at the film thinning velocity the normal stress condition is satisfied on an integral basis. The assumption of a plane-parallel film and the use of an integral form of the normal stress condition is self-contradicting. Based on these assumptions, the film thinning velocity is given by

$$V'_{Re} = -\frac{dh'}{dt'} = \frac{8h'^3}{3\mu' R'^2}\Delta p' \tag{1}$$

where h' is half-film thickness, t' is time, μ' is viscosity of film liquid, and $\Delta p'(=p'_c - \pi')$ is driving force per unit area. Here p'_c is capillary pressure, and π' is disjoining pressure.

The present analysis acknowledges the experimental observation that the film remains essentially plane-parallel during the process of film thinning (Scheludko, 1967; Rao et al. 1982; Manev et al. 1984a). However, the deformation at the Plateau borders is accounted for in this analysis.

To keep the mathematics tractable, we need to make the following simplifying assumptions:

1. The interfaces bounding the draining liquid are axisymmetric.
2. The film remains essentially plane-parallel throughout the process of thinning.
3. Film radius, R', is defined as the farthest radial distance where the film has the minimum thickness. (All dimensional quantities are denoted with a prime.)
4. The flow in the film as well as in the Plateau borders obeys the Reynolds lubrication approximation (valid for $h'/r' \ll 1$ and low Reynolds number).
5. Bulk liquids and adsorbed layers are Newtonian fluids with constant physical properties.
6. The effect of gravity is negligible.
7. The effect of mass transfer on velocity distribution is neglected.
8. There is enough surfactant present in the system to completely retard the tangential motion of the interface.
9. Sufficiently far away from the film, the interface has essentially spherical curvature.
10. The film forms a macroscopic contact angle with its associated Plateau borders. This contact angle is assumed to be independent of time.
11. Viscous effects are negligible in the drop phase.
12. Since drainage is a slow process, a pseudosteady-state approach is employed.

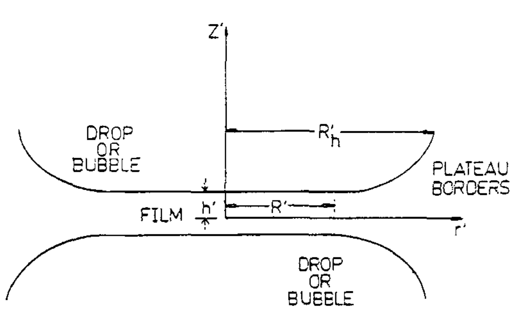

Figure 1. Film configuration and coordinate system.

Because of assumptions 8 and 11, the flow in the dispersed phase no longer needs to be considered. Hence, one needs to combine two different flows in the continuous phase: flow between plane-parallel surfaces for $0 < r' < R'$ (film) and flow with deformable surfaces for $R' < r' < R'_h$ (Plateau borders). R'_h is the radial location where the flow has no effect on the shape of the interfaces. We must keep in mind assumption 4, which requires the distance of separation between the bounding interfaces to be much smaller than the radial distance.

Governing equations in the Plateau borders

Using the preceding assumptions and an order of magnitude analysis, the Navier-Stokes equations in the Plateau borders can be simplified to the following dimensionless form.

$$\frac{\partial p}{\partial r} = \frac{\partial^2 V_r}{\partial z^2} \tag{2}$$

$$\frac{\partial p}{\partial z} = 0 \tag{3}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(rV_r) + \frac{\partial V_z}{\partial z} = 0. \tag{4}$$

The dimensionless quantities are defined as

$$r = \frac{r'}{R'_0}, \quad z = \frac{z'}{h'_0}$$

$$V_r = \frac{R'^3_0 \mu'}{h'^3_0 \sigma'_0} V'_r, \quad V_z = \frac{R'^4_0 \mu'}{h'^4_0 \sigma'_0} V'_z$$

$$p = \frac{R'^2_0}{\sigma'_0 h'_0} p'$$

with R'_0 and h'_0 being the film radius and film thickness at time $t' = 0$. ρ' and μ' are respectively the bulk density and the viscosity of the continuous phase liquid. σ'_0 is the equilibrium interfacial tension between the continuous phase liquid and the dispersed phase fluid. V_r and V_z denote the velocity components in the r and z directions, respectively; p denotes pressure.

In view of assumption 8, we do not need to consider the transport of the surfactant from the bulk phases onto the interface. Hence, we do not need to formulate the surfactant conservation equations for the bulk phases and sufactant mass balance equation at the interface.

