Nonlinear evolution equations for thin liquid films with insoluble surfactants

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The dynamics of a free-liquid film with insoluble surfactants is followed until film rupture with a simple model based on three nonlinear evolution equations for the film thickness, the surfactants concentration and the tangential velocity of the fluid in the film. This model is derived asymptotically from the full Navier–Stokes equations for free films and incorporates the effect of van der Waals attraction, capillary forces and Marangoni forces due to gradients of surface tension. Different stability regimes are observed numerically for periodic and fixed boundary conditions and several initial conditions. Furthermore, the role of the relevant parameters (Hamaker constant, tension, Marangoni number) on the rupture time is assessed and comparison is made with the flow dynamics for a liquid film with insoluble surfactants on a solid substrate.

I. INTRODUCTION

The hydrodynamic stability of thin liquid films has been widely studied over the last two decades, allowing many applications in chemical or biomedical engineering. Two different generic geometries of these films have been considered: first, a thin liquid film on a solid substrate,[1] which is involved in wetting of surfaces, evaporation or surfactant spreading; second, a free-film geometry,[2] involved for instance in rupture of soap films and coalescence of droplets or emulsions. In the biological domain, these two geometries can be recognized respectively in the case of adhesion of cells to solid substrates and in the case of aggregation or fusion of vesicles and cells.[3,4] In both cases, the rupture instability, first introduced by Sheludko,[5] result from an amplification of spontaneous fluctuations by long range molecular forces due to van der Waals attraction, which are always operative for ultrathin liquid films (100–1000 Å). Such fluctuations and waves have been detected experimentally at the surface of free-liquid films by dynamic light scattering. Two collective modes of motion were observed on soap films:[6,7] the bending mode (BE), also called the undulation mode, which maintains the thickness of the film, and the squeezing mode (SQ), or in other words the peristaltic mode, which involves symmetric thickness fluctuations. This squeezing mode is the one considered when studying film rupture.

In order to describe this rupture, Felderhof[8] has applied a linear stability analysis to a thin free film, accounting for the van der Waals dispersion forces and the double layer forces, but for an inviscid flow. Lucassen–Reynders and Lucassen[9] have extended this treatment to a viscous film with capillary waves. Gummerman and Homsy[10] examined the linear stability of radially bounded thinning films. However, a linear analysis ceases to be valid at finite size deformation and does not enable to follow the dynamics of the induced flow. Recently, nonlinear methods have appeared based on the long-wave nature of the response. They provide nonlinear evolution equations (NEE) derived asymptotically from the Navier–Stokes equations and whose solutions are obtained either by bifurcation analysis or by numerical methods. Such nonlinear evolution equations have already been considered in different systems, which allows now some classification.

- A single NEE is sufficient to describe the evolution of the thickness h of the film, in the case of a thin film on a solid substrate (Williams and Davis,[11] Burelbach *et al.*,[12] Hatziavramidis[13]) or in the case of a free film with tangential immobile surfaces (Prevost and Gallez,[14] Gallez *et al.*[15]).
- A pair of NEE are needed if surfactants are present in variable concentration for a liquid film on a solid substrate: one equation for h and a second one to describe the evolution of the concentration of the surfactants (see, for example, the case of a multistable chemical reaction treated by Dagan and Pismen,[16] the spreading of surfactants on a viscous film examined by Jensen and Grotberg[17,18] or the problem of adhesion of cells to a solid substrate[19]). However, it has been recently recognized by Erneux and Davis[20] that for free films without surfactants, the presence of two stress-free boundaries requires a higher-order analysis which leads also to a system of two NEE (one equation for h and the other one for the tangential velocity of the fluid in the film).

In this paper, we extend these nonlinear approaches to study the rupture of a free film with insoluble surfactants. We show that a system of three coupled NEE describing the evolution of the thickness h, the concentration of the surfactants Γ and the tangential velocity u of the fluid is required to describe the evolution of the symmetric mode (SQ mode) of the free film with insoluble surfactants. Analytical and numerical study of the derived model give insight into the role

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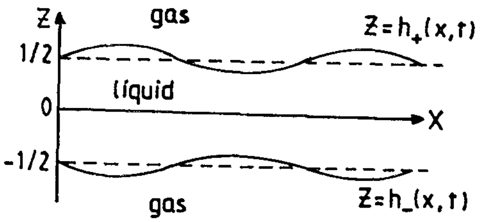

FIG. 1. Sketch of a free film with fluctuating surfaces. The free surfaces are described by the equations $z=h_{\pm}(x,t)$. The dashed lines indicate their mean position at $h=\pm 1/2$. The squeezing mode, for which the fluctuations of the thickness are symmetric with regard to the axis $z=0$, leads to rupture.

of the different parameters on the rupture time, as well as on the dynamics of the rupture. Eventually, we underline the difference between the behavior of a free film with that of a film on a solid substrate.

