

Note

Hydrodynamic instability of a thin viscous film between two drops

Leslie Y. Yeo and Omar K. Matar *

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BZ, UK

Received 20 August 2002; accepted 28 January 2003

Abstract

Linear stability analysis is employed to derive analytical expressions for the growth rate of disturbances applied to a thin plane-parallel film trapped between two drops. From these expressions, the band of unstable wavenumbers and the “most dangerous” wavenumber are identified for systems in the absence and presence of insoluble surfactant. Marangoni effects are shown to exert a stabilizing influence and reasonably good agreement with experimental observations is found. Subsequent nonlinear analysis indicated amplification of the disturbance growth rate beyond that suggested by linear theory as the film proceeded toward rupture.

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Keywords: Thin film; Stability; Rupture; Emulsions; Insoluble surfactant; Marangoni effect

1. Introduction

Hydrodynamic inhomogeneities in thin emulsion films have long been known to exist [1]. In the experiments of Manev et al. [2], interfacial irregularities were observed during the film drainage process close to the critical film thickness. Sharma and Ruckenstein [3] suggested that these interfacial waves were likely to grow as the film thinned due to increasing contributions of the van der Waals force. This growth was demonstrated to enhance the thinning velocity by generating a “pumping” action on the fluid, thereby decreasing the lifetime of the film.

While previous work has considered the amplitude of the interfacial waves [4] and the implications of these waves on the thinning velocity [3], we consider the other important characteristic of these disturbances, namely the instability wavelength. In particular, we attempt to identify the band of wavelengths over which the imposed instability is amplified. The “most dangerous” wavelength, for which the growth rate of the disturbance is maximized, is also identified. In addition, we compare the rate at which the instability arising from the disturbance grows with typical velocities at which the film drains hydrodynamically due to an applied external force in the absence of any imposed disturbances, as predicted by Reynolds’ law. This provides

vital information on whether the disturbance provides a significant contribution to the rupture of the film.

Although surfactant effects on the thinning velocity have been studied [5], the analysis was limited to low viscosity ratios due to the omission of the coupling between the film and the dispersed phase. Moreover, a *quasi-steady-state* approximation was adopted where all system variables depended adiabatically on time through the local film thickness. In this Note, however, the full dynamic coupling between the evolution of the film thickness and the interfacial surfactant concentration is considered in addition to the coupling between the film and dispersed-phase flows. Given the latter consideration, the present study is therefore valid over a wider range of viscosity ratios.

2. Governing equations

Starting from the usual lubrication equations to describe the flow in the film and in the adjacent dispersed phases, the evolution equation for the film thickness, $h(x, t)$, has been derived for a system in which an initially thin plane-parallel continuous phase film is bounded by two drops [6–8]:

$$\frac{\partial h}{\partial t} = -\frac{1}{12} \frac{\partial}{\partial x} \left[h^3 \left(C \frac{\partial^3 h}{\partial x^3} + \frac{mB}{h^{m+1}} \frac{\partial h}{\partial x} \right) \right] + \frac{\partial}{\partial x} \left\{ \frac{hL}{2\lambda} \left[\frac{\partial \Gamma}{\partial x} - \frac{h}{2} \left(C \frac{\partial^3 h}{\partial x^3} + \frac{mB}{h^{m+1}} \frac{\partial h}{\partial x} \right) \right] \right\}. \quad (1)$$

* Corresponding author.

E-mail address: o.matar@imperial.ac.uk (O.K. Matar).

t denotes time, Γ denotes the interfacial surfactant concentration, and C is a capillary parameter; $\lambda \equiv \mu^*/\mu_d^*$ and $L \equiv L_i^*/L_f^*$, where μ^* and μ_d^* are the continuous and dispersed phase viscosities, and, L_i^* and L_f^* are the characteristic length scales of drop i and that of the local thinning region in the film, respectively. The asterisk (*) indicates dimensional quantities. Here, we adopt $L = 4$. We have scaled the streamwise and vertical directions, x^* and z^* , with L_f^* and h_0^* , respectively, and t^* scales as $\mu^*L_f^*/\epsilon S^*$, h_0^* being the initially flat film thickness between the drops and, S^* , the spreading pressure. For lubrication theory to hold, $\epsilon \ll 1$, where $\epsilon \equiv h_0^*/L_f^*$. In (1), B is the Hamaker constant, defined as $B \equiv B^*/S^*h_0^{*m-1}$, where $m = 3$ for $h^* \leq 120 \text{ \AA}$.