With assumptions 6, 7, 8, and 11, the tangential and normal stress boundary conditions at $z = h$ reduce to

$$V_r = 0 \tag{5}$$

$$p_g - p = \frac{1}{R_1} + \frac{1}{R_2} + \Pi(h) \tag{6}$$

where

$$\frac{1}{R_1} = \frac{\dfrac{1}{r}\dfrac{\partial h}{\partial r}}{\left[1 + \epsilon^2\left(\dfrac{\partial h}{\partial r}\right)^2\right]^{1/2}}$$

and

$$\frac{1}{R_2} = \frac{\dfrac{\partial^2 h}{\partial r^2}}{\left[1 + \epsilon^2\left(\dfrac{\partial h}{\partial r}\right)^2\right]^{3/2}}$$

with $\epsilon = h'_0/R'_0$. R_1 and R_2 are the two radii of curvature of the interface. Π is the disjointing pressure, comprised of long-range van der Waals attractive forces, electrostatic repulsive forces, and forces due to steric hindrance in closely packed monolayers of long-chain surfactant molecules.

Using assumption 7, the kinematic boundary condition can be written as

$$V_z = \frac{d_m h}{dt} = \frac{\partial h}{\partial t} + V_r\frac{\partial h}{\partial r} \quad \text{at } z = h \tag{7}$$

where

$$t = \frac{h_0'^3 \sigma_0'}{R_0'^4 \mu'} t'.$$

Employing assumption 4, the above equation reduces to

$$V_z = \frac{\partial h}{\partial t}. \tag{8}$$

Due to the natural symmetry of the system, we have at $z = 0$

$$\frac{\partial V_r}{\partial z} = 0 \tag{9}$$

$$V_z = 0. \tag{10}$$

The assumption of a macroscopic contact angle between the film and its associated Plateau borders can be written as

$$\frac{\partial h}{\partial r} = \frac{1}{\epsilon}\tan\theta' \quad \text{at } r = R \tag{11}$$

where θ' is the contact angle between the film and the Plateau borders.

According to assumption 9, the two radii of curvature at $r = R_h$ are independent of time, i.e.,

$$\left(\frac{\partial h}{\partial r}\right)_t = \left(\frac{\partial h}{\partial r}\right)_{t=0} \quad \text{at } r = R_h \tag{12}$$

$$\left(\frac{\partial^2 h}{\partial r^2}\right)_t = \left(\frac{\partial^2 h}{\partial r^2}\right)_{t=0} \quad \text{at } r = R_h. \tag{13}$$

Since the distance of separation between the two interfaces at radial location $r = R_h$ is large, the disjoining pressure can be neglected at $r = R_h$, in which case Eqs. 6, 12, and 13 combine to give

$$P_g - p = \frac{\left(\dfrac{1}{r}\dfrac{\partial h}{\partial r}\right)_{t=0}}{\left[1 + \epsilon^2\left(\dfrac{\partial h}{\partial r}\right)^2_{t=0}\right]^{1/2}} + \frac{\left(\dfrac{\partial^2 h}{\partial r^2}\right)_{t=0}}{\left[1 + \epsilon^2\left(\dfrac{\partial h}{\partial r}\right)^2_{t=0}\right]^{3/2}} \quad \text{at } r = R_h. \tag{14}$$

Governing equations in the film

The flow in the film can be described by the set of equations

$$\frac{\partial p^f}{\partial r} = \frac{\partial^2 V_r^f}{\partial z^2} \tag{15}$$

$$\frac{\partial p^f}{\partial z} = 0 \tag{16}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(rV_r^f) + \frac{\partial V_z^f}{\partial z} = 0. \tag{17}$$

where the superscript f refers to quantities in the film phase. It should be pointed out that the film is assumed to be plane-parallel, i.e., $h_f \neq h_f(r)$. h_f is the film thickness.

Solution

Flow in the Plateau borders

Integrating Eq. 2 twice with respect to z with Eq. 5 and 9, the radial velocity, V_r, can be written as

$$V_r = \frac{z^2 - h^2}{2}\frac{\partial p}{\partial r}. \tag{18}$$

Substituting Eq. 18 into Eq. 4, integrating with respect to z, and employing Eqs. 8 and 10, we obtain

$$\frac{\partial h}{\partial t} = \frac{1}{3}\nabla_r\left(h^3\frac{\partial p}{\partial r}\right) \tag{19}$$

where

$$\nabla_r = \frac{1}{r}\frac{\partial}{\partial r}r.$$

Defining $t^* = t/3$, the above equation can be reduced to

$$\frac{\partial h}{\partial t^*} = \nabla_r\left(h^3\frac{\partial p}{\partial r}\right). \tag{20}$$

In the early stages of film thinning the disjoining pressure is negligible. However, as the thickness of the film becomes sufficiently small (<100 nm), the disjoining pressure becomes significant. If there is an excess of electrolyte present in the continuous phase, the electrostatic component of the disjoining pressure can be neglected. Furthermore, for small-chain surfactant molecules the forces due to steric hindrance are insignificant. In the absence of electrostatic and steric forces, the disjoining pressure can be expressed as $\Pi' = -K'/8h'^3$, in which case Eq. 6 can be written as

$$p_g - p = \frac{1}{R_1} + \frac{1}{R_2} - \frac{K}{h^3} \tag{21}$$

where

$$K = \frac{R_0'^2}{8h_0'^4\sigma_0'}K'$$

and K' is Hamaker's constant.

