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Instability and Dewetting of Thin Films Induced by Density Variations

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A recently proposed new mechanism of thin film dewetting (Wensink, K. D.; Jérôme, B. *Langmuir* **2002**, *18*, 413) is revisited, and conditions are established under which rupture of a thin film can be engendered by the density variations caused by changes in its local thickness. An increase in the density with the increasing film thickness can actually stabilize a thermodynamically unstable film. In the opposite case of decrease in the density with increasing film thickness, a thermodynamically stable thin film can be destabilized. Nonlinear simulations confirm the validity of the linear stability analysis. Morphological characteristics of this novel density variation induced instability closely resemble the well-known spinodal dewetting at constant density.

Introduction

Spontaneous dewetting of thin films has been extensively studied theoretically^{1–13} because of its importance in areas as diverse as coatings, paints, adhesives, flotation, multilayer adsorption, wetting, and tear film breakup, etc. In addition to its scientific content, the problem of spontaneous pattern formation during dewetting is of increasing interest because of its promise in the creation of desired micro- and nanoscale patterns for a host of nanotechnology applications.

There are two known mechanisms responsible for the instability and spontaneous dewetting of isothermal thin fluid films without any applied external field. First, a thin film on a homogeneous substrate undergoes instability by a spinodal mechanism whenever the second derivative of the excess intermolecular interaction energy becomes negative on a nonwetable substrate.^{1–11} Another mechanism of thin film instability has also been proposed in which the dewetting is driven by the spatial gradient of microscale wettability^{12,13} rather than by the nonwettability of the substrate itself. This mechanism is important for real substrates that are chemically or physically heterogeneous on nanometer to micrometer scales because of the substrate nonuniformity, contaminants, trapped cavities, etc.

Wensink and Jérôme¹⁴ recently proposed another variant of the heterogeneous mechanism in which the surface instability may be engendered by fluctuations of its local density (which cause a gradient of van der Waals forces)

rather than by the gradient of force caused by the substrate heterogeneities. The density variations are coupled to the local film thickness because of the confinement, layering, and restructuring effects in the polymer films.^{15–28} Diblock copolymers with different affinities to the air and substrate can also result in different types of restructuring within the film depending on the film thickness.²⁷ In addition, at the substrate–film interface, low-density defects such as nanobubbles,²⁶ voids due to chain packing constraints, or even partial delamination can occur rather readily.²⁸ All of these factors can lead to variations of the local mean film density along the substrate because of changes in the local film thickness.

We revisit the analysis of Wensink and Jérôme¹⁴ to establish the general conditions under which density variations can induce film instability and rupture in otherwise stable thin films. It is found that density variations can change the stability behavior of thin films very profoundly. A thermodynamically stable film may become unstable in some cases, and equally interestingly, an unstable film may even be stabilized under another set of conditions (a case not considered in the earlier study¹⁴). In the latter case, true dewetting (formation of dry spots) can change into pseudo-dewetting (formation of a stable adsorbed film on a dewetted spot) and then to complete stability as the density variations become stronger. Our results regarding the conditions for the instability and its length and time scales are different

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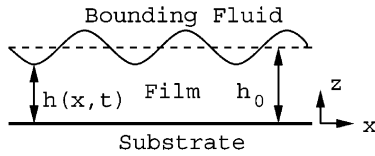


Figure 1. Schematic diagram of an unstable thin film on a solid substrate.

from the previous study¹⁴ of the same phenomenon. The results of the linear stability analysis are directly verified by numerical solutions of the nonlinear governing equation for the film thickness. In particular, we also show that the instability due to density variations can be physically interpreted and understood within the framework of the well-known^{1–11} spinodal dewetting of constant density films by an appropriate redefinition of the spinodal parameter. The density variation induced instability closely mimics the morphological behavior of spinodal dewetting, so that the true mechanism of dewetting may be easily disguised in the experiments. In fact, a motivation for the new mechanism comes from the experiments showing that even the films that are expected to be spinodally stable on the high surface energy substrates (a much-studied case being dewetting of polystyrene on silicon wafers) are observed to dewet in ways similar to some of the expectations of the spinodal theory.

Theory

Thin Film Equation. We consider a Newtonian nonslipping liquid film sandwiched between a solid substrate and a bulk fluid phase as shown in Figure 1; x and z are coordinates parallel and normal to the solid surface, respectively. The mean density (ρ) of the film averaged over local film thickness ($0 < z < h$) is assumed to vary along the substrate in the x -direction. The equation of continuity and the z - and x -direction Navier–Stokes equations in the long-wave approximation are^{1–11,14}

$$\rho_t + (\rho u)_x + (\rho w)_z = 0 \quad (1)$$

$$p_z + \phi_z = 0 \quad (2)$$

$$\mu u_{zz} = p_x + \phi_x \quad (3)$$

where subscripts denote differentiation, u and w are the x and z components of velocity, p is pressure, μ is viscosity, and ϕ is the excess body force due to intermolecular interactions. The boundary conditions are

solid surface ($z = 0$)

$$u = 0 \text{ and } w = 0 \quad (4)$$

free surface ($z = h$)

$$u_z = 0 \text{ and } p_x = -\gamma h_{xx} \quad (5)$$

where γ is the surface tension of the liquid film.

