Instability of Thin Liquid Films by Density Variations: A New Mechanism that Mimics Spinodal Dewetting

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Based on the linear stability analysis and nonlinear simulations, conditions are established under which instability and dewetting of a thin liquid film can be engendered solely by the density variations (for example, due to confinement, layering, defects, and restructuring) related to changes in the local film thickness. An increase in the density with the increasing film thickness can stabilize a thermodynamically unstable film, and, equally interesting, a decrease in the density with increasing film thickness can render a thermodynamically stable film unstable. Morphological characteristics of this novel density variation induced instability closely resemble the well-known spinodal dewetting.

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Theoretical understanding of thin (< 100 nm) film stability, dynamics, dewetting, and morphology has attracted much attention [1–3] because of diverse technological applications of thin liquid films in optoelectronic coatings, adhesives, flotation, biological membranes, and nanotechnology. In addition to its technological content, a thin liquid film is a model mesoscale system involving a host of fundamental scientific issues such as intermolecular forces, self-organization, confinement and finite size effects, microscale dewetting, multilayer adsorption, and phase transitions. There are two well-known mechanisms for the instability of isothermal thin fluid films: (i) spinodal dewetting on a homogeneous nonwettable substrate [1,2], and (ii) heterogeneous dewetting or "nucleation" engendered by the microscale wettability contrasts on a heterogeneous substrate [3]. We analyze here a third possibility [4] in which the surface instability is caused by the fluctuations of local density, which produces a gradient of the van der Waals force. The density variations are coupled to the local film thickness due to the confinement, layering, restructuring, and defect mediated effects in the polymer films [5,6]. We show that density variations can lead to profound qualitative changes in the stability behavior of thin films. We also show that 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 [7–11] showing that even the films that are expected to be spinodally stable are observed to dewet in ways similar to the expectations of the spinodal theory. In what follows, x and z are coordinates parallel and normal to the solid substrate, respectively; the mean density (ρ) of the film averaged over its local thickness ($0 < z < h$) is assumed to vary along the substrate in the x direction; subscripts denote differentiation; u and w are the x and z components of velocity; μ is viscosity; ϕ is the excess body force due to intermolecular interactions (conjoining pressure); p is pressure at the free surface; and γ is surface tension. The equation of motion in the thin film approximation, $\mu u_{zz} = (p + \phi)_x$, together with the equation of continuity (mass balance), $\rho_t + (\rho u)_x + (\rho w)_z = 0$, equation of capillarity, $p_x = -\gamma h_{xxx}$, and the kinematic condition, $h_t + u h_x = w$, give the equation that describes the stability, dynamics, and morphology, $h = h(x, t)$, of a thin film (boundary conditions are $\mu u_z = 0$ at $z = h$ and $u = w = 0$ at $z = 0$):

$$3\mu(\rho h)_t + [\rho h^3(\gamma h_{xx} - \phi)_x]_x = 0. \tag{1}$$

For constant density, Eq. (1) reduces to the form used extensively [2]. The van der Waals conjoining pressure is given by [1,5]: $\phi = A(\rho)/6\pi h^3$, where A is an effective Hamaker constant determined by the liquid-liquid (A_{LL}) and solid-liquid (A_{SL}) Hamaker constants, $A = A_{LL} - A_{SL}$. $A > 0$ implies attractive force leading to spinodal dewetting, whereas $A < 0$ corresponds to thermodynamic stability and perfect wetting [1,2]. The binary Hamaker constants are given by [4,5] $A_{LL} = \alpha_{LL}\rho^2$ and $A_{SL} = \alpha_{SL}\rho_S\rho$, where ρ_S and ρ are the densities of the substrate and liquid film, respectively. The variation in the local density of the film (ρ) causes the Hamaker constants to change locally. This causes a gradient of intermolecular force engendering flow in the film from the regions of lower (more negative) ϕ to the regions with higher ϕ. The dispersion relation resulting from the linear stability analysis of Eq. (1) is [$h = h_0 + \epsilon \sin(kx)e^{\omega t}$; $\rho = \rho_0 + \hat{\rho}\sin(kx)e^{\omega t}$]:

$$\omega = (h_0^3 k^2/3\mu)[-\gamma k^2 - \Psi_{h0}](1 + \hat{\rho} h_0/\epsilon\rho_0)^{-1}, \tag{2}$$

where $\Psi_{h0} = (\partial\Psi/\partial h)_0$ is evaluated at the mean film thickness (h_0), and can be referred to as a modified spinodal parameter given by

$$\Psi_{h0} = -A_0/2\pi h_0^4 + (A_{LL0} + A_0)(\hat{\rho}/\epsilon)/6\pi h_0^3\rho_0, \tag{3}$$

where ρ_0 is evaluated at the mean film thickness h_0, ϵ is the surface amplitude ($\ll h_0$), $\hat{\rho}$ is the amplitude of

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variation in the density, k is the wave number, and ω is the growth rate of instability. For any arbitrary variation of $\rho = f(h)$, the first order expansion for the density is $\rho = \rho_0 + (\partial\rho/\partial h)_{h0}\epsilon$, which implies a relation $(\partial\rho/\partial h)_0 = \hat{\rho}/\epsilon = f_{h0}$. For $\hat{\rho} = 0$, Eq. (2) reduces to the well-known result for the spinodal instability of a constant density thin film [1]. The term, $[A_{LL0}(\partial\rho/\partial h)_0/6\pi h_0^3\rho_0]$, in Eq. (2) is absent in the earlier analysis [4], and is destabilizing when $(\partial\rho/\partial h)_0$ is negative since the liquid phase Hamaker constant increases (ϕ becomes more negative) as the film thins locally. 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 [5], and, unlike A_0, which can be either positive or negative, A_{LL0} is always positive. Equation (2) is identical to the relation in the absence of density fluctuations [1], except for a numerical factor, $\chi = (1 + \hat{\rho}h_0/\epsilon\rho_0)$, and a reinterpretation of the spinodal parameter according to Eq. (3). Thus, for $\chi > 0$, which is usually the case, the necessary condition for the instability ($\omega > 0$) formally remains the same as for a constant density film, namely, $\Psi_{h0} < 0$. The dominant wave number (k_m) is obtained by $\partial\omega/\partial k = 0$, which gives $k_m = (-\Psi_{h0}/2\gamma)^{1/2}$. The dominant instability wavelength (λ_m) is $\lambda_m = 2\pi/k_m$ and the corresponding growth rate is $\omega_m = (h_0^3/12\mu\gamma)(\Psi_{h0})^2(1 + \hat{\rho}h_0/\epsilon\rho_0)^{-1}$. An estimate for the instability time scale is $t_m = (1/\omega_m)\ln(h_0/\epsilon)$. We illustrate some of the results with the help of a simple form:

$$\rho = \rho_b + a(1 + bh/h_*)^{-1} = f(h), \tag{4}$$

where ρ_b denotes the bulk density, the constants a and b are given by $a = \rho_i - \rho_b$, $b = (\rho_i - \rho_*)/(\rho_* - \rho_b) > 0$, where ρ_i is the interfacial density ($h \to 0$), and ρ_* is the density at an intermediate thickness h_*. 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 thickness [4–6]. We emphasize that a particular form, Eq. (4), is chosen merely for illustration, but 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 [5,6]. Thus, the sign of $(\partial\rho/\partial h)_0$ can even change periodically with thickness, offering a host of interesting possibilities for the nonlinear evolution of instability. The evolution Eq. (1) can be nondimensionalized for the most compact representation of results by introducing [2] $X = (A_{LLb}/2\pi h_0^4\gamma)^{1/2}x$; $T = (A_{LLb}^2/12\pi^2 h_0^5\mu\gamma)t$; $H = h/h_0$; $\Phi = (2\pi h_0^3/A_{LLb})\phi$; $\Gamma = \rho/\rho_b$, where A_{LLb} is the liquid Hamaker constant evaluated at the bulk density ρ_b. The 2D analog of Eq. (1) can now be written in a compact nondimensional form as

$$(\Gamma H)_T + [\Gamma H^3(H_{XX} + H_{YY} - \Phi)_X]_X + [\Gamma H^3(H_{XX} + H_{YY} - \Phi)_Y]_Y = 0, \tag{5}$$