Flow in the film

Following a procedure similar to that outlined above, film thinning can be described by

$$V_r^f = \frac{z^2 - h_f^2}{2}\frac{\partial p^f}{\partial r} \tag{22}$$

$$\frac{\partial h_f}{\partial t} = h_f^3\nabla_r\left(\frac{\partial p^f}{\partial r}\right) \tag{23}$$

Integrating Eq 23 with respect to r, we obtain

$$\frac{\partial h_f}{\partial t} = \frac{2h_f^2}{R}\left(\frac{\partial p^f}{\partial r}\right) \quad \text{at } r = R \tag{24}$$

with R being the dimensionless film radius given by

$$R = \frac{R'}{R_0'}.$$

Matching the two solutions

In order to match the solutions given by Eqs. 20 and 23, we equate the outgoing flux from the film phase, Q^f, to the flux in the Plateau borders, Q^p, at the film periphery. Q^f is given by

$$Q^f = 2\pi R\int_0^{h_f}(V_r^f)_{r=R}\,dz. \tag{25}$$

Substituting Eqs. 22 and 25, one obtains

$$Q^f = -\frac{\pi}{3}Rh_f^3\left(\frac{\partial p^f}{\partial r}\right)_{r=R} \tag{26}$$

Integration of Eq. 18 with respect to z gives flux Q^p in the Plateau border at the film rim

$$Q^p = -\frac{\pi}{3}Rh^3\left(\frac{\partial p}{\partial r}\right)_{r\rightarrow R^+}, \tag{27}$$

where $r \rightarrow R^+$ means $r \rightarrow R$ when $r > R$.

Employing Eqs. 26 and 27 and equating the two fluxes, we obtain

$$\left(\frac{\partial p^f}{\partial r}\right)_{r=R} = \left(\frac{\partial p}{\partial r}\right)_{r\rightarrow R+} = \left(\frac{\partial p}{\partial r}\right)_{r=R}. \tag{28}$$

Combining Eqs. 24 and 28 results in

$$\frac{\partial h}{\partial t} = \frac{2h^3}{R}\frac{\partial p}{\partial r} \quad \text{at } r = R. \tag{29}$$

Equation 20 can be integrated with respect to t using the boundary conditions of Eqs. 11–14 and 29, provided the macroscopic contact angle (between the film and the Plateau borders) and the initial shape of the Plateau borders are known.

Initial shape of the Plateau borders

Scheludko and his coworkers (1968) in a series of experimental papers dealing with measurements of contact angle between thin liquid films and the bulk adjoining liquid have shown that the shape of the Plateau borders can be represented by a quadratic equation. They have clearly stated that if the film radius is small in comparison with the radius of the tube containing the drop or bubble, then a parabola represents an accurate description of the Plateau borders. In view of this, we assume that the initial shape of the Plateau borders can be represented by the following polynomial form

$$h = a_0 + a_1r + a_2r^2. \tag{30}$$

The above equation has three unknowns a_0, a_1, and a_2. Also, we must identify the radial location $r = R_h$ where the flow has insignificant effect on the balance of forces and also where assumption 4 is not violated. Hence, we need four conditions to evaluate the unknowns a_0, a_1, a_2, and R_h. It is desirable to choose R_h as large as possible in order to make the pressure gradient at this point negligibly small. But if R_h is assigned too large a value, the lubrication approximation will be violated. Since differential Eq. 20 is linear in time, the choice of film thickness at time $t = 0$ is rather arbitrary. It is assumed that at time $t = 0$, film thickness $h_0' = 400$ nm. Furthermore, R_h is identified as the radial location where the thickness $h = 12$. We need two additional conditions to evaluate the unknowns. The assumption that the curvature of the interface is essentially spherical at $r = R_h$ provides one condition. The second condition is obtained by the assumption that the film forms a macroscopic contact angle with its associated Plateau borders. Thus, the four conditions necessary for calculation of the initial shape of the Plateau borders can be represented by

$$\frac{\partial h}{\partial r} = \frac{1}{\epsilon} \tan \theta' \quad \text{at } r = 1 \tag{31}$$

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{\epsilon R_c} \quad \text{at } r = R_h \tag{32}$$

$$h_0' = 4.0 \times 10^{-7} \text{m} \quad \text{at } r = 1 \tag{33}$$

$$h = 12 \quad \text{at } r = R_h. \tag{34}$$

Method of Solution

Equations 20 and 21 were reduced to a finite-difference form with error $0(\Delta r^2 + \Delta t^2)$ using the Crank-Nicolson approach. The resultant set of nonlinear equations were solved using the two-slice tridiagonal elimination method (Malhotra, 1984). Convergence of the numerical scheme was checked by varying time and space intervals.