By solving eqs 1–5 together with the kinematic condition, $h_t + uh_x = w$, the equation of evolution for the film thickness is obtained as

$$3\mu(\rho h)_t + [\rho h^3(\gamma h_{xx} - \phi)_x]_x = 0 \quad (6)$$

This form of the thin film equation is quite general as specific functional dependencies of the conjoining pressure (ϕ) and density on the local film thickness have not been specified. We consider now the case where the dominant

excess intermolecular interactions are due to the long-range Lifshitz–van der Waals (LW) forces. The conjoining pressure in this case is given by¹⁵

$$\phi = A(\rho)/6\pi h^3 \quad (7)$$

where A is an effective Hamaker constant given by the difference between the liquid–liquid (A_{LL}) and solid–liquid (A_{SL}) Hamaker constants, $A = A_{LL} - A_{SL}$. Positive values of A imply attractive LW interactions leading to spinodal dewetting, whereas negative values correspond to LW repulsion leading to thermodynamic stability and perfect wetting in the absence of density variations. The individual binary Hamaker constants depend on the film density and are given by¹⁵

$$A_{LL} = (N_A^2 \pi^2 \beta_{LL} / M_L^2) \rho^2 = \alpha_{LL} \rho^2 \quad (8)$$

$$A_{SL} = (N_A^2 \pi^2 \beta_{SL} / M_S M_L) \rho_S \rho = \alpha_{SL} \rho_S \rho \quad (9)$$

where N_A is Avogadro's number; M_S and M_L are the molecular weights of the solid and liquid films, respectively; β denotes the strength of pairwise interaction potential; and ρ_S and ρ are the densities of the solid and liquid films, respectively. The variation in ρ causes the values of binary A to change, thereby changing the value of A_0 . This causes a gradient of intermolecular force field engendering flow in the film.

Linear Stability Analysis. The initial evolution of the instability in the thin films can be described by the linearized equation whenever the amplitude of the initial disturbance is much smaller than the mean film thickness. The dimensional evolution equation is linearized by substituting the following expressions for h and ρ :

$$h = h_0 + \epsilon \sin(kx)e^{\omega t}; \rho = \rho_0 + \hat{\rho} \sin(kx)e^{\omega t} \quad (10)$$

where h_0 is the mean thickness of the film, ρ_0 is the density of the film evaluated at the mean thickness, ϵ is the amplitude ($\ll h_0$), $\hat{\rho}$ is the amplitude of the fluctuation in the density, k is the wavenumber, and ω is the growth rate of the initial disturbance. For any arbitrary variation of $\rho = f(h)$, the first-order expansion for the density is

$$\rho = \rho_0 + (\partial \rho / \partial h)_{h_0} \epsilon = \rho_0 + (\partial f / \partial h)_{h_0} \epsilon \quad (11)$$

The above implies a relation:

$$\hat{\rho} / \epsilon = (\partial f / \partial h)_{h_0} = f_{h_0} \quad (12)$$

The expression for ϕ due to density variations is obtained in first orders of ϵ and $\hat{\rho}$ by using eq 10.

$$\phi = \phi_0 + (\partial \phi / \partial h)_{h_0, \rho_0} (h - h_0) + (\partial \phi / \partial \rho)_{h_0, \rho_0} (\rho - \rho_0) \quad (13)$$

$$\phi = \phi_0 - (A_0 / 2\pi h_0^4) \epsilon \sin(kx)e^{\omega t} + (2\alpha_{LL}\rho_0 - \alpha_{SL}\rho_S) \hat{\rho} \sin(kx)e^{\omega t} / (6\pi h_0^3) \quad (14)$$

$$\phi = \phi_0 - (A_0 / 2\pi h_0^4) \epsilon \sin(kx)e^{\omega t} + (A_{LL0} + A_0) \hat{\rho} \sin(kx)e^{\omega t} / 6\pi h_0^3 \rho_0 \quad (15)$$

$$\phi = \phi_0 + \hat{\phi} \sin(kx)e^{\omega t} \quad (16)$$

Equation 6 after linearizing yields

$$3\mu(\rho_0\epsilon + h_0\hat{\rho})\omega \sin(kx)e^{\omega t} + \rho_0 h_0^3 (\gamma\epsilon k^4 + \hat{\phi}k^2) \sin(kx)e^{\omega t} = 0 \quad (17)$$

The resulting linear dispersion relation is obtained after substituting the value of $\hat{\phi}$ and is given by

$$\omega = (h_0^3 k^2 / 3\mu) [-\gamma k^2 + (A_0 / 2\pi h_0^4) - (2A_{LL_0} - A_{SL_0})(\hat{\rho}/\epsilon) / 6\pi h_0^3 \rho_0] (1 + \hat{\rho} h_0 / \epsilon \rho_0)^{-1} \quad (18a)$$

The above can also be written as

$$\omega = (h_0^3 k^2 / 3\mu) [-\gamma k^2 + (A_0 / 2\pi h_0^4) - (A_{LL_0} + A_0)(\hat{\rho}/\epsilon) / 6\pi h_0^3 \rho_0] (1 + \hat{\rho} h_0 / \epsilon \rho_0)^{-1} \quad (18b)$$

In the above equation, $(\partial\rho/\partial h)_0 = \hat{\rho}/\epsilon = f_{h_0}$. For $\hat{\rho} = 0$, the above reduces to the well-known result for the spinodal instability of a thin film without density variations. The term, $[A_{LL_0}(\partial\rho/\partial h)_0 / 6\pi h_0^3 \rho_0]$ in eq 18b is absent in the earlier analysis¹⁴ of the same problem. As will be shown, this term has the most profound influence on the stability characteristics, since the effective Hamaker constant is usually much smaller than the liquid phase Hamaker constant ($A_0 = A_{LL_0} - A_{SL_0} < A_{LL_0}$), and unlike A_0 (which can be positive or negative), A_{LL_0} is always positive.

