STABILITY OF THIN LIQUID FILMS

N. A. Dunaevskii, V. P. Reshetin,
and R. I. Soloukhin*

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In many practical problems, the thickness of liquid films spread on solid surfaces is of the order of 10-100 nm. Organic liquids form films of such thickness on molecular crystal surfaces; dyes, lubricants, etc., that wet the surface, completely or partially, form similar films [1]. Films of similar thickness are also formed under laser melting and demetallization as a result of rapid heating. Liquid film stability is an important problem for the analysis of interaction between radiation and substance (absorption, scattering, etc.), and also for ensuring high quality of film under laser processing.

Even though a macroscopic description is generally applicable, the fluid mechanics of thin films and film stability are determined by van der Waals forces (vdW), and also by electrostatic double-layer forces localized near the phase separation boundary. Models of such interactions [1-3] are used in the present paper to determine the conditions of dynamic film stability and to obtain estimates for the growth increment of small perturbations of the film surface.†

The energy density of van der Waals forces E(δ) is determined by the following [1, 2, 5]:

$$E(\delta)=\begin{cases}\dfrac{\hbar\omega_0}{16\pi^2\delta^2}, & \delta<\bar{\lambda},\\[2mm] \dfrac{\alpha_0\hbar\omega_0\bar{\lambda}}{16\pi^2\delta^3}, & \delta>\bar{\lambda}.\end{cases}$$

Here δ is the film thickness, $\hbar$ is Planck's constant, ω_0 is the characteristic frequency, $\alpha_0 \sim 1$ is a dimensionless constant, and $\lambda = 2\pi\lambda \sim 8\cdot10^{-8}$ m. The sign of ω_0 depends on the force (attraction or repulsion) that acts on the film.

An electrostatic double layer of opposite charges forms at the water—solid interface. The corresponding force of "wedging" pressure (due to the double layer) is calculated in [6]. Thus, for $\delta \geqslant k_d^{-1}$ (k_d^{-1} ~ 30 nm is the shielding length), we have

$$E(\delta) = C\exp(-2k_d\delta)/2k_d. \tag{1}$$

For univalent ions $C = 64nk_dT\tanh(\Psi_0 e/k_dT)$, where Ψ_0 is the surface potential of the solid surface and n is the ion density. Due to the large dielectric permeability of water, the electrostatic field outside the liquid film is negligible. (According to experimental data [1] for films of thickness ~$4\cdot10^{-8}$m, the density of energy of long-range forces is E(δ) ~ in δ.)

We will investigate the development of small perturbations at the surface of thin films. When the film thickness is altered by $\varepsilon = \delta - \delta_0$, where δ_0 is the film thickness in the absence of perturbations, the pressure at the free liquid surface changes by

$$\delta p = (-\alpha\Delta\varepsilon + \rho g\varepsilon + E''(\delta_0)\varepsilon)$$

where $E'' = d^2E/d\delta^2|_{\delta=\delta_0}$, and α is the surface tension coefficient at the free surface of the film. Linearizing the equations of fluid mechanics with regard to the small amplitude of perturbations (the small parameter max $\{\varepsilon/\lambda;\ \varepsilon/\delta_0\} \ll 1$, where λ is the wavelength), we can easily obtain the dispersion relationship for gravitational-capillary waves [7] modified for long-range forces:

$$\omega^2 = (ak + \alpha k^3/\rho)\,\mathrm{th}k\delta_0\ \ (a = g + E''(\delta_0)/\rho). \tag{2}$$

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*Deceased.

†The thermodynamic stability of thin films was studied systematically, for example, in [4].

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The sign and amplitude of acceleration a can vary depending on the properties of the liquid and solid. Consider some typical cases. For $\omega_0 < 0$, when the long-range force is repulsive, the film surface may be unstable for small perturbations. The condition of instability

$$g + E''(\delta_0)/\rho < 0, \tag{3}$$

enables us to determine the critical film thickness δ_* below which the film is unstable (for $\delta_0 < \delta_*$). When van der Waals forces act at the solid–liquid interface, the critical thickness δ_* is determined by

$$\delta_* = \begin{cases} \left(\dfrac{3}{8}\dfrac{\hbar|\omega_0|}{\pi^2\rho g}\right)^{1/4}, & \delta_* < \bar{\lambda}, \\ \left(\dfrac{3}{4}\dfrac{\hbar|\omega_0|\alpha\bar{\lambda}}{\pi^2\rho g}\right)^{1/5}, & \delta_* > \bar{\lambda}. \end{cases}$$

Figure 1 shows the variation of the instability increment γ with wave number k. When $k_{\max} = (|a|\rho/2\alpha)^{1/2}$ and $k\delta_0 \ll 1$, the instability increment reaches the maximum

$$\gamma_{\max} = \operatorname{Im}\omega = (\delta_0\rho/\alpha)^{1/2}a/2. \tag{4}$$

