Dynamics of Thin Liquid Films with Nonsoluble Surfactants: Weakly Nonlinear Analysis

B. Y. Rubinstein and A. M. Leshansky*

Department of Chemical Engineering, Technion—I.I.T., Haifa 32000, Israel

Received October 26, 1999. In Final Form: December 15, 1999

Amplitude equations for Turing instabilities for two models describing dynamics of thin liquid films with nonsoluble surfactants are derived. Analytical expressions for the film rupture time were obtained, and the comparison with the results of previous numerical simulations was performed. It was shown that the Marangoni effect due to insoluble surfactants cannot prevent the film rupture.

1. Introduction

It is now well known that the thin liquid films exhibit hydrodynamic instability due to the long range molecular forces. These forces result from van der Waals attractions, and the instability leads to the film rupture. Two different *generic* geometries are usually considered: liquid film on a solid substrate and a liquid layer bounded by two free surfaces separating the liquid from a passive gas or another liquid. The former case is important in surface wetting and evaporation while the latter case is involved in coalescence of drops and emulsions and in cell membranes.

The presence of surfactants can drastically change the dynamics of the film motion. The nonuniform surfactant distribution in the film will cause the surface tension gradients, which result in tangential velocity along the interface (Marangoni effect). The Marangoni effect can either destabilize or stabilize the liquid film, depending on the particular situation. The combined effect of surfactants and van der Waals forces is an interesting issue, since Marangoni forces can compete with the van der Waals attractions and lead to the suppression of the film rupture. Probably, the most significant is the importance of the subject toward the fluid particle and emulsion coalescence.

Recently developed nonlinear stability theory, based on the long-wave nature of the response, provide nonlinear evolution equations, which can be solved numerically or by means of bifurcation analysis. Such evolution equations have already been considered for different situations. The detailed review of an application of this theory to different thin film problems can be found in the review by Oron et al.[1] The van der Waals attraction potential, which is given in general by some nonlocal operator, can be simplified in the long scale limit.[2]

It has been shown that a pair of coupled equations is required in the case of the free film subjected to the van der Waals attractions without surfactants[3] due to the presence of two stress-free boundaries (one equation for h and the other one for the tangential velocity of the liquid in film, u). Also a pair of equations are required if surfactants are present in a thin liquid film on a solid substrate (one for h and the other one for the concentration Γ of surfactants.[4,5] De Wit et al.[5] showed that a system of three coupled nonlinear evolution equations describing h, Γ, and u is needed to describe the evolution of a squeezing mode (SQ) of the free film subjected to the van der Waals attractions with *insoluble* surfactants (SQ mode involves symmetric thickness fluctuations and most directly leads to the film rupture). They provided the linear stability analysis and a numerical study of their model in both geometries.

Sharma and Ruckenstein[6] developed a nonstandard approach to the problem of thin film rupture. They consider the finite amplitude disturbance by perturbing the *spatially inhomogeneous* stationary solution of the nonlinear evolution equation. This approach results in a linear differential equation with inhomogeneous coefficients which they reduced to a problem with constant coefficients. The linear stability analysis of the latter problem gives an estimate of rupture time as a function of various system parameters and the amplitude of the initial perturbation of the base state from the spatially homogeneous solution.

In this paper we investigate two problems considered in ref 5 by means of weakly *nonlinear* analysis in the vicinity of a steady bifurcation point. The coefficients of the resulting nonlinear amplitude equations are obtained analytically with the help of a symbolic program[7,8] written in *Mathematica*. We think that development and usage of symbolic software for bifurcation analysis of nonlinear problems in hydrodynamics look very promising. Further analysis of the amplitude equation provides an analytic estimate of the *nonlinear* rupture time as a function of different parameters of the model. These rupture times are compared with the numerical results obtained in ref 5. The presented results give a deeper insight into the role of surfactants on the dynamics of the thin film rupture in the weakly nonlinear region of parameters.

2. Problem Formulation

We consider, first, the model describing the evolution of free film subjected to van der Waals attractions with insoluble surfactants for the thickness h of the film, the

(1) Oron, A.; Davis, S. H.; Bankoff, S. G. *Rev. Mod. Phys.* **1997,** *69,* 931.
(2) Maldarelli, C.; Jain, R. K.; Ivanov, I. B.; Ruckenstein, E. *J. Colloid Interface Sci.* **1980**, *78*, 118.
(3) Erneux, T.; Davis, S. H. *Phys. Fluids, A* **1993**, *5*, 1117.
(4) Jensen, O. E.; Grotberg, J. B. *Phys. Fluids, A* **1993**, *5*, 58.
(5) De Wit, A.; Gallez, D.; Christov, C. I. *Phys. Fluids, A* **1994**, *6*, 3256.
(6) Sharma, A.; Ruckenstein, E. *J. Colloid Interface Sci.* **1986**, *113*, 2.
(7) Pismen, L. M.; Rubinstein, B. Y.; Velarde, M. G. *Int. J. Bif. Chaos* **1996**, *6*, 1.
(8) Pismen, L. M.; Rubinstein, B. Y. *Int. J. Bif. Chaos* **1999**, *9*, 983.

