

Nonlinear Rupture Theory of a Thin Free Liquid Film with Insoluble Surfactant

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Effects of insoluble surfactant on the dynamic rupture of a thin free film are investigated. The integral method is applied to derive the strong nonlinear evolution equations. Then the numerical method is used to analyze the nonlinear rupture process. The results show that the Marangoni effect due to the concentration gradient of insoluble surfactant delays the rupture process. Furthermore, the rupture time predicted by the evolution equations derived by the integral theory is always longer than that predicted by the evolution equations derived by the long-wave expansion method. Besides, it is shown that the stronger the Marangoni effect becomes, the larger the difference between the rupture time predicted by both above two models becomes.

KEYWORDS: thin liquid film, nonlinear rupture, van der Waals potential, Marangoni effect, integral method

§1. Introduction

The hydrodynamic stability of thin liquid films has been widely studied due to its widespread applications in chemical, mechanical and biomedical engineering, *et al.* A liquid film is unstable when its thickness is thinner than 1000 Å. To realize the mechanism through which the instability of the thin film presents, the parameter "disjoining pressure", which is generated by the van der Waals potential (VDWP), was introduced as a measure of the corresponding change in the thermodynamic properties and to distinguish between the properties of the thin film and those of bulk phase.¹⁾ When electric double-layer forces are considered, the added disjoining pressure component is positive and the competition between these and VDWP can lead to the formation of black films.²⁾

In the case of a thin coating film on a solid substrate, the critical length and the linear rupture time of the thin film, which are related to the surface tension and VDWP, can be obtained by the hydrodynamic stability theory.^{3,4)} While, in the nonlinear analysis, two effects are reported to influence the rupture process, which include the nonlinearity in both the surface tension and VDWP that would accelerate the rupture process.⁵⁻⁸⁾ Moreover, for catching the high-order nonlinear effect such as inertia and high-order dissipation, the integral method can be used to derive the evolution equations of the thin films in a more compact form than those obtained by traditional long-wave expansion method.^{7,8)} Besides, in refs. 7 and 8, it is reported that the inertia could increase the instability of the thin films while the high-order dissipation decreases it.

Another important geometry of the film is a free film bounded by two free surfaces. The results of the linear analysis shows that the instability of a free film is more unstable than that of a film on a plate.⁴⁾ Prévost and Gallez^{9,10)} attempted to investigate the nonlinear

rupture process of the free films. It has been assumed by them that the boundary condition at the free surface is immobile (no-slip condition). This condition is consistent to the fact that a modest concentration of the added surfactant is sufficient to keep the free surface immobile.²⁾ However, it is unreasonable for the free films of pure liquid. Sharma and Ruckenstein¹¹⁾ also studied this problem by considering the linearized Navier-Stokes equations, linearized stress boundary conditions and mobile free surfaces. Nevertheless, Erneux and Davis¹²⁾ indicated that the high-order nonlinear effects in the governing equations and boundary conditions should also be considered in the rupture process of the free films. They derived the nonlinear evolution equations involving the effects of the high-order nonlinear contributions mentioned above. However, the estimation of the order of the magnitude of the variables and physical parameters are rough. Also in this study, the low-order velocity profile is used to correlate itself to the high-order nonlinear contributions of the governing equations, so that some of the high-order effects in both the momentum equation in the vertical direction and the stress boundary conditions are neglected. In addition, there have also been some research concerned with the spreading of the surfactant added to the thin film.¹³⁻¹⁹⁾ When a localized nonuniform distribution of surfactant is deposited as a monolayer on the surface of a thin film, the resulting gradients of the surface tension generate flows that makes the surfactant spread. Effects of insoluble surfactant on the nonlinear rupture process of a free and a coating film on a plate had been studied by De Wit *et al.*²⁰⁾ which extends the formulation and the methodology used by Erneux and Davis.

In some of the research,^{5-7,9-13,20)} the order of the magnitude of the dimensionless parameter (*e.g.* the dimensionless surface tension and the dimensionless Hamaker constant related to the strength of VDWP, etc.) is estimated to be large for retaining the main physi-

cal effects in the leading-order nonlinear evolution equations. However, the magnitudes of those dimensionless parameters of real materials (*e.g.* water and ethanal) are small. Moreover, some other nonlinear contributions of the governing equations, which should be appeared with those parameters, are usually neglected in those research. Therefore, in the present work, first the order of the magnitude of each variable and parameter is adopted by considering the long-wave nature of the response and the small magnitude of the parameters.^{5,6)} Then the simplified equations of motions and pertinent boundary conditions are formulated, and the high-order nonlinear contributions in the governing equations are considered. Finally, the integral method^{21,22)} is applied with a specific velocity profile to derive the nonlinear evolution equations. This velocity profile includes an unknown function to correlate shear-stress balance boundary condition at the interface. In this study, the evolution equations are used to simulate the nonlinear rupture processes and the numerical analysis results based on our model will be compared with those derived by De Wit *et al.* systematically.

