Morphological Instability of Solid-on-Liquid Thin Film Structures

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ABSTRACT

Subject to a compressive membrane force, a solid film on a liquid layer may form wrinkles. When the solid film is very thin, surface stresses contribute to the membrane force. When the liquid layer is very thin, the two interfaces bounding the liquid interact with each other through forces of various physical origins. We formulate the free energy of the solid-on-liquid structure, and carry out a linear perturbation analysis. A dimensionless parameter is identified to quantify the relative importance of flexural rigidity, membrane force, and interfacial force. Depending on the nature of the interfacial force, several intriguing behaviors are possible; for example, the solid film may remain flat under a compressive membrane force, or form wrinkles under a tensile membrane force.

INTRODUCTION

A thin liquid layer, lying on a solid substrate by itself, can rupture to form islands and dry spots [1-4]. The instability is driven by long-range attractive interactions between the two interfaces that bound the liquid layer. The surface energy of the liquid can stabilize perturbations of short wavelengths, but not those of long wavelengths. As a result, perturbations of long wavelengths grow and the liquid layer is unstable.

If the liquid layer is covered by a thin solid film, as shown in Fig. 1, several differences are expected. The flexural rigidity of the solid film provides resistance against instability. If the solid film is subject to a residual stress, tension stabilizes the film, and compression destabilizes it. The long-range interactions between the interfaces can be attractive or repulsive, destabilizing or stabilizing the system. Yet another difference is about surface energy. As first pointed out by Gibbs [5], for a solid-liquid interface, the change of surface energy depends on the elastic strain. Unlike the surface energy density at an air-liquid interface, which is a positive constant and always tends to stabilize the liquid layer, the surface stress at a solid-liquid interface can be
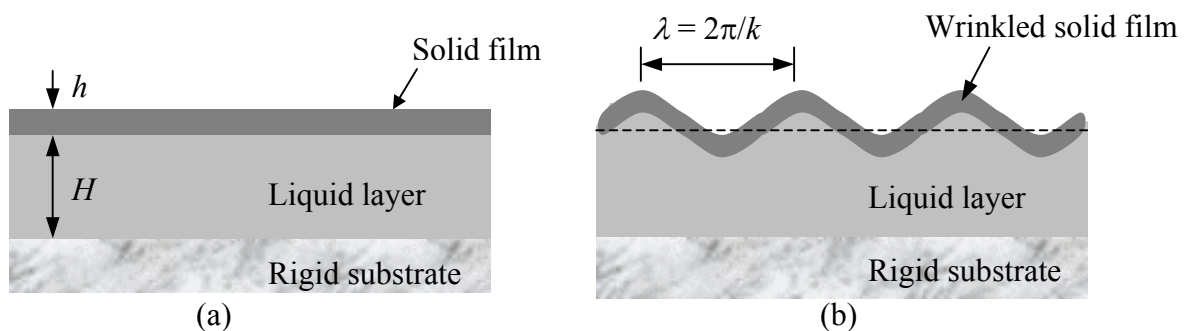

Figure 1: Illustration of a solid-on-liquid thin film structure: (a) flat and reference state; (b) wrinkled state.

either positive or negative [6-9], and thus can either stabilize or destabilize the solid-on-liquid (SOL) structure.

Recently, we and others have studied the stability of a SOL structure by considering the elastic deformation of the solid and the viscous flow of the liquid, but ignoring the effects of surface stresses and interfacial forces [10-13]. The analysis is valid as long as both the solid film and the liquid layer are sufficiently thick. In that case, a compressed solid film is always unstable and forms wrinkles. This paper aims to elucidate the effects of the surface stresses and the interfacial forces on the stability of SOL thin film structures.