The paper is therefore organized as follows. Section II is devoted to the derivation of the model. In Sec. III, a linear stability analysis will provide insight on the role of the relevant parameters on rupture time while in Sec. IV, numerical results will show the stability properties and the dynamic behavior of the system in different conditions. Finally, in Sec. V, we compare these results to those obtained for a liquid film on a solid substrate.

II. BASIC EQUATIONS AND FORMULATION OF THE MODEL

Consider a thin liquid layer bounded by two surfaces. The longitudinal direction is denoted by x while z corresponds to the transverse direction. The film is bounded by two free surfaces located at $z=h_{\pm}(x,t)$ separating the liquid from the gas (Fig. 1). The analysis will be based on the squeezing mode, which is symmetric along the x axis, since it leads to film rupture and is the most unstable.

The liquid layer is assumed to be thin enough so that van der Waals forces are effective and yet thick enough so that a continuum theory of the liquid is applicable. The film is supposed to be of finite extent, its length L far exceeding its thickness h_0. The free surfaces possess surface properties like surface tension and surface coverage. Consequently, if the surfactants are free to diffuse along the surface, the surface tension will vary in accordance with surface concentration (Marangoni effect[21]). The liquid film is described as a Newtonian viscous fluid having viscosity μ, density ρ, and kinematic viscosity ν. Dimensionless variables are introduced using the following scales: length h_0, time h_0^2/ν, velocity ν/h_0 and pressure $\rho\nu^2/h_0^2$. In addition, we use the equilibrium value Γ_0 as a unit measure for the concentration of the surfactants. The two-dimensional motion of the liquid in the film phase is given by the dimensionless Navier–Stokes equations[2]:

$$(u_t+uu_x+vu_z)=-(p+W)_x+(u_{XX}+u_{ZZ}), \tag{1}$$

$$(v_t+uv_x+vv_z)=-(p+W)_z+(v_{XX}+v_{ZZ}), \tag{2}$$

together with the continuity equation

$$u_x+v_z=0, \tag{3}$$

where u and v are, respectively, the tangential and normal velocities in the Cartesian coordinate system (x,z). The suffices indicate differentiation while p is the mechanical pressure. The van der Waals potential is given by

$$W(\mathbf{r})=\int w(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}')d\mathbf{r}' \tag{4a}$$

and

$$w(|\mathbf{r}-\mathbf{r}'|)\approx\Lambda/(|\mathbf{r}-\mathbf{r}'|)^6.$$

Here the dimensionless London constant Λ is related to the dimensional constant Λ_D by $\Lambda=\Lambda_D/(h_0^2\rho\nu^2)$. In general, W is a function of x, z, and t. However, as indicated by Maldarelli *et al.*,[22] this formulation can be simplified in the long wavelength limit, and it has been customary to use the following simplified model, where the attractive van der Waals potential W depends on the film thickness h as

$$W=A(h_+-h_-)^{-3}, \tag{4b}$$

where the dimensionless Hamaker constant A can be linked to the dimensional constant A_{H} as $A=A_{\mathrm{H}}/(h_0^2\rho\nu^2)$.