§2. Formulation

The physical model for present study is shown in Fig. 1. The liquid is a Newtonian viscous fluid having kinematic viscosity ν and constant density ρ . In addition, we use the equilibrium value Γ_0 as a unit for measuring the concentration of the surfactants. It is as-

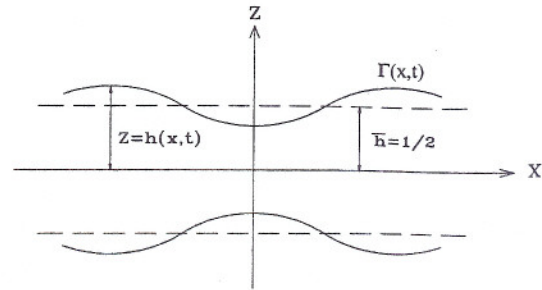


Fig. 1. The physical model of a thin free liquid film.

sumed that the gravity effect is neglected and the effect of VDWP is considered because of thin film thickness. Scaling the coordinate by the equilibrium thickness h_0 , time by h_0^2/ν , velocity by ν/h_0 , pressure by $\rho\nu^2/h_0^2$, concentration of the surfactant by Γ_0 , we have the modified Navier-Stokes equations given by¹²⁾

$$u_t + uu_x + wu_z = -p_x - \phi_x + u_{xx} + u_{zz}, \quad (1)$$

$$w_t + uw_x + ww_z = -p_z - \phi_z + w_{xx} + w_{zz}, \quad (2)$$

$$u_x + w_z = 0, \quad (3)$$

with the boundary conditions:

at $z = 0$,

$$u_z = w = 0, \quad (4)$$

at the interface, $z = h(x, t)$,

$$(u_z + w_x) - 4u_x h_x (1 + h_x^2)^{-1} = -M\Gamma_x (1 + h_x^2)^{1/2}, \quad (5)$$

$$-p + 2[(1 - h_x^2)w_z - h_x(u_z + w_x)](1 + h_x^2)^{-1} = (T - M\Gamma)h_{xx}(1 + h_x^2)^{-3/2}; \quad (6)$$

$$\Gamma_t + [(u\Gamma)_x + h_x(w\Gamma)_x](1 + h_x^2)^{-1} = D_s \nabla_s^2 \Gamma, \quad (7)$$

and the kinematic condition at the free surface is given by

$$h_t + uh_x = w, \quad (8)$$

where the surface gradient ∇_s is defined as²³⁾

$$\nabla_s = \left[\begin{array}{c} \frac{1}{1 + h_x^2} \frac{\partial}{\partial x} \\ \frac{h_x}{1 + h_x^2} \frac{\partial}{\partial x} \end{array} \right].$$

Equation (1) and (2) are momentum equations in x and z directions, respectively, and eq. (3) is the continuity equation. Equations (5) and (6) are shear and normal stress balance condition at the free surface. Equation (7) is a conservation equation for the concentration of the surface active substance. u , w , p and D_s are the dimensionless x -component velocity, the z -component velocity, pressure, and the surface diffusion coefficient of the surfactant, respectively, and the subscripts represent the partial derivatives. The second term in the left-hand side of eq. (7) represents of the rate of change of the concentration due to the dilatation of the free surface and the convection of the surfactant. In the research of De Wit *et al.*, the surface gradient effect is not considered.

The VDWP is represented through the potential function ϕ which depends on the film thickness as $\phi = \phi(h)$. We follow the reports of Ernueux & Davis¹²⁾ and De Wit *et al.*²⁰⁾ to write the potential function as

$$\phi = A(2h)^{-3}. \quad (9)$$

The dimensionless parameters in eqs. (1)–(9) are

$$M = -[\Gamma_0 h_0 / (\rho\nu^2)] (\partial\sigma/\partial\Gamma), \quad T = \sigma_0 h_0 / (\rho\nu^2),$$

$$A = A' / (6\pi h_0 \rho\nu^2), \quad \text{and} \quad D_s = D'_s / \nu,$$

where A' is the dimensional Hamaker constant, σ surface tension, and D'_s surface diffusion coefficient. It shows that A represents the ratio between the VDWP with the viscous dissipation and T represents the constant part of the tension σ_0 at equilibrium concentration Γ_0 . M is the dimensionless tension Marangoni number for the variation $\partial\sigma/\partial\Gamma$ of the dimensional tension σ versus the dimensional concentration Γ .

After solving the exact linear stability problem of eqs. (1)–(8) (please refer to the Appendix in detail), one can find that the neutral state of the system is present at the cut-off wave number given by

$$k_c = \left(\frac{6A}{T-M} \right)^{1/2}. \quad (10)$$

As is mentioned above, the real magnitudes of the dimensionless parameters are small. For example, $A = 10^{-5} \sim 10^{-3}$, $T = 10^{-2} \sim 3$, $M = 10^{-5} \sim 1$, and $D_s = 10^{-3} \sim 10^{-1}$ for water.²⁰⁾ Accordingly, the order of the magnitude of A , T , M and D are assumed as

$$T = O(1), \quad M = O(\epsilon), \quad A = O(\epsilon^4), \quad \text{and} \quad D_s = O(\epsilon), \quad (11)$$

where ϵ is a small parameter. Introducing eq. (11) into eq. (10), then the order of unstable wave number, k , can be represented as

$$k \doteq O(\epsilon^2). \quad (12)$$

The order of other dimensionless variables are^{5,6)}

$$\begin{aligned} u &= O(1), \quad w = O(k), \quad p = O(k^{-1}), \\ x &= O(k^{-1}), \quad z = O(1), \quad t = O(k^{-1}). \end{aligned} \quad (13)$$