For a film with parameters $\delta_0 \sim 10^{-6}$ cm, $\rho \sim 2$ g/cm^3, $\alpha \sim 20$ erg/cm^2, the maximum instability increment is of the order of $\gamma_{\max} \sim |a|/3g$ sec for $k_{\max} \sim 7\ (|a|/g)^{1/2}$ cm^{-1}. For example, when $\omega_0 \sim 10^{14}$ sec^{-1} and $\delta_0 \sim 10^{-6}$ cm, we have $|a|/g \sim 3\hbar|\omega_0|/(8\pi^2\delta_0^4\rho g) \sim 10^7$, $\gamma_{\max}^{-1} \sim 0.3$ μsec and $k_{\max}^{-1}$ 1 μm. When the condition of instability (3) is satisfied, the liquid pressure decreases in the direction of the solid surface. The force that develops as film thickness changes causes the amplitude of perturbations to increase. Capillary forces at the free surface are sufficient to stabilize shortwave perturbations with $k > \sqrt{2}\,k_{\max}$.

When $a > 0$ ($\omega_0 > 0$, $\omega_0 < 0$), the "gravitational"-capillary waves are stable; by preserving the term "gravitational"-capillary waves, we would like to emphasize that for $|a| \gg g$ the role of "gravitational" forces are played by van der Waals forces or double-layer forces. The dispersion relationship is simplified, $\omega = \sqrt{a\delta_0}k$, when the following inequalities are satisfied: $a \gg g$, and $k \gg (\rho g/\alpha)^{1/2}$. The wave phase velocity in a thin liquid film is determined by the long-range forces near the solid–liquid interface.

When the heating is inhomogeneous, the "gravitational"-capillary waves at the surface of liquid films may be unstable even if the condition of instability (3) is not satisfied [8]. The substitution $g \to a$ should be made in the equations developed by Levchenko and Chernyakov [8] in the calculations of the instability increment and threshold. This substitution can lead to significant numerical differences. The ratio of instability thresholds with and without taking into account the van der Waals forces when $k\delta_0 \ll 1$ equals a/g. The dependence of the instability increment on a is more complicated [8].

We present calculations of acceleration a for liquid films whose steady-state properties are described in [1, 9]. For $\omega_0 > 0$ and complete wetting, volatile liquids form, on a dry solid surface, films of thickness

$$\delta_{01} = \left(\frac{\hbar\omega_0\bar{\lambda}}{6\pi^2\rho g}\right)^{1/5}, \tag{5}$$

which is of the order of 30 nm. In the derivation of Eq. (5) it was assumed that $\Delta = \alpha_{SO} - \alpha_{SL} - \alpha = 0$, where α_{SO}, α_{SL}, and α are the surface tension coefficients for the following interfaces: dry solid surface–air, solid surface–liquid, and liquid–vapor; Δ determines the spreading capability of the film. When the film is spreading on a wet foundation, we have [1]

$$\delta_{02} = [\hbar\omega_0\bar{\lambda}/16\pi^2\rho g]^{1/5}. \tag{6}$$

For $0 < \Delta < 1$ the film thickness is [8]

$$\delta_{03} = [\hbar\omega_0/64\pi^3\Delta]^{1/2} \quad (\delta_{03} < \bar{\lambda}); \tag{7}$$

and when electrostatic forces (1) are applied [1]

$$\delta_{04} = (1/2k_d)\ln(C/\Delta k_d). \tag{8}$$

Substituting Eqs. (5)-(8) into (2), we obtain

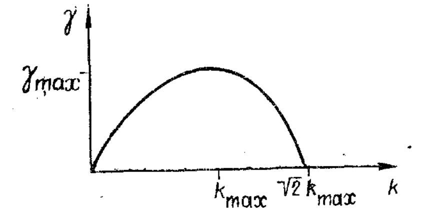

Fig. 1

$$a=\begin{cases}2.5g, & \delta=\delta_{01},\\ 5g, & \delta=\delta_{02},\\ \left(\dfrac{3\hbar\omega_0}{8\pi^2\delta_{03}^4\rho g}+1\right)g, & \delta=\delta_{03},\\ \left[\dfrac{2k_dC}{\rho g}\exp(-2k_d\delta_{04})+1\right]g, & \delta=\delta_{04}.\end{cases}$$

When $\delta = \delta_{03}$ and $\delta = \delta_{04}$, the acceleration a exceeds the gravitational acceleration by an order of magnitude. Thus the attractive van der Waals or double-layer forces are stabilizing, which significantly increases the instability threshold of nonuniformly heated liquid films.

The growth of small perturbations at the liquid surface can cause breakdown of the liquid film at the nonlinear stage of instability. The formation of an incipient pattern on liquid films of melt obtained by laser melting is also of importance, since it determines subsequent scattering and absorption at the surface.

It should be noted that the scale of the long-range forces, as a rule, does not exceed ~$5\cdot10^{-8}$ m. Exceptions are polymer melts with a high molecular weight ($M \sim 10^6$) for which the range of action of the force at the interface between two phases is ~10 μm, and in some cases ~1 mm [1]. This difference should be taken into account in estimates of the instability increment (4).

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