The initial shape of the Plateau borders was determined by solving the set of nonlinear Eqs. 30–34 using the Newton-Raphson method. As mentioned earlier, it is desirable to choose R_h as large as possible in order to make the pressure gradient at this point negligible. But too large a value of R_h would violate assumption 4. In order to check the sensitivity of R_h on drainage time, the computations were repeated with $h = 9$ and $h = 15$ in Eq. 34. This procedure changes the value of R_h. These computations showed that drainage time changed less than 1% and hence $h = 12$ in Eq. 34 is reasonable.

Results and Discussion

For a capillary radius $R_c' = 2 \times 10^{-3}$ m, Figure 2 shows the variation of dimensionless drainage time t^+ (the time for a film to drain from a thickness, $h' = 100$ to 25 nm) as a function of film radius, R_0', for various values of dimensionless Hamaker's constant, K^+. We redefined the dimensionless time and Hamaker's constant so that their definitions involve only system properties and not the film radius. These are now defined as

$$t^+ = \frac{\sigma_0'}{3\mu' h_0'} t'$$

$$K^+ = \frac{K'}{8 h_0'^2 \sigma_0'}$$

The initial shape was calculated using Eqs. 30–34. Table 1 lists the values of the various constants used in calculating the initial shape of the Plateau borders for different values of film radii.

The initial shape of Plateau borders calculated with Eqs. 29–31 and 33 and $h_0' = 400$ nm at $r = 1$ was utilized with Eqs. 11–13, 19, 20, and 23 to arrive at the shape of the Plateau borders at a film thickness of 100 nm. This shape was employed to predict the drainage time from an initial film thickness of 100 to 25 nm. Other values of h_0' (such as $h_0' = 1{,}000$ nm and $h_0' = 300$ nm) were also employed to estimate the shape of the Plateau borders;

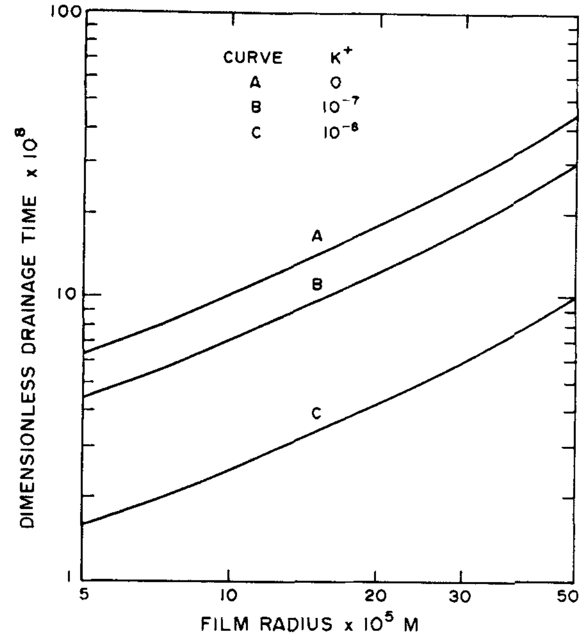

Figure 2. Dimensionless drainage time as a function of film radius R_0 for various values of dimensionless Hamaker's constant K^+.
Drainage time t^+ from thickness $h' = 100$ to 25 nm

the calculated values of drainage time from 100 to 25 nm were essentially unaffected (<2%). It needs to be pointed out that the governing equations, Eqs. 19 and 20, are linear with respect to time t. Furthermore, Manev et al. (1984a) have measured the contact angle between the film and the Plateau borders and found it to be very small (<5°). Therefore, we set it equal to zero in comparing our theoretical predictions with the experimental data.

It is clear from Figure 2 that for a constant range of thicknesses, the drainage time increases with film radius. An increase in Hamaker's constant results in increased disjoining pressure and hence reduced drainage time.

Comparisons with experimental data

In our laboratory, Manev et al. (1984a) and DiNardo (1984) have taken extensive data on drainage of aqueous foam and emulsion films as a function of film radius and surfactant concentration. Sodium dodecyl sulfate (SDS, an anionic surfactant) and octanoic acid (a nonionic surfactant) solutions were

Table 1. Constants in Eq. 30 for Evaluating Initial Shape of Plateau Borders for Parametric Study

R_0' $\times 10^5$ m	R_h' $\times 10^5$ m	a_0' $\times 10^7$ m	$-a_1'$ $\times 10^2$	a_2' $\times 10^{-2}$ m^{-1}
5	17.5	11.33	2.93	2.93
10	21.9	36.63	6.53	6.53
20	31.1	152.57	14.86	14.86
30	40.7	363.54	23.97	23.97
40	50.5	632.32	33.46	33.46
50	60.3	1082.74	43.15	43.15

used to form films of the dispersion medium, and both toluene and decane were used as a dispersed phase. The experiments were performed with microscopic circular horizontal films of radii 5 to 50 × 10^{-5} m, applying the technique developed by Scheludko (1967) that has been used in our recent studies of foam and emulsion films (Rao et al., 1982; Manev et al. 1982, 1984a,b). The film thickness was estimated from the intensity of the reflected monochromatic light (wavelength = 546 nm). The drainage time and film thinning velocity as well as the critical thickness (i.e., the thickness at which the film ruptures) were recorded.

