



# THE DRAINAGE AND RUPTURE OF THE FILM BETWEEN COLLIDING DROPS IN THE PRESENCE OF SURFACTANT

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The understanding of the coalescence process between two drops is essential in determining the stability of liquid-liquid systems. By solving the equation governing the evolution of the continuous phase film trapped between two drops colliding at constant velocity coupled with that describing the surfactant interfacial concentration in the lubrication approximation, we show that the interface is rendered immobile due to the presence of a small amount of surfactant. Film rupture is therefore delayed due to the Marangoni effect retarding the drainage of the film. In this study, the effects of the viscosity ratio, surface diffusivity, approach velocity and the van der Waals interaction force are reported.

## INTRODUCTION

During the approach of two drops in a dispersion of two immiscible liquids, a thin film of the continuous phase is trapped between the interface of the drops. This film then proceeds to drain as the interfaces deform under the influence of the interaction forces acting on the drops. If the film succeeds in draining to a thickness at which van der Waals forces become significant in the time at which the drops are in contact with each other, the film ruptures resulting in the coalescence of the drops. The study of the film drainage and rupture process is therefore vital in the determination of the stability of liquid-liquid systems.

In practical systems of interest, surface active agents are often present. Due to spontaneous deformations at the drop interface, concentration gradients arise resulting in the Marangoni effect. The influence of surfactant on the drainage and rupture of the film between two drops colliding at a constant approach force has been investigated by Chesters and Bazhlekov [1]. In this paper, we consider the constant approach velocity case which is more appropriate for inertial collisions, which is often more relevant in practical liquid-liquid systems.

## PROBLEM FORMULATION

The approach of two drops with radii,  $R_i^*$  ( $i = 1,2$ ), at a velocity,  $V^*$  (\* indicating a dimensional quantity), is considered (Figure 1). The following simplifying approximations have been adopted:

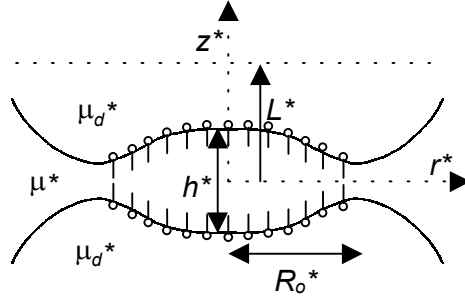


Figure 1. Schematic diagram of the film drainage region.

1. The film is sufficiently thin compared to the radial extent ( $\epsilon = h_o^*/R_o^* \ll 1$ , where  $h_o^*$  is the initial film thickness and  $R_o^*$  is the initial rim radius of the film) such that the lubrication approximation applies. Symmetry relative to the plane  $z^* = 0$  can also be assumed since the effect of drop size on the film curvature is negligible as a result. An equivalent radius,  $R^*$ , can then be defined as follows:

$$\frac{1}{R^*} = \frac{1}{2} \left( \frac{1}{R_1^*} + \frac{1}{R_2^*} \right). \quad (1)$$

As a consequence of symmetry, it can also be assumed that the interfacial properties are the same at both interfaces and hence the interfacial concentration of surfactant,  $\Gamma^*$ , and the interfacial tension,  $\gamma^*$ , are equal at both the drop interfaces [2].

2. In the drop, there is a characteristic penetration length,  $L^*$ , of magnitude  $\epsilon R^*$  from the interface at which the velocity and the velocity gradient approach zero [2,3].
3. A dilute and uniformly distributed amount of surfactant is present at the interface initially. The surfactant is assumed to be insoluble in both the dispersed and continuous phases. A linear surfactant equation of state, justifiable for dilute concentrations, is adopted:

$$\gamma^* = \gamma_o^* - \left( \frac{\partial \gamma^*}{\partial \Gamma^*} \right) \Gamma^*, \quad (2)$$

where  $\gamma_o^*$  is the interfacial tension when the interface is free of surfactant.

