Notes

Dynamics of Thin Liquid Films on a Coated Solid Surface with Insoluble Surfactants: Weakly Nonlinear Analysis

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It is now well known[1] that thin liquid films exhibit hydrodynamic instability due to long-range molecular forces. With an apolar liquid these forces result from van der Waals attractions and the instability leads to film rupture. It was shown that nonlinear effects accelerate rupture when the rupture time is compared with that estimated on linear theory basis (see also ref 2 on similar calculations for a free film subject to Marangoni forces). The long-wave evolution equations used in refs 1 and 2 were generalized in ref 3 for a volatile fluid on a heated flat surface to include evaporative mass change, vapor thrust, and Marangoni and surface wave effects along with van der Waals attractive and surface tension forces. A detailed review of the application of nonlinear stability theory (based on the long-wave nature of the response) to different thin film problems is given by Oron et al.[4] This approach provides nonlinear evolution equations, which can be solved numerically or by means of bifurcation analysis. Such evolution equations have already been considered for different situations. In ref 5, the relatively long-range repulsive forces, owing to the effect of an adsorbed layer (such as corrosion or contamination) on the solid surface, were included in the long-wave model for dynamics of a volatile film under the additional action of Marangoni and surface tension forces. The conjoining pressure is significant at actual surfaces instead of "pure" surfaces, obtained only by cleavage of crystals under carefully controlled conditions. For pure surfaces the conjoining pressure is from Born repulsion at atomic distances. A weakly nonlinear theory was developed for the nonvolatile case, which showed that the inclusion of the repulsive forces can lead to stabilization of small, short-scale perturbations of a uniform stationary basic profile.

The presence of surfactants can drastically change the dynamics of the film motion. The nonuniform surfactant distribution in the film will cause 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, because Marangoni forces can compete with the van der Waals attractions and lead to suppression of the film rupture. The long-wave model corresponding to this case was derived in ref 6; the numerical simulations performed there showed that the film ruptures for all values of parameters checked, and the rupture time was found. In ref 7, the weakly nonlinear analysis was performed analytically. It was shown that for common liquids the influence of surfactant-driven Marangoni forces could slow the rupture process, but cannot stabilize short-scale perturbations. Rupture time estimates based on nonlinear analysis results were close to numerical values found in ref 6.

In this communication we generalize a model considered in refs 6 and 7 to a case of body potential including both disjoining and conjoining pressures. The amplitude equation describing evolution of a small perturbation valid in a close vicinity of a bifurcation point is derived, using the approach described in ref 8. The analysis of this equation enables us to construct a bifurcation diagram showing that the perturbation is stable in a very narrow region of dimensionless Hamaker constants determining the contribution of pressures in the body potential. It appears that even a small influence of conjoining pressure stabilizes the perturbed film in a narrow range of disjoining pressures. This range grows with an increase of conjoining pressure, then decreases again, shrinking to zero at some critical value of conjoining pressure, which is determined by other parameters of the problem.

We consider a model describing the evolution of the thin film with insoluble surfactants on a solid substrate (see ref 6), subjected to van der Waals attractions and shorter-scale repulsions, for the thickness h of the film and the concentration Γ of the surfactants:

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

$$\Gamma_t = \Gamma_{xx}/S + (M\Gamma_x \Gamma h - \Gamma\phi_x h^2/2)_x \qquad (1)$$

with

$$\phi(x,t) = -\frac{A}{h^3} + \frac{B}{h^4} + Th_{xx} \qquad (2)$$

where M is a dimensionless Marangoni number, T is a dimensionless surface tension, S is a Schmidt number, and A and B are dimensionless Hamaker constants for van der Waals long-range attractions and shorter-range repulsions, respectively. The basic solution is the spatially uniform stationary state $\mathbf{u}_0 = \{h_0, \Gamma_0\} = \{1,1\}$.

