Effect of van der Waals Interactions on the Fingering Instability of Thermally Driven Thin Wetting Films

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Received June 19, 2000. In Final Form: April 5, 2001

The effect of van der Waals forces on the fingering instability of a thin liquid film wetting a solid substrate and moving under the action of a thermal gradient applied along the film is investigated. Both horizontal films and films climbing a vertical wall are considered. A linear stability analysis shows the stabilizing action of the van der Waals forces. The effect of gravity forces can be either stabilizing or destabilizing, depending on the relative strength of the effects of gravity and surface-tension gradients. A weakly nonlinear analysis of the unstable wetting front shows that the frontal evolution is described by the Kuramoto–Sivashinsky equation, revealing the possibility of chaotic behavior of fingerlike patterns near the instability threshold.

1. Introduction

The motion and stability of a three-phase (gas–liquid–solid or liquid–liquid–solid) contact line plays an important role in many processes encountered in modern technologies, such as printing, dyeing, coating, separation processes in chemical engineering such as distillation, absorption in packed columns, and so forth, cleaning of oil films from water surfaces, oil recovery from porous rocks, drying and cleaning in the electronics and microprocessor industries, and others. It is also a challenging fundamental problem that has been attracting wide attention during the past decade and is still far from being completely resolved.[1–4] Its complexity (and challenge for fundamental science) is in the coupling between the macroscopic hydrodynamical processes governing the motion of a liquid film and the microscopic processes connected with the intermolecular forces controlling the creation of new interfaces in the moving contact line region.

If a thermal gradient is applied along a solid surface supporting a liquid film, the latter starts to flow because of the surface-tension gradient at the film's free surface. Such thermally driven liquid films have been recently attracting a great deal of attention because of the importance of this mechanism for the control of liquid flow in microfabricated devices.[5–8] A wetting liquid film spreads over the solid surface under the simultaneous action of van der Waals forces and the surface-tension gradient. Such thermally assisted spreading can lead to the propagation of a stationary wave consisting of a nearly flat liquid film, a thin precursor film with a decaying thickness, governed by the van der Waals forces, and a narrow intermediate region associated with a moving "contact line". This propagating contact line is often unstable exhibiting the formation of growing fingers.[9–11] This phenomenon is schematically shown in Figure 1. A similar instability is observed in gravity-driven films (see refs 12–14 and references therein) as well as in films with spreading surfactants.[17]

The linear stability analysis performed in refs 10–14 took into account the presence of the precursor film with a fixed thickness as an independent parameter which is assumed to be known from experiments. The evolution of this precursor film is governed by van der Waals forces. In the present paper, we focus on the investigation of the effect of van der Waals forces on the dynamics of the precursor film and its coupling to the fingering instability of the contact line region of a thermally driven wetting film. We shall demonstrate that the van der Waals forces have a stabilizing effect on the fingering instability as has been speculated in refs 15 and 16.

2. Governing Equation

Consider a liquid film supported by an inclined solid substrate with a constant thermal gradient, β, applied downward along the substrate. Because of the dependence of the film surface tension σ on temperature T, which is assumed to be linear, $\sigma = \sigma_0 - \sigma_T(T - T_0)$, with σ_T = const > 0 which is the case for most liquids, the film is spreading upward, in the direction opposite to the direction of the applied thermal gradient. Because in experiments liquid

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10.1021/la000859u CCC: $20.00
Published on Web 05/31/2001

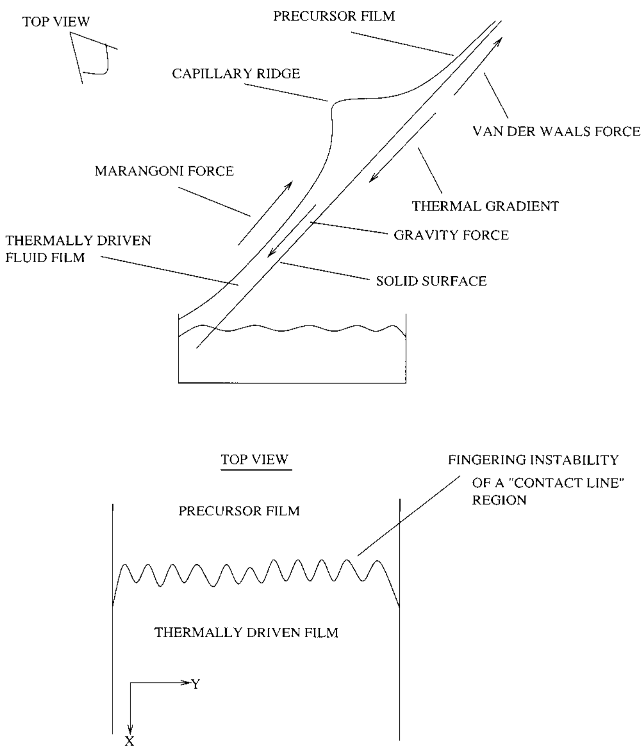

Figure 1. Schematic representation of a thermally driven liquid film and its fingering instability.

