

Nonlinear rupture of thin liquid films on solid surfaces

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In this letter we investigate the rupture instability of thin liquid films by means of a bifurcation analysis in the vicinity of the *short-scale* instability threshold. The rupture time estimate obtained in closed form as a function of the relevant dimensionless groups is in striking agreement with the results of the numerical simulations of the original nonlinear evolution equations. This suggests that the weakly nonlinear theory adequately captures the underlying physics of the instability. When antagonistic (attractive/repulsive) molecular forces are considered, nonlinear saturation of the instability becomes possible. We show that the stability boundaries are determined by the van der Waals potential alone.

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It is well known that a liquid film on a planar solid surface may become unstable due to long-range molecular forces. The forces originating from van der Waals attractions [1] accelerate thinning in regions of film depression leading to film rupture and subsequent dewetting [2]. On the other hand, electrical double layers on the solid surface may give rise to intermolecular repulsions stabilizing thin films against rupture [3].

In recent years, much effort has been put into theoretical modeling the dewetting phenomena [4–12]. A nonlinear theory of the film evolution based on the long-wave nature of the response was first posed in Ref. [4]. This approach, which has already been considered for different situations [5], yields nonlinear partial differential equations that describes the evolution of the interface shape, surfactant concentration, and others. Linear stability analysis is routinely applied to predict the onset of the instability and the characteristic wavelength, but the rupture time estimate obtained from the linear theory turns out to be rather poor: It underestimates the rupture time due to the highly nonlinear nature of the response. The most common and straightforward approach is to solve the evolution equations numerically [6,7,10–14]. The obvious disadvantage of the numerical simulation is that for a complex problem that involves many parameters, full parametric study of the rupture is quite elaborate.

A bifurcation technique was first applied in Ref. [8] to arrive at the nonlinear estimate for the rupture time in the vicinity of a steady bifurcation point. It was demonstrated that nonlinear terms owing to van der Waals attractions contribute to rapid acceleration of the rupture beyond the linear regime. Analysis of the nonlinear evolution of small disturbances leads to a dynamic Landau equation for the perturbation amplitude. The closed-form solution of the amplitude equation provides a time for “blowup” of the initial small-amplitude disturbance that was proposed to be a good estimate of the nonlinear rupture time. In particular, it was demonstrated that the ratio of the linear and the nonlinear

estimates increases as $\ln \epsilon^{-1}$ as criticality $\epsilon \rightarrow 0$. The approach has never been given enough attention perhaps because the analysis involves rather tedious algebra and can only be done “by hand” for some simple cases. It has been demonstrated in Ref. [9] that the derivation of the amplitude equation can be automatized by using a previously developed symbolic algorithm for bifurcation analysis [15]. Although the closed-form nonlinear estimate of the rupture time of the thin film in presence of insoluble surfactant was derived in Ref. [9], the lack of parametric study of the problem by simulations did not allow a proper comparison of the two approaches. Recently, an extensive numerical study of the thin film rupture driven by van der Waals attractive forces in the presence of insoluble surfactant and hydrodynamic slip was reported in Ref. [10]. We have developed a generalized theory of thin-film rupture for an arbitrary intermolecular potential; further, we compare the rupture time estimate from our theory with the results of simulations by Ref. [10] for the purely attractive potential and come up with some predictions for the competing (attractive/repulsive) potential.

We consider a model describing the evolution of a thin liquid film a solid substrate subject to a van der Waals force in the presence of a slip and insoluble surfactant. The dimensionless film thickness h and surfactant concentration Γ are governed by a system of coupled evolution equations derived in the long-wave approximation [10],

$$h_t = \left[\mathcal{M} \Gamma_x h \left(\frac{h}{2} + \beta \right) - \mathcal{F}_x h^2 \left(\frac{h}{3} + \beta \right) \right]_x, \quad (1)$$

$$\Gamma_t = \frac{\Gamma_{xx}}{\mathcal{P}} + \left[\mathcal{M} \Gamma \Gamma_x (\beta + h) - \Gamma \mathcal{F}_x h \left(\frac{h}{2} + \beta \right) \right]_x, \quad (2)$$

with

$$\mathcal{F}(x, t) = -\varphi(h) + \mathcal{C} h_{xx}$$

and where \mathcal{M} is a Marangoni number, \mathcal{P} is a Peclet number, β is a Navier slip coefficient, \mathcal{C} is a surface tension parameter, and $\varphi = (\partial \Delta G / \partial h)$ is the van der Waals potential (all

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dimensionless). For nonslipping films ($\beta=0$) Eqs. (1) and (2) are equivalent to those in Ref. [7].