The data of Manev et al. (1984a) and DiNardo (1984) satisfy the major assumptions of the present model, i.e.:

1. The surfactant concentration is sufficiently high to render the film surfaces tangentially immobile (Malhotra 1984)
2. The film remains essentially plane-parallel during the process of thinning

Therefore, we have employed this data to verify the predictions of the present model.

All the films investigated by Manev et al. (1984a) and DiNardo (1984) had an excess of electrolyte to suppress the electrostatic component of the disjoining pressure. The radius of the film holder (R'_c) was 1.79 × 10^{-3} m for foam films and 1.58 × 10^{-3} m for emulsion films. Since no contact angle data are available for the systems studied by Manev et al. and DiNardo, the contact angle was assumed to be zero (i.e., a smooth transition between the film and the Plateau borders). The reported data are for aqueous films at 25 ± 0.1°C, hence the viscosity of the continuous phase (film phase) was taken to be equal to 0.89 mPa · s for making the comparisons between the experimental values and the theoretical predictions.

Manev et al. have reported drainage data for two cases:

1. Drainage data for a constant range of film thicknesses (from an initial thickness $h' = 100$ nm to final thickness $h' = 25$ nm) as a function of film radius.
2. Film lifetimes as a function of film radius. Lifetime represents the drainage time up to the critical thickness. In this case critical thickness is that thickness at which the film becomes unstable and ruptures.

The data utilized for making theoretical predictions for aqueous foam films are given in Table 2. Hamaker's constant, $K' = 2 \times 10^{-21}$ J was employed for making theoretical predictions (Scheludko, 1967). The electrostatic component of the disjoining pressure was assumed to be negligible due to the presence of excess salt in the system. In Figures 3–5 we have plotted drainage time (for the film to drain from a thickness $h' = 100$ to 25 nm) on a log scale as function of film radius. As first pointed out by Manev et al. (1984a), these plots yield a linear dependence with a slope of about 0.8, a value much smaller than the slope of 2.0 required by all the available theoretical expressions including Reynolds Eq. 1.

Figures 3–5 show the comparison between the predictions of the present model and the experimental data. The present model predicts results that are in good agreement with experimental data for the whole range of radii investigated by Manev et al. It is interesting to note that the present model is in better agreement with the experimental data for systems 1 and 2 as compared with systems 3 and 4. We suspect that this is due to the uncertainty in the value of Hamaker's constant employed for making theoretical predictions. The value of Hamaker's constant employed for the comparison accounts for the interaction between water-water molecules only. There are no available data nor any theory to describe how the presence of surfactants affects the Hamaker constant.

Figure 6 displays the comparison for the same system as above but now the theoretical drainage time is the time required for the film to drain from a thickness $h' = 100$ nm to the critical thickness. The experimental points represent the lifetime of the films, i.e., the time elapsed between film formation and its rupture. The values of critical thickness employed for making theoretical predictions are given in Table 3. Manev et al. observed that the critical thickness is independent of both the surfactant and electrolyte concentration. Once again, the present model is in good agreement with the experimental data.

Table 4 presents the data employed for making theoretical predictions for emulsion films. The composite Hamaker's constant was calculated from the individual Hamaker's constants

Table 2. Data Used for Predictions for Comparison with Experimental Data of Manev *et al.* (1984a) on Drainage of Aqueous Foam Films Stabilized with SDS

System	Surface Tension × 10^3 N/m
1	44.5
2	37.0
3	34.0
4	34.0

$T' = 25°C'$, $R'_c = 1.79 \times 10^{-3}$m; $K' = 2 \times 10^{-21}$ J
Systems:
1. Film-water + 4.3 × 10^{-4} kmol/m³ SDS + 0.1 M NaCl
2. Film-water + 4.3 × 10^{-4} kmol/m³ SDS + 0.25 M NaCl
3. Film-water + 3.5 × 10^{-3} kmol/m³ SDS + 0.25 M NaCl
4. Film-water + 8.7 × 10^{-4} kmol/m³ SDS + 0.25 M NaCl