The evolution equation governing the transport of the surfactant monolayer along the interface reads [6–8]

$$\frac{\partial \Gamma}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{\Gamma L}{2\lambda} \left[\frac{\partial \Gamma}{\partial x} - \frac{h}{2} \left(C \frac{\partial^3 h}{\partial x^3} + \frac{mB}{h^{m+1}} \frac{\partial h}{\partial x} \right) \right] \right\} + \frac{1}{Pe} \left(\frac{\partial^2 \Gamma}{\partial x^2} \right), \quad (2)$$

where Pe is the surface Péclet number defined by $Pe \equiv S^*h_0^*/\mu^*D_s^*$, and D_s^* is the surface diffusivity. Here, $\Gamma \equiv \Gamma^*/\Gamma_m^*$ and $C = \epsilon^2\gamma_m^*/2S^*$, where $S^* = \gamma_0^* - \gamma_m^*$ and $\gamma \equiv (\gamma^* - \gamma_m^*)/S^*$, in which γ_0^* is the interfacial tension of the pure system or that of the uncontaminated region, while γ_m^* is the interfacial tension corresponding to a region saturated with surfactant at concentration Γ_m^* , respectively. Closure was obtained via a linear surfactant equation of state, which in dimensionless terms reads $\gamma = 1 - \Gamma$ [6–8].

Equations (1) and (2) therefore describe the dynamic coupling between the evolution of the film thickness and the interfacial surfactant concentration. For pure systems, $S^* = \gamma_0^*$ and $C = \epsilon^2/2$. It should be noted that although the magnitudes of B and C are of order ϵ^2 , the terms containing these dimensionless groups in (1) and (2) are retained because these terms could potentially be significant due to the magnitudes of $1/h^{m+1}$ at small film thicknesses and curvature, respectively. The term $1/Pe$ is retained to control the relative magnitudes of the diffusional and Marangoni processes.

3. Linear stability analysis

We linearize (1) and (2) about the base state $h = 1$ and $\Gamma = \Gamma^{(0)}$; $\Gamma^{(0)}$ is a parameter. Keeping only linear terms in the film and surfactant concentration perturbations and using a normal modes decomposition, we can write down the relationship for the growth rate of the disturbance, ω ,

$$\omega = \frac{k^2}{2} \left[P(mB - Ck^2) - \frac{1}{Pe} - Q \right] \pm \frac{k^2}{2} \left\{ \left[Q + \frac{1}{Pe} - P(mB - Ck^2) \right]^2 \right\}^{1/2}, \quad (3)$$

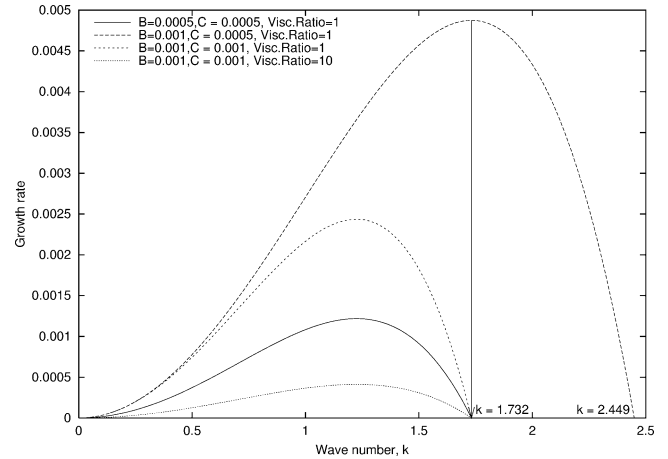


Fig. 1. The effect of the dimensionless Hamaker constant, B , the capillary parameter, C , and the viscosity ratio, λ , on the growth rate, ω , over the range of wavenumbers, k , for pure systems. The critical wavenumber, k_c , and the wavenumber that maximizes the growth rate, k_m , for the case $B = 0.001$, $C = 0.0005$, and $\lambda = 1$ are identified. In this case, $k_m = 1.732$ and $k_c = 2.449$.