The linear stability analysis of the uniform stationary state $\mathbf{u}_0=\{h_0, \Gamma_0\}$ results in a critical value of the wave number corresponding to a stationary bifurcation point $k_c = [-\varphi'(h_0)/\mathcal{C}]^{1/2}$. Following a standard procedure, we choose \mathcal{C} as a bifurcation parameter. In a bounded domain, $0 < x < \mathcal{L}$, the basic solution \mathbf{u}_0 changes stability (becomes spinodally unstable) with $k=k_c$ and when $\mathcal{C} < \mathcal{C}_c = -\varphi'(h_0)\mathcal{L}^2/4\pi^2$, where \mathcal{C}_c correspond to a steady bifurcation point.

To investigate the nonlinear problem in the vicinity of the bifurcation point, we expand the bifurcation parameter as $\mathcal{C} = \mathcal{C}_c + \epsilon^2\mathcal{C}_2 + \dots$, where ϵ is a small criticality, introduce a slow time scale suggested by the linear theory, $\tau = \epsilon^2 t$, and seek the solution in power series of ϵ as $\mathbf{u} = \mathbf{u}_0 + \epsilon\mathbf{u}_1 + \dots$. Substitution of this expansion into the system (1) and (2) to the first order in ϵ yields $\mathbf{u}_1 = [A(\tau)e^{ik_c x} + \text{c.c.}]\mathbf{U}$, where $\mathbf{U} = \{1, 0\}$ is a solution of the linearized zero-eigenvalue problem. The complex amplitude A satisfies the dynamic Landau equation which is determined to $\mathcal{O}(\epsilon^3)$ of the perturbation theory:

$$\frac{\partial A}{\partial \tau} = \alpha A + \kappa |A|^2 A, \quad (3)$$

where the linear coefficient α and the Landau coefficient κ are given by

$$\alpha = -\delta k_c^4 \mathcal{C}_2, \quad \kappa = \frac{\delta}{6\mathcal{C}_c} (\varphi''^2 + 3\varphi' \varphi'''), \quad (4)$$

respectively, and

$$\delta = \frac{h_0^2 [4(h_0 + 3\beta) + h_0(h_0 + 4\beta)\theta]}{12[1 + (h_0 + \beta)\theta]}, \quad \theta = \mathcal{M}\mathcal{P}\Gamma_0.$$

The closed-form solution of the amplitude Eq. (3) can be easily obtained given the initial value of the amplitude $A_0 = A(0)$. The blowup time, corresponding to the infinite growth of the amplitude A and providing a nonlinear estimate of the rupture time (in the original time scale), in the vicinity of the bifurcation point, as $\mathcal{C}_2 \rightarrow 0$ is determined solely by the cubic coefficient

$$t_{\text{rup}} \approx (2A_0^2 \kappa)^{-1}, \quad (5)$$

where A_0 is now $\mathcal{O}(\epsilon)$. An important observation is that despite the complicated nature of the original evolution equations, the structure of the cubic coefficient κ in Eq. (4) is very simple: Terms in brackets contain only derivatives of the intermolecular potential φ , and a factor δ/\mathcal{C}_c incorporates the dependence on the rest of parameters. Since $\delta > 0$, it is readily seen from Eq. (4) that for purely attractive potential, κ is always positive and the rupture is inevitable. For the most commonly encountered attractive potential $\varphi = \mathcal{A}/h^c$, with $c=3, 4$ (unretarded and retarded case, respectively), we calculate the rupture time from Eq. (5) and compare to the results of numerical simulations of the original evolution Eqs. (1) and (2) reported in Ref. [10]. $\mathcal{A} = \mathcal{A}^*/6\pi\rho^2 h_*^{c-2}$ is the scaled Hamaker constant with h_* being the mean film