FREE ENERGY

Refer to Fig. 1 again. Take the configuration with all interfaces flat and parallel as the reference state (Fig. 1a). At the wrinkled state (Fig. 1b), the solid film deflects, and the free energy in the system changes. The energy change consists of the changes in the bulk elastic energy within the solid film (U_B), the surface energy at the solid-liquid interface and the solid-air interface (U_S), and the interaction energy associated with interfacial forces (U_L), i.e.,

$$\Delta U = \Delta U_B + \Delta U_S + \Delta U_L. \tag{1}$$

If the total free energy increases for any arbitrary wrinkle, the flat film is stable, and the wrinkle will decay. Otherwise, the flat film is unstable, and the wrinkle will grow.

Assume that the solid film is isotropic and elastic with Young's modulus E and Poisson's ratio ν. At the wrinkled state (Fig. 1b), the solid film has a deflection, $w(x,y)$, and the in-plane displacements, $u_x(x,y)$ and $u_y(x,y)$. According to the von Karman plate theory [14], from the reference state to the wrinkled state, the in-plane strain changes by

$$\Delta\varepsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial w}{\partial x_\alpha}\frac{\partial w}{\partial x_\beta}\right) - \frac{\partial^2 w}{\partial x_\alpha \partial x_\beta}z, \tag{2}$$

where $z = 0$ at the middle plane and $z = \pm h/2$ at the top and bottom surfaces of the solid film. The change of the bulk elastic energy per unit area is

$$\Delta U_B = \frac{\sigma_{\alpha\beta}h}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial w}{\partial x_\alpha}\frac{\partial w}{\partial x_\beta}\right) + \frac{D}{2}\left[\left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2}\right)^2 + 2(1-\nu)\left(\left(\frac{\partial^2 w}{\partial x \partial y}\right)^2 - \frac{\partial^2 w}{\partial x^2}\frac{\partial^2 w}{\partial y^2}\right)\right],$$

$$\tag{3}$$

where $\sigma_{\alpha\beta}$ is the in-plane residual stress in the film at the reference state, and $D = Eh^3/12(1-\nu^2)$ is the flexural rigidity. We adopt the convention that a repeated Greek subscript implies summation over the two in-plane coordinates.

Following Cahn [6], we define the surface energy density referring to the surface area of the undeformed state, so that the surface energy density is

$$U_S = \Gamma_0 + f_{\alpha\beta}\varepsilon^s_{\alpha\beta}, \tag{4}$$

where Γ_0 is the surface energy density in the undeformed state, $f_{\alpha\beta}$ is the surface stress tensor, and $\varepsilon^s_{\alpha\beta}$ is the strain at the solid surface. Thus, the changes of strain at both top and bottom surfaces of the solid film, from Eq. (2) with $z = \pm h/2$, leads to the change of the surface energy per unit area

$$\Delta U_S = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial w}{\partial x_\alpha}\frac{\partial w}{\partial x_\beta}\right)\bar{f}_{\alpha\beta} - \frac{\partial^2 w}{\partial x_\alpha \partial x_\beta}\frac{h}{2}\tilde{f}_{\alpha\beta},$$ (5)

where $\tilde{f}_{\alpha\beta}$ equals the surface stress of the top surface (solid-air interface) minus that of the bottom surface (solid-liquid interface), and $\bar{f}_{\alpha\beta}$ is the sum of the two surface stresses.

The long-range forces between the interfaces separated by a liquid lead to the interaction energy. Following a common practice in the literature [15, 16], we take the interaction energy per unit area as a function of the separation, $U_L(H)$. Thus, from the reference state to the wrinkled state of the SOL structure, the change of the interaction energy per unit area is

$$\Delta U_L = U_L(H + w) - U_L(H).$$ (6)

The explicit expression of the interaction energy will be given later for specific interfacial forces.

LINEAR PERTURBATION ANALYSIS

Perturb the reference state with a sinusoidal deflection

$$w = q\sin(kx),$$ (7)

where q is the amplitudes and k is the wavenumber. By integrating the change of the energy density over one period ($\lambda = 2\pi/k$) of the perturbation and then dividing by the period, we obtain the free energy change per unit area, to the leading order of the perturbation amplitude,

$$\Delta\bar{U} = \frac{q^2}{4}\left[Dk^4 + Nk^2 + U_L''\right],$$ (8)

where $N = \sigma h + \bar{f}$ is the net membrane force of the solid film combining the residual stress and the surface stresses, and $U_L'' = \partial^2 U_L/\partial H^2$. The surface stresses contribute to the net membrane force. For representative values, $\bar{f}$ = 1 N/m and σ = 100 MPa, and the contribution of the surface stresses is negligible unless the film thickness is around 10 nm or less.