Alternatively, we can write ω from eq 18b in another physically illuminating form as

$$\omega = (h_0^3 k^2 / 3\mu) (-\gamma k^2 - \phi_{h_0}) (1 + \hat{\rho} h_0 / \epsilon \rho_0)^{-1} \quad (19)$$

where ϕ_{h_0} is the first derivative of ϕ with respect to h , $(\partial\phi/\partial h)_0 = \phi_{h_0}$, evaluated at h_0 . ϕ_h (force per unit volume), referred to as the spinodal parameter in this study, is known to govern the instability of thin films by the mechanism of spinodal dewetting.¹⁻¹¹ A positive spinodal parameter (ϕ_h) value means a stable and completely wetting film, whereas a negative spinodal parameter value leads to spinodal dewetting. The modified spinodal parameter (ϕ_{h_0}) due to density variations is given by

$$\phi_{h_0} = -A_0 / 2\pi h_0^4 + (A_{LL_0} + A_0)(\hat{\rho}/\epsilon) / 6\pi h_0^3 \rho_0 \quad (20)$$

where

$$\hat{\rho}/\epsilon = (\partial\rho/\partial h)_0$$

A_0 is the effective Hamaker constant and A_{LL_0} is the liquid Hamaker constant for ρ_0 . The first term in the above equation is the spinodal parameter without the density variation. For a film to be unstable, ω should be positive. The form of eq 19 is identical to the dispersion relation obtained in the absence of density fluctuations except for a numerical factor, $\chi = (1 + \hat{\rho} h_0 / \epsilon \rho_0)$ and a reinterpretation of ϕ_{h_0} according to eq 20. Thus, for $\chi > 0$ (which is usually the case) the necessary condition for the instability formally remains the same as for a constant density film, $\phi_{h_0} < 0$. For $\hat{\rho} = 0$, eq 21 reduces to the well-known result for the spinodal instability of a constant density thin film.¹⁻¹¹ The term $[A_{LL_0}(\partial\rho/\partial h)_0 / 6\pi h_0^3 \rho_0]$ in eq 21 (which was absent in the earlier analysis)¹⁴ is destabilizing when $(\partial\rho/\partial h)_0$ is negative since A_{LL_0} increases (ϕ becomes more negative) as the film thins locally. However, this term has the most profound influence on the stability characteristics, since A_0 is usually much smaller than A_{LL_0} ,¹⁵ and

unlike A_0 , which can be either positive or negative, A_{LL_0} is always positive.

In the above analysis, the interfacial tension (γ) is assumed to be constant, which should be evaluated at the mean film density. In particular, for a completely apolar van der Waals liquid²⁹

$$\gamma = A_{LL_0} / 24\pi d_0^2 = A_{LL_0} (\rho/\rho_0)^2 / 24\pi d_0^2 \quad (21)$$

where d_0 (~ 0.158 nm) is a cutoff distance for the van der Waals forces. The linear stability of eq 6 in this case produces a slightly modified dispersion relation (where γ is replaced by $\gamma_0 = A_{LL_0}^2 / 24\pi d_0^2$)

$$\omega = (h_0^3 k^2 / 3\mu) [-\gamma_0 k^2 + (A_0 / 2\pi h_0^4) - (A_{LL_0} + A_0)(\hat{\rho}/\epsilon) / 6\pi h_0^3 \rho_0] (1 + \hat{\rho} h_0 / \epsilon \rho_0)^{-1} \quad (22)$$

The theoretical analysis and the numerical computations in this study are based on a constant value of γ so that underlying physics can be illustrated without bringing in the nonessential details.

For an unstable film, the dominant wavenumber (k_m), which corresponds to the maximum growth factor (ω_m), is obtained by $\partial\omega/\partial k = 0$ and is obtained as $k_m = (-\phi_{h_0} / 2\gamma)^{1/2}$. The dominant wavelength (λ_m) of the instability is given by $\lambda_m = 2\pi/k_m$.

The maximum growth rate is obtained by substituting k_m in the dispersion relation given by eq 19:

$$\omega_m = (h_0^3 / 12\mu\gamma) (\phi_{h_0})^2 (1 + \hat{\rho} h_0 / \epsilon \rho_0)^{-1} \quad (23)$$

The linear theory predicts unhindered growth of the surface deformations leading to rupture whenever the conditions for the instability are satisfied. An estimate for the time of rupture from the linear theory is obtained by setting $h = 0$ in eq 10. The minimum time of rupture (t_m) is obtained for k_m and is given by

$$t_m = (1/\omega_m) \ln(h_0/\epsilon) \quad (24)$$

Although all of the above results are valid for any arbitrary variation of density, $\rho(h)$, we illustrate some of the results with the help of a particularly simple form

$$\rho = \rho_b + a(1 + bh/h_*)^{-1} = f(h) \quad (25)$$

where ρ_b denotes the bulk density of a thick film, and the constants a and b are given by the following expressions:

$$a = \rho_i - \rho_b \quad b = (\rho_i - \rho_*) / (\rho_* - \rho_b) > 0 \quad (26)$$

where ρ_i is the density of an ultrathin fluid film ($h \rightarrow 0$) that can be substantially different from its bulk value because of increased importance of confinement near the solid surface, and ρ_* is the density of the film evaluated at some arbitrary intermediate thickness h_* . For this particular functional form, the density variation ($\hat{\rho}$) is then given by

$$\hat{\rho}/\epsilon = (\partial\rho/\partial h)_{h_0} = (-ab/h_*) (1 + bh_0/h_*)^{-2} \quad (27)$$

The film density may increase ($\hat{\rho}/\epsilon = (\partial\rho/\partial h)_0 > 0$; $a < 0$), or decrease ($\hat{\rho}/\epsilon = (\partial\rho/\partial h)_0 < 0$; $a > 0$) with the film

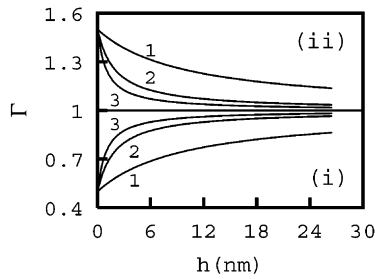


Figure 2. Variation of nondimensional density ($\Gamma = \rho/\rho_b$) with h as given by eq 32. Panels i and ii correspond to in-phase (density increasing with film thickness, $a^* = -0.5$) and out-of-phase (density decreasing with the film thickness, $a^* = +0.5$) density variations, respectively.

thickness. Figure 2 shows the density variation with the film thickness for both the cases for different values of $B = b/h^*$.