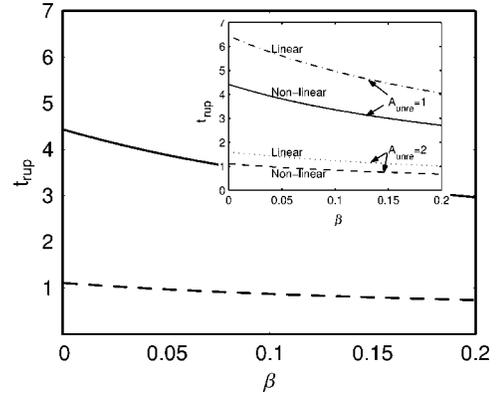


FIG. 1. Variation of rupture time vs β with $A_0=0.106$, $h_0=1$, $\mathcal{C}=1$, $\mathcal{M}=1$, $\mathcal{P}=100$, $\Gamma_0=0.5$, $c=3$, and $\mathcal{A}=1$ (—), $\mathcal{A}=2$ (---). The inset shows analogous results of the numerical simulations [16] (A_{unre} corresponds to the unretarded potential with $c=3$).

thickness (here and thereafter dimensional quantities are marked with *). Typical evolution of the film thickness in numerical simulations shows an accelerated thinning of the film in the depressed region due to the initial disturbance at some unstable wavelength $\lambda > 2\pi/k_c$ with a subsequent film rupture [5,7]. This scenario suggests that the acceleration of the film rupture could be adequately described by the cubic nonlinearity in the amplitude Eq. (3), leading to a blowup in a finite time [Eq. (5)].

Figure 1 shows the dependence of t_{rup} on β estimated from Eq. (5) and that from the simulation results [10] (the inset) for two distinct values of \mathcal{A} . It is readily seen that there is a very close agreement between the two. Since the numerical simulations refer to the fastest growing mode, the amplitude of the initial perturbation chosen here ($A_0 = 0.106$) is different than that used in Ref. [10] ($A_0 = 0.01$). Nevertheless, a very close agreement between our theory (with the fixed value of A_0) and the numerical simulations upon varying other parameters (Figs. 2 and 3) validates unequivocally that the near-critical theory can be adequately applied to model rupture far from the instability threshold [17]. An obvious advantage of the present analysis over the

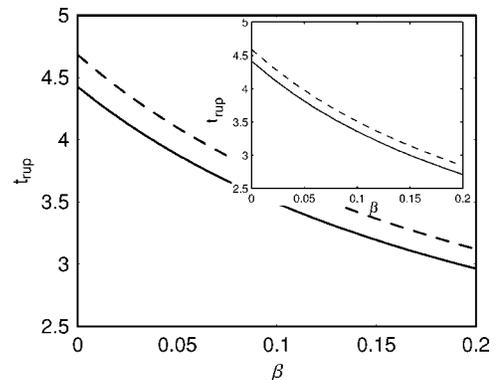


FIG. 2. Variation of rupture time with β for $A_0=0.106$, $\mathcal{A}=1$, and the same values of other parameters as in Fig. 1 except we vary \mathcal{M} : $\mathcal{M}=1$ (—), $\mathcal{M}=100$ (---). The inset shows analogous results of the numerical simulations [16].

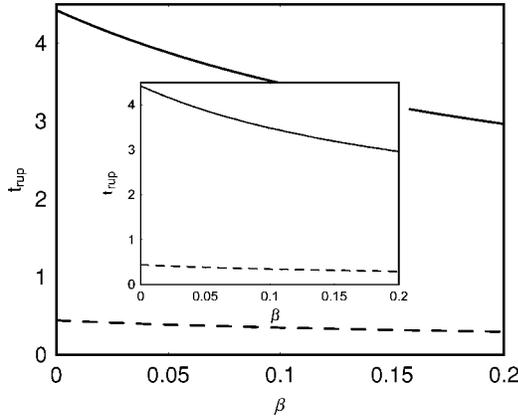


FIG. 3. Variation of rupture time with β for $A_0=0.106$, $\mathcal{A}=1$, and the same values of other parameters as in Fig. 1 except now we vary C : $C=1$ (—); $C=0.1$ (---). The inset shows analogous results of the numerical simulations [16].

numerical simulation is that the simple closed-form expression for the nonlinear rupture time is available for a general van der Waals potential.