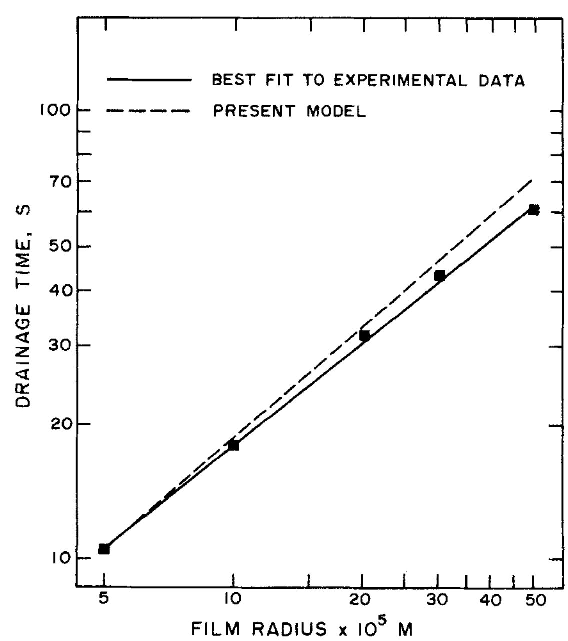

Figure 3. Theoretical and experimental drainage times for aqueous foam films.
Drainage times from thickness $h' = 100$ to 25 nm
Foam films containing 4.3 × 10^{-4} kmol/m³ SDS + 0.1 M NaCl

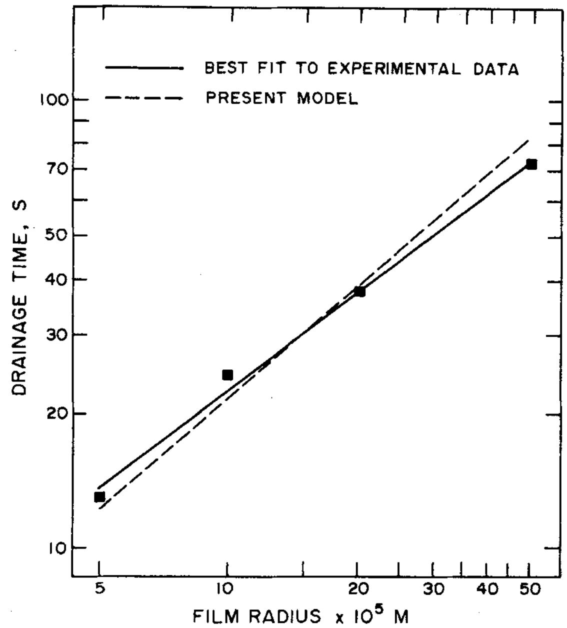

Figure 4. Theoretical and experimental drainage times for aqueous foam films.
Drainage times for thickness $h' = 100$ to 25 nm
Foam films containing 4.3×10^{-4} kmol/m^3 SDS + 0.25 M NaCl

using the equation (Visser, 1972)

$$K' = c(\sqrt{K'_{11}} - \sqrt{K'_{22}}) \quad (34)$$

where K' is the Hamaker constant for material 1 embedded in material 2. K'_{11} and K'_{22} are the Hamaker constants for interaction between 1-1 and 2-2 materials respectively. c is a constant

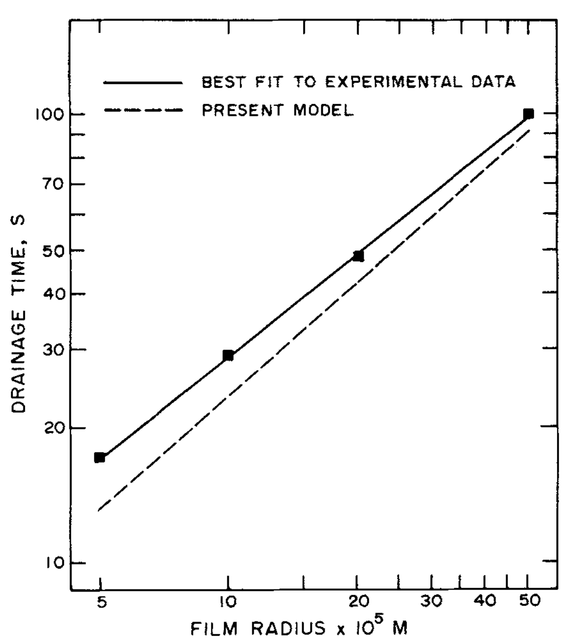

Figure 5. Theoretical and experimental drainage times for aqueous foam films.
Drainage times from thickness $h' = 100$ to 25 nm
Foam films containing 3.5×10^{-3} kmol/m^3 SDS + 0.25 M NaCl