films are usually very thin (a few micrometers thick), following the suggestion in ref 10, we neglect the temperature variation across the film, thereby assuming the film surface temperature to be equal to that of the solid substrate. The effect of molecular forces in the precursor film can be described by the van der Waals potential ϕ, which, in the long-wave approximation, can be taken as $\phi = A_0/h^3$, where h is the local film thickness and $A_0 = A/(6\pi)$ is the Hamaker constant. The evolution of the film is described by[18]

$$\mu h_t - \sigma_T\beta h h_x + \rho g_{\|} h^2 h_x + \nabla\cdot\left[\frac{1}{3}h^3\nabla(-\rho g_{\perp} h + \sigma_0\nabla^2 h + A_0 h^{-3})\right] = 0 \quad (1)$$

where μ and ρ are the liquid viscosity and density, respectively, $g_{\|} = g \sin \theta$, $g_{\perp} = g \cos \theta$, where g is the acceleration of gravity, and θ is the inclination angle of the solid substrate ($\theta = 0$ corresponds to a horizontal film); x is the coordinate along the substrate whose direction is chosen so that the film propagates in the direction of negative x.

Introducing the scaling $x \to \lambda x$, $t \to \tau t$, $h \to H_0 h$, where H_0 is the liquid film thickness at $x \to \infty$, far from the leading edge, and

$$\lambda = \left(\frac{\sigma_0 H_0^{\,2}}{3\beta\sigma_T}\right)^{1/3} \qquad \tau = \frac{\lambda\mu}{\beta H_0 \sigma_T} \quad (2)$$

one rewrites eq 1 in the dimensionless form:

$$h_t + (Kh - 1)hh_x + \nabla\cdot[h^3\nabla(-Gh + \nabla^2 h + Vh^{-3})] = 0 \quad (3)$$

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Equation 3 contains three dimensionless parameters, G, K, and V:

$$G = \left(\frac{\rho g_{\perp} H_0^{\,2}}{\sigma_0}\right)\left(3\beta H_0\frac{\sigma_T}{\sigma_0}\right)^{-2/3} \qquad K = \frac{\rho g_{\|} H_0}{\beta\sigma_T}$$
$$V = \left(\frac{A}{6\pi\sigma_0 H_0^{\,2}}\right)\left(3\beta H_0\frac{\sigma_T}{\sigma_0}\right)^{-2/3} \quad (4)$$

The parameter G characterizes the effect of hydrostatic pressure normal to the substrate relative to the effect of capillary and Marangoni (surface tension gradient driven) forces, the parameter K characterizes the strength of the gravity-induced flow along the substrate relative to the Marangoni flow ($K = 0$ for a horizontal film), and the parameter V characterizes the effect of the van der Waals forces relative to surface-tension forces. Taking $A = 10^{-19}$ J, $g = 9.81$ m/s^2, and $\theta = 45°$, for a 2 μm thick film of a silicon oil with $\rho = 0.9$ g/cm^3, $\sigma = 20$ dyn/cm, and $\sigma_T = 0.07$ dyne/(cm K), with the applied thermal gradient $\beta = 4$ K/cm, one obtains $V = 1.6 \times 10^{-4}$, $G = 3.1 \times 10^{-3}$, and $K = 0.46$. Note that none of the parameters V, G, or K depends on the viscosity of the film; the latter affects only the characteristic time scale of the film dynamics but neither the conditions of the fingering instability nor its characteristic spatial scale.

3. Uniformly Spreading Thermally Driven Films

We are interested in a solution of eq 3 describing a uniformly spreading thermally driven film. This solution has the shape of a front, $h(x + Ut)$, uniformly moving from right to left with a constant speed U. Far to the right, as $x \to \infty$, $h \to H_0$. Far to the left, as $x \to -\infty$, one can consider one of two boundary conditions: (i) $h \to b = \text{const} > 0$ and (ii) $h \to 0$. Condition i corresponds to the existence of a precursor film of constant thickness b. This case was considered in refs 10–14; the precursor film thickness b is an additional parameter which is assumed to be known from experiments. It is assumed in this case that the characteristic time of the precursor film formation is much smaller than that of the spreading of the thermally (or gravitationally) driven film. Condition ii corresponds to a precursor film whose thickness gradually decays to zero far from the contact line region. In this case, it is assumed that the characteristic time of the precursor film formation (governed by the van der Waals forces) is of the same order of magnitude as that of the driven film spreading under the action of Marangoni or gravity forces. The conditions of the fingering instability can thus be expected to depend strongly on the interplay between the van der Waals forces and thermocapillary forces driving the film spreading. Note that because the formation of the precursor film is a slow process, both cases usually correspond to rather thin films or to films on inclined planes whose thermocapillary flow rate is retarded by viscosity or gravity.