Equation (8) reduces to that for Euler instability of a compressed elastic film if the interaction energy and the surface stresses are ignored, and it reduces to that for a thin liquid film if the flexural rigidity and the residual stress are absent. A comparison between the first two terms in the bracket of Eq. (8) defines a length,

$$b = \left(\frac{D}{|N|}\right)^{1/2}.$$ (9)

When considering all three terms in Eq. (8), we define a dimensionless parameter,

$$\xi = \frac{DU_L''}{N^2}.$$ (10)

Figure 2 shows the normalized free energy change as a function of the wavenumber for various values of ξ. For a tensile net membrane force ($N > 0$), there are two cases: (1) If $\xi > 0$,
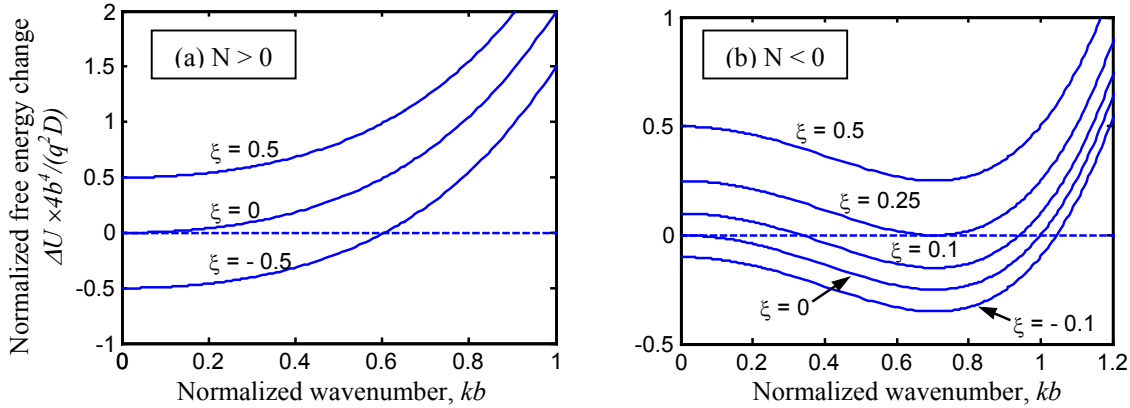
Figure 2: Normalized free energy change vs normalized wavenumber for various values of ξ.

the energy change is positive for all wavenumbers, which means the flat film is unconditionally stable; (2) If $\xi < 0$, however, the energy change becomes negative for wavenumbers less than a critical wavenumber, and thus the film is unstable and wrinkles of small wavenumbers can grow. The critical wave number is given by

$$(kb)^2 = \frac{1}{2}\left(\sqrt{1-4\xi} - 1\right). \tag{11}$$

For a compressive net membrane force ($N < 0$), there are three cases: (1) If $\xi > 0.25$, the energy change is positive for all wavenumbers, and the flat film is unconditionally stable; (2) If $0.25 > \xi > 0$, the energy change is negative for intermediate wavenumbers and the flat film is unstable. The boundaries of the unstable wavenumbers are given by