10.1021/la9914099 CCC: $19.00
Published on Web 02/05/2000

concentration Γ of the surfactants, and the tangential velocity u of the fluid in the film[5]

$$h_t = -(uh)_x$$

$$\Gamma_t = \Gamma_{xx}/Sc - (\Gamma u)_x$$

$$(u_t + uu_x - Th_{xxx} + W_x)h = (-M\Gamma + 4hu_x)_x \quad (1)$$

where M is a dimensionless Marangoni number, T is a dimensionless surface tension, Sc is a Schmidt number, and W is an attractive van der Waals potential, $W = A(2h)^{-3}$, while A is a dimensionless Hamaker constant. Taking $\Gamma = 0$ identically the above model reduces to a system of two coupled equations derived previously by Erneux and Davis.[3] Second, we consider the model describing the evolution of the thin film with insoluble surfactants on a solid substrate[5]

$$h_t = (M\Gamma_x h^2/2 - \phi_x h^3/3)_x$$

$$\Gamma_t = \Gamma_{xx}/Sc + (M\Gamma_x \Gamma h - \Gamma \phi_x h^2/2)_x \quad (2)$$

with

$$\phi(x,t) = -A/h^3 + Th_{xx} \quad (3)$$

3. Linear Analysis

In this section we briefly repeat results of linear analysis for two models performed in ref 5. Consider model 1, its basic stationary uniform solution is

$$\mathbf{w}_0 = \{h_0 = 1/2,\ G_0 = 1,\ u_0 = 0\}$$

Expanding a phase variables vector $\mathbf{w} = \{h, \Gamma, u\}$ around the point $\mathbf{w}_0$

$$\mathbf{w} = \mathbf{w}_0 + \mathbf{A}\exp(ikx + i\omega t)$$

and retaining only linear terms we find the bifurcation condition (for $\omega = 0$) in the form

$$k^4(Tk^2 - 6A) = 0$$

which leads to the critical value of wavenumber $k_{cm}^{I} = (6A/T)^{1/2}$.

Similar calculations show that model 2 also permits the monotonic short-scale instability with critical wavenumber $k_{cm}^{II} = (3A/T)^{1/2}$. Oscillatory instability is not detected in this case.

4. Nonlinear Analysis

Automated derivation of amplitude equations for the model considered consists of several steps. The program written in *Mathematica* implements the method of multiple scale expansion. Input of the program specifies the following data: the system of equations under consideration $\mathbf{F}(\partial/\partial t, \partial/\partial x, \mathbf{w}(x,t), R)$, which should admit trivial (zero) basic solution; array of the phase variables $\mathbf{w}(x,t)$; time t, space x variables, bifurcation parameter R, and its critical value R_c; scaling for space and time variables used in the expansion process and scaling for the phase variables; eigenvector $\mathbf{U}$ of the linearized problem, and eigenvector $\mathbf{U}^\dagger$ of the adjoint problem; expansion parameter E; critical value of wavenumber k_c and (for Hopf bifurcations) of the frequency ω_c.

The program starts with the expansion of time and space variables, phase variables, and the bifurcation parameter into the series in the small parameter ϵ:

$$t = t_0 + \epsilon t_1 + \epsilon^2 t_2 + \ldots$$

$$x = x_0 + \epsilon^\gamma x_1$$

$$\mathbf{w} = \mathbf{w}_0 + \epsilon \mathbf{w}_1 + \epsilon^2 \mathbf{w}_2 + \ldots$$

$$R = R_0 + \epsilon R_1 + \epsilon^2 R_2 + \ldots \quad (4)$$

Here γ is a scaling of space variable x. The expansion of x and t is effectively rewritten as expansion of the corresponding derivatives

$$\partial/\partial t = \partial/\partial t_0 + \partial/\partial t_1 + \epsilon^2 \partial/\partial t_2 + \ldots$$

$$\partial/\partial x = \partial/\partial x_0 + \epsilon^\gamma \partial/\partial x_1$$

The above expansions are applied to the system of equations, and the resulting equations in different orders of ϵ are produced. The linear approximation $L\ \mathbf{w}_1 = 0$ is retrieved in the first order in ϵ; the program checks whether the specified eigenvalue verifies the linear problem at given critical values of k_c, ω_c, and R_c. Then it proceeds to the second order in ϵ which has a form of inhomogeneous linear problem

$$L\ \mathbf{w}_2 = \mathbf{g}_2 \quad (5)$$

A solvability condition for this equation can be written in the form $\mathbf{g}_2\mathbf{U}^\dagger = 0$. It can be shown that this condition is a linear equation for an amplitude of the perturbation, slowly varying in time and space (at the characteristic scales x_1 and t_1). In most cases this equation can be reduced to the trivial one by switching to a comoving frame that is performed automatically. Then the program substitutes the solution into eq 5 and solves it, trying to find a solution orthogonal to the first-order solution (proportional to $\mathbf{U}$). This procedure is repeated until the nontrivial amplitude equation is produces at some step.