The linear analysis provides the critical value of the wavenumber corresponding to Turing bifurcation $k_c = [(3A - 4B)/T]^{-1}$, which imposes the condition on the Hamaker constants $A > 4B/3$. The eigenvectors $\mathbf{U}, \mathbf{U}^\dagger$ of both

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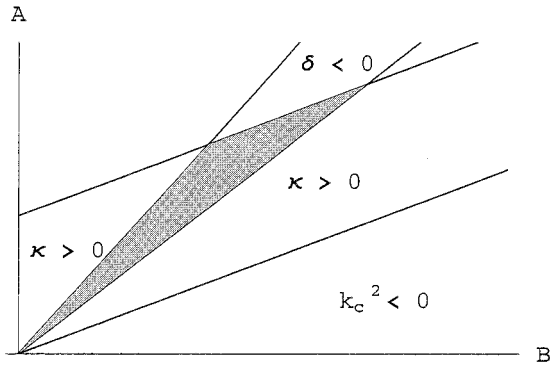(8) Pismen, L. M.; Rubinstein, B. Y. *Int. J. Bif. Chaos* **1999**, *9*, 983.

Figure 1. Bifurcation stability diagram of the perturbed film for $S = 34.5$, $M = 0.02$ and various values of the Hamaker constants A and B. The stability region is shown gray.

linearized and adjoined linearized problems corresponding to zero eigenvalue are determined as

$$\mathbf{U} = \{1,0\}, \quad \mathbf{U}^{\dagger} = \left\{- 2 - \frac{2}{MS}, 1\right\}$$

The surface tension T is selected as a bifurcation parameter with critical value T_c; in a bounded domain of the length L with periodic boundary conditions this value is found as

$$T_c = (3A - 4B) \frac{L^2}{4\pi^2}$$

Introduce the small criticality $\epsilon = T - T_c$, slow time $\tau = \epsilon^2 t$, long spatial coordinate $\xi = \epsilon x$, and expand the solution and bifurcation parameter in a series in ϵ:

$$\mathbf{u} = \mathbf{u}_0 + \epsilon\mathbf{u}_1 + \epsilon^2\mathbf{u}_2 + ..., \quad T = T_c + \epsilon T_1 + \epsilon^2 T_2 + ... \tag{3}$$

Substitution of the expansion (eq 3) into the system (eq 1) to the first order of ϵ, one obtains

$$\mathbf{u}_1 = (A(\xi,\tau)e^{ik_c x} + \text{cc})\,\mathbf{U}$$

where cc denotes complex conjugation. In the third order of ϵ the Ginzburg−Landau amplitude equation is obtained

$$\frac{\partial A}{\partial \tau} = \alpha A + \kappa|A|^2\,A + \delta\frac{\partial^2 A}{\partial \xi^2} \tag{4}$$

The signs of the Landau constant κ and diffusional

coefficient δ determine the stability of the stationary uniform solution

$$A_{st} = \sqrt{-\frac{\alpha}{\kappa}}$$

of the amplitude equation (eq 4), namely, it is stable at $\kappa < 0$ and $\delta > 0$. The linear coefficient $\alpha = -k_c^4\,T_2/2$ is proportional to the second-order deviation of the bifurcation parameter. The expression for the Landau constant reads as

$$\kappa = \frac{171A^2 - 570AB + 460B^2}{3\,T_c}$$

and for diffusional coefficient one has

$$\delta = \frac{k_c^2 T_c}{2(1 + MS)^2}\,(5(1 + MS)^2 - MS^2 k_c^2 T_c)$$

The bifurcation diagram depicting the stability region of the perturbed film in the plane of Hamaker constants $\{A,B\}$ is shown in Figure 1. For small B the range of stable perturbed solution is narrow in A, and it grows with increase of B. If one neglects dependence of the perturbation amplitude A on the large-scale spatial variable ξ, then the diffusional term in eq 4 can be dropped, and the stability region width continues to grow. Influence of weak spatial modulation at larger scales leads to shrinking of the stability region, which eventually vanishes at

$$B = \frac{95}{4}\left(1 - \sqrt{\frac{15}{19}}\right)\frac{(1 + MS)^2}{MS^2}$$

This simple analysis enables us to pose a question about the significance of the spatial dependence effects (which clearly may be neglected for systems in bounded region with size of several wavelengths $L = 2n\pi/k_c; n\sim 1$) on the stability of perturbed film.

Thus, the conjoining pressure stabilizes the film in a narrow region of parameters $\{A,B\}$ at small B, but eventually for large B results in absolute instability. This stabilization is a novel feature in thin film dynamics driven by surface tension inhomogeneities and shorter scale molecular interactions.