Introducing eqs. (11)–(13) into eqs. (1)–(8) and neglecting the terms higher than $O(\epsilon^6)$, we can formulate the following simplified system,

$$u_t + uu_x + wu_z = -p_x - \phi_x + u_{xx} + u_{zz}, \quad (14)$$

$$w_t + uw_x + ww_z = -p_z + w_{zz}, \quad (15)$$

$$u_x + w_z = 0; \quad (16)$$

at $z = 0$

$$u_z = w = 0, \quad (17)$$

and at the interface, $z = h(x, t)$,

$$u_z = 4u_x h_x - w_x - M\Gamma_x \left(1 + \frac{3}{2}h_x^2 \right), \quad (18)$$

$$-p - (T - M\Gamma)h_{xx} = 2u_x + 2h_x u_z, \quad (19)$$

$$\Gamma_t + (u\Gamma)_x - D_s\Gamma_{xx} = h_x^2(u\Gamma)_x - h_x(w\Gamma)_x - D_s[h_x^2\Gamma_{xx} + h_x h_{xx}\Gamma_x], \quad (20)$$

$$h_t + uh_x = w. \quad (21)$$

One can find that the above system is similar to that of Prokopiou²⁴⁾ except for the momentum equation in z -direction, eq. (15), which includes the inertia and shear stress terms. The high-order dissipation terms are the normal stress in x -momentum equation, shear stress in z -momentum equation, and the interfacial shear, normal stress, and surfactant distribution in the right-hand side of dynamic boundary conditions (18)–(20) which are caused by large deformation. The above high-order terms are important when the evolution of the rupture processes reach the nonlinear stage.

The mass balance relationship is obtained by rewriting eq. (21) as

$$h_t + q_x = 0, \quad (22)$$

where q is the local flow rate and it can be expressed as

$$q = \int_0^h u \, dz.$$

A specific profile must now be imposed in the integral method. For highly turbulent flow, a flat profile is usually assumed. However, for the flow of interest here, Alekseenko *et al.*²¹⁾ have experimentally established that a parabolic profile is more appropriate. Therefore, we impose the following second-order self-similar profile of u as

$$\begin{aligned} q_t + \left(G^2 h + \frac{2}{3}GLh^3 + \frac{1}{5}L^2h^5 \right)_x &= \frac{3}{8}Ah^{-3}h_x + f + \frac{1}{3}L_{xx}h^3 + h[(T - M\Gamma)h_{xx}]_x + 2G_{xx}h \\ &+ 2h(Lh^2)_{xx} \left\{ -\frac{2}{3}L_xh^3 + \frac{1}{3}G_{xt}h^3 + \frac{1}{15}L_{xt}h^5 + \frac{1}{3}h^3[(GG_x)_x - 2G_x^2] + \frac{1}{15}h^5[3(LG_x)_x + (GL_x)_x \right. \\ &\left. - 8G_xL_x] + \frac{1}{21}h^7[(LL_x)_x - 2L_x^2] \right\}_x. \end{aligned} \quad (24)$$

$$u = qh^{-1} - \frac{fh}{6} \left[1 - 3\left(\frac{z}{h}\right)^2 \right],$$

where $f(x, t)$ is an unknown correlation function. This velocity profile satisfies boundary condition at the center of film and $u_z = f(x, t)$ at free surface. Applying the continuity equation and eq. (18), the shear-stress balance boundary condition at free surface can be given by the following form,

$$\begin{aligned} f &= 4G_xh_x + 4L_xh^2h_x + G_{xx}h + \frac{1}{3}L_{xx}h^3 \\ &- M\Gamma_x \left(1 + \frac{3}{2}h_x^2 \right), \end{aligned} \quad (23)$$

where

$$G(x, t) = qh^{-1} - \frac{1}{6}fh,$$

and

$$L(x, t) = \frac{1}{2}fh^{-1}.$$

Equation (23) represents the nonlinear shear stress equilibrium relation at the interface and the unknown function f now is correlated to h and q in the rupture process. Furthermore, integrating eq. (14) over the film thickness and applying eq. (15) with other boundary conditions, one can obtain the averaged x -momentum equation as

Finally, substituting the surface velocities (e.g. u and w at the free surface) into eq. (19), the diffusion equation of insoluble surfactant can be rewritten as

$$\Gamma_t + (1 - h_x^2)(G\Gamma + L\Gamma h^2)_x - \frac{1}{3}h_x(3G_x\Gamma h + L_x h^3\Gamma)_x = D_s[(1 - h_x^2)\Gamma_{xx} - \Gamma_x h_x h_{xx}]. \quad (25)$$

Equations (22)–(25) are the nonlinear evolution system with the film thickness h , local flow rate q , correlation function f , and concentration Γ . If f and the high-order terms in the diffusion equation is neglected, the evolution system is equivalent to that derived by De Wit *et al.* Here, eqs. (22)–(25) are denoted as SNEF

(the strong nonlinear evolution equation for free films), and the evolution equations derived by De Wit *et al.* are DWE.