At the free interfaces $h_{\pm}(x,t)$, we have the following boundary conditions:[23] the normal stress balance (Laplace condition) is given by

$$\begin{aligned}-p+1/(1+h_{\pm x}^2)[2v_z(1-h_{\pm x}^2)-h_{\pm x}(v_x+u_z)]\\=\pm\Sigma\ h_{\pm xx}/(1+h_{\pm x}^2)^{3/2},\end{aligned} \tag{5}$$

where we have assumed that the pressure of the gas is zero. If we neglect surface viscosity, the dimensionless surface tension Σ is given by the following constitutive relation:

$$\Sigma=T-M\Gamma, \tag{6}$$

where

$$T=\sigma_0h_0/(\rho\nu^2) \tag{7}$$

is the dimensionless tension for the constant part of the tension σ_0 at equilibrium concentration Γ_0 and

$$M=-[\Gamma_0h_0/(\rho\nu^2)](\partial\sigma/\partial\Gamma) \tag{8}$$

is the dimensionless Marangoni number for the variation $\partial\sigma/\partial\Gamma$ of the dimensional tension σ versus the dimensional concentration Γ; $\Gamma=\Gamma/\Gamma_0$ is the dimensionless surfactants concentration.

The tangential stress balance (Marangoni condition) reads

$$[(u_z+v_x)(1-h_{\pm x}^2)+2h_{\pm x}(v_z-u_x)]=\Sigma_x(1+h_{\pm x}^2)^{1/2}. \tag{9}$$

The kinematic boundary conditions are given by

$$v=h_{\pm t}+h_{\pm x}u. \tag{10}$$

In addition, a conservation equation is needed for the concentration of the surface active substance:

$$\Gamma_t+(\mathring{a}/2a)\Gamma+(\Gamma u)_x=(D_s/\nu)\Gamma_{xx}, \tag{11}$$

where D_s is the surface diffusion coefficient of the surfactant. The second term in the left-hand side (LHS) of Eq. (11) represents the rate of change of concentration due to the dilatation of the surface.[24] This term is small for large curvature radius a and will be neglected in the following. The possible generation mechanisms for the variation of surfactants concentration (surface chemical reaction, adsorption–desorption from the film bulk phase or surfactant spreading) will not be considered explicitly here, since we are above all interested in deriving a simple model. These effects could be added afterwards by introducing a source term in the equation of conservation of surface mass.[11]

Last, the perturbations at the two surfaces are symmetric for the squeezing mode in which

$$h_+(x,t) = -h_-(x,t). \tag{12}$$

From now on, we write the dimensionless thickness as $h_+(x,t) = h(x,t)$ and will consider only the upper part of the symmetric film $[0 \leqslant z \leqslant h_+(x,t)]$. The conditions for the SQ mode are then

$$u_z = v = 0 \quad \text{at the center of the film } z=0. \tag{13}$$

The behavior of the film is thus completely determined by the hydrodynamic equations (1)–(3) along with the boundary conditions (5), (9), (13), the kinematic equation (10) and the conservation equation (11). The linear stability analysis of this system may be performed in order to determine the conditions for marginal stability of the free film with a finite quantity of surfactants toward infinitesimal disturbances. This analysis cannot, however, follow the dynamics of the film up to the rupture: experimental evidence on soap films shows indeed that films rupture when disturbances have reached a large size. The behavior of the system in that regime can be correctly understood only by taking into account the nonlinearities of the evolution equations governing the behavior of finite disturbances.

To take such terms into account, a long wavelength approximation is used in a nonlinear theory to obtain successive approximations to the solutions of the equations of motion (1) and (2). The solutions derived for each component of the velocity field will then be substituted in the kinematic equation (10) and in the conservation equation (11). We formalize the long wavelength theory by rescaling the variables with a small parameter ϵ inversely proportional to the wavelength of the disturbance which is supposed to be much larger than the film thickness. We define thus new dimensionless rescaled variables as follows:

$$\begin{gathered} X = \epsilon x, \quad Z = z, \\ U = u/\epsilon, \quad V = v/\epsilon^2, \\ \tau = \epsilon^2 t, \quad P = p/\epsilon^2, \quad H = h. \end{gathered} \tag{14}$$

The rescaled variables and derivatives with respect to the upper case variables are all unit order as $\epsilon \to 0$.

The dynamical equations (1) and (2) are then expressed as follows:

$$U_\tau + UU_X + VU_Z = [U_{XX} + U_{ZZ}/\epsilon^2 - (P+W')_X], \tag{15}$$

$$V_\tau + UV_X + VV_Z = (V_{XX} + V_{ZZ}/\epsilon^2 - P_Z/\epsilon^2), \tag{16}$$

where we have assumed that

$$W' = A'/h^3 \text{ with } A' = A/\epsilon^2 = O(1). \tag{17}$$

The continuity equation (3) becomes

$$U_X + V_Z = 0. \tag{18}$$

The ratio U/V is of the order of ϵ to preserve the continuity equation (3) with the stretching transformation.