$$+ 4 \left[\left(PQ + \frac{P}{Pe} - \frac{LQ}{4\lambda} \right) (mB - Ck^2) \right]^{1/2}, \quad (3)$$

where

$$P \equiv \frac{1}{4} \left(\frac{1}{3} + \frac{L}{\lambda} \right), \quad Q \equiv \frac{L\Gamma^{(0)}}{2\lambda}. \quad (4)$$

In the absence of surfactant, (3) reduces to

$$\omega = k^2 P (mB - Ck^2), \quad (5)$$

which is similar to that obtained in [3]. Disturbances having $\text{Re}[\omega] > 0$ are amplified while those with $\text{Re}[\omega] < 0$ decay. The competition between the destabilizing and stabilizing mechanisms is clear: van der Waals forces promote growth while capillary forces act to damp out short-wavelength disturbances. There therefore exists a range of growing modes having wavenumbers between $k = 0$ and $k = k_c$, k_c being the critical cut-off wavenumber beyond which $\text{Re}[\omega] < 0$. From (5) it can be shown that $k_c = (Bm/C)^{1/2}$, and $k_m = k_c/\sqrt{2}$, where k_m is the so-called “most dangerous mode” at which the growth rate is maximized. Thus the range of unstable wavenumbers depends only on van der Waals and capillary forces; λ and L do, however, exert an influence on the disturbance growth rate. These conclusions are in accordance with the results shown in Fig. 1, which depicts the parametric dependence of ω as a function k on B , C , and λ . We note that ω , k_c , and k_m decrease, that is, the system becomes more stable, with increasing C and decreasing B , consistent with the mechanism described above. Increasing λ also serves to decrease ω as the internal viscous effects of the dispersed phase dampen the instability.

For typical values of B and C , k_c ranges from 0.25 to 54.8. Typical critical cut-off wavelengths above which instability is obtained are therefore in the range from 10^{-3} to 10^{-1} cm for characteristic film length scales of 10^{-2} cm.

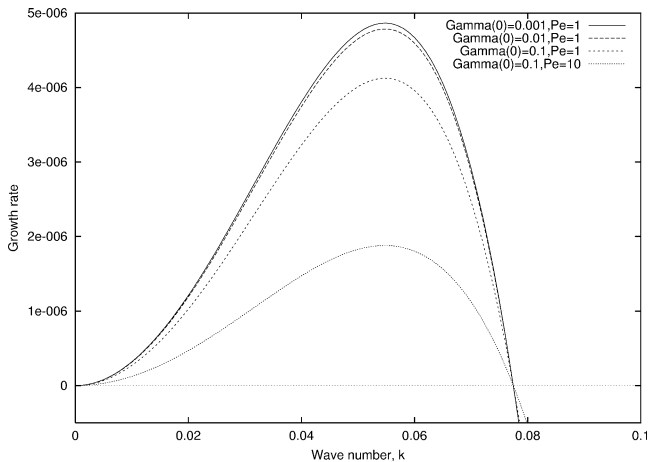


Fig. 2. Parametric dependence of the growth rate, ω , as a function of the wavenumber, k , on the surface Péclet number, Pe , and the surfactant base state concentration, $\Gamma^{(0)}$, for systems in which trace amounts of surfactant are present, i.e., $S^* \sim O(\epsilon^2 \gamma_m^*)$. Here, $B = 10^{-3}$, $C = 0.5$, and $\lambda = 1$.

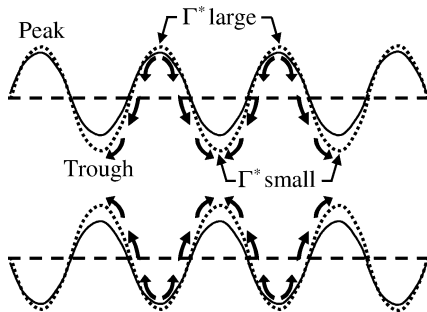


Fig. 3. Simplified illustration indicating the action of surfactant distribution and spreading along the interface. The dashed and dotted curves represent the base state of the film and the imposed periodic disturbance, respectively. The arrows indicate the direction of the interfacial motion due to the Marangoni stresses that arise out of the surfactant concentration gradients. The solid curve typically depicts the resultant state of the disturbance wave as a consequence of the action of the Marangoni stresses on the interface stabilizing the film.