§3. Nonlinear Rupture Theory

It is instructive to analyze the linear stability of the steady-state solution $(q, h, f, \Gamma) = (0, 0.5, 0, 1)$. Introducing the deviation $h' = h - 0.5$, $q' = q$, $f' = f$, and $\Gamma' = \Gamma$ into eqs. (22)–(25) and admit solutions of the form

$$(h', q', f', \Gamma') = (H_0, Q_0, F_0, \Gamma_0)e^{\omega t + ikx},$$

one can find the following characteristic equation for the growth rate ω :

$$\begin{aligned} & \frac{1}{960}(-60k^2 - k^4 - 720)\omega^3 + \left[\frac{1}{5760}Mk^2(k^2 - 12) + \frac{1}{16}k^2(k^2 - 36) - \frac{1}{5760}k^2(6D_s + M)(60k^2 + k^4 + 720) \right]\omega^2 \\ & - \left\{ \frac{1}{96}Mk^2(k^2 - 12)^2 + \frac{1}{96}k^4(k^2 - 36)(6D_s + M) + \frac{3}{8}[6A - (T - M)k^2] \right\}\omega \\ & + \frac{1}{16}k^4(6D_s + M)[6A - (T - M)k^2] = 0. \end{aligned} \quad (26)$$

Equation (26) admits a zero ω if the last coefficient is equal to zero. This leads the cut-off wave number k_c to be

$$k_c = \left(\frac{6A}{T - M} \right)^{1/2}, \quad (27)$$

which agrees with the exact linear results. The solutions to the characteristic equation for various M values are shown in Fig. 2. The peak of each $\omega - k$ curve denotes the maximum growth rate ω_m and the corresponding wave number k_m . It is clear that an increase in M results in a decrease in the maximum growth rate ω_m which is inversely proportional to the rupture time of the free film as described in refs. 5–7. This means that the film will become more stable as we increase the concentration Γ_0 of surfactants in the film or the rate $(-\partial\sigma/\partial\Gamma)$ in order to increase the Marangoni number. If we increase the surface tension T , then the cutoff wave number k_c will decrease. The film is thus more stable as the domain

of possible unstable wave number shrinks. It is obvious that as ω_m decreases, the rupture time of the film will be postponed, which is in agreement with the fact that films with a higher interfacial tension are more stable.

The nonlinear rupture process of the film is revealed by solving SNEF and DWE numerically. Equations are discretized by using the finite-difference method. Center differences are employed in space while the midpoint rule is used for time. The calculation domain is fixed on interval $0 \leq x \leq 2\pi/k_m$, where k_m is the wave number of the maximum growth rate. The periodic boundary conditions are considered in this problem. The initial-value conditions are

$$h(x, 0) = 0.5 + H_0 \cos k_m x, \quad 0 \leq x \leq 2\pi/k_m \quad (28)$$

$$q(x, 0) = -\frac{\omega_m}{k_m} H_0 \sin k_m x, \quad 0 \leq x \leq 2\pi/k_m \quad (29)$$

$$f(x, 0) = -\omega_m k_m H_0 \sin k_m x, \quad 0 \leq x \leq 2\pi/k_m \quad (30)$$

$$\Gamma(x, 0) = 1.0, \quad 0 \leq x \leq 2\pi/k_m \quad (31)$$

where H_0 is the initial disturbance. In all the numerical results mentioned below, the initial disturbance 0.05. The Newton-Raphson iteration scheme is introduced to calculate the difference equations and the convergent tolerance is 10^{-5} .

The profiles of the film thickness predicted by SNEF and DWE at $t = 5320$ are shown in Fig. 3. It shows that the nonlinear rupture process predicted by DWE is completed while that predicted by SNEF is still around the initial disturbance of the film. Figure 4 shows the nonlinear evolution of $h_{\min}$ (the minimum thickness of the film) predicted by both DWE and SNEF for $T = 1$, $A = 0.001$ and $M = 0.01$. It reveals that the rupture processes predicted by DWE are faster than those predicted by SNEF. The effect of inertia is included in both models. The nonlinear rupture process accelerates very fast during the range of $0.3 \leq h_{\min} \leq 0.4$. However, those predicted by SNEF do not proceed acceleratively

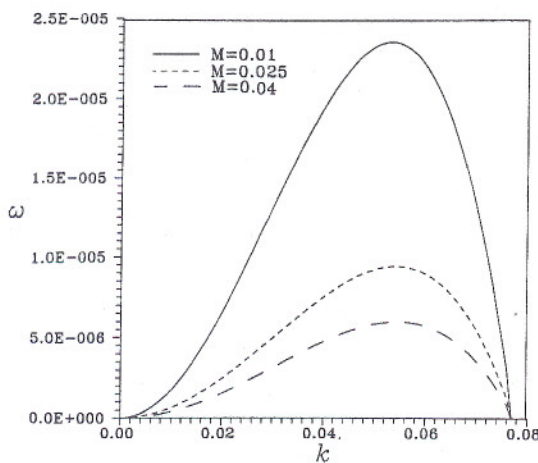


Fig. 2. ω versus k for various M value. The value of A is 0.001, T 1.0 and D_s 0.1.