where $\Gamma = 1 + a_*(1 + BHh_0)^{-1}$, $a_* = a/\rho_b$, and $B = b/h_*$. The above equations were discretized using a central differencing method with half node interpolation. The resultant set of stiff coupled ordinary differential equations was solved using Gear's algorithm with an initial volume preserving random perturbation and periodic boundary conditions. Depending on the effects of confinement, restructuring, cavitation, and the specific interactions with the substrate and air, the mean density may either decrease [$(\partial\rho/\partial h)_0 = \hat{\rho}/\epsilon < 0$] or increase ($\hat{\rho}/\epsilon > 0$). In what follows, we consider these two general cases, each with two different possibilities: (i) the film is spinodally stable ($A_0 > 0$) in the absence of density variation, and (ii) the film is unstable ($A_0 > 0$) in the absence of density variations. The mean effective Hamaker constant is given by [5] $A_0 = A_{LL0} - A_{SL0} = A_{LL0}^{1/2}(A_{LL0}^{1/2} - A_{SS0}^{1/2})$.

Case I, decrease in density with decreasing film thickness, $(\hat{\rho}/\epsilon) = (\partial\rho/\partial h)_0 > 0$.—The necessary and sufficient conditions for a film to be unstable (i.e., $\omega > 0$) are, respectively, $\Psi_{h0} < 0$ and $k^2 < -\Psi_{h0}/\gamma$, which imply a long-wave instability. *(i)* $A_0 < 0$*, implying* $A_{LL0} < A_{SS0}$ *(constant density film is spinodally stable).*

The conditions for the growth of density variation induced instability are $|A_0| > A_{LL0}$, and $(\partial\rho/\partial h)_0 = (\hat{\rho}/\epsilon) > 3(\rho_0/h_0)[|A_0|/(|A_0| - A_{LL0})]$. The first necessary condition and the last factor, $\beta_1 = [|A_0|/(|A_0| - A_{LL0})] > 1$, which involves the ratio of Hamaker constants, were missing in the earlier analysis [4] of the same case. Thus, unless the density variation with thickness is very strong, the above conditions for the instability are unlikely to be satisfied. For example, the condition for instability is not satisfied for a reasonable example of density variation, Eq. (4), even when the interfacial density is only 1% of the bulk density. *(ii)* $A_0 > 0$*, implying* $A_{LL0} > A_{SS0}$ *(constant density film is spinodally unstable).*

The expression for modified spinodal parameter with density variation becomes

$$\Psi_{h0} = -|A_0|/2\pi h_0^4 + (A_{LL0} + |A_0|)(|\hat{\rho}/\epsilon|)/6\pi h_0^3\rho_0$$

The condition for instability despite density variations is

$$(\partial\rho/\partial h)_0 = (\hat{\rho}/\epsilon) < 3(\rho_0/h_0)[|A_0|/(|A_0| + A_{LL0})]. \tag{6}$$

The factor $\beta_2 = [|A_0|/(A_{LL0} + |A_0|)] < 1$ and, thus, weak to moderate density variations can even stabilize an otherwise unstable film when the above condition is violated. This can happen rather readily if the effective Hamaker constant is small, i.e., surface tensions of the solid and liquid are close. The dominant wavelength of instability in this case is $\lambda_m = (-8\pi^2\gamma/\Psi_{h0})^{1/2} = \{(8\pi^2\gamma)/[|A_0|/2\pi h_0^4 - (A_{LL0} + |A_0|)(\hat{\rho}/\epsilon)/6\pi h_0^3\rho_0]\}^{1/2}$. Thus, the additional term in ψ_{h0} due to density fluctuation has a stabilizing influence and increases the length scale of instability. Although a constant density film in this case is unstable to the extent of true rupture or dry spot formation since $\Psi_h < 0$ for all thicknesses, a modified spinodal parameter due to density variation can lead to pseudodewetting [Fig. 1(A)] or even complete stability depending on the strength and thickness dependence of $(\partial\rho/\partial h)_0$. Moderate values of $(\partial\rho/\partial h)_0$ lead to pseudodewetting [Fig. 1(A)], defined by the situation where an equilibrium film is left on the substrate after dewetting [2]. *In essence, modification of the spinodal parameter due to density changes in this case mimics the effect of a repulsive force in a constant density film.* An example of density variation induced pseudodewetting is shown in Fig. 1(B) based on numerical solutions of the 1D nonlinear thin film equation. Figure 1(C) shows the complete 3D morphology of dewetting based on numerical solutions of the 2D nonlinear Eq. (5). 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 2D, since approximately nine holes form in a domain of size $3\lambda_m \times 3\lambda_m$. We now turn to the analysis of the case when the film density has an antagonistic relation with the film thickness.

