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Linear stability of ultrathin slipping films with insoluble surfactant

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To study the dewetting process of ultrathin slipping films, the stability characteristics of the surfactant-covered ultrathin films with slippage are analyzed with linear theory. A set of nonlinear equations for the film thickness and the concentration of surfactant is derived based on lubrication approximation for Newtonian viscous fluid. Results show slippage can always enhance the development of perturbations, and reduce the number density of holes when rupture occurs. A prominent characteristic of the stability is that two branches of solutions are found in the dispersion relation. This might lead to an inflexion in the growth rate curve of the most unstable modes, and a cusp point in the corresponding wave number curve for infinite slippage, which indicates that the slip has a profound effect on the linear stability of the films. The influences of the Marangoni number $\mathcal{M}$, equilibrium distance l_c, and the base concentration of surfactant Γ_0 on the linear stability are also discussed for different slip lengths in the present study. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2017229]

Liquid thin film flows are commonly encountered in nature and numerous practical applications, e.g., chemical engineering, materials process, or microelectronic systems. A great deal of theoretical studies have been performed to understand the stability, dynamics and dewetting of the flows.[1] For an ultrathin film (film thickness h less than 100 nm) on a solid substrate, previous studies showed that the van der Waals forces will come into action and enhance the development of small disturbances, and finally lead to rupture of the film and formation of holes, in the sense that the local film thickness becomes zero in a finite time period.

Most of the current theoretical studies focused on the films satisfying no-slip velocity condition on substrates. Recent experiments and computations based on molecular dynamics simulation indicated that slipping velocity can be evidently found in macromolecular polymer films.[2–4] Various ranges of slip length were reported in different experiments, varying from a few nanometers to a thousand micrometers. In mathematical modeling the boundary condition widely adopted for tangential velocity is written as $u = \beta u_z$ on the substrate, which implies the slip coefficient β is proportional to the shear stress at the wall. It might be expected that the slippage has great influences on their hydrodynamic behavior. A linear stability analysis was conducted by Sharma *et al.* for Newtonian fluid to take into account the effect of slippage.[5] Results showed slippage will encourage the development of the perturbations and film rupture, and reduce the number density of holes for sufficiently strong slip. To understand the nonlinear evolution and morphology of the flow, numerical simulations were performed henceforth based on the Navier–Stokes equations with lubrication or long wave approximation for both weak and strong slip.[6,7] The ratio of rupture time between the nonlinear computations and linear analysis is always less than 1, which reveals the nonlinear effects accelerate the breakup of the films.

The presence of a surfactant affects the surface tension of the interface and dynamics of films.[8] The transport equation for concentration of surfactant adopted in most of the related work available was derived by Stone using a simplified method.[9] Hereafter, numerous investigations were carried out to study the roles of surfactant, such as the bifurcation structures and pattern formation,[10] shock evolution, and rupture.[11] Recently Warner *et al.*[12] conducted stability analysis and numerical simulation to explore the dewetting process of ultrathin no-slip films with insoluble surfactant. The molecular potential extended from Sharma's work[13] was used in their study, which allowed the Hamaker coefficients to vary with surface tension or concentration of surfactant. The stability and dynamics of surfactant driven films overlying a hydrophobic epithelium were investigated by Zhang *et al.*[14] with the presence of slip, in which the van der Waals potential was considered to describe molecular interaction. Analogical with the case of the surfactant-free flows, the linear theory predicted that the slip leads to a significant reduction of the rupture time and the cutoff wave numbers are independent of the slip length β.

Following the work of Warner *et al.*,[12] the influence of slippage on the linear stability of surfactant-covered films is investigated in this Brief Communication. The mathematical model of the viscous ultrathin films is described by the Navier–Stokes equations involving the molecular interaction force or the disjoining pressure term, together with the boundary conditions at the free surface and on the solid substrate. To take both apolar and polar interactions into account, the molecular potential is given as[12]

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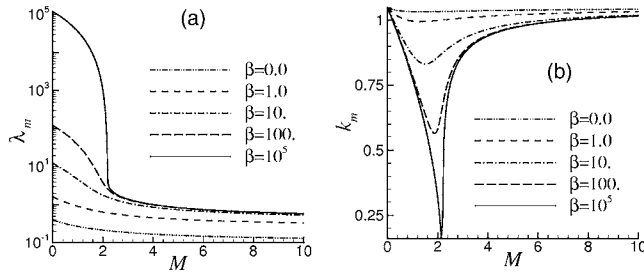
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FIG. 1. The variation of growth rate (a) and wave number (b) of the most unstable mode with the Marangoni number for different slip coefficient. The Hamaker and Born coefficients are constant and equal to 1. Others parameters are given as Pe=1, l_c=0.2, m=2, n=3.