This is in reasonable agreement with the experiments in [4], where surface inhomogeneities were observed to have a wavelength of 5×10^{-3} cm. Our predictions also agree with those in [3], where it was suggested that the wavelength observed in [4] applies for large film radii above 10^{-2} cm, whereas the wavelengths could vary between 2.5×10^{-3} cm and 10^{-2} cm for smaller film radii.

We now devote our attention to systems in which insoluble surfactant resides at the interfaces. The dispersion relation, Eq. (3), is plotted in Fig. 2 for different values of $\Gamma^{(0)}$. We also note from (3) that the effect of surfactant is always stabilizing and the band of unstable wavenumbers is independent of $\Gamma^{(0)}$ and Pe . The maximal growth rate, however, decreases with increasing $\Gamma^{(0)}$ and Pe : $\text{Re}[\omega]$ is up to several orders smaller when surfactant is present in trace amounts, i.e., $S^* \sim O(\epsilon^2 \gamma_m^*)$ [6,7], than in the case of pure systems.

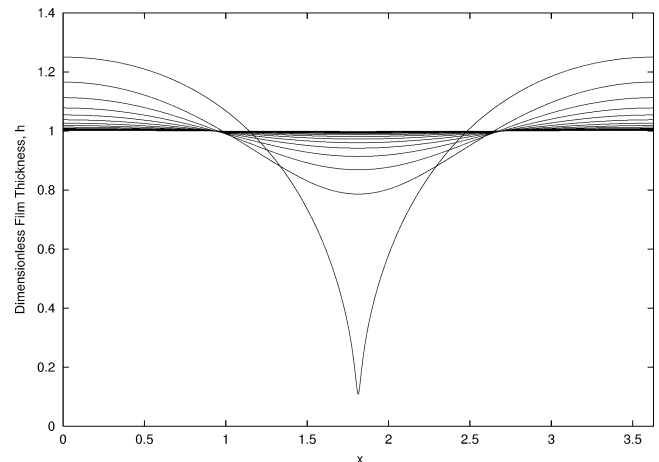


Fig. 4. Evolution profiles of the film thickness, h , at 15 equal time steps up to $t = 1124.27$ initiated by a small-amplitude disturbance wave with the fastest growing mode predicted by linear theory ($k = 1.732$). The other parameters used in the simulation are $B = 0.001$, $C = 0.0005$, and $\lambda = 1$.

The stabilizing mechanism is fairly well understood and is illustrated in Fig. 3. Any interfacial deformations resulting from the introduction of the perturbation onto the film lead to nonuniformities in the interfacial surfactant concentration. At the troughs of the imposed periodic wave where the influence of the van der Waals forces is largest, the film thins more severely than in the other regions. As a result, surfactant is depleted from these regions, resulting in a lower interfacial concentration. Marangoni stresses, therefore, act to spread the surfactant back into these regions from the peaks of the interfacial wave where the surfactant concentration is high. This redistribution process drags the fluid in the film back into the troughs, therefore decreasing the perturbation amplitude and retarding the growth of the instability. As Pe increases, the relative contribution of Marangoni-dominated spreading to surface diffusion is increased, thereby dampening out the perturbation, as reflected by the decrease in $\text{Re}[\omega]$. Similarly, when more surfactant is present (i.e., $\Gamma^{(0)}$ increases), the concentration gradients arising from the disturbance becomes larger, therefore increasing the Marangoni spreading rate and consequently decreasing $\text{Re}[\omega]$.