We again emphasize that a particular form (eq 27) is chosen merely for illustration but that the general linear stability analysis involves only the local density variation, $(\partial\rho/\partial h)_0$, and can be used for any form of ρ . For example, oscillating density due to layering, which can cause 10%–50% changes in the density, is commonly encountered.^{15–25} In such cases, the sign of $(\partial\rho/\partial h)_0$ depends on the local mean thickness and changes periodically with thickness, offering a host of interesting possibilities for the nonlinear evolution of instability.

Nondimensionalization and Numerical Methods

The evolution eq 6 is nondimensionalized for the most compact representation of results. The following nondimensional variables are introduced:^{6,8,9,11}

$$X = (A_{LLb}/2\pi h_0^4 \gamma)^{1/2} x \quad T = (A_{LLb}^2/12\pi^2 h_0^5 \mu \gamma) t \quad (28)$$

$$H = h/h_0 \quad \Phi = (2\pi h_0^3/A_{LLb})\phi; \Gamma = \rho/\rho_b \quad (29)$$

where A_{LLb} is the liquid film Hamaker constant evaluated at the bulk density ρ_b for a thick film. Introduction of the above nondimensional scalings in the equation of evolution produces the following nondimensional equation that describes the spatio-temporal evolution of a thin film:

$$(\Gamma H)_T + [\Gamma H^3(H_{XX} - \Phi)]_X = 0 \quad (30)$$

Equation 30 is a fourth-order nonlinear partial differential equation. A straightforward extension of the above in the 2-D space (X – Y) is given by

$$(\Gamma H)_T + [\Gamma H^3(H_{XX} + H_{YY} - \Phi)]_X + [\Gamma H^3(H_{XX} + H_{YY} - \Phi)]_Y = 0 \quad (31)$$

Equation 31 gives the complete 3-D morphology of the film $H = H(X, Y)$. The above equations were discretized in space using a central differencing method with half node interpolation. The resultant set of coupled ordinary differential equations (ODEs) was very stiff. This set of ODEs was solved as an initial value problem with an initial volume preserving random perturbation and periodic boundary conditions. These were integrated in time using NAG library subroutine DO2EJF, which employs Gear's algorithm suitable for stiff equations.

The nondimensionalized form of the density function is

$$\Gamma = 1 + a^*(1 + BHh_0)^{-1} \quad (32)$$

where the two constants (a^* and B) are given by $a^* = a/\rho_b$ and $B = b/h^*$.

Results and Discussion

Depending on the confinement effects, restructuring, cavitation, and specific interactions of film molecules (e.g., polymer chains) with the substrate and air, the mean density may either decrease $((\partial\rho/\partial h)_0 = \hat{\rho}/\epsilon < 0)$ or increase $((\partial\rho/\partial h)_0 = \hat{\rho}/\epsilon > 0)$ with the local film thickness. In what follows, we consider these two general cases, each with two different possibilities: (a) the film is spinodally stable ($A_0 < 0$) in the absence of density variations, and (b) the film is unstable ($A_0 > 0$) in the absence of density variations. A_0 at the mean film thickness is given by

$$A_0 = A_{LL0} - A_{SL0} = A_{LL0}^{1/2}(A_{LL0}^{1/2} - A_{SS}^{1/2}) \quad (33)$$

Decrease in Density with Decreasing Film Thickness ($\hat{\rho}/\epsilon > 0$). We now consider the case when the density of the film decreases with the decreasing film thickness and vice versa. As $(\hat{\rho}/\epsilon) = (\partial\rho/\partial h)_0$ is positive in this case, the factor $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ is always positive in eq 19. Therefore, the necessary and sufficient conditions for a film to be unstable (i.e., $\omega > 0$), respectively, are

$$\phi_{h_0} < 0 \text{ and } k^2 < -\phi_{h_0}/\gamma \quad (34)$$

The instability conditions are established for ω to be positive for different values of A_0 evaluated at h_0 .

Case 1: $A_0 = 0$ (Critical Case). A_0 is zero whenever A_{LL0} is equal to A_{LS0} . The expression for modified ϕ_{h_0} in this case is

$$\phi_{h_0} = A_{LL0}(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0 \quad (35)$$

Since variation of density leads to $\phi_{h_0} > 0$, the density variations in this case are always stabilizing. The necessary condition of instability given by eq 34 can never be satisfied, and the film is always stable. Hence, the effect of density fluctuations occurring in the film is to make it stable to small amplitude perturbations.