When the antagonistic attractive/repulsive intermolecular interactions are present, nonlinear saturation of the rupture instability is possible as κ may change sign (supercritical bifurcation). Let us consider the general representation of the antagonistic van der Waals potential [11,12]

$$\varphi(h) = \frac{\mathcal{A}}{h^c} - \frac{\mathcal{B}}{h^d} - (S_p/l_p)\exp(-h/l_p), \quad (6)$$

where \mathcal{A} is defined as before, $\mathcal{B}=\mathcal{B}_*/\rho\nu^2h_*^{d-2}$, $S_p=S_p^*h_*^2/\rho\nu^2$, and $l_p=l_p^*/h_*$. It follows from Eq. (4) that the stationary nonruptured solution with amplitude $A=(-\alpha/\kappa)^{1/2}$ is stable if

$$d\gamma_1 + H\gamma_2 < c, \quad \sum_{i,j} \sum_{i+j \leq 2} a_{ij}\gamma_1^i\gamma_2^j < 0, \quad (7)$$

where the first inequality is imposed by the linear theory, $\gamma_1=\mathcal{B}h_0^{c-d}/\mathcal{A}$, $\gamma_2=(S_p/l_p)h_0^c e^{-H}/\mathcal{A}$, $H=h_0/l_p$, and a_{ij} are some polynomial functions of c , d , and H only.

When the interplay between algebraic potentials is considered ($\gamma_2=0$), the nonlinear stability region is defined by γ_1 alone. For exponents $(c,d)=(3,4)$ (repulsive retarded van der Waals force) the film is stable if $0.51 < \gamma_1 < 0.73$. For the exponents $(3,9)$ (short-range Born repulsion) the stability window is shifted to lower values of γ_1 and the film is stable whenever $0.066 < \gamma_1 < 0.30$. For instance, using the values of the Hamaker constants measured for a polystyrene film on oxidized Si wafers with $\mathcal{A}_*=2.2 \times 10^{-20}$ J and $\mathcal{B}_*=5.04 \times 10^{-75}$ J m⁶ [13] the nonlinear analysis predicts a stable film thickness of $h_0 \approx 2$ nm ($\gamma_1=0.068$), while the linear theory results in 1.56 nm and the equilibrium thickness determined from the minimum of ΔG is only 1.3 nm [13]. For thicker films, γ_1 is rapidly decreasing as h_0^{-6} , e.g., $\gamma_1 \approx 0.00125$ for $h_0=3.9$ nm. Although, a qualitative difference in the morphology of dewetting in Ref. [13] was observed for thicker films (3.9 nm vs 4.9 nm), we speculate that the

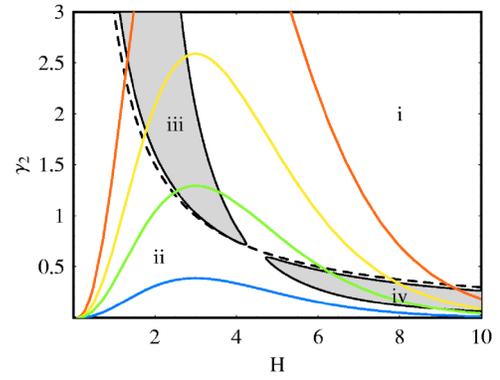


FIG. 4. (Color online) Stability diagram for an antagonistic exponential/algebraic potential ($\gamma_1=0$) in plane of parameters $\gamma_2=(S_p/l_p)h_0^c e^{-h_0/l_p}/\mathcal{A}$ and $H=h_0/l_p$. The dashed curve corresponds to marginal stability boundary with $c=3$. The regions of stationary nonruptured states are shown in gray. Colored curves show the dependence γ_2 vs H for varying hydrophobicity of the substrate from hydrophilic (blue curve) to hydrophobic (red curve) using parameters from [12].

qualitative change is due to approach to the nonlinear stability boundary as h_* approaches the thickness of 2 nm.