$$\phi = \frac{1}{h^{m+1}}\left[A(\Gamma) - B(\Gamma)\left(\frac{l_c}{h}\right)^{n-m} \right], \tag{1}$$

where Γ is the concentration of surfactant. $A(\Gamma)$ and $B(\Gamma)$ are the Hamaker and Born coefficients dependent on the concentration of surfactant, respectively. l_c is defined as the equilibrium separation distance to measure the competition between polar and apolar forces. Previous researches demonstrated that the van der Waals (apolar) attraction is the dominant mechanism for film rupture, whereas the Born (polar) repulsion is helpful to stabilize the process.[10]

By applying the lubrication approximation to the hydrodynamic equations, a set of two nonlinear equations for the film thickness h and the concentration of surfactant in non-dimensional form can be written as

$$\Gamma_t = \left[\Gamma\left(\frac{h^2}{2} + \beta h\right)(-h_{xx} + \phi)_x + \mathcal{M}\Gamma\Gamma_x(h+\beta) \right]_x + \frac{\Gamma_{xx}}{\text{Pe}}, \tag{2}$$

$$h_t = \left[\left(\frac{h^3}{3} + \beta h^2\right)(-h_{xx} + \phi)_x + \mathcal{M}\left(\frac{h^2}{2} + \beta h\right)\Gamma_x \right]_x \tag{3}$$

in which x, t represent for horizontal coordinate and time, $\mathcal{M}$ and Pe are the Marangoni and Peclét number, respectively. The subscripts denote partial differentiation. Detailed derivation and mathematical denotations are analogical with the work of Warner *et al.*, and the system will reduce to their equations (26) and (27) for the no-slip case, β=0.

Using normal mode method, substituting $h=1+\hat{h}e^{ikx+\lambda t}$, $\Gamma=\Gamma_0+\hat{\Gamma}e^{ikx+\lambda t}$ to the linearized system of (2) and (3), and expanding the Hamaker and Born coefficients as $A(\Gamma)=A(\Gamma_0)+\hat{\Gamma}A_\Gamma(\Gamma_0)e^{ikx+\lambda t}$ and $B(\Gamma)=B(\Gamma_0)+\hat{\Gamma}B_\Gamma(\Gamma_0)e^{ikx+\lambda t}$, yield the dispersion relation for the perturbation with the growth rate λ and wave number k:

$$\left| \begin{array}{cc} \lambda + \left(\frac{1}{3} + \beta\right)k^2(k^2 - Q) & k^2\left[\left(\frac{1}{2} + \beta\right)\mathcal{M} + \left(\frac{1}{3} + \beta\right)P \right] \\ \Gamma_0\left(\frac{1}{2} + \beta\right)k^2(k^2 - Q) & \lambda + k^2\Gamma_0\left[(1+\beta)\mathcal{M} + \left(\frac{1}{2} + \beta\right)P \right] + \frac{k^2}{\text{Pe}} \end{array} \right| = 0, \tag{4}$$

where Γ_0 is the base concentration of surfactant, $Q=[(m+1)A(\Gamma_0)-(n+1)B(\Gamma_0)l_c^{n-m}]$, and $P=A_\Gamma(\Gamma_0)-l_c^{n-m}B_\Gamma(\Gamma_0)$. Similar to the no-slip films, if $k^2-Q<0$ it will produce a band of unstable modes with the wave number $0<k<k_c$, where the cutoff wave number k_c is independent of the Marangoni number and the slip coefficient. Since k_c decreases with the increase of the equilibrium separation distance l_c, the enhancement of the Born repulsion will narrow the band of unstable perturbations.

The variations of the maximal growth rate λ_m and the corresponding wave number k_m with the Marangoni number $\mathcal{M}$ are shown in Fig. 1 for different slip coefficients, providing the Hamaker and Born coefficients remain fixed. Generally λ_m decreases with the Marangoni number, while increases with the slip length. These results indicate that the slippage accelerates the film rupture whereas the Marangoni effect plays a stabilizing role, as were predicted in the previous work for the no-slip or the surfactant-free films.[5,12] It can be found in Fig. 1(b) that the wave number k_m declines for smaller $\mathcal{M}$ whereas it ascends for larger $\mathcal{M}$ for the no-slip case, which forms a "valley" in the $k_m \sim \mathcal{M}$ curve. This valley becomes more and more sharp with the increase of the

slip length, and nearly comes to be a cusp point at $\mathcal{M} \approx 2.2$ when $\beta \rightarrow \infty$. To explain this phenomenon, the growth rate obtained from (4) can be written as follows for infinite β:

$$\lambda_\pm = \frac{\beta k^2}{2}\left[-(k^2 - R) \pm \sqrt{(k^2 - R)^2 - \frac{4(k^2 - Q)}{\text{Pe}\,\beta}} \right], \tag{5}$$