Case 2: $A_0 < 0$, Implying $A_{LL0} < A_{SS}$ (Constant Density Film Is Spinodally Stable). The negative value of A_0 means that the constant density film is thermodynamically stable and completely wets the substrate. This is the only case considered in the paper of Wensink and Jérôme.¹⁴ The expression for the modified spinodal parameter, ϕ_{h_0} is

$$\phi_{h_0} = |A_0|/2\pi h_0^4 + (A_{LL0} - |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0 \quad (36)$$

The first term in this equation, which corresponds to a constant density film, is positive and therefore stabilizing. The necessary conditions for the growth of instability are

$$|A_0| > A_{LL0}, \text{ which implies } A_{SL0} > 2A_{LL0} \quad (37)$$

where $|A_0| = |A_{LL0} - A_{SL0}| = |A_{LL0}^{1/2}(A_{LL0}^{1/2} - A_{SS}^{1/2})|$. When condition eq 37 is satisfied, instability is ensured by the following condition:

$$(\partial\rho/\partial h)_0 = (\hat{\rho}/\epsilon) > 3(\rho_0/h_0)(|A_0|/(|A_0| - A_{LL0})) \quad (38)$$

The necessary condition (eq 37) and the last factor ($\beta_1 = [|A_0|/(|A_0| - A_{LL0})] > 1$) that involve the ratio of A were missing in the earlier analysis¹⁴ of the same case. Thus, unless the density variation with thickness is very strong, conditioning eq 38 for the instability is unlikely to be

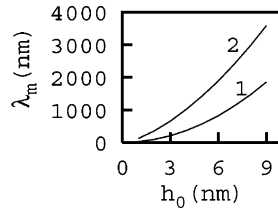


Figure 3. Dependence of the length scale of instability (λ_m) on the mean h_0 for the case of $\partial\rho/\partial h > 0$ and $A_0 > 0$ (constant density film is unstable). Curves 1 and 2 correspond to a constant density film ($\bar{\Gamma} = 0$) and a variable density film ($a^* = -0.5$, $B = 0.1$), respectively. The other parameter values are: $A_{LLb} = 2 \times 10^{-18}$ J, $A_{SLb} = 1 \times 10^{-18}$ J.

satisfied. Interestingly, a very high A for the solid (as obtained for metals in a vacuum without an oxide layer) is more conducive for engendering instability *because of density variations* since $\beta_1 \approx 1$ for $A_{SS} \gg A_{LL0}$. On the other hand, for *constant density films*, the condition $A_{SS} \gg A_{LL0}$ promotes stability and perfect wetting!

The nondimensional parameter a^* is negative in eq 32, and its feasible range is from -0.01 to -0.99 . Physically, these values correspond to the variation of interfacial density (ρ_i) from 99% to 1%, respectively, of the bulk density (ρ_b). Magnitude of parameter B governs the rapidity of changes in the density with the film thickness. Higher B corresponds to more prominent density variation for thinner films. A wide range from 0.1 to 10 is used for B for illustration of some of the results. For these wide range of parameter values, the maximum value of $[(\partial\rho/\partial h)_0/(3\rho_0/h_0)]$ is approximately 0.82, which is less than the minimum value of β_1 (> 1). Hence the condition in eq 38 for instability is not satisfied for this in particular but is a reasonable example of density variation.

Case 3: $A_0 > 0$, Implying $A_{LL0} > A_{SS}$ (Constant Density Film Is Spinodally Unstable). A positive value of A_0 implies spinodally unstable films in the absence of density variations. The expression for modified ϕ_{h_0} with density variation becomes

$$\phi_{h_0} = -|A_0|/2\pi h_0^4 + (A_{LL0} + |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0 \quad (39)$$

The necessary condition for the film to remain unstable in the face of density variations is

$$(\partial\rho/\partial h)_0 = (\hat{\rho}/\epsilon) < 3(\rho_0/h_0)(|A_0|/(|A_0| + A_{LL0})) \quad (40)$$

Clearly, the factor $\beta_2 = [|A_0|/(A_{LL0} + |A_0|)] < 1$, and thus moderate to strong density variations can even stabilize an otherwise unstable film when the above condition is violated. This can happen rather readily if A_0 is small (i.e., surface tensions of the apolar solid and liquid are nearly the same).

The dominant wavelength of instability is

$$\lambda_m = (-8\pi^2\gamma/\phi_{h_0})^{1/2} = (8\pi^2\gamma)^{1/2} [|A_0|/2\pi h_0^4 - (A_{LL0} + |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0]^{-1/2} \quad (41)$$

The additional term in eq 41 because of density fluctuation has a stabilizing influence and increases the length scales of instability. In Figure 3, the length scales of instability are compared for the cases of constant density and variable density for different mean thicknesses (h_0).

Although a constant density film is unstable to the extent of true rupture or dry spot formation since $\phi_h < 0$ for all thicknesses, density variation can lead to pseudo-dewetting or even complete stability. To understand these

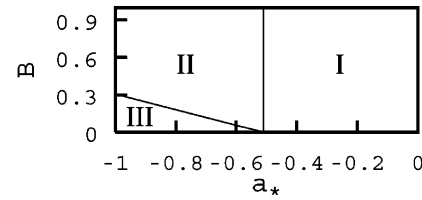


Figure 4. Regimes of true dewetting (regime I), pseudo-dewetting (regime II), and complete wetting (regime III) for the density function of eq 32 and $\partial\rho/\partial h > 0$ and $A_0 > 0$. The mean film thickness is 5 nm, and $A_{LLb} = 2 \times 10^{-18}$ J, $A_{SLb} = 1 \times 10^{-18}$ J.

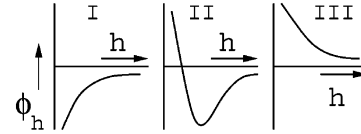


Figure 5. Qualitative behavior of the modified spinodal parameter curve for the different regimes shown in Figure 4.

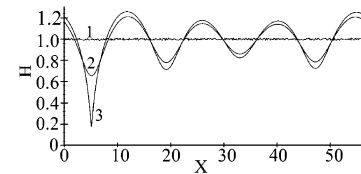


Figure 6. Evolution of instability in a 5 nm film corresponding to regime I in Figure 4 ($a^* = -0.1$, $B = 0.1$). The domain size is $4\lambda_m$. Curves 1–3 correspond to nondimensional time (T) of 0, 103, and 143, respectively.