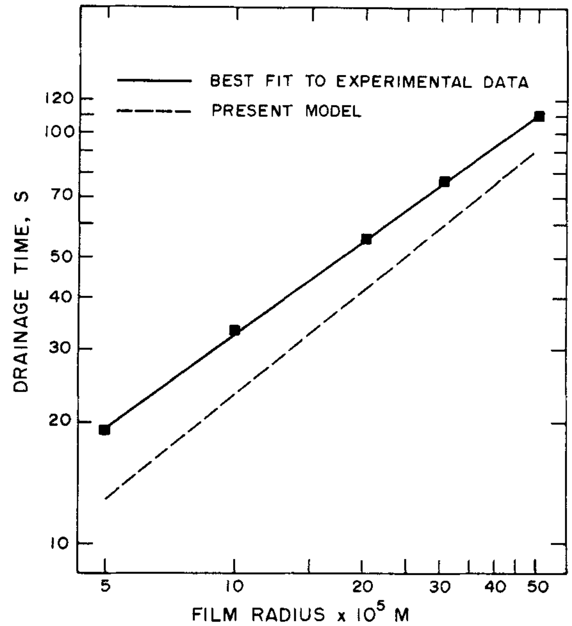

Figure 6. Theoretical and experimental drainage times for aqueous foam films.
Drainage times from thickness $h' = 100$ to 25 nm
Foam films containing 8.7×10^{-4} kmol/m^3 SDS + 0.25 M NaCl

Table 3. Values of Critical Thickness Employed for Prediction of Drainage Time of SDS Stabilized Aqueous Foam Films

Film Radius $\times 10^5$ m	Critical Thickness $\times 10^{10}$ m
5	250 ± 10
10	300 ± 10
20	350 ± 10
30	400 ± 10
50	470 ± 10

Table 4. Values of Interfacial Tension Used for Predictions for Comparison with Experimental Data of Manev *et al.* (1984a) on Drainage of SDS Stabilized Aqueous Emulsion Films

System	Interfacial Tension $\times 10^3$ N/m
5	15.0
6	7.9

Systems:
5. Film-water + 5.6×10^{-3} kmol/m^3 SDS + 0.3 M NaCl; dispersed phase toluene
6. Film-water + 4.3×10^{-4} kmol/m^3 SDS + 0.1 M NaCl; dispersed phase toluene

equal to 1.6 if material 2 is water, and 1.7 if the material is polystyrene; for all other materials c can be taken as unity. In the present study materials 1 and 2 refer to water and toluene, respectively. Visser recommends respective Hamaker's constants of 2.3×10^{-21} J and 5.3×10^{-21} J for K'_{11} and K'_{22}. This results in a composite Hamaker's constant, $K' = 6 \times 10^{-22}$ J. A

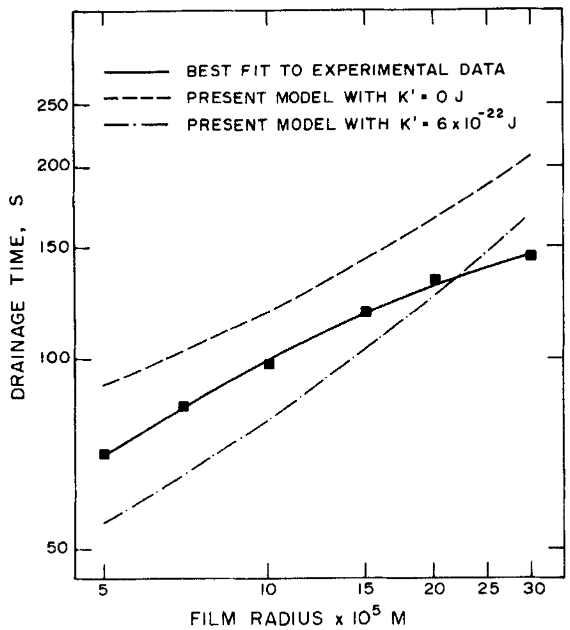

Figure 7. Theoretical and experimental drainage times for aqueous emulsion films.
Drainage times from thickness $h = 100$ nm to critical thickness
Emulsion films containing 5.6×10^{-3} kmol/m^3 SDS + 0.3 M NaCl with toluene as dispersed phase

20% uncertainty in values of K'_{11} and K'_{22} can lead to a factor of four difference in K'. For this reason, the comparison has been done for $K' = 0$ J and $K' = 6 \times 10^{-22}$ J.

Figure 7 compares the theoretical predictions with the experimental data for SDS-stabilized emulsion films. The theoretical drainage time is the time required for the film to drain from $h' = 100$ nm to the critical thickness. The experimental data points represent film lifetimes (i.e., time elapsed between the film formation and its rupture). The values of critical thickness employed for making theoretical predictions are given in Table 5. Since small variation in an individual Hamaker's constant can result in a significant variation in the composite Hamaker's constant, the comparison has been made for two values of Hamaker's constants, $K' = 0$ J and $K' = 6 \times 10^{-22}$ J. The present model is in reasonable agreement with the experimental results for the whole range of radii. Furthermore, the experimental results lie within the predictions of the present model for $K' = 0$ J and $K' = 6 \times 10^{-22}$ J.