Case II, increase in density with decreasing film thickness, $\hat{\rho}/\epsilon = (\partial\rho/\partial h)_0 < 0$.—The factor $\chi = (1 + \hat{\rho} h_0/\epsilon\rho_0)$ still stays positive in realistic cases, as can be seen, for example, from Eq. (4) even when the interfacial density (ρ_i) is increased by a factor of 10 compared to the bulk density. In any event, negative values of χ imply a short wave instability, $\Psi_{h0} < 0$ and $k^2 \geq -\Psi_{h0}/\gamma$, which cannot be considered in the framework of the long-wave instabilities. *(i)* $A_0 > 0$ *(constant density film is spinodally unstable).*

The expression for the modified spinodal parameter in this case is $\Psi_{h0} = -|A_0|/2\pi h_0^4 - (A_{LL0} + |A_0|)(|\hat{\rho}/\epsilon|)/6\pi h_0^3\rho_0$. Thus, Ψ_{h0} is always negative, and the film remains unstable with density variations. Density changes merely make the instability stronger by reducing its length scale and its time of rupture, with no qualitative changes in the stability behavior. *(ii)* $A_0 < 0$ *(constant density film is spinodally stable).*

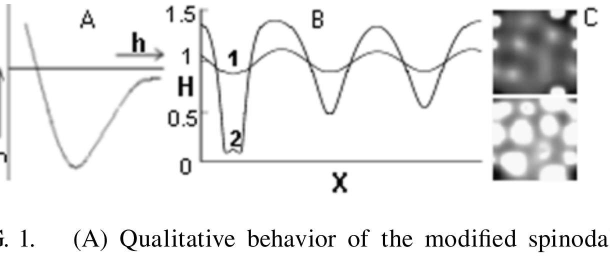

FIG. 1. (A) Qualitative behavior of the modified spinodal parameter in the pseudodewetting regime. (B) Evolution of instability in a 5 nm film corresponding to regime in (A) ($A_{LLb} = 2 \times 10^{-18}$ J, $A_{SLb} = 1 \times 10^{-18}$ J, $a_* = -0.6$, $B = 0.5$). The domain size is $3\lambda_m$. For curves 1 and 2 nondimensional time, $T = 419$ and 524, respectively. (C) Pseudodewetting in a 2 nm film; $B = 1$. Pictures are at nondimensional time of 664 and 740, respectively.

The expression for modified spinodal parameter becomes

$$\Psi_{h0} = |A_0|/2\pi h_0^4 - (A_{LL0} - |A_0|)(|\hat{\rho}/\epsilon|)/6\pi h_0^3\rho_0$$

The conditions for the instability are

$$A_{LL0} > |A_0| \quad \text{and} \quad (|\partial\rho/\partial h|)_0 = (|\hat{\rho}/\epsilon|) > 3(\rho_0/h_0)[|A_0|/(A_{LL0} - |A_0|)]. \tag{7}$$