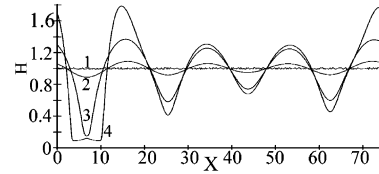


Figure 7. Evolution of instability in a 5 nm film corresponding to regime II in Figure 4 ($a^* = -0.6$, $B = 0.5$). The domain size is $4\lambda_m$. Curves 1–4 correspond to $T = 0, 404, 525$, and 538 , respectively.

observations, it is instructive to examine the form of a modified spinodal parameter (ϕ_h vs h from eq 39) due to density variation. Figure 4 shows the region of stability for different a^* and B for a given A_{LLb} and A_{SLb} . The change in the behavior of thin film stability can be explained by the shape of the modified spinodal parameter curve (ϕ_h vs h from eq 39) in the presence of density variation. Figure 5 shows the qualitative behavior of the modified spinodal parameter curve from eq 39 for the three different regimes shown in Figure 4. ϕ_h is always negative in the unstable regime I, where density variation merely changes the length and time scales of instability. The nature of modified ϕ_h changes regime II, giving rise to pseudo-dewetting where an equilibrium film is left on the substrate after dewetting.^{6–11} The form of the spinodal parameter also implies that ultrathin films less than some critical thickness (h_c) are stabilized since ϕ_h becomes positive. Finally, ϕ_h is always positive in regime III, signifying a stable thin film.

The initial evolution of instability, based on a numerical solution of the 1-D nonlinear thin film equation (eq 30) is shown in Figures 6 and 7 for films corresponding to regimes I and II. The length scale of instability is quite accurately predicted by the linear theory (eq 41). In the first case, true rupture of the film occurs ($h = 0$), whereas in the second case, pseudo-dewetting on an equilibrium

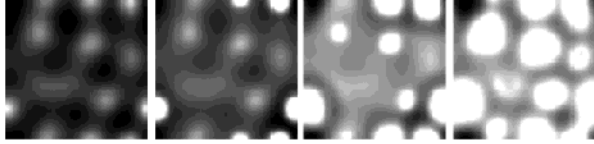


Figure 8. Evolution of 3-D morphology in a 2 nm film corresponding to regime II in Figure 4 ($a^* = -0.6$, $B = 1$). The domain size ($X-Y$) is $3\lambda_m \times 3\lambda_m$. Pictures from left to right correspond to $T = 636, 664, 693$, and 740 , respectively.

film is seen. In essence, modification of the spinodal parameter due to density changes has the same effect as the presence of a short-range repulsive force in this regime.

Figure 8 shows the complete 3-D morphology of dewetting for the same case as shown in Figure 7, based on numerical solutions of the 2-D nonlinear eq 31. The growth of (pseudo-) dewetted regions occurs by the formation of largely circular holes that grow and coalesce. The linear theory prediction of the length scale is also well respected in 2-D, since approximately nine holes form in a domain of size $9\lambda_m^2$, where λ_m is the dominant wavelength of the instability.

In regime III, this stabilizing influence is strong enough to completely dominate the tendency of the film to dewet because of the van der Waals attractive forces at constant density. We now turn to the analysis of the case when the film density has an antagonistic relation with the film thickness.

Increase in Density with Decreasing Film Thickness ($\hat{\rho}/\epsilon < 0$). In this case, the density of the film increases with the decreasing film thickness and vice versa. As $(\hat{\rho}/\epsilon) = (\partial\rho/\partial h)_0$ is negative in this case, the factor $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ in eq 19 can be either positive or negative, even though as shown later, this factor is unlikely to be negative. In general, the condition for χ to be positive is

$$(|\partial\rho/\partial h|)_0 = |\hat{\rho}/\epsilon| < \rho_0/h_0 \quad (42)$$

When condition eq 42 is satisfied, the necessary and sufficient condition from eq 19 for a film to be unstable (i.e., $\omega > 0$), respectively, is

$$\phi_{h_0} < 0 \text{ and } k^2 < -\phi_{h_0}/\gamma \quad (43)$$

The condition for $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ to be negative is

$$(|\partial\rho/\partial h|)_0 = |\hat{\rho}/\epsilon| > \rho_0/h_0 \quad (44)$$

When condition eq 44 is satisfied, the conditions for a film to be unstable (i.e., $\omega > 0$) are

$$\text{either } \phi_{h_0} > 0 \text{ or } \phi_{h_0} < 0 \text{ and } k^2 > -\phi_{h_0}/\gamma \quad (45)$$

The latter condition implies a short-wave instability and is therefore not considered further in this study of the long-wave instabilities. We now establish the conditions for instability for different signs of A_0 .

Case 1: $A_0 = 0$ (Critical Case). The expression for modified ϕ_{h_0} becomes

$$\phi_{h_0} = A_{LL_0}(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0 \quad (46)$$

As $(\hat{\rho}/\epsilon) = (\partial\rho/\partial h)_0$ is negative in this case, ϕ_{h_0} is always negative. When factor $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ is positive, the necessary condition of instability (eq 43) is always satisfied, and the film is unstable to small amplitude perturbations.

The parameters a^* and B in the density variation given by eq 32 were varied from 0.1 to 10. Physically, these

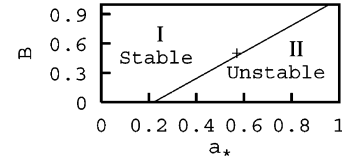


Figure 9. Regimes of instability and stability depending on the values of constants a^* and B for the density function of eq 32, and $\partial\rho/\partial h < 0$ and $A_0 < 0$. The mean film thickness is 5 nm, and $A_{LLb} = 1 \times 10^{-20}$ J, $A_{SLb} = 1.2 \times 10^{-20}$ J.