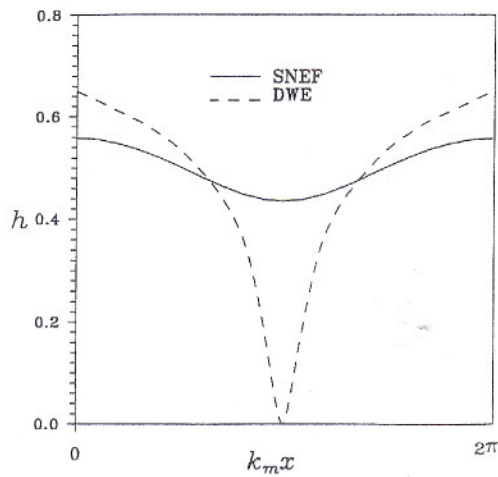


Fig. 3. The film profile predicted by SNEF and DWE theory at $t = 5320$. $A = 0.001$, $T = 1.0$, $M = 0.01$ and $D_s = 0.1$

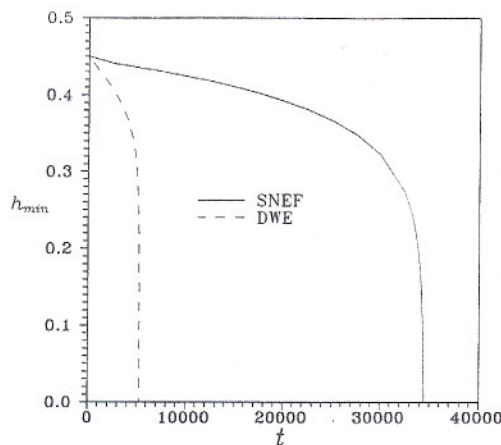


Fig. 4. The nonlinear evolution of $h_{\min}$ predicted by SNEF and DWE. $A = 0.001$, $T = 1.0$, $M = 0.01$ and $D_s = 0.1$.

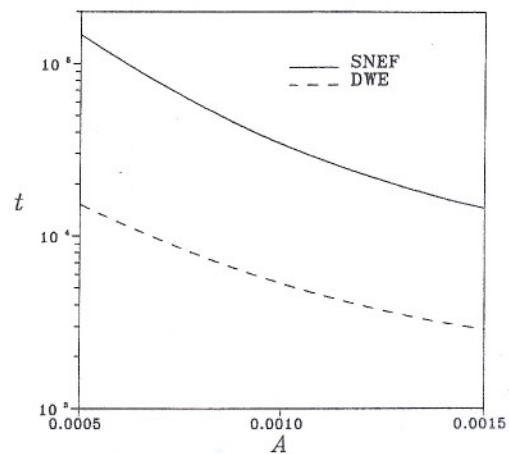


Fig. 5. Rupture time versus A values for SNEF and DWE. $M = 0.01$, $T = 1.0$ and $D_s = 0.1$.

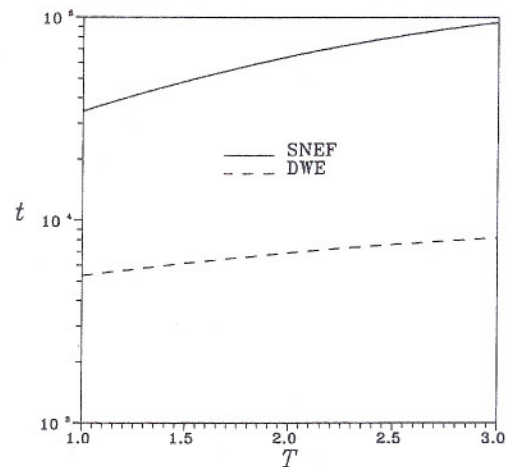


Fig. 6. Rupture time versus T values for SNEF and DWE. $A = 0.001$, $M = 0.01$ and $D_s = 0.1$.

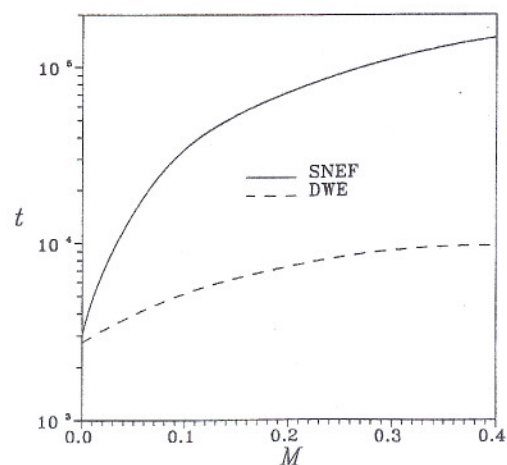


Fig. 7. Rupture time versus M values for SNEF and DWE. $A = 0.001$, $T = 1.0$ and $D_s = 0.1$

until $0.2 \leq h_{\min} \leq 0.3$. This phenomenon is considered to be caused by the more complete high-order viscous dissipation effects. The high-order shear force on the interface could slow down the rupture process.²⁴⁾ However, for the case of a film on a flat plate, the rupture process predicted by the evolution equation derived by the long-wave expansion is slower than that predicted by the equations derived by the integral method. It is because for the film on a plate, the effect of inertia and high-order dissipation are neglected during the formulation of the equation by the long-wave expansion, and those are the destabilizing factors for the rupture process.⁴⁻⁸⁾

Figure 5 presents the nonlinear rupture time predicted by two models versus various A values. The larger the value of A turns to be, the shorter the rupture time predicted by both models will become. While the difference between the rupture times predicted by two models decreases slightly when VDWP is weakened. The rupture time predicted by DWE is shorter than by SNEF about 90% to 80% as the value of A increases from 0.0005 to 0.00015. Figure 6 presents the nonlinear rupture time predicted by two models versus various T values. The rupture time predicted by both models and the difference

between them increase slightly together as the effect of the surface tension becomes stronger. The rupture time predicted by DWE is shorter than that by SNEF about 85% to 91% as the value of T increases from 1 to 3.