Figures 8 and 9 summarize the comparison between the measured and predicted drainage times for foam and emulsion systems, respectively. The results of our model are compared with the experimental data of Manev *et al.* (1984a), DiNardo (1984), and Traykov et al. (1977). It should be pointed out that all the data are for high surfactant concentrations where the interface is immobile. It is evident that there is reasonable agreement between the predicted and experimentally measured drainage times. The larger deviation between the calculated and measured drainage times for emulsion systems is due to the uncertainty in the values of Hamaker's constant employed for comparison.

In conclusion, a theoretical model has been developed to predict the rate of drainage of surfactant stabilized foam and emulsion films. The analysis is restricted to plane-parallel films containing enough surfactant to render the interface tangentially immobile. The model predicts the experimentally observed de-

Table 5. Critical Thickness Data Used for Prediction of Drainage Time of SDS Stabilized Aqueous Emulsion Films

Film Radius $\times 10^5$ m	Critical Thickness $\times 10^{10}$ m
5	250 ± 10
7	270 ± 10
10	300 ± 10
15	320 ± 10
20	350 ± 10
30	380 ± 10

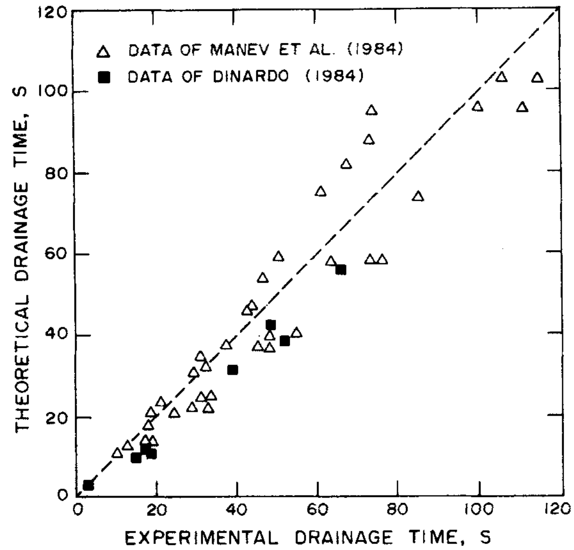

Figure 8. Theoretical and experimental drainage times for foam films.

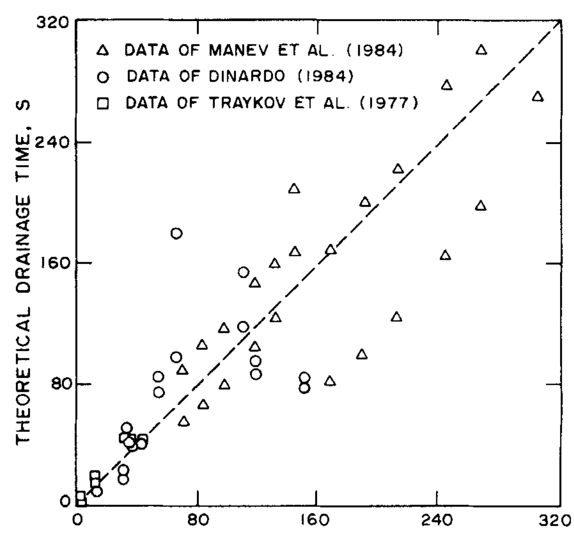

Figure 9. Theoretical and experimental drainage times for emulsion films.

pendence of film radius on drainage time from the knowledge of physicochemical properties.

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Notation

a_0, a_1, a_2 = constants in Eq. 30 to describe the initial shape of Plateau borders
c = material constant in Eq. 34
h = half thickness
h_f = half film thickness
h_o = half film thickness at time, $t = 0$
K = Hamakers constant
K_{11} = Hamakers constant for Material 1
K_{22} = Hamakers constant for Material 2
K^* = dimensionless Hamakers constant
p = pressure
p_c = capillary pressure
p_g = uniform pressure in the dispersed phase
Δp = pressure difference causing drainage
r = radial distance in cylindrical coordinates
R = film radius
R_c = capillary radius
R_h = radial distance where liquid flow has no effect on the shape of Plateau borders
R_o = film radius at time, $t = 0$
R_1, R_2 = two radii of curvature associated with the shape of Plateau borders
t = time
t^* = dimensionless time
t^+ = dimensionless time
Δt = drainage time
V_r = radial velocity
V_z = axial velocity
V_{Re} = Reynolds velocity of thinning
z = axial distance in cylindrical coordinates

Greek letters

ϵ = film aspect ratio (h_o/R_o) at time, $t = 0$
θ = contact angle between the film and the Plateau borders
μ = viscosity of film liquid
π = disjoining pressure
ρ = bulk density of film liquid
σ_0 = equilibrium interfacial tension between the continuous phase and the dispersed phase

Superscripts

$'$ = dimensional quantity
f = film
p = Plateau borders

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