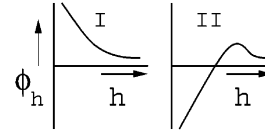


Figure 10. Qualitative behavior of the modified spinodal parameter for the different regimes shown in Figure 9.

values correspond to an increase in the interfacial density (ρ_i) by a factor of 1.1:11 as compared to ρ_b . Thus, for a wide range of density variations, the factor $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ always comes out to be positive, implying that short wavelength instability is indeed not likely.

Case 2: $A_0 < 0$ (Constant Density Film Is Spinodally Stable). The expression for modified ϕ_{h_0} becomes

$$\phi_{h_0} = |A_0|/2\pi h_0^4 + (A_{LL_0} - |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0 \quad (47)$$

When factor $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ is positive, the first term is stabilizing. For instability to grow, the necessary conditions are

$$A_{LL_0} > |A_0| \quad (48)$$

$$(|\partial\rho/\partial h|)_0 = |\hat{\rho}/\epsilon| > 3(\rho_0/h_0)(|A_0|/(A_{LL_0} - |A_0|)) \quad (49)$$

Clearly, the factor $\beta_3 = [|A_0|/(A_{LL_0} - |A_0|)] > 0$ when the film is unstable. If A_{LL_0} is much larger than A_0 , then $\beta_3 \ll 1$, and the condition for the density variation induced instability can be easily satisfied.

When $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ is negative (which is an unlikely case, but included here for the sake of completeness), the condition for instability, $\phi_{h_0} > 0$ in eq 45 implies

$$|A_0| > A_{LL_0} \quad (50)$$

Also, the second condition in eq 45 implies

$$A_{LL_0} > |A_0| \quad \hat{\rho}/\epsilon < (3\rho_0/h_0)(|A_0|/(A_{LL_0} - |A_0|)) \quad (51)$$

Since the condition $\chi < 0$ is unlikely, the most likely conditions of instability for a spinodally stable constant density film are eqs 48 and 49, which will be more fully discussed below.

Conditions for instability implied by eq 49 are satisfied at some critical value of $\partial\rho/\partial h$ or beyond some corresponding value of parameter a^* (in the density function, eq 32). Figure 9 shows the stability characteristics in the parameter space. This can be explained from the shape of the modified spinodal curve (eq 47) shown in Figure 10 for parameters corresponding to different regimes. The spinodal parameter (ϕ_h) remains positive in regime I, implying a stable film. When a^* exceeds a critical value, which depends on parameter B , ϕ_h becomes negative (regime II) for films thinner than a certain thickness (where ϕ_h changes sign). Thus, constant density stable thin films can be destabilized solely because of density variations. However, films that are thicker than where ϕ_h

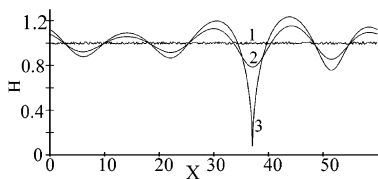


Figure 11. Evolution of instability in a 5 nm thick film corresponding to regime I in Figure 9 ($a^* = +0.6$, $B = 0.1$). The domain size is $4\lambda_m$. Curves 1–3 correspond to $T = 0$, 98, and 147, respectively.

changes from negative to positive remain stable and completely wetting. For example, for the case considered in Figure 9, films thicker than 27 nm are stable. In essence, density variations can modify the spinodal parameter of a perfectly stable constant density film so that it resembles the spinodal parameter due to a combination of long-range repulsion combined with a shorter range attraction (Figure 10II).

Finally, Figure 11 (on the basis of numerical solutions of eq 30) shows the evolution of density variation induced instability for a 5 nm thick film. Such a film would have been spinodally stable in the absence of density variations.

The most interesting conclusion is that density variations can even render a spinodally stable film unstable and induce dewetting. This scenario may be applicable to the experiments of the kind discussed by Demirel and Jérôme,¹⁷ who observed dewetting for thinner films and re-entrant wetting for thicker films. This was attributed to a dynamic effect due to the restructuring of the molecules at the solid–liquid interface.¹⁷ It is instructive to examine the length and time scale of instability induced by density variations to make some connection with experiments.

The dominant wavelength of instability is

$$\lambda_m = (8\pi^2\gamma)^{1/2} [-|A_0|/2\pi h_0^4 + (A_{LL_0} - |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0]^{-1/2} > 0 \quad (52)$$

The minimum time of rupture (t_m) is

$$t_m = (12\mu\gamma/h_0^3)(|A_0|/2\pi h_0^4 + (A_{LL_0} - |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0)^{-2}(1 + \hat{\rho}h_0/\epsilon\rho_0) \ln(h_0/\epsilon) \quad (53)$$

The density variation induced instability is dominated by the second term of eq 52 when the conditions in eqs 48 and 49 are met. Thus, the length scale of instability shows a variable order dependence on the film thickness, $\lambda_m \propto h_0^n$, where the exponent n can range from 1.5 (for a linear local density variation with thickness) to 2.5 (for a rather extreme variation, $\partial\rho/\partial h \propto 1/h^2$). It may be recalled that spinodally unstable films with nonretarded van der Waals forces show a fixed exponent of 2, which is also close to the range obtained for the density variation induced instability. The length scale arguments alone are therefore not sufficient for discriminating the true mechanism of instability. In view of these considerations, let us consider the somewhat enigmatic dewetting of polystyrene films on silicon wafers, where A_0 is likely to be negative since silicon (as well as silicon oxide) has a larger Hamaker constant than the polymer. Polystyrene films should therefore be spinodally stable but were observed to breakup with the scaling, $\lambda_m \propto h_0^n$, where n was found close to 2 in one study^{30,31} and variable order in another³²