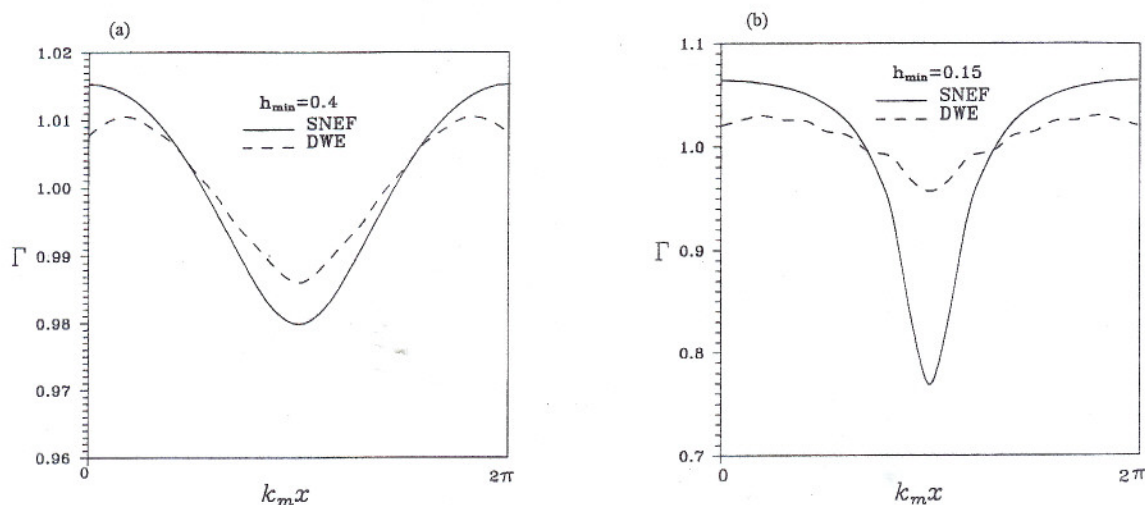


Fig. 8. (a) The concentration profile of insoluble surfactant predicted by long wave and integral theory at $h_{min} = 0.4$. $A = 0.001$, $T = 1.0$, $M = 0.01$ and $D_s = 0.1$. (b) The concentration profile of insoluble surfactant predicted by long wave and integral theory at $h_{min} = 0.15$. $A = 0.001$, $T = 1.0$, $M = 0.01$ and $D_s = 0.1$.

The nonlinear rupture times predicted by both two model versus M are presented in Fig. 7. The rupture times predicted by both models are postponed explicitly as the Marangoni effect tends to strong. This is because the re-distribution of surfactant at free surface makes the concentration of surfactant at the peak region of the disturbed wave more stable than that of the bottom region of the wave. Accordingly, a gradient of the surface tension is present, and the surface tension is stronger at the bottom than at the peak. The flow of the liquid from the weaker surface tension regions to the stronger ones is the Marangoni flow. Since this flow is in a direction opposite to the flow generated due to VDWP to slow down the thinning of the film, it delays the process of thinning and thus extends the rupture time of the film.²⁵ Another tendency shown in Fig. 7 is the difference between the rupture times predicted by two models increases explicitly as the Marangoni effect tends to stronger. The time difference is about 9% at $M = 0$ and enlarge dramatically to 93.46% at $M = 0.04$. It can be expected that the high-order effect, especially the high-order nonlinear terms in shear-stress balance condition and surfactant diffusion equation, will magnify the concentration gradient of insoluble surfactant. This phenomenon can be realized clearly as demonstrated in Figs. 8(a)–8(b). In these figures, It is found that the concentration difference along the film surface predicted by SNEF is larger than that predicted by DWE and therefore induces a stronger Marangoni flow.

As is shown in Fig. 9, the nonlinear rupture times predicted by two models vary with the value of D_s . The stronger the effect of the surface diffusion tends to be, the shorter the rupture times predicted by SNEF and DWE will become. The diffusion effect could mitigate the non-uniform distribution of surfactant at free surface, and thus the Marangoni effect is reduced. Additionally, the difference between the rupture time predicted by SNEF and DWE decreases as the effect of surface diffusion tends to stronger. The rupture time predicted by

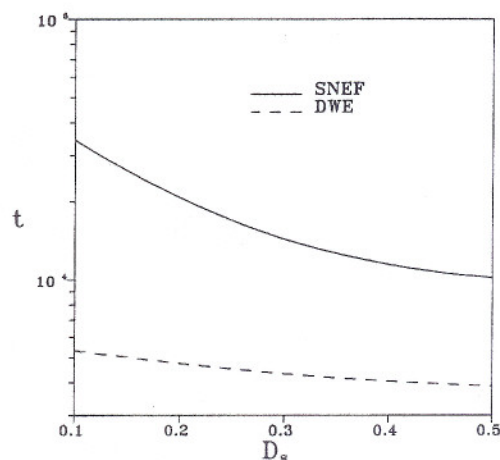


Fig. 9. Rupture time versus M values for SNEF and DWE. $A = 0.001$, $T = 1.0$ and $M = 0.01$.