The following transformations are applied to render the variables dimensionless:

$$\begin{aligned} r &\equiv \frac{r^*}{R_o^*}; & R_i &\equiv \frac{R_i^*}{R_o^*}; & z &\equiv \frac{z^*}{h_o^*}; & h &\equiv \frac{h^*}{h_o^*}; & t &\equiv \frac{\epsilon S^* t^*}{\mu^* R_o^*}; & p &\equiv \frac{h_o^* p^*}{S^*}; \\ \lambda &\equiv \frac{\mu^*}{\mu_d^*}; & \Gamma &\equiv \frac{\Gamma^*}{\Gamma_m^*}; & \gamma &\equiv \frac{(\gamma^* - \gamma_m^*)}{S^*}; & B &\equiv \frac{B^*}{S^* h_o^{*m-1}}; & S^* &\equiv \gamma_o^* - \gamma_m^*, \end{aligned} \quad (3)$$

where  $h$  is the film thickness,  $t$  is the time,  $S^*$  the spreading pressure and  $p$  the film pressure;  $\mu^*$  and  $\mu_d^*$  are the continuous and the dispersed phase viscosities, respectively;  $\gamma_m^*$  is the interfacial tension when the interfacial surfactant concentration is at its saturation,  $\Gamma_m^*$ .  $B$  is the dimensionless Hamaker constant and  $m$  is a parameter for which value of 3 is assumed [4].

The lubrication equations can then be written both for the film and in the drops:

$$\frac{\partial p}{\partial r} = \frac{\partial^2 v}{\partial z^2}; \quad \frac{\partial p_i}{\partial r} = \lambda \frac{\partial^2 v_i}{\partial z^2}, \quad (4)$$

where  $v$  is the radial velocity in the film, and,  $p_i$  and  $v_i$  are the pressure and radial velocity in drop  $i$ , respectively. Taking into account the tangential shear stress balance at the interfaces,

$$\frac{\partial v}{\partial z} - \lambda \frac{\partial v_1}{\partial z} = \frac{\partial \gamma}{\partial r}, \quad (5)$$

$$\lambda \frac{\partial v_2}{\partial z} - \frac{\partial v}{\partial z} = \frac{\partial \gamma}{\partial r}, \quad (6)$$

where equation (5) applies to the interface above  $z = 0$  and equation (6) applying to the bottom interface, it can then be shown [2,5] by integration of the lubrication equations (the boundary conditions being the velocity and velocity gradient in the drop diminishing at the characteristic penetration length, symmetry at  $z = 0$  and continuity of velocities at the interface) that:

$$\frac{\partial h}{\partial t} = \frac{1}{12r} \frac{\partial}{\partial r} \left( rh^3 \frac{\partial p}{\partial r} \right) - \frac{1}{r} \frac{\partial}{\partial r} (rhv_{int}). \quad (7)$$

Here,  $v_{int}$  is the interfacial velocity which is given by:

$$v_{int} = \frac{R}{2\lambda} \frac{\partial \gamma}{\partial r} - \frac{hR}{4\lambda} \frac{\partial p}{\partial r}. \quad (8)$$

The dimensionless film pressure can be written as:

$$p = \frac{2\epsilon \gamma_m^*}{RS^*} - \frac{1}{2} \frac{\epsilon^2 \gamma_m^*}{S^*} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) \right] + \frac{B}{h^m}, \quad (9)$$

and the equation describing the evolution of surfactant interfacial concentration reads:

$$\frac{\partial \Gamma}{\partial t} = \frac{1}{Pe_s} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Gamma}{\partial r} \right) \right] - \frac{1}{r} \frac{\partial}{\partial r} (rv_{int}\Gamma), \quad (10)$$

where  $Pe_s$  is the surface Péclet number ( $Pe_s = S^*h_o^*/\mu^*D_s$  where  $D_s$  is the surface diffusivity).

Given an initially undeformed spherical drop with uniform concentration,  $\Gamma_o$ ,

$$h = h_{oo} + \frac{r^2}{\epsilon R} \quad \text{and} \quad \Gamma = \Gamma_o \quad \text{at} \quad t = 0, \quad (11)$$

where  $h_{oo}$  is the initial film thickness at  $t = 0$ . The following boundary conditions apply:

$$\begin{aligned} \frac{\partial h}{\partial r} = 0; \quad \frac{\partial^3 h}{\partial r^3} = 0; \quad \frac{\partial \Gamma}{\partial r} = 0 \quad \text{at} \quad r = 0, \\ \frac{\partial h}{\partial t} = -V; \quad p = 0; \quad \frac{\partial \Gamma}{\partial r} = 0 \quad \text{at} \quad r = \infty, \end{aligned} \quad (12)$$

where  $V = V^*\mu^*/\epsilon^2 S^*$ .