Substitute the anzatz $h(x + Ut)$ in eq 3 and integrate from $-\infty$ to ∞ to obtain the spreading velocity of the driven film as

$$U = \frac{1}{2}(1 + b) - \frac{K}{3}(1 + b + b^2) \quad (5)$$

For $b = 0$, one obtains $U = 1/2 - K/3$. One can see that the solution in the form of a uniformly spreading film exists only if $K < 1.5$ or, in dimensional variables, if $3\beta\sigma_T > 2\rho g_{\|} H_0$. This is the condition for the net mass flux in the liquid film in the direction of its motion to be positive, that is, for the surface tension gradient induced driving force to be sufficient to overcome gravity and to pull the film upward. For $b = 0$ and $K = 0$ (horizontal film), one obtains $U = \beta H_0 \sigma_T / 2\mu$.

Consider now the asymptotic behavior of the precursor film far ahead of the contact line region. The equation for the stationary wave $h_0(\xi)$ (where $\xi = x + Ut$) reads

$$(U + Kh_0^{\,2} - h_0)h_{0\xi} + [h_0^{\,3}(-Gh_0 + h_{0\xi\xi} + Vh_0^{\,-3})_\xi]_\xi = 0 \quad (6)$$

The asymptotic behavior of the precursor film is described by the equation

$$Uh_{0\xi} - \left(\frac{3V}{h_0}h_{0\xi}\right)_\xi = 0 \quad (7)$$

Integration of (7) with the boundary condition $h \to b$ as $\xi \to -\infty$ gives

$$h_0 = \frac{b}{1 - C_1 \exp[bU\xi/(3V)]} \quad (8)$$

and the boundary condition $h \to 0$ as $\xi \to -\infty$ gives

$$h_0 = -\frac{1}{C_2 + U\xi/(3V)} \quad (9)$$

where C_1 and C_2 are integration constants to be determined by matching with the solution in the outer region.

One can see that if the formation of the precursor film with a constant thickness ahead of the contact line region is much faster than the thermally driven spreading, the film profile approaches the constant thickness exponentially. If the formation of the precursor film governed by the van der Waals forces occurs on the same time scale as the film spreading caused by the surface-tension gradient, the precursor film thickness decreases algebraically as $1/\xi$.

In the following sections, we will be interested in the case when the characteristic time of the precursor film formation governed by the van der Waals forces is comparable to the characteristic time of spreading caused by the surface tension gradient driven forces, that is, the case described by the boundary condition $h \to 0$ as $\xi \to -\infty$. In this case, the interplay between the van der Waals forces and the Marangoni forces is most important.

On the other side of the film, far from the contact line region on the right, as $x \to \infty$, the film profile approaches the constant value $h = 1$ in an oscillatory manner (see refs 10 and 11), which can be found by linearizing eq 6 around $h = 1$ and solving the corresponding linear equation for $\tilde{h} = h - 1$. One finds that as $\xi \to \infty$ (for the case $b = 0$, $U = 1/2 - K/3$) $h \sim 1 + Ce^{\lambda_r \xi}\cos(\lambda_i \xi)$, where $\lambda_r < 0$ and λ_i are the real and imaginary parts of two complex conjugate roots of the cubic equation

$$\lambda^3 - (3V + G)\lambda - 1/2 + 2K/3 = 0 \quad (10)$$

In the following sections, we shall perform the linear stability analysis of the stationary wave solutions $h_0(x + Ut)$ of eq 3 for two cases: (i) when the film spreads along a horizontal surface and (ii) when the film climbs up a vertical wall.

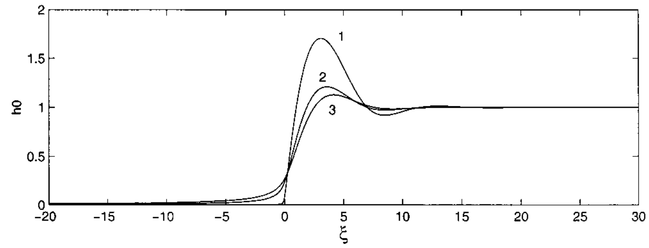

Figure 2. Shape of a uniformly propagating thermally driven film corresponding to the solution of eq 6 for $G = 0.001$ and (1) $V = 0.0006$, (2) $V = 0.02$, and (3) $V = 0.04$.