In [3], typical hydrodynamic thinning velocities of order 10 \AA/s are reported. In comparison, the thinning velocity predicted by Reynolds [9] is of order 1 \AA/s . From our results, ω for systems in which trace quantities of surfactant are present is of order 10^{-6} , which corresponds to growth rates of order 100 \AA/s , suggesting that the rate at which the instability grows is still significant compared to the rate at which the film thins hydrodynamically due to an external approach force, in the absence of any imposed periodic disturbances. Increasing the initial surfactant concentration, $\Gamma^{(0)}$, leads to a reduction in the growth rates, as shown in Fig. 2, so that saturation of the interface with surfactant retards the instability to the extent that the hydrodynamic rate of thinning overtakes the growth rate of the instability. Therefore,

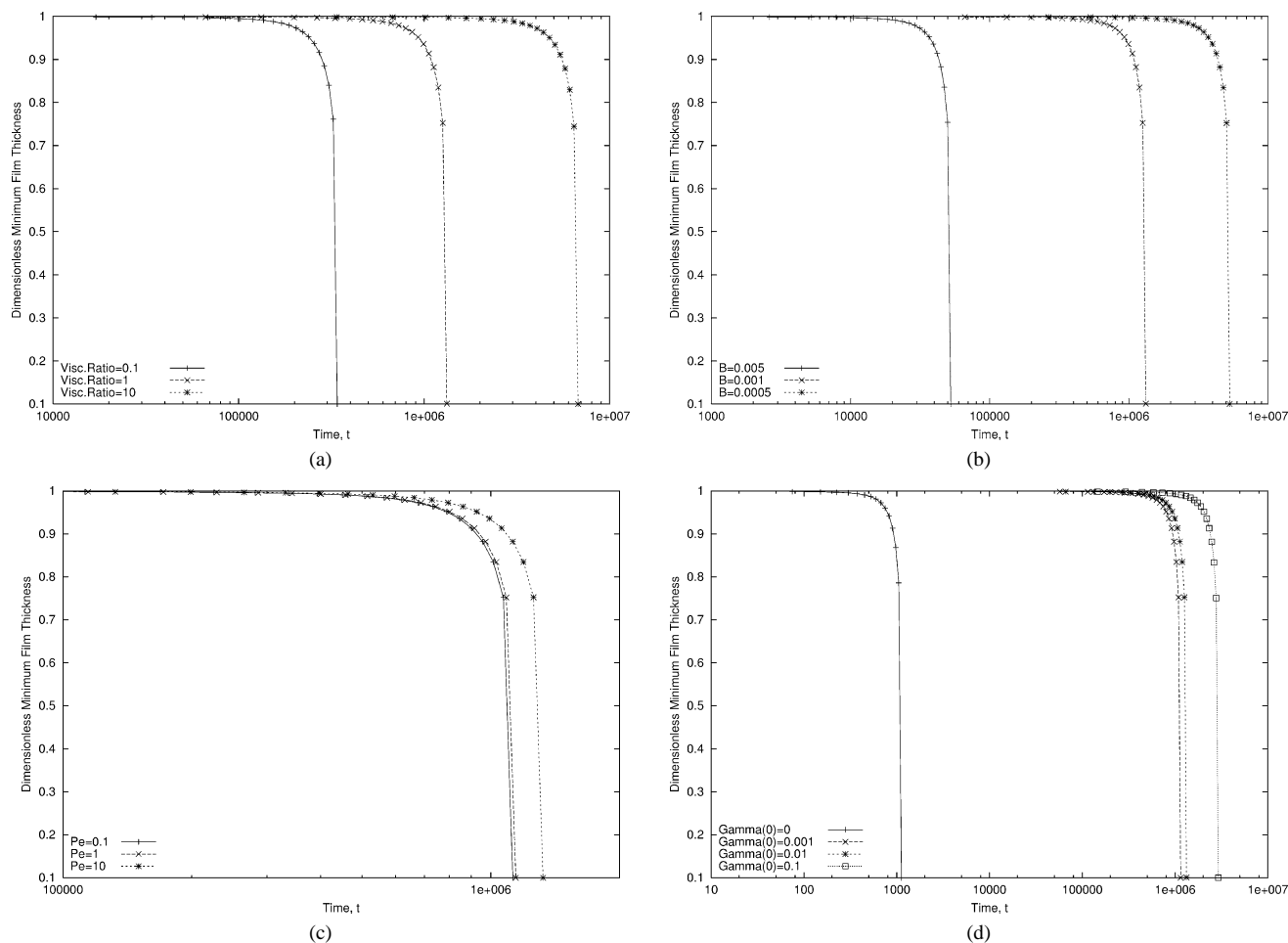


Fig. 5. Plots of the minimum film thickness against time for (a) variation of the viscosity ratio, λ , (b) variation of the Hamaker constant, B , (c) variation of the surface Péclet number, Pe , and (d) variation of the initial surfactant concentration, $\Gamma^{(0)}$. The base case is $\lambda = 1$, $B = 0.001$, $C = 0.5$, $Pe = 10$, and $\Gamma^{(0)} = 0.01$ for systems in which trace amounts of surfactant are present, i.e., $S^* \sim O(\epsilon^2 \gamma_m^*)$. Each plot indicates the result of varying a single parameter in the base case for the fastest growing mode; all other parameters were held constant. For the pure system in (d), $C = 0.0005$ to be consistent with the definition of the capillary parameter.

the role of the disturbance wave in the film rupture process in these surfactant-loaded systems is minimal.

4. Nonlinear effects

We now consider nonlinear effects of the instability by solving the film and surfactant concentration evolution equations given by Eqs. (1) and (2) with no-flux boundary conditions at both ends of the solution domain: $\partial h / \partial x = \partial^3 h / \partial x^3 = \partial \Gamma / \partial x = 0$. Film thinning and subsequent evolution of the surfactant concentration are initiated by imposing a small-amplitude monochromatic wave perturbation as the initial condition:

$$h(x, 0) = 1 + 0.001 \cos(kx). \quad (6)$$

The partial differential equation solver PDECOL [10] was employed for the numerical solutions, in which discretization of the spatial variables was carried out by finite element collocation, whereas the method of lines was adopted for

time integration. The computations were carried out using 2000 grid points for the spatial domain of length $2\pi/k$ and halted at film thicknesses of 0.1 when difficulties arose in the accurate resolution of the increasingly singular spatial derivatives in the rupture region.