The two coupled fourth-order nonlinear parabolic partial differential equations describing the evolution of the film and the interfacial concentration of surfactant as given by equations (7) and (10) were solved starting from the initial conditions, equation (11), subject to the boundary conditions, equation (12), using the numerical Method of Lines [6]. Spatial derivatives were discretised using fourth-order centred differences and Gear's method was used to advance the solution in time. A uniform grid of up to 1000 points was used, the grid being refined to achieve convergence. In the case of film rupture, the computations were halted at a film thickness of approximately 0.1 as the increasingly singular spatial derivatives near the rupture region posed a difficulty for it to be resolved. In the simulations, we assume  $R = 4$  [3] and  $\gamma_m^* = S^* = 40$  dynes/cm;  $h_{oo}$  was taken to be 1 unless otherwise stated.

## RESULTS

### Interface Immobilisation

The effect of surfactant on film drainage can be seen in Figure 2. It is seen that the drainage of the film is retarded even at the addition of a small amount of surfactant. As the initial concentration of surfactant is increased, the drainage profile tends to that of a surfactant-free system with immobile interfaces (*i.e.*,  $v_{int} = 0$ ) for which the flow is only driven by the radial pressure gradient. These results are in agreement with previous theoretical and experimental findings [7-9] which report interfacial immobilisation in the presence of a small quantity of surfactant. A typical surfactant interfacial concentration evolution profile is illustrated in Figure 3(a) indicating that the initial deformation of the interface due to the approach of the drops results in depletion of surfactant at the centre. This gives rise to the Marangoni effect where interfacial tension gradients arise to oppose the flow of liquid out from the drainage region. Consequently, the surfactant gets replenished in the deformation region. The corresponding film thickness evolution profile is shown in Figure 3(b) showing the formation of a dimple. Surfactant is observed to deplete at the dimple rim as fluid is expelled away from this region.

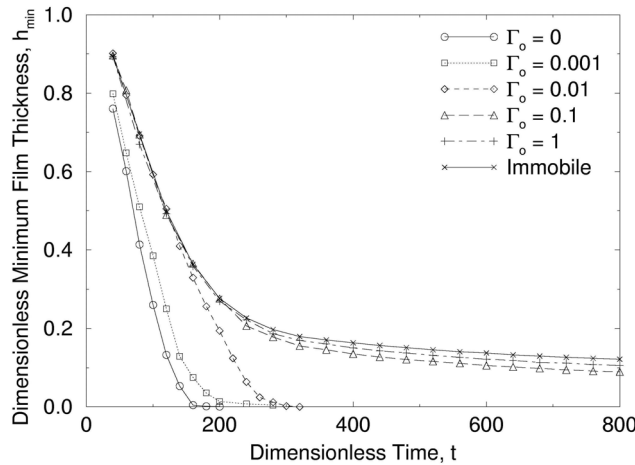


Figure 2. Minimum film thickness as a function of time for various surfactant loadings. The rest of the parameters are  $\lambda = 1$ ,  $Pe_s = 1000$  (where applicable),  $B = 0$  &  $V = 0.01$ . Also shown is the solution for the surfactant-free immobile interface.

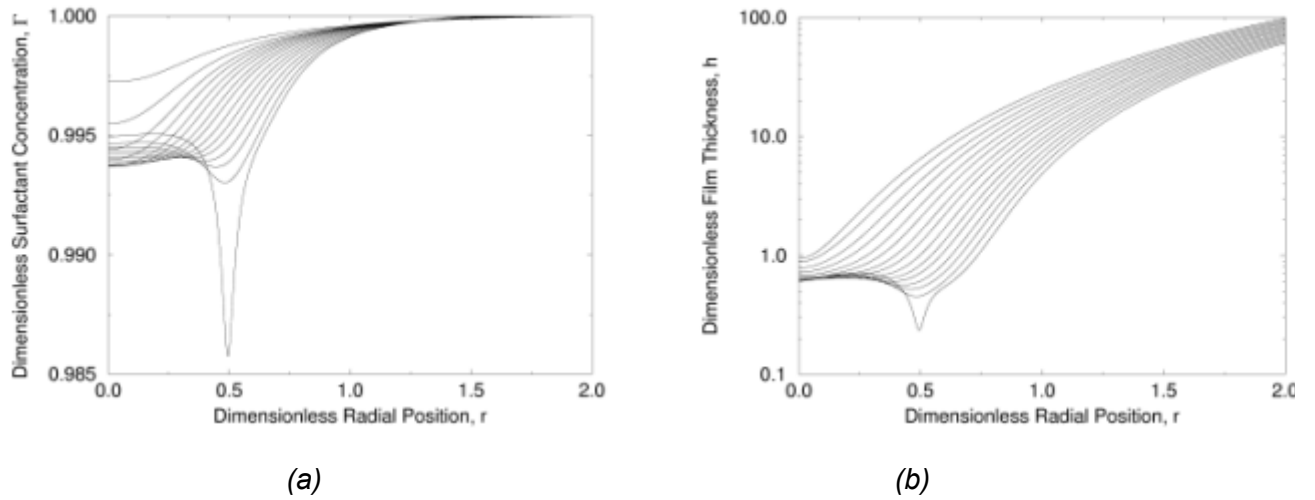


Figure 3. Surfactant concentration (a) & film thickness (b) evolution profiles for 15 equal time steps up to  $t = 117.1$ . Other parameters are  $\lambda = 1$ ,  $Pe_s = 1000$ ,  $\Gamma_o = 1$ ,  $B = 10^{-3}$  &  $V = 0.5$ .