DWE is shorter than that predicted by SNEF about 84% to 62% as the value of D_s increases from 0.1 to 0.5. The high-order dissipation, especially the high-order nonlinear terms in the diffusion equation of surfactant, reduces the effect of diffusion to make the gradient of the concentration of surfactant explicit.

§4. Conclusion

The effect of insoluble surfactant on the instability of a liquid film bounded by two free surfaces is studied. The exact linear analysis provides the information about the neutral state which is used to correlate k to the surface tension S , Marangoni effect M , the surface diffusivity D_s , and the Hamaker constant A . Sequentially, the leading-order governing equations and the corresponding boundary conditions are obtained, and the strong nonlinear evolution equations are derived by the integral method. Finally, the numerical method are used to solve the nonlinear evolution system for studying the rupture process. It is concluded that the nonlinear rup-

ture time predicted by present model is longer than that predicted by De Wit *et al.* The rupture time difference between the above two models enlarges explicitly when the Marangoni effect becomes stronger. It is because a complete high-order dissipation effect in present model has been considered, and induce a larger local concentration difference of insoluble surfactant than that derived by De Wit *et al.* While in the results derived by De Wit *et al.* with the long-wave expansion, an incomplete high-order dissipation effect has been considered with the low-order velocity profile being used to correlate itself to the high-order contributions of the governing equations. The effect of the surface diffusivity could reduce the elongation of the rupture time due to the Marangoni effect. On the other hand, the difference in the rupture times predicted by these two models discussed above seems not to vary much as the effect of VDWP or surface tension is enlarged.

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Appendix

The base states of eqs. (1)–(8) are

$$\bar{u} = 0, \quad \bar{w} = 0, \quad \bar{p} = 0, \quad \bar{\Gamma} = 1,$$

and

$$\bar{h} = 0.5.$$

And we assume the perturbation of the velocity vector (u', w'), the pressure p' , the concentration Γ' , and the height of free surface h' have the form

$$(u', w', p', \Gamma', h') = (\hat{u}(z), \hat{w}(z), \hat{p}(z), \hat{\Gamma}, a) e^{\omega t + ikx}, \quad (\text{A.1})$$

where k is dimensionless wave number, ω is the dimensionless complex characteristic value, and a is the amplitude of the disturbance. Taking eq. (A.1) into account, we can write the linearized equations for disturbances in the form:

$$ik(\hat{p} - 6Aa) = [D^2 - (k^2 + \omega)]\hat{u}, \quad (\text{A.2})$$

$$D\hat{p} = [D^2 - (k^2 + \omega + ik)]\hat{w}, \quad (\text{A.3})$$

$$ik\hat{u} + D\hat{w} = 0. \quad (\text{A.4})$$

The boundary conditions at the center of free film and the free surface have the form:

$$D\hat{u} = \hat{w} = 0, \quad (\text{at } z = 0) \quad (\text{A.5})$$

$$\hat{w} = a\omega, \quad (\text{at } z = \bar{h}) \quad (\text{A.6})$$

$$D\hat{u} + ik\hat{w} = -Mik\hat{\Gamma}, \quad (\text{at } z = \bar{h}) \quad (\text{A.7})$$

$$\hat{p} + 2ik\hat{u} = k^2(T - M)a, \quad (\text{at } z = \bar{h}) \quad (\text{A.8})$$

$$\omega\hat{\Gamma} + ik\hat{u} = -k^2D_s\hat{\Gamma} \quad (\text{at } z = \bar{h}) \quad (\text{A.9})$$

where D denotes d/dz . The system (A.2)–(A.4) can be conveniently reduced to a single Orr-Sommerfeld equation for $\hat{w}(z)$:

$$[D^4 - (2k^2 + \omega)D^2 + k^2(k^2 + \omega)]\hat{w} = 0, \quad (\text{A.10})$$

and the boundary conditions (A.5)–(A.9) become

$$\hat{w} = D^2\hat{w} = 0, \quad (\text{at } z = 0) \quad (\text{A.11})$$

$$\hat{w} = a\omega, \quad (\text{at } z = \bar{h}) \quad (\text{A.12})$$

$$(D^2 + k^2)\hat{w} = 0, \quad (\text{at } z = \bar{h}) \quad (\text{A.13})$$

$$[D^3 - (3k^2 + \omega)D + Ak^2\omega^{-1} - (T - M)k^4\omega^{-1}]\hat{w} = 0, \quad (\text{at } z = \bar{h}) \quad (\text{A.14})$$

$$[D^2(\omega + D_s k^2) + Mk^2D + (\omega k^2 + D_s k^4)]\hat{w} = 0. \quad (\text{at } z = \bar{h}) \quad (\text{A.15})$$