4. Linear Stability of a Uniformly Spreading Thermally Driven Film

To study the linear stability of the solution $h_0(\xi)$ of eq 6 corresponding to the stationary spreading wave, we consider the perturbations $\tilde{h} = h - h_0$ in the form

$$\tilde{h} = u(\xi, t)\exp(\omega t + iky) \quad (11)$$

where k is the wavenumber of harmonic perturbations in the transverse direction y along the contact line. Substituting (11) in (3), one obtains the following eigenvalue problem for the perturbations u:

$$\omega u + \frac{d}{d\xi}L_0 u + k^2 L_2 u + k^4 h_0^{\,3} u = 0 \quad (12)$$

where

$$L_0 = f_3 \frac{d^3}{d\xi^3} + f_1 \frac{d}{d\xi} + f_0 \quad (13)$$

$$L_2 = -\frac{d}{d\xi} f_3 \frac{d}{d\xi} - f_3 \frac{d^2}{d\xi^2} - f_1 \quad (14)$$

with

$$f_3 = h_0^{\,3} \qquad f_1 = -\frac{3V}{h_0} - Gh_0^{\,3} \qquad f_0 = \frac{1}{2}h_0 - 2U + \frac{12V}{h_0^{\,2}}h_{0\xi} \quad (15)$$

We consider the cases of a film spreading on a horizontal substrate and the case of a film climbing along a vertical wall separately.

4.1. Horizontal Film. In the case of a horizontal film, $K = 0$ and $U = 1/2$. Figure 2 shows numerical solutions of eq 3 obtained by means of a finite difference method in a co-moving frame ($\xi = x + Ut$) in a large interval $\xi \in [-L_1, L_2]$ with the boundary conditions $h_\xi = h_{\xi\xi\xi} = 0$ for $\xi = L_2 > 0$ and $h = 6V/L_1$, $h_\xi = 6V/L_1^{\,2}$ for $\xi = -L_1 < 0$. We have used a semi-implicit Crank–Nicolson discretization scheme which appears to be highly stable and did not produce any divergence in higher derivatives.

The eigenvalue problem (12) has been solved numerically, by using the numerical solution for h_0 described above, that is, by discretizing eq 12 on the interval $[-l_1, l_2] \in [-L_1, L_2]$, and solving the eigenvalue problem for the corresponding system of linear equations numerically.

Because the original problem is formulated in an infinite region and the eigenvalue problem can be solved numerically only in a finite region, we need to choose appropriate boundary conditions for the numerical solution of the eigenvalue problem. In the infinite region, the natural boundary conditions correspond to the decay of the perturbation u and its derivatives far from the contact

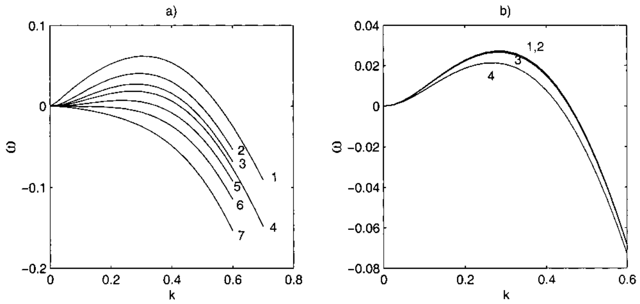

Figure 3. (a) Dispersion curves $\omega(k)$ for the perturbations of thermally driven spreading films for $G = 0.001$ and (1) $V = 0.0006$, (2) $V = 0.001$, (3) $V = 0.002$, (4) $V = 0.004$, (5) $V = 0.01$, (6) $V = 0.02$, and (7) $V = 0.04$. (b) Dispersion curves $\omega(k)$ for the perturbations of thermally driven spreading films for $V = 0.002$ and (1) $G = 0.0$, (2) $G = 0.001$, (3) $G = 0.01$, and (4) $G = 0.1$.

line region. In a *finite* computational region, appropriate boundary conditions are those which mimic the asymptotic behavior of the perturbation u at $\pm\infty$. Obviously, this behavior also exhibits the decay of the perturbation and its derivatives. Therefore, the boundary conditions for the perturbation u and its derivatives should be uniform, that is, $c_1^{(0)}u + c_1^{(1)}u_\xi + c_1^{(2)}u_{\xi\xi} + ... = 0$ for $\xi = -l_1$ and $c_2^{(0)}u + c_2^{(1)}u_\xi + c_2^{(2)}u_{\xi\xi} + ... = 0$ for $\xi = l_2$. The coefficients $c_{1,2}^{(i)}$ should be chosen in such a way that the perturbation u is affected by the *finite* length of the computational domain as little as possible. The mode which is most vulnerable to this effect is the zero eigenmode $u = h_{0\xi}$ corresponding to $\omega = k = 0$ which is present because of the translational invariance of the problem. This mode is also crucial for the computation of the nonlinear behavior of the system near the instability threshold where the instability is long-wave. Therefore, we have chosen the coefficients $c_{1,2}^{(i)}$ so that the zero eigenmode $u = h_{0\xi}$, whose asymptotic behavior at the left end of the interval ($\xi = -l_1$) is $u \sim 3V/(U\xi^2)$ and at the right end of the interval ($\xi = l_2$) is $u \sim \exp(\lambda\xi)$, with λ determined by eq 10, satisfies these boundary conditions, namely,

$$u_\xi - \frac{2}{l_1}u = u_{\xi\xi\xi} - \frac{4}{l_1}u_{\xi\xi} = 0 \qquad \xi = -l_1 \tag{16}$$

$$\begin{aligned} u_{\xi\xi} + 2\lambda_r u_\xi + ({\lambda_r}^2 + {\lambda_i}^2)u &= \\ u_{\xi\xi\xi} + 2\lambda_r u_{\xi\xi} + ({\lambda_r}^2 + {\lambda_i}^2)u_\xi &= 0 \qquad \xi = l_2 \end{aligned} \tag{17}$$

The interval $[-l_1, l_2]$ has been chosen so that the basic solution h_0 essentially coincides with its asymptotic behavior at the ends of the interval. We have checked, by significantly changing the interval $[-l_1, l_2]$, that the effect of its length on the result of the stability analysis (the dispersion curve $\omega(k)$) was negligible (because the asymptotic behavior has been achieved at the ends of the interval).