### Viscosity Ratio

The effect of the viscosity ratio on the drainage process is illustrated in Figure 4. It can be seen that the viscosity ratio has little effect on film drainage. This is consistent with the experimental observations in [9]. The viscosity ratio is not expected to significantly influence the drainage of the film because of the resulting immobility of the interface due to the presence of surfactant, as discussed previously [1,9]. Since the flow in the dispersed phase is insignificant for immobile interfaces, the drop phase viscosity therefore no longer influences the interface.

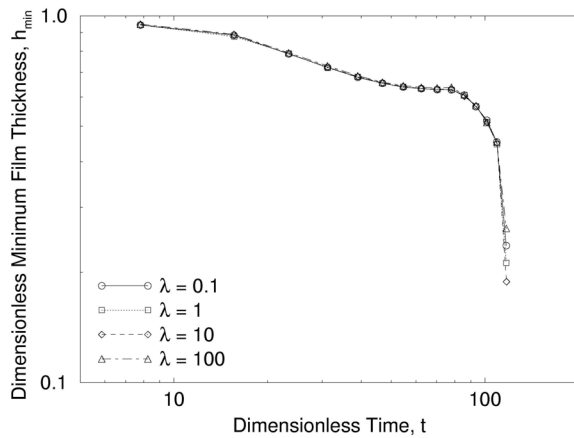


Figure 4. Effect of viscosity ratio,  $\lambda$ , on the minimum film thickness. The rest of the parameter values are  $Pe_s = 1000$ ,  $\Gamma_o = 1$ ,  $V = 0.5$  &  $B = 10^{-3}$ .

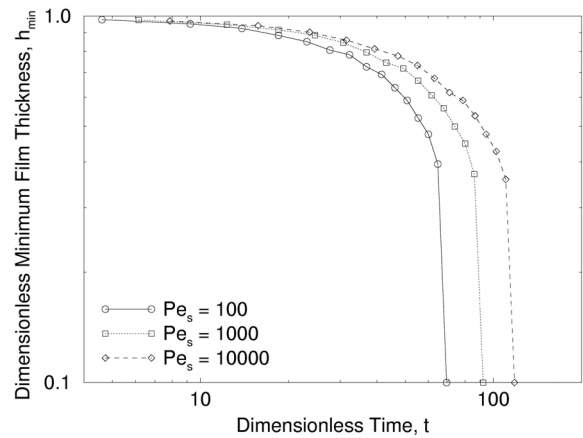


Figure 5. Minimum film thickness as a function of the surface Péclet number  $Pe_s$ . Other parameter values are  $\lambda = 1$ ,  $\Gamma_o = 0.0025$ ,  $V = 0.01$  &  $B = 10^{-4}$ .

### Surface Péclet Number

The surface Péclet number,  $Pe_s$ , represents the significance of surfactant transport by Marangoni convection relative to that by surface diffusion. Low  $Pe_s$  values indicate the dominance of surface diffusion whereas high  $Pe_s$  values indicate that the spreading of surfactant due to Marangoni stresses is the dominant mechanism. Figure 5 depicts the effect of  $Pe_s$  on the dynamics of the film drainage process. As Marangoni convection becomes increasingly significant with increasing

$Pe_s$ , it can be seen that the latter stages of film drainage is affected, the film taking longer to drain. It should be noted that there is little difference in the early stages of the film drainage because the surfactant concentration gradient at the interface is small. However, as the drops approach each other, interfacial deformation takes place leading to a large negative concentration gradient being present in the drainage region. For systems with high  $Pe_s$ , the Marangoni stresses that arise as a consequence of these concentration gradients act to retard the interfacial velocity and thus the drainage of the film. For systems with low  $Pe_s$  on the other hand, there is little effect of the surfactant on the interfacial dynamics since diffusion serves to distribute the surfactant quickly with little disturbance caused to the interface.