After calculating the solution of eq. (A.10) with boundary conditions (A.11)–(A.15), the secular determinant would lead to a relation among the parameters in the following form

$$F(\omega, k, A, T, M)$$

$$\begin{aligned} &= (\beta_1^2 - \beta_2^2)(G_1 G_4 - \beta_2 R F) \sin \alpha_1 \cos \alpha_2 + (\beta_1^2 - \beta_1^2)(G_2 G_3 - \beta_1 R F) \cos \alpha_1 \sin \alpha_2 \\ &\quad + (\beta_2^2 - \beta_1^2)(G_1 R - G_2 R) \sin \alpha_1 \sin \alpha_2 + (\beta_1^2 - \beta_2^2)(G_2 \beta_2 F - G_4 \beta_1 F) \cos \alpha_1 \cos \alpha_2 \\ &= 0, \end{aligned} \quad (\text{A.16})$$

where $\beta_1, \beta_2, \alpha_1, \alpha_2, G_1, G_2, G_3, G_4, R$ and F are defined as follow:

$$\beta_1^2 = -(\omega + k^2 + ik), \quad \beta_2^2 = -k^2,$$

$$\alpha_1 = \beta_1/2, \quad \alpha_2 = \beta_2/2,$$

$$G_1 = -\beta_1^2(\omega + D_s k^2) - \omega k^2 + D_s k^4, \quad G_2 = -\beta_2^2(\omega + D_s k^2) - \omega k^2 + D_s k^4,$$

$$G_3 = \beta_1^3 \omega + \beta_1 \omega (3k^2 + 1), \quad G_4 = \beta_2^3 \omega + \beta_2 \omega (3k^2 + 1),$$

$$R = 6Ak^2 - (T - M)k^4, \quad \text{and} \quad R = -Mk^2.$$

The neutral state of system implies the real part of ω is zero, and from eq. (A.16), it is easy to find the cut-off wave number

$$k_c = \left(\frac{6A}{(T-M)} \right)^{1/2}. \quad (\text{A.17})$$

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- 1) A. Sheludko: *Adv. Colloid Interface Sci.* **1** (1967) 391.
 - 2) J. T. G. Overbeek: *J. Phys. Chem.* **64** (1960) 1178.
 - 3) A. Vrij: *Discuss. Faraday Soc.* **42** (1966) 23.
 - 4) E. Ruckenstein and R. K. Jain: *J. Chem. Soc. Faraday Trans. II* **70** (1974) 132.
 - 5) M. B. Williams and S. H. Davis: *J. Colloid Interface Sci.* **90** (1982) 220.
 - 6) J. P. Burelbach, S. G. Bankoff and S. H. Davis: *J. Fluid Mech.* **195** (1988) 463-494.
 - 7) J.-L. Chen and C.-C. Hwang: *J. Colloid Interface Sci.* **167** (1994) 214.
 - 8) C.-C. Hwang, J.-L. Chen and L.-F. Shen: *Phys. Rev. E* (revised).
 - 9) M. Prévost and D. Gallez: *J. Chem. Phys.* **84** (1986) 4043.
 - 10) M. Prévost and D. Gallez: *AIChE Symp. Ser.* **252** (1986) 123.
 - 11) A. Sharma and E. Ruckenstein: *AIChE Symp. Ser.* **252** (1986) 130.
 - 12) T. Erneux and S. H. Davis: *Phys. Fluids A* **5** (1993) 1117.
 - 13) M. S. Borgas and J. B. Grotberg: *J. Fluid Mech.* **193** (1988) 155.
 - 14) D. P. Gaver III and J. B. Grotberg: *J. Fluid Mech.* **213** (1990) 127.
 - 15) S. M. Troian, E. Herbolzheimer and S. A. Safran: *Phys. Rev. Lett.* **65** (1990) 333.
 - 16) O. E. Jensen and J. B. Grotberg: *J. Fluid Mech.* **240** (1992) 259.
 - 17) F. F. Espinosa, A. H. Shapiro, J. J. Fredberg and R. D. Kamm: *J. Appl. Physiol.* **75** (1993) 2028.
 - 18) H. S. Khesghi and L. E. Scriven: *Chem. Engng. Sci.* **46** (1991) 519.
 - 19) D. P. Gaver III and J. B. Grotberg: *J. Fluid Mech.* **235** (1992) 399.
 - 20) A. De Wit, D. Gallez and C. I. Christov: *Phys. Fluids* **6** (1994) 3256.
 - 21) S. V. Alekseenko, V. Ye. Narkoryakov and B. G. Pokusaev: *AIChE J.* **31** (1985) 1446.
 - 22) Th. Prokopiou, M. Cheng, and H.-C. Chang: *J. Fluid Mech.* **222** (1991) 665.
 - 23) C. E. Weatherburn: *Differential Geometry of Three Dimensions* (Cambridge University Press, New York, 1927) Chap. 12, p. 233.
 - 24) C.-C. Hwang, J.-L. Chen, L.-F. Shen and C.-I. Weng: *Physica A* (accepted).
 - 25) A. Sharma and E. Ruckenstein: *J. Colloid Interface Sci.* **113** (1986) 456.
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