Clearly, the factor, $\beta_3 = [|A_0|/(A_{LL0} - |A_0|)] > 0$ when the film is unstable. If the liquid Hamaker constant is much larger than the effective Hamaker constant (as is the case for polystyrene films on silicon oxide [5]), then $\beta_3 \ll 1$, and the condition for the density variation induced instability can be easily satisfied. The condition for instability implied by Eq. (7) is satisfied at some critical value of $(\partial\rho/\partial h)$. Figure 2(A) shows the nature of the modified spinodal parameter as $(\partial\rho/\partial h)$ is increased. *In this regime, the modified spinodal parameter mimics the behavior of a constant density film subjected to a short range attraction combined with a long range repulsion, as has indeed been suggested* [9] *to be the case for the polystyrene films on silicon wafers based on the observations of the instability.* Thus, constant density stable thin films can be destabilized solely due to density variations. In such systems, films thicker than a critical thickness (where Ψ_h becomes positive) remain stable and completely wetting, as was also observed [9,10]. Figure 2(B) shows the evolution of density variation induced instability for a 5 nm thick film, which would have been spinodally stable in the absence of density variation. The most interesting conclusion is that density variations can even render a spinodally stable film unstable and induce dewetting. In addition to polystyrene films, this scenario may also be applicable to the experiments of the kind discussed by Demirel *et al.* [11], who observed dewetting for thinner films and reentrant wetting for thicker films. This was attributed to a dynamic effect due to the restructuring of the molecules at the solid-liquid interface [4,11]. It is instructive to examine the length scale of density variation induced instability

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

The density variation induced instability is dominated by the second term of the above equation when the conditions in Eq. (7) 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 constant $\partial\rho/\partial h$) 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 theoretical exponent of 2 [1,2], which is also close to the range obtained for the density variation induced instability. The length scale arguments alone

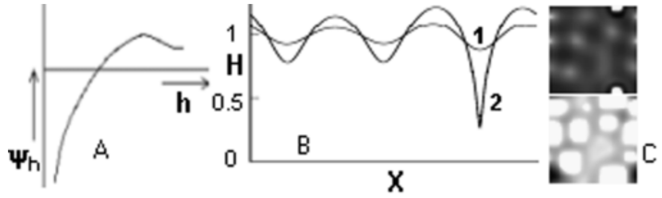

FIG. 2. (A) Qualitative variation of the modified spinodal parameter for a spinodally stable film with $(\partial\rho/\partial h) < 0$. (B) Evolution of instability in a 5 nm thick film ($A_{LLb} = 1 \times 10^{-20}$ J $A_{SLb} = 1.2 \times 10^{-20}$ J, $a_* = +0.6$, $B = 0.1$). The domain size is $3\lambda_m$. For curves 1 and 2 nondimensional time, $T = 161$ and 186, respectively. (C) Evolution of 3D morphology. 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 correspond to nondimensional times of 182 and 200, respectively.

are therefore not sufficient for discriminating the true mechanism of instability. In fact, if one examines the variation of λ_m with mean thickness, and assumes spinodal dewetting with constant density to be the cause, one would conclude that the spinodal parameter shows signatures of a short range van der Waals force combined with a long range van der Waals force. Such a conclusion is, however, misleading if density variations are important. These considerations may be relevant to enigmatic dewetting of polystyrene films that are expected to be spinodally stable on silicon wafers (since $A_{SS} > A_{LL}$ [5,7–10]). However, such films were observed to break up with the scaling, $\lambda_m \propto h_0^n$, where n was found close to 2 in one study [7], and variable order in another [8] which used different conditions for the preparation of films. Ref. [8] also implicated the formation of nanovoids and sensitivity to preparation conditions as possible factors in the breakup (or the lack of it), which may relate to density variations. Another interesting aspect of density variation induced dewetting is that the morphology during dewetting [Fig. 2(C)] is also identical to spinodal dewetting [2]. Figure 2(C), for example, shows the 3D 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.

In conclusion, the density variations due to confinement, restructuring, layering, defects, and interactions at 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 pseudodewetting (formation of stable adsorbed film on dewetted spot), and then to complete stability as the density variations become stronger. On the other hand, if density decreases with decreasing 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 scale and time scale of instability. We also show that the instability due to density variations can be interpreted by an appropriate redefinition of the spinodal parameter, which involves additional attractive or repulsive forces due to density variation. Thus, the inverse problem of determination of true thin film potential from the measurement of instability length scale is subject to the uncertainty of density variations, which depend on the preparation conditions and on the substrate-film materials. The proposed theory should lead to a more rational design and interpretation of thin film experiments.

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