### Approach Velocity

The role of the approach velocity on the dynamics of film thinning is described in Figure 6. As the drops collide with increasing velocities, dimpling begins to occur as seen by the rim position for larger velocities in the figure. For low velocities, dimpling does not occur since there are insufficient hydrodynamic forces to cause deformation to the film. As such, the film drains quickly and proceeds towards rupture, as shown by the minimum film thickness curves in Figure 6.

### van der Waals Interaction Forces

As the film thins to thicknesses of the order 1000 Angstroms, intermolecular interactions such as the van der Waals attraction become significant. As a result, there is a negative contribution to the disjoining pressure leading towards the rupture of the film as observed in Figure 3(b). The liquid in the film is expelled together with surfactant away from the rupture region thereby causing a sharp depletion of surfactant as shown in Figure 3(a). Figure 7 shows the rate of film thinning as a function of the dimensionless Hamaker constant,  $B$ . Clearly, as the magnitude of  $B$  increases, the film tends to rupture quickly at a large critical rupture thickness since the van der Waals attraction is strong. In Figure 7, it can be seen that for  $B = 10^{-6}$ , the effect of the van der Waals force, which is extremely weak in this case, is not significant even at a film thickness of 0.1 dimensionless units and hence rupture does not occur even at this stage.

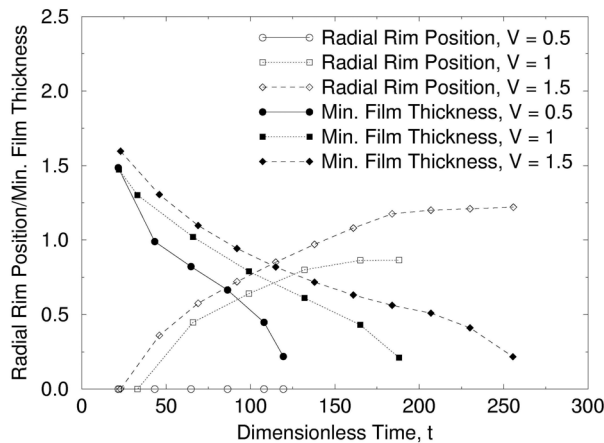


Figure 6. Radial rim position & minimum film thickness as a function of the approach velocity  $V$ . The rest of the parameters are  $\lambda = 1$ ,  $Pe_s = 1000$ ,  $\Gamma_o = 1$ ,  $B = 10^{-3}$  &  $h_{oo} = 2.63$ .

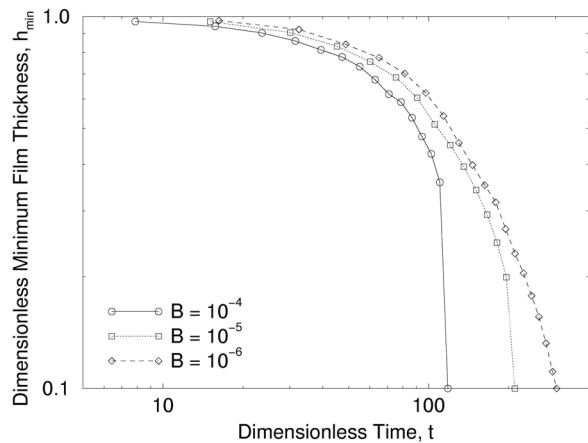


Figure 7. Variation of the minimum film thickness with the dimensionless Hamaker constant  $B$ . The other parameters are  $\lambda = 1$ ,  $Pe_s = 10000$ ,  $\Gamma_o = 0.0025$  &  $V = 0.01$ .

## CONCLUSIONS

The drainage of the film trapped between two drops colliding at constant approach velocity in the presence of insoluble surfactant has been studied. The interface is rendered immobile even when small amounts of surfactant are present, thereby retarding the drainage of the film and hence film rupture. This is a consequence of concentration gradients that arise out of deformations caused to the film during the approach of the drops. These concentration gradients seek to replenish the surfactant locally depleted in the film deformation region therefore retarding interfacial mobility by opposing the flow of the liquid outwards.

The role of the viscosity ratio, surface Péclet number, approach velocity and van der Waals force have been investigated. Viscosity ratio is not found to have any influence on film drainage since the interface is immobilised and thus there is no flow in the dispersed phase. As the surface Péclet number is increased, Marangoni forces become increasingly dominant thereby retarding the drainage of the film. When the drops collide at higher approach velocities, dimpling of the film is observed and hence the film takes longer to drain as compared to low velocity collisions. Finally, the effect of van der Waals forces on film drainage and rupture was examined.

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