where $R=Q-\Gamma_0(\mathcal{M}+P)$. The solutions of (5) can be divided into two branches according to the sign of k^2-R. If $k^2-R<0$, the second term in the radical sign can be ignored, and the growth rate concerned reads,

$$\lambda_+ = -\beta k^2(k^2 - R). \tag{6}$$

Then the wave number of the most unstable mode is $k_m = \sqrt{R/2}$. The growth rate is proportional to the slip coefficient, as shown in Fig. 1 for smaller $\mathcal{M}$. Suppose $\mathcal{M}$ is larger enough such that $k^2-R>0$ and the second term in the radical sign is higher order compared with the first one, the growth rate can be given asymptotically as
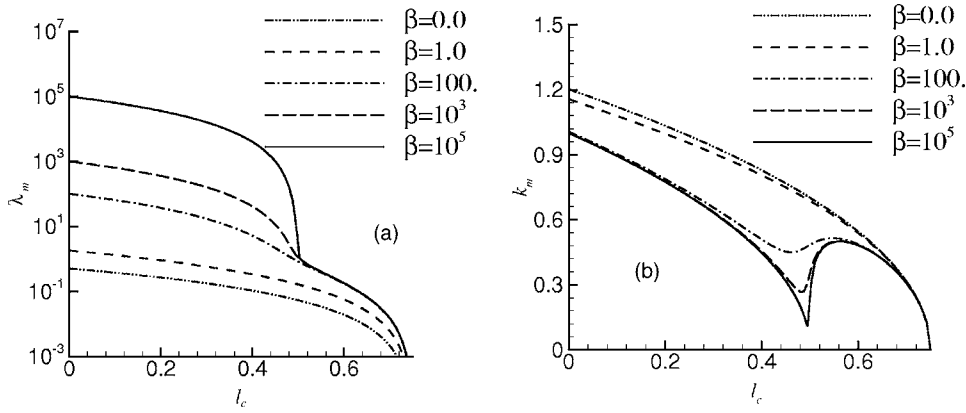
FIG. 2. The variation of growth rate (a) and wave number (b) of the most unstable mode with l_c for different slip coefficient. The Hamaker and Born coefficients are constant and equal to 1. Others parameters are given as Pe $=1$, $\mathcal{M}=1$, $m=2$, $n=3$.

$$\lambda_+ = -\frac{(k^2 - Q)k^2}{\text{Pe}(k^2 - R)}, \tag{7}$$

which is independent of β, and tends to be constant as $\mathcal{M}$ increases. The wave number of the maximal growth mode is $k_m^2 = R + \sqrt{-R\Gamma_0(\mathcal{M}+P)}$. Therefore k_m does not rely on β for any given $\mathcal{M}$, as shown in Fig. 1(b). Considering k^2 is quite small for infinite β, one can calculate the Marangoni number at the cusp approximately simply using $R=0$. These results show the slip and Marangoni effects have more important influences on the linear stability behavior when the the growth rate λ_+ is located on the first branch of the solutions.

To study the effects of the molecular potential, the dependence of stability characteristics on the equilibrium dis-