Both models produce similar amplitude equations in the time scale t_2 having the form of the dynamic Landau equation (LE)[9]

$$\partial a/\partial t_2 = \alpha a + \beta |a|^2 a \quad (6)$$

In both cases we chose tension T to be a bifurcation parameter, its critical value is denoted as T_c, and second-order deviation is T_2. Below are the values of the coefficients of LE. For model 1 the following values are found:

$$\alpha^{I} = -9G^2 T_2/(12G + MSc)$$

$$\beta^{I} = 456 T_c G^2/(12G + MSc)$$

where $G = A/T_c$. In order to check this result we set $M = 0$ effectively reducing model 1 to the simpler one considered in ref 3, where the analytical expressions for the coefficients α and β were derived. It can be easily seen that for $M = 0$, formula 7 reduced to that found in ref 3.

(9) Generally, the Ginsburg−Landau equation (GLE) is produced, but in both present models we must set the spatial modulation term, $\delta\partial^2 a/\partial x_1^2$, to be zero, since $k_{cm}^{I,II}$ corresponds to the longest possible spatial scale of the perturbation, $k_{cm}^{I,II} = \min_k T_c$.

For the second model (2), we find the following:

$$\alpha^{II} = -3/4G^2T_2(4 + MSc)/(1 + MSc)$$

$$\beta^{II} = 19T_cG^2(4 + MSc)/(1 + MSc)$$

5. Rupture of Films

Consider dynamics of the perturbation amplitude determined by the values of α and β. General solution of Landau amplitude equation (6) is given by

$$a(t) = a_0e^{\alpha t}\left(\frac{\alpha}{\alpha + \beta a_0^2(1 - e^{2\alpha t})}\right)^{1/2} \quad (7)$$

Film rupture corresponds to the infinite growth of the perturbation amplitude. The rupture time is determined as

$$t_r = \frac{1}{2\alpha}\ln\left(1 + \frac{\alpha}{a_0^2\beta}\right) \quad (8)$$

It can be shown that rupture is inevitable for positive values of β.

Having analytical expressions for coefficients α and β, one can easily make estimations of rupture times for different values of model parameters. Here are formulas for the rupture time:

$$t_r^{I} = -\frac{MSc + 12G}{18T_2G^2}\ln\left(1 - \frac{3T_2}{152a_0^2T_c}\right)$$

$$t_r^{II} = -\frac{2(MSc + 1)}{3T_2G^2(4 + MSc)}\ln\left(1 - \frac{3T_2}{76a_0^2T_c}\right) \quad (9)$$

It is interesting to receive the above expressions in a limit case $T_2 \to 0$, which corresponds to the negligibly small deviation of the bifurcation parameter from its critical value.

$$t_r^{IL} = \frac{MT_cSc + 12A}{912a_0^2A^2}$$

$$t_r^{IIL} = \frac{T_c(1 + MSc)}{38a_0^2A^2(4 + MSc)} \quad (10)$$

The last relations enable us to analyze influence of different parameters on the rupture time in both cases. We assume for simplicity sake that the Schmidt number *Sc* and initial amplitude a_0 of perturbation are fixed. Consider model 1 with a rupture time t_r^{IL}. It can be easily seen that film will rupture more slowly if one either adds surfactants *(M* increasing) or chooses a fluid with higher interfacial tension *T* or lower van der Waals attraction *A*. This qualitatively corresponds to the results of numerical simulations for this model obtained in ref 5; our estimates (10) of rupture time give different values but the same order of magnitude. A possible explanation of this discrepancy is that numerics were made for perturbations with the wavenumber value far from the critical one, and therefore, these results were strongly influenced by high nonlinearities.

For another model the influence of *M* on the film rupture is weaker, and the rupture time is affected mainly by changes of attraction coefficient or interfacial tension. Again, the comparison of our estimates with numerical results in ref 5 is not ideal for the above reason. For example, for the following set of parameters

$$A = 5, \quad T_c = 30, \quad Sc = 10, \quad M = 0.1, \quad a_0 = 0.1$$

we have $t_r^{IIL} = 1.27$, compared with $t_r = 1.6$ in ref 5.

In conclusion, we perform derivation of amplitude equations valid in a small vicinity of the critical points for Turing bifurcation for two models describing dynamics of thin liquid films with nonsoluble surfactants. Analytical expressions for the film rupture time were obtained, and comparison with the results of previous numerical simulations shows qualitative agreement. We show that the Marangoni effect, due to insoluble surfactants, cannot saturate the rupture instability in a weakly nonlinear region of parameters.

Acknowledgment. A.M.L. thanks Dr. A. A. Golovin for helpful discussions during the course of this investigation. B.Y.R. acknowledges financial support of the Israel Science Foundation and the Ministry of Science and Arts of Niedersachsen.

LA9914099