A conservative discretization scheme, described in Appendix A, has been used. The resulting eigenvalue problem has been solved by means of MATLAB software, and the behavior of the largest eigenvalue $\omega(k)$ with the variation of the parameters V and G has been studied. The instability was found to be monotonic. Figure 3a shows the dependence $\omega(k)$ for $G = 0.001$ and selected values of V, and Figure 3b presents the dependence $\omega(k)$ for $V = 0.002$ and selected values of G.

One can see, for example, that the thermally driven film with $G = 0.001$ and $V < 0.0188$ is linearly unstable with respect to transverse perturbations with a finite wavenumber, which results in the formation of a periodic cellular structure at the moving contact line region (fingering instability). The wavelength of the most unstable mode depends on the parameters V and G. One can also see that the dispersion curves for $G < 0.01$ are practically the same as for $G = 0$. The decrease of V and the increase of G promote the film instability. This shows the interplay between the capillary pressure and viscous, gravity, and van der Waals forces. As has been shown in refs 10 and 11, the primary cause of the fingering instability is the formation of a capillary ridge in the contact line region (see Figure 2: (a) film is unstable, (b) film is neutrally stable, and (c) film is stable). Gravity tends to flatten the film and to diminish the ridge height, and van der Waals forces *pull* the film toward the region of smaller thickness, thus also tending to flatten it. On the other hand, the applied thermal gradient *pushes* the film, thus promoting the ridge formation in the contact line region. The increase of the film thickness decreases the drag effect of the viscous forces and promotes ridge formation.

One can see also that there exists a threshold value $V^*(G)$ at which the fingering instability occurs. Because of the weak dependence of the dispersion curves on G for small G corresponding to realistic physical situations, one can set $G = 0$ and obtain a single threshold value for the fingering instability, $V_{cr} = V^*(0)$. We have computed the threshold value V_{cr} in the following way. For small wavenumbers k, the perturbation growth rate $\omega(k) = \omega_2(V, G)k^2 + \omega_4(V, G)k^4 + ... \approx \omega_2(V, 0)k^2 + \omega_4(V, 0)k^4 + ...$ The threshold value V_{cr} corresponds to $\omega_2(V, 0) = 0$. Expanding $u = u_0 + k^2u_2 + ...$, one obtains from eq 12 the following problem for u_2:

$$\frac{d}{d\xi}L_0u_2 \equiv L_0'u_2 = -\omega_2u_0 - L_2u_0 \tag{18}$$

whose solvability condition gives

$$\omega_2 = -\frac{\int_{-\infty}^{\infty} L_2u_0u_0^* d\xi}{\int_{-\infty}^{\infty} u_0u_0^* d\xi} \tag{19}$$

Here, u_0 is the null eigenvector of L_0' corresponding to $\omega = 0$, and u_0^* is the conjugate null eigenvector which can easily be found by solving the described eigenvalue problem with the transposed matrix.

Using (4), one obtains $V_{cr} = 0.0188$ (for $G = 0$). This allows one to get a relation between the physical parameters which gives the threshold for the fingering instability of a thermally driven horizontal film to occur. Namely, the instability occurs if

$$\frac{A}{\sigma^{1/3}{H_0}^{8/3}(\beta\sigma_T)^{2/3}} \leq 0.737 \tag{20}$$

The condition (20) allows one to predict and control the fingering instability of a thermally driven horizontal film on the basis of physically measurable and controllable quantities (film thickness H_0 and applied thermal gradient β) and physical properties of the system (surface tension σ, Hamaker constant A, and the derivative of the surface-tension dependence on temperature σ_T). For the values of physical parameters typical of experiments on thermally driven films,[19,20] one gets $A\sigma^{-1/3}{H_0}^{-8/3}(\beta\sigma_T)^{-2/3}$