$$(kb)^2_{1,2} = \frac{1}{2}\left(1 \pm \sqrt{1-4\xi}\right); \tag{12}$$

(3) If $\xi < 0$, the energy change becomes negative for wavenumbers less than a critical wavenumber, and the critical wave number is given by
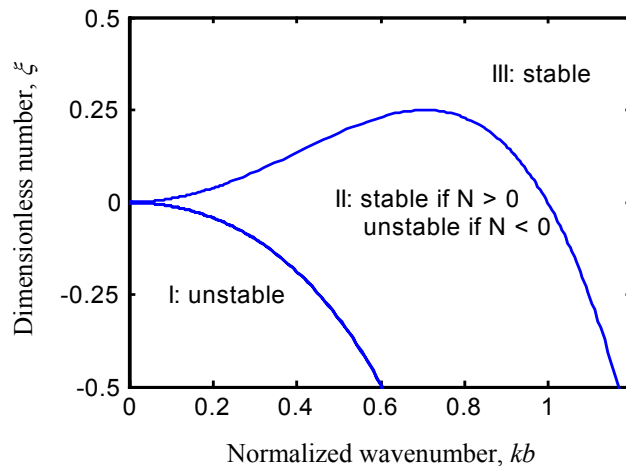
$$(kb)^2 = \frac{1}{2}\left(\sqrt{1-4\xi} + 1\right). \tag{13}$$

Figure 3: Stable and unstable regions in the ξ-kb diagram.

To summarize, Figure 3 shows the stable and unstable regions in the ξ - kb diagram. In region I, the film is unstable. In region III, the film is stable. In region II, the film is unstable if N < 0 and stable if N > 0. From Eq. (10), the sign of ξ depends on the interaction energy. In the cases of negative ξ, the flat film can be unstable even under a tensile membrane force. On the other hand, if ξ > 0.25, the structure is stable even the film is under compression.

SPECIFIC INTERFACIAL FORCES

Interfacial forces may result from various physical origins. To illustrate the effects of interfacial forces on the stability of the SOL structures, we consider several specific examples.

Photon dispersion

Phonon dispersion leads to the dispersion force or van der Waals force [16]. The interaction energy per unit area takes the form

$$U_L(H) = -\frac{A}{12\pi H^2},$$
(14)

where A is the Hamaker constant, and H is the separation between two interfaces. According to Eq. (8), an attractive dispersion force ($A > 0$) destabilizes the system and a repulsive dispersion force ($A < 0$) stabilizes the system. The effect manifests when the thickness of the liquid layer is small, in the order of 10nm or less by a rough estimation.

Electrical double layer

When a body is immersed in a polar solvent such as water, the surface charge and the diffuse layer of counter-ions constitute an electrical double layer [15, 16]. An approximate expression for the interaction energy is given by

$$U_L(H) = B\exp(-\kappa H),$$
(15)

where B and κ are positive constants depending on the number density and the valence of the cationic species, the dielectric permittivity of the solvent, the surface potential, and the temperature.

The interfacial force resulting from electrical double layers is always repulsive, and thus stabilizes the SOL structure. The effect depends on the electrolyte concentration, the surface potential, and the solvent permittivity, and decays exponentially as the thickness of the liquid layer increases. The Debye length, κ^{-1}, usually is in the order of a few nanometers.

Electron confinement

For a metal film on a substrate, it is common that a native oxide forms on top of the metal. At an elevated temperature, the metal creeps, but the oxide remains to be solid. The native oxide is typically very thin, just a few nanometers, and is subject to an in-plane residual stress due to the oxidation process. A recent model has highlighted forces of two origins in a metal film: quantum confinement and charge transfer [17, 18]. An estimate of the interaction energy, considering electron confinement only, gives an asymptotic expression [18]

$$U_L(H) = \frac{C}{H},$$
(16)

where *C* is a positive constant depending on the number of free electrons per unit volume. Equation (17) leads to a repulsive interfacial force, which tends to stabilize the SOL structure. The effect decays as the metal thickness (*H*) increases, but not as fast as for the forces due to photon dispersion and electrical double layer.

CONCLUSIONS

A linear perturbation analysis was performed to study the stability of solid-on-liquid thin film structures. The relative importance of the flexural rigidity of the solid film, the net membrane force, and the interfacial force was quantified by a dimensionless parameter ξ. Surface stresses at the solid-liquid and solid-air interfaces contribute to the net membrane force. The effects of interfacial forces were illustrated by specific interactions resulting from photon dispersion, electrical double layer, and electron confinement.

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