tance l_c is exhibited in Fig. 2 for different slip lengths β. Two branches of solutions can be easily identified when the slippage is sufficiently strong. An inflexion at $l_c \approx 0.5$, calculated by $R=0$, can be found in Fig. 2(a) to separate the curve into two segments. Before the point λ_m falls rapidly by several orders of magnitude, whereas the tendency is relatively smooth for $l_c > 0.5$. The cusp can be also observed in the associated wave-number curves [Fig. 2(b)]. The reduction of λ_m with increasing l_c shows that the polar repulsion has a stabilizing effect on the rupture process, which agrees with the bifurcation analysis for the surfactant-free film.[10] For the parameters given in the figure, the films will be always spinodally stable when $l_c > 0.75$, then the Born repulsion be-
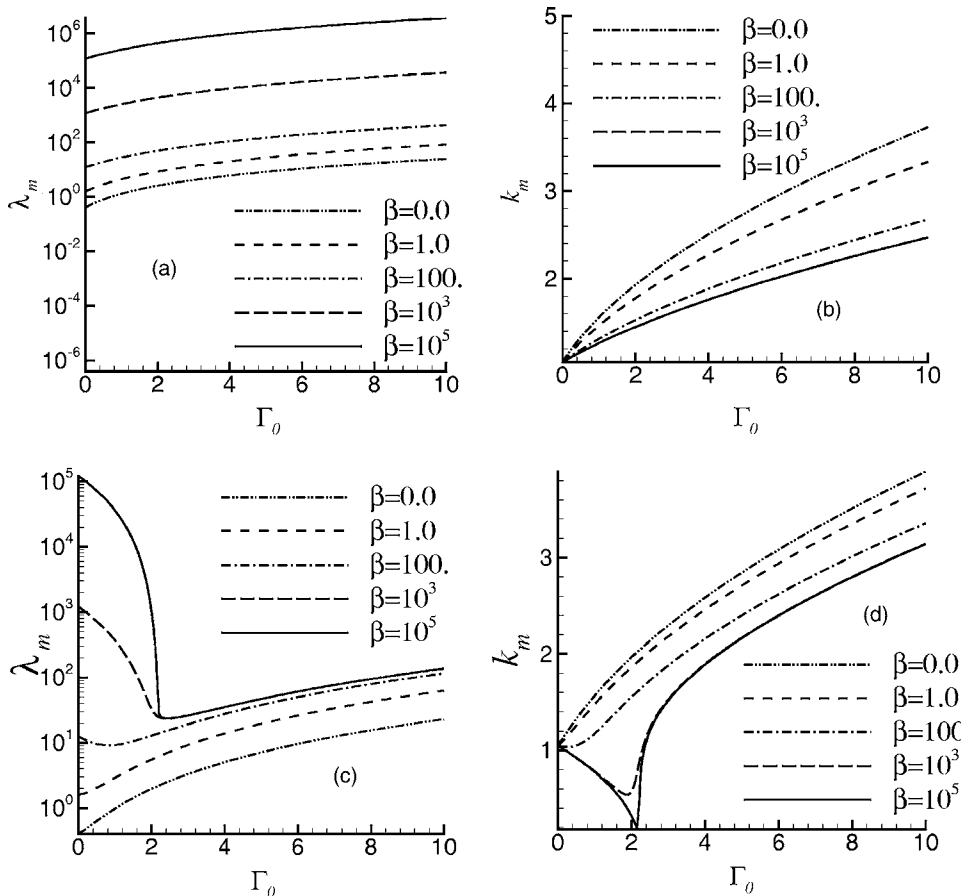

FIG. 3. The variation of growth rate and wave number of the most unstable mode with the base concentration Γ for different slip coefficient. The Marangoni number $\mathcal{M}=1$ in (a) and (b) while $\mathcal{M}=3$ in (c) and (d). The Hamaker coefficient $A(\Gamma)=1+\Gamma$, and the Born coefficient $B(\Gamma)=1$. Others parameters are given as Pe$=1$, $l_c=0.2$, $m=2$, $n=3$.

comes the dominant mechanism over the van der Waals force. Although k_m does not vary monotonously, it decreases with the equilibrium distance on the whole, which illustrates that the enhancement of the Born repulsion might reduce the number density of holes when rupture occurs.

Figure 3 depicts the influences of the slippage and the base concentration Γ_0 on the stability characteristics for different Marangoni numbers, in which the Hamaker coefficient is allowed to vary with the concentration by $A(\Gamma)=1+\Gamma$. The behaviors of the linear perturbations are quite different for weak or strong Marangoni effects. When $\mathcal{M}=1$, both the maximum of growth rate and associated wave number increase monotonously with Γ_0 for any value of β, therefore the presence of the surfactant will promote the evolution of the perturbations and raise the number density of holes. For the flows with $\mathcal{M}=3$, the influences of the concentration of the surfactant are opposite for $\Gamma_0 < 2.2$ and sufficiently large slippage. It is because that k^2-R is always negative if the Marangoni number is less than 2, thus λ_m will be on the first branch of solutions for any Γ_0. These results reveal that the surfactant has twofold effects on stability, dependent on the parameters considered. As shown in (5), it might enhance the action of the van der Waals force by increasing the Hamker coefficient, and thus lead to the film rupture; or restrain the development of the unstable modes by enhancing the Marangoni stabilizing effect.

In conclusion, the slipping velocity on the solid substrate has considerable influence on the linear stability characteristics of surfactant-covered ultrathin films, especially for large slip coefficient. The mathematical expression obtained shows that the cutoff wave number only relies on the molecular potential and the base concentration of surfactant, and is independent of the Marangoni number and slip length. In general, the slippage destabilizes the linear perturbations whearas the Marangoni effect restrains their development. Introducing the polar force in molecular potential allows us to study the competition between the van der Waals attaction and the Born repulsion. It is found that the λ_m decreases with the equilibrium distance l_c, which reveals that the polar repulsion has stabilizing effect on the film rupture. For the molecular potential considered in (1), the role of the concentration of the surfactant Γ_0 depends on the interaction between the van der Waals force and the Marangoni effect. It is possible to promote development of the perturbations and the film rupture by enhancing the action of the van der Waals force, or to restrain the process by strengthening the Marangoni effect. Two branches of the solutions with different characteristics are found in the dispersion relation according to the sign of k^2-R. The influences of the slip length and the Marangoni number are more evident when λ_m is located on the first branch. The next goal of the present study is to confirm these theoretical results, and examine the nonlinear evolution of the films by numerical simulations.

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