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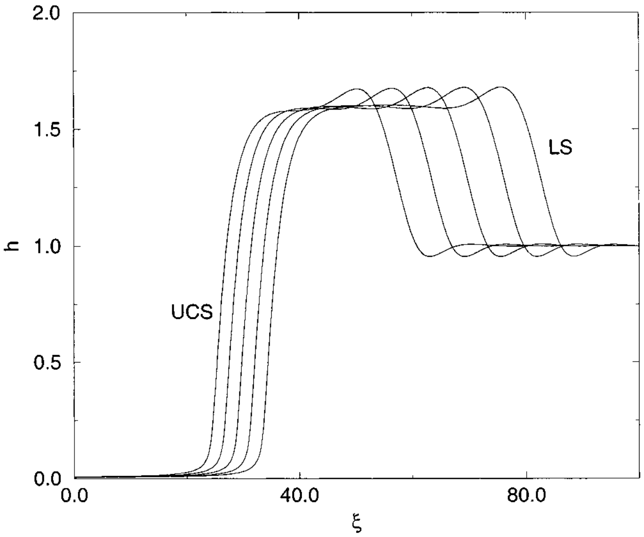

Figure 4. Double-shock structure of a widening capillary ridge of a thermally driven film: solution of eq 3 for $V = 0.01$, $K = 0.6$. Successive curves correspond to equal time intervals $\Delta t = 200$. UCS, undercompressive shock; LS, Lax shock.

≈ 0.02 which is far beyond the instability threshold. This explains the well-developed fingering usually observed in experiments.

4.2. Vertical Film. Consider now a liquid film climbing up a vertical plane under the action of a surface-tension gradient induced by the thermal gradient applied down the plane. As already mentioned, solutions of eq 3 in the form of a uniformly propagating stationary wave exist for $K < 1.5$; otherwise, gravity is too strong and pulls the fluid down and therefore does not allow the film to climb up and to form a uniformly propagating wave. Note also that because, as shown above, the gravity component normal to the film surface is not important, all conclusions about vertical films are also true for a film climbing up an inclined surface, except for those with very small slopes.

We have performed a linear stability analysis of the stationary wave solution of eq 3 in this case which is completely analogous to that described in the previous subsection for the case of a horizontal film. However, unlike the case of a horizontal film, we have observed two types of instability. The first type is observed when the parameter K is not large: one observes the usual transverse fingering instability of a uniformly propagating film with a capillary ridge in the contact line region (see Figure 2). The second type is found for larger K: one no longer observes a uniformly propagating film, but the ridge region starts to widen forming a structure containing two shocks, the so-called "undercompressive shock", near the precursor film, and the "Lax shock", between the almost flat ridge and the uniform film far from the contact line region (see Figure 4). These two shocks move with different speeds so that the ridge region constantly widens (see Figure 4) and one never observes a uniformly traveling film with an unchanged shape. This double shock structure is rather robust and was observed for different initial and boundary conditions. (As initial conditions, we used arctangent-shaped functions as well as linear functions, with values at the ends of the computational interval close to those prescribed by the asymptotic behavior. Different boundary conditions were also chosen in such a way that the asymptotic solution would satisfy them, for example, $h = 3V/(UL_1)$, $h_\xi = 3V/(UL_1^2)$ at the left end and $h = 1$, $h_\xi = 0$ at the right end or $h - L_1 h_\xi = h_\xi - (L_1/2)h_{\xi\xi} = 0$ at the left end and $h_\xi = h_{\xi\xi\xi} = 0$ at the right end.) The double-shock structure of a widening capillary ridge of a thermally driven fluid film climbing along an inclined solid surface was observed in refs 21 and 22, and the theory of such two-shock structures has been developed in refs 21, 23, and 24.

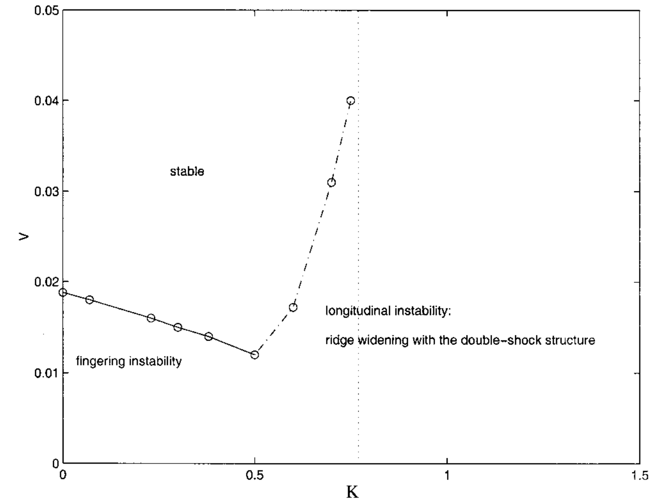

Figure 5. Stability regions for a thermally driven film climbing along a vertical solid surface.