Figure 4 illustrates the film thinning process instigated by an initial perturbation wave with a wavelength associated with the “most dangerous mode,” i.e., $k = k_m$. The film proceeds to thin and rupture at the trough of the wave where the influence of the van der Waals forces is largest. The initial growth rate of the instability calculated in the numerical solutions was found to be linear and consistent with that predicted by Eq. (3) using linear theory. The plots of minimum film thickness as a function of time in Fig. 5 indicate that while the thinning of the film is initially linear, nonlinear effects become increasingly evident close to the end of the lifetime of the film as the film tends toward rupture. Given that linear theory already predicts a comparable if not significant growth rate for the instability in pure systems and in systems containing trace amounts of surfactant, as contrasted with

typical hydrodynamic thinning velocities, nonlinear theory suggests that the instability arising out of interfacial perturbations could grow and rupture the film at much higher rates.

A parametric study of the minimum film thickness plots in Figs. 5a–5d shows the effect of λ , B , Pe , and $\Gamma^{(0)}$ on the film thinning process, consistent with the results of previous related studies [6–8]. Film thinning and rupture is seen to be retarded by increasing λ , Pe , and $\Gamma^{(0)}$ and accentuated by increasing magnitudes of B .

5. Conclusions

Analytical expressions for the growth rate of an imposed spatial periodic disturbance on a localized plane-parallel film trapped between two drops have been derived using linear stability analysis in the lubrication approximation for both pure and surfactant-laden systems. From these expressions, the critical cut-off wavenumber, below which all wavenumbers lead to amplification of the instability, as well as the “most dangerous” wavenumber, at which the growth rate of the instability is maximized, have been identified. The presence of insoluble surfactants at the interface is found to stabilize the film: the Marangoni effect dampens the growth of the instability due to the redistribution of surfactant and hence fluid along the interface. Comparisons of typical wave-

lengths with experimental and analytical observations show that our predictions are reasonable and of similar orders of magnitude. When large amounts of surfactants are present, such that the spreading is Marangoni-dominated, the growth rate of the instability is insignificant compared to the velocity at which the film thins hydrodynamically. Nonlinear effects are observed to amplify the instability growth rates beyond that suggested by linear theory as the film proceeds toward rupture in finite time.

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