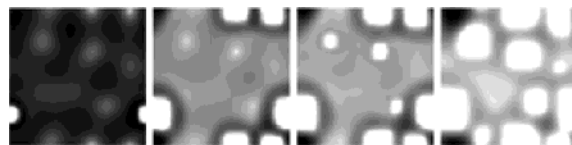


Figure 12. Evolution of 3-D morphology in a 5 nm film corresponding to regime II in Figure 9 ($a^* = 0.6$ and $b = 0.1$). The domain size for the simulation is $3\lambda_m \times 3\lambda_m$, which eventually produces ≈ 9 holes in line with the expectations of the linear analysis. Pictures from left to right correspond to $T = 182, 189, 192$, and 200 , respectively.

that used different conditions for the preparation of films. It is therefore entirely possible that dewetting of thin polystyrene films on silicon wafers is caused by density variations rather than by attractive van der Waals forces. Ref 32 also implicated the formation of nanovoids as a possible factor in the breakup, which may relate to density variations.

Another interesting aspect of density variation induced dewetting is that the precise morphology during dewetting is also identical to spinodal dewetting. The latter occurs by the formation of largely circular holes.^{9,11} Figure 12, for example, shows the 3-D nonlinear evolution of morphology for a thin film that is spinodally stable in the absence of density fluctuations. The formation and growth of holes is therefore again not an exclusive indicator of spinodal dewetting but is shared equally by the density induced dewetting.

Case 3: $A_0 > 0$ (Constant Density Film Is Spinodally Unstable). The expression for the modified ϕ_{h_0} is

$$\phi_{h_0} = -|A_0|/2\pi h_0^4 + (A_{LL_0} + |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3 \rho_0 \quad (54)$$

ϕ_{h_0} is always negative; therefore, when $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ is positive, the film remains linearly unstable to small amplitude perturbations. The term due to density fluctuation in eq 54 makes ϕ_{h_0} even more negative. This makes the instability stronger by reducing its length scale and its time of rupture. However, in the unlikely case when $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ is negative, the film can remain unstable only if the following conditions of instability, given by eq 43, are also satisfied (since ϕ_{h_0} is strictly negative).

$$k^2 > |A_0|/2\pi\gamma h_0^4 - (A_{LL_0} + |A_0|)(\hat{\rho}/\epsilon)/6\pi\gamma h_0^3 \rho_0 \quad (55)$$

However, the above implies a short-wave instability and cannot be analyzed within the long-wave framework pursued here. Also, as explained earlier for rather wide feasible ranges of a^* and B values, the factor $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$ is in fact positive.

Conclusions

The density variations due to confinement, restructuring, layering, defects, and interactions at solid–liquid and solid–air interfaces can change the stability behavior of a thin film very profoundly. A thermodynamically unstable film can be completely stabilized when the density of the film decreases with decreasing film thickness. In such a case, true dewetting (formation of dry spots) can change into pseudo-dewetting (formation of a stable adsorbed film on a dewetted spot) and then to complete stability as the density variations become stronger. On the other hand,

(30) Reiter, G. *Phys. Rev. Lett.* **1992**, *65*, 78.

(31) Reiter, G. *Langmuir* **1993**, *9*, 1344.

(32) Jacobs, K.; Seeman, R.; Schatz, G.; Herminghaus, S. *Langmuir* **1998**, *14*, 4961.

Table 1. Summary of Results

form of density variation	sign of factor $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$	sign of effective Hamaker constant	conditions of instability	conclusions
$(\hat{\rho}/\epsilon) = (\partial\rho/\partial h)_0 > 0$; increase in density with increased film thickness	since $(\hat{\rho}/\epsilon)$ is positive, χ is always positive	$A_0 < 0$; constant density film is stable	eqs 37 and 38	density variations can lead to instability, but in most cases the condition for the instability is unlikely to be satisfied
		$A_0 > 0$; constant density film is unstable	eq 40	density variations can lead to pseudo-dewetting or even complete stability
		$A_0 < 0$; constant density film is stable	eqs 48 and 49	density variations can destabilize the film, especially if A_{LL0} is much larger than A_0
$(\hat{\rho}/\epsilon) = (\partial\rho/\partial h)_0 > 0$; decrease in density with increased film thickness	χ is positive, which means $ \hat{\rho} / \epsilon < \rho_0/h_0$	$A_0 > 0$; constant density film is unstable	always unstable	density variations lead to stronger instability, shortening of length scale, and reduced time of rupture
	χ is negative (<i>unlikely case</i>), which means $ \hat{\rho} / \epsilon > \rho_0/h_0$	$A_0 > 0$; constant density film is unstable	eq 53	short-wave instability is implied, which cannot be analyzed within the long wavelength framework

if density increases with increasing film thickness, a stable thin film can be destabilized to the extent of true rupture. Also, density variations occurring in the film change the length and time scales of instability. Our results regarding the conditions for the instability and its length and time scales are different from the previous study¹⁴ of the same phenomenon. The results of the linear stability analysis are directly verified by numerical solutions of the nonlinear governing equation for the film thickness. We also show that the instability due to density variations can be interpreted (by an appropriate redefinition of the spinodal parameter) within the framework of the well-known spinodal dewetting of constant density films.^{1–11} However, the modified spinodal parameter involves not only the

true forces at constant density but also additional attractive or repulsive forces due to density variation. Thus, the inverse problem of determination of true thin film potential from the measurements of instability length scale is subject to the uncertainty of density variations that depend on the preparation conditions in addition to the substrate–film material properties. The proposed theory should lead to a more rational design and interpretation of thin film experiments. Finally, the conditions for the density variation induced instability for different cases are summarized in Table 1 for a ready reference.

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