The stability diagram in the (K, V) parameter plane is shown in Figure 5. The solid line depicts the boundary of the fingering instability of a uniformly propagating film with a contact line region, whose shape is similar to those shown in Figure 2. One can see that the threshold value V_{cr} decreases with increasing K. This is the result of the interplay between van der Waals and gravity forces. As discussed in the previous subsection, larger van der Waals forces (growing V) stabilize the thermally driven film because they push the fluid into the region of the precursor film thus diminishing the height of the bump. In the case of a vertical film, gravity pulls the fluid downward, which also diminishes the bump height. Thus, because of the additional stabilizing action of gravity forces, the fingering instability occurs at $V_{cr}(K)$ which is smaller than $V_{cr}(0) = 0.188$, corresponding to a horizontal film. For $0.5 < K < 0.76$, the effect of gravity is so strong that it drives the longitudinal instability of a thermally driven film and leads to the formation of the double-shock structure shown in Figure 4. The boundary of this instability is shown in Figure 5 by the dashed line. For $K > 0.76$, the film climbing up the vertical wall, with a precursor film ahead (as shown in Figure 2), is always unstable with respect to formation of the double-shock structure.

For $0.012 < V < 0.0188$, the film is stable only in a finite interval of K. Thus, with the decrease of K (e.g., the decrease of the slope of the solid surface along which the film is climbing) one observes the fingering instability, and with the increase of the slope (increase of K) one will see that the film will become unstable with respect to the double-shock structure formation. For $K > 0.76$, there is no stable vertical film climbing uniformly under the action of the thermal gradient.

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5. Nonlinear Analysis

It is interesting to study the nonlinear evolution of the fingering instability of a thermally driven film. For values of V close to $V_{cr}(K)$ on the solid line of Figure 5, the instability is *long-scale*, that is, it occurs for small wavenumbers, $k < k* = O(\epsilon) \ll 1$, where $k*$ is the wavenumber corresponding to $\omega = 0$ (see Figure 3), and $\epsilon^2 \sim V - V_{cr}(K)$. One can then employ a long-wave analysis and consider perturbations of a uniformly propagating film profile in the form

$$h = h(\xi + \epsilon^2\phi(Y, T)) \tag{21}$$

where $\xi = x + Ut$, $Y = \epsilon y$ is the large-scale transverse coordinate, $T = \epsilon^4 t$ is the slow time, and $\phi(Y, T)$ is a function describing the shape of contact line perturbations.

Substituting (21) into eq 3, one obtains, to order $O(\epsilon^6)$ of the perturbation theory, the Kuramoto−Sivashinsky (KS) equation for $\phi(Y, T)$, describing the nonlinear evolution of the fingering instability:

$$\phi_T + \gamma\phi_{YY} + \chi\phi_{YYYY} + \nu{\phi_Y}^2 = 0 \tag{22}$$

where

$$\gamma = -\frac{1}{2}\frac{\partial^2\omega}{\partial k^2} \qquad \chi = -\frac{1}{24}\frac{\partial^4\omega}{\partial k^4}$$

can both be computed from the dispersion relation, and the nonlinear coefficient ν is obtained in terms of the basic solution $h_0(\xi)$ by means of our bifurcation analysis code written using the Mathematica symbolic computations package. The expression for ν is given in Appendix B. For example, in the case of a horizontal film, $K = 0$, eq 22 reads

$$\phi_T = 25.5(V - V_{cr})\phi_{YY} - 0.9\phi_{YYYY} + 0.0027{\phi_Y}^2 \tag{23}$$

Note that all terms in this equation are $O(\epsilon^6) = O((V - V_{cr})^3)$. Because the governing eq 1 was itself derived in the long-wave approximation for $h_x = O(\delta) \ll 1$, with terms $O(\delta^2)$ in the averaged velocity profiles being uniformly omitted, eq 22 is asymptotically correct for $(h_x)^2 \ll (V - V_{cr})^3 \ll 1$. Note also that, because of the translation invariance of the problem, eq 22 contains only derivatives of ϕ. An equation similar to (22) was recently obtained for the nonlinear evolution of the fingering instability of a gravity-driven contact line with a precursor film.[25]

Equation 22 is known to exhibit cellular solutions resembling fingers forming at the unstable contact line of a thermally driven film. Depending on the values of the coefficients, this equation is also known to exhibit complex oscillations, traveling and modulated waves as well as chaotic spatiotemporal dynamics, in which the birth and death of cells (fingers) occur in a chaotic manner.[26−28] It is important that eq 22 can be reduced to a standard form by appropriate scaling transformations so that there is only one bifurcation parameter, namely, the *dimensionless length* of the region, L, where the instability develops. According to the numerical computations performed in ref 27, chaotic behavior would be observed for $L > 34.05$. In our case, this corresponds to the domain $\sim 45.6(V - V_{cr})^{-0.5}$ which for the chosen parameter values and the supercriticality $V - V_{cr} \sim 1 \div 10\%$ corresponds to an actual physical domain which is approximately several meters long along the contact line! This is due to the fact that eq 22 describes the system behavior near the bifurcation point where the growing perturbations are long. Experiments with thermally driven contact lines made so far corresponded to conditions far from the bifurcation point $V = V_{cr}$ where the system dynamics is not described by eq 22. On one hand, this explains why the fingering dynamics observed in experiments differs strongly from the KS dynamics. On the other hand, our computations of the critical conditions for the fingering instability with van der Waals forces and the computed coefficients of eq 22 may encourage experiments near the bifurcation point in order to verify possible complex KS dynamics of the fingering instability of a thermally driven contact line.