When the interplay between algebraic and exponential potentials is considered ($\gamma_1=0$), the nonlinear stability diagram can be defined in terms of γ_2 and H as in Fig. 4. The dashed lines correspond to the boundary of linear stability, while the regions of nonlinear stability corresponding to $\kappa < 0$ are shown in gray (iii and iv). Note that, if the long-range attraction is combined with the shorter-range repulsion ($\mathcal{A} > 0$, $S_p > 0$), the spinodally unstable region is under the dashed curve (region ii in Fig. 4), and nonlinear saturation occurs for $H \geq 4.5$ and small values of γ_2 (region iv). In the opposite case ($\mathcal{A} < 0$, $S_p < 0$), the spinodally unstable region lies above the dashed curve (region i) and stabilization occurs for thinner films, $H \leq 4$, and moderate values of γ_2 (region iii).

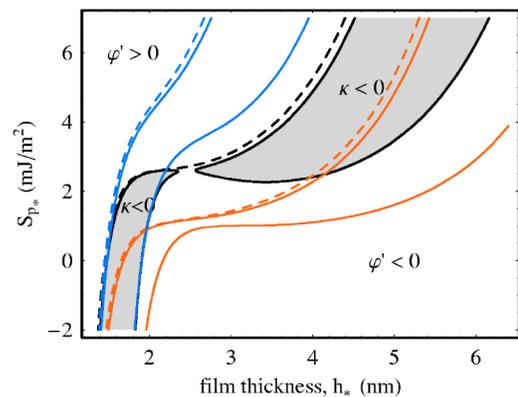


FIG. 5. (Color online) Stability diagram for a general van der Waals potential (6). The regions right to the dashed curves are spinodally unstable and the regions between the solid curves correspond to stationary nonruptured state. Black curves correspond to $\mathcal{A}_*=3.0 \times 10^{-20}$ J, $\mathcal{B}_*=5.04 \times 10^{-75}$ J m⁶, and $l_p^*=0.6$ nm (nonlinear stability regions are shown in gray). The color curves correspond to the same values of the parameters except $l_p^*=0.4$ nm (blue curves) and $\mathcal{A}=1.4 \times 10^{-20}$ J (red curves).

For instance, for aqueous films on Si substrates with $c=3$, $\mathcal{A}_*=-1.41 \times 10^{-20}$ J, and $l_{p_*}=0.6$ nm [12], we plot γ_2 vs H in Fig. 4 (color curves) for different values of S_{p_*} varying from -0.61 mJ/m² (blue) to -8.5 mJ/m² (red) due to increasing hydrophobicity of the substrate [12]. It is evident from Fig. 4 that the emergence of nonruptured ultrathin films is possible on nonhydrophilic substrates as the color curves cross region (iii), while on hydrophilic substrates (the blue curve) the film of any thickness is stable, in accord with Ref. [12].

Even more interesting is the behavior for competing short-range algebraic and exponential potentials. In this case, $\gamma_1, \gamma_2 \neq 0$ and as they both vary with h_0 we chose to depict the stability diagram in terms of dimensional quantities, S_{p_*} and h_* as in Fig. 5. It is evident that stabilization is possible for a wide range of film thicknesses, h_* . When the magnitude of the exponential repulsion is small, the steady nonruptured state is only possible for ultrathin films; for moderate values of S_{p_*} the band of stable solutions widens. For instance,

when $S_{p_*}=1.1$ mJ/m², with parameters corresponding to the red curve in Fig. 5, nonlinear theory predicts that the film is stable below a thickness of ~ 4 nm, whereas linear stability provides a value of ~ 2.2 nm.

In conclusion, we have developed a nonlinear theory for the rupture of a thin liquid film subject to a general van der Waals potential. The comparison between the prediction of the weakly nonlinear analysis and the results of numerical simulations is provided; the close agreement between the nonlinear rupture time estimate found from the near-critical theory and the simulation was found. When an antagonistic potential is considered, the saturation of the small-amplitude-initial perturbations beyond the instability threshold is possible, while the stability boundary is determined solely by the intermolecular potential.

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 [17] The Galerkin method can be applied for derivation of the amplitude equation for the “most dangerous” linear mode. The resulting amplitude equation is the same as Eq. (3) with α given by the linear stability and κ that differs from the near-critical expression Eq. (4). The preliminary analysis shows that in case with no surfactant, the nonlinear rupture time estimate is in excellent agreement with results of numerical simulations [10] for the same value of the initial amplitude A_0 . The theory of the nonlinear rupture far from the instability threshold is a subject of a separate paper.