The normal stress balance (5) at $Z = H(X,\tau)$ reads

$$\begin{aligned} -P + 1/(1+\epsilon^2 H_X^2)[2V_Z(1-\epsilon^2 H_X^2) - H_X(\epsilon^2 V_X + U_Z)] \\ = (T - \epsilon^2 M'\Gamma) H_{XX}/(1+\epsilon^2 H_X^2)^{3/2}, \end{aligned} \tag{19}$$

where we have assumed that $M' = M/\epsilon^2 = O(1)$ and $T = O(1)$.

Using the same definition for the rescaled Marangoni number M', the tangential stress balance (9) at $Z = H(X,\tau)$ becomes

$$\begin{aligned} (U_Z + \epsilon^2 V_X)(1 - \epsilon^2 H_X^2) + 2\epsilon^2 H_X (V_Z - U_X) \\ = -\epsilon^2 M' \Gamma_X (1+\epsilon^2 H_X^2)^{1/2}. \end{aligned} \tag{20}$$

Moreover, we have

$$U_Z = V = 0 \quad \text{at } Z = 0. \tag{21}$$

Last, the kinematic equation and the conservation equation for the concentration of the surfactants can be written at $Z = H(X,\tau)$ as

$$V = H_\tau + UH_X, \tag{22}$$

$$\Gamma_\tau + (\Gamma U)_X = \Gamma_{XX}/S_c, \tag{23}$$

where $S_c = \nu/D_S$ is the dimensionless Schmidt number. Approximate solutions of this new system of equations can be obtained by introducing the following regular perturbation expansion for U, V, and P into equations (15)–(23):

$$(U,V,P) = (U_0,V_0,P_0) + \epsilon^2(U_1,V_1,P_1) + \cdots . \tag{24}$$

We have assumed $A = O(\epsilon^2)$ and $T = O(1)$ to retain at lowest order both effects of van der Waals interactions and of surface tension. The problem is to obtain the velocity field which is the solution of Eqs. (15)–(18), consistent with the boundary conditions on normal and tangential stress together with the SQ mode condition. In particular, consistence between the tangential stress condition (20) at $Z = H(X,\tau)$ and condition $U_Z = 0$ at $Z = 0$ for the SQ mode at the lowest order has lead us to take $M = O(\epsilon^2)$. The zeroth-order problem reads then

$$U_{0ZZ} = 0, \tag{25a}$$

$$V_{0ZZ} = P_{0Z}, \tag{25b}$$

$$U_{0X} + V_{0Z} = 0, \tag{25c}$$

$$-P_0 + 2V_{0Z} - H_X U_{0Z} = TH_{XX} \quad \text{at } Z = H, \tag{25d}$$

$$U_{0Z} = 0 \quad \text{at } Z = H, \tag{25e}$$

$$V_0 = U_{0Z} = 0 \quad \text{at } Z = 0, \tag{25f}$$

$$V_0 = H_\tau + U_0 H_X \quad \text{at } Z = H, \tag{25g}$$

$$\Gamma_\tau + (\Gamma U_0)_X = \Gamma_{XX}/S_c \quad \text{at } Z = H. \tag{25h}$$

A straightforward integration[20] of Eqs. (25a)–(25c) using boundary conditions (25d)–(25f) leads to the following velocity and pressure fields:

$$U_0=B(X,\tau), \tag{26}$$

$$V_0=-B_X Z, \tag{27}$$

$$P_0=-2B_X-TH_{XX}, \tag{28}$$

where B, an unknown function of X and τ becomes a new variable of the problem, i.e., the tangential velocity of the fluid. We straight away remark that the normal velocity V_0 is an antisymmetric function of Z while the tangential velocity U_0 is a symmetric function of Z, in agreement with the definition of the SQ mode. The form for U_0 [Eq. (26)] is substituted into (25g) and (25h) to obtain

$$H_\tau=-(BH)_X, \tag{29}$$

$$\Gamma_\tau=\Gamma_{XX}/S_c-(\Gamma B)_X. \tag{30}$$

Since we obtain two NEE [Eqs. (29) and (30)] for three variables: H, Γ, and B, a third relation between them is needed. To this end, we analyze the next order of the ϵ expansion where we have for U_1

$$U_{0\tau}+U_0U_{0X}+V_0U_{0Z}=[U_{0XX}+U_{1ZZ}-(P_0+W')_X], \tag{31a}$$

$$U_{1Z}+V_{0X}+2H_X(V_{0Z}-U_{0X})-U_{0Z}H_X^2$$
$$=-M'\Gamma_X \quad \text{at } Z=H, \tag{31b}$$

$$U_{1Z}=0 \quad \text{at } Z=0. \tag{31c}$$

Solving this system of equations finally gives an additional partial differential equation governing the spatiotemporal evolution of the tangential velocity $B(X,\tau)$:

$$(B_\tau+BB_X-TH_{XXX}+W_X')H=(-M'\Gamma+4HB_X)_X. \tag{32}$$

Finally, we rewrite Eqs. (29), (30), and (32) in terms of the original variables using (14) and (26) and reminding that $M'=M/\epsilon^2$ and $W'=W/\epsilon^2$. We obtain a simple model describing the evolution of free films with insoluble surfactants thanks to three coupled NEE for the thickness h of the film, the concentration Γ of the surfactants and the tangential velocity u of the fluid in the film, i.e.,

$$h_t=-(uh)_x, \tag{33a}$$

$$\Gamma_t=\Gamma_{xx}/S_c-(\Gamma u)_x, \tag{33b}$$

$$(u_t+uu_x-Th_{xxx}+W_x)h=(-M\Gamma+4hu_x)_x. \tag{33c}$$

III. LINEAR STABILITY THEORY

If we suppose that the free film is initially homogeneous, model (33) admits a whole family of steady states denoted as $(h_{SS},\Gamma_{SS},u_{SS})$. In the following, we choose to analyze the stability of the steady-state solution $(h_{SS},\Gamma_{SS},u_{SS})=(1/2,1,0)$ corresponding to a plane film with the fluid at rest. We perturb this basic state by small perturbations (α,γ,β) i.e.,

$$h=1/2+\alpha, \tag{34a}$$

$$\Gamma=1+\gamma, \tag{34b}$$

$$u=\beta. \tag{34c}$$

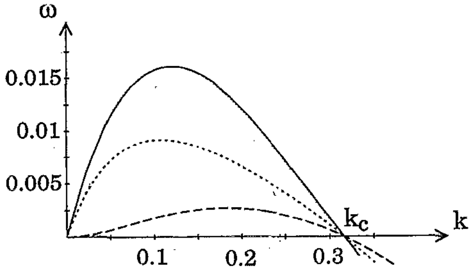

FIG. 2. Growth rate ω of the unstable mode versus its wave number k for increasing values of M. The straight, dotted, and dashed lines correspond, respectively, to M: 0.025, 0.05, and 0.1 with $A=0.05$; $T=3$; $S_c=10$. The growth rate is positive for all $k<k_c$. The variation of M does not affect k_c while increasing M leads to a decrease of $\omega_{\max}$ and hence to an increase of the rupture time.

We obtain by inserting Eqs. (34) in Eqs. (33) a linearized problem that, in a system with periodic boundary conditions on a bounded domain $0\leqslant x\leqslant L$, admits solutions of the form

$$(\alpha,\gamma,\beta)=\sum_m (\alpha_m,\gamma_m,\beta_m)\exp(\omega t+ik_m x) \tag{35}$$

while in a system with fixed boundary conditions, the solutions are

$$(\alpha,\gamma,b)=\sum_m (\alpha_m,\gamma_m,b_m)\exp(\omega t)\sin(k_m x), \tag{36}$$

where $b=\beta_x$ and ω is the growth rate of the disturbance while $k_m=m\pi/L$ $(m=1,2,\ldots)$ is its wave number. For both cases, the corresponding characteristic equation for ω reads

$$\omega(\omega+k^2/S_c)(\omega+4k^2)+k^2/2(\omega+k^2/S_c)(Tk^2-6A)$$
$$+2Mk^2\omega=0. \tag{37}$$

The critical wave number k_c for which ω=0 corresponds to

$$k_c^2=6A/T \tag{38}$$

which agrees with the linear theory result of Ruckenstein and Jain.^{2} The dispersion relation has three roots. Two of them have a real part which remains always negative while the third one, ω_3