Acknowledgment. We are grateful to Professor A. A. Nepomnyashchy and Dr. L. Braverman for useful discussions. We also would like to thank the anonymous reviewers for many helpful suggestions. This work was supported by the Israel Science Foundation.

Appendixes

A. Discretization Scheme for the Linear Eigenvalue Problem. A conservative discretization scheme, described in Appendix A, has been used, such that, for example,

$$\frac{d}{d\xi}[f_3u'''] = \frac{1}{\Delta}[f_3^{(j+1/2)}u'''_{j+1/2} - f_3^{(j-1/2)}u'''_{j-1/2}]$$

where j denotes the node value of the function on the mesh and Δ is the spatial step. Equation 12 yields the following system of equations with a five-diagonal matrix:

$$A_ju_{j-2} + B_ju_{j-1} + C_ju_j + D_ju_{j+1} + E_ju_{j+2} = \omega u_j \tag{A1}$$

where $(A_j, B_j, C_j, D_j, E_j) = (A_j^{(0)}, B_j^{(0)}, C_j^{(0)}, D_j^{(0)}, E_j^{(0)}) + k^2(0, B_j^{(2)}, C_j^{(2)}, D_j^{(2)}, 0) + k^4(0, 0, f_3^{(j)}, 0, 0)$ and

$$A_j^{(0)} = \frac{1}{\Delta^4}f_3^{(j-1/2)}$$

$$B_j^{(0)} = \frac{1}{\Delta^4}(-f_3^{(j+1/2)} - 3f_3^{(j-1/2)}) + \frac{1}{\Delta^2}f_1^{(j-1/2)} - \frac{1}{2\Delta}f_0^{(j-1)}$$

$$C_j^{(0)} = \frac{3}{\Delta^4}(f_3^{(j+1/2)} + f_3^{(j-1/2)}) - \frac{1}{\Delta^2}(f_1^{(j+1/2)} + f_1^{(j-1/2)})$$

$$D_j^{(0)} = \frac{1}{\Delta^4}(-3f_3^{(j+1/2)} - f_3^{(j-1/2)}) + \frac{1}{\Delta^2}f_1^{(j+1/2)} + \frac{1}{2\Delta}f_0^{(j+1)}$$

$$E_j^{(0)} = \frac{1}{\Delta^4}f_3^{(j+1/2)}$$

$$B_j^{(2)} = -\frac{1}{\Delta^2}(f_3^{(j-1/2)} + f_3^{(j)})$$

$$C_j^{(2)} = \frac{1}{\Delta^2}(f_3^{(j+1/2)} + 2f_3^{(j)} + f_3^{(j-1/2)} - f_1^{(j)})$$

$$D_j^{(2)} = -\frac{1}{\Delta^2}(f_3^{(j+1/2)} + f_3^{(j)})$$

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Boundary conditions (16) and (17) give

$$u_{-1} = u_1 + \frac{4\Delta}{\xi_{\min}} u_0 \tag{A2}$$

$$u_{-2} = u_2 + \frac{16\Delta}{\xi_{\min}} u_1 + \left(-\frac{8\Delta}{\xi_{\min}} + \frac{32\Delta^2}{\xi_{\min}{}^2}\right) u_0$$

$$u_{N+1} = \frac{2 - (a^2 + b^2)\Delta^2}{1 + a\Delta} u_N + \frac{a\Delta - 1}{a\Delta + 1} u_{N-1}$$

$$u_{N+2} = u_{N+1}(2 - 4a\Delta - (a^2 + b^2)\Delta^2) + u_N(8a\Delta) + u_{N-1}(-2 - 4a\Delta + (a^2 + b^2)\Delta^2) + u_{N-2}$$

B. Nonlinear Coefficient in KS Equation. Proceeding with the perturbation theory up to sixth order and applying the solvability condition, one obtains the following expression for the nonlinear coefficient ν in eq 22:

$$\nu = \frac{\langle f, u_0^* \rangle}{\langle h_0', u_0^* \rangle} \tag{B1}$$

where

$$f = h_0' + 2Kh_0'\left(h_0{}^2 - \frac{1}{3}\right) - 2h_0h_0' + \frac{3V}{h_0}\left(\frac{h_0'^{\,2}}{h_0} - h_0''\right)$$

Here, $h_0(\xi)$ is the solution of eq 6, prime denotes the derivative with respect to the running coordinate $\xi = x + Ut$, the inner product $\langle a(\xi), b(\xi) \rangle = \int_{-\infty}^{\infty} a(\xi) b(\xi)\, d\xi$, and u_0^* is the zero eigenvalue solution of the linear problem adjoint to (12). For $K = 0$ (horizontal film), one obtains from (B1) that $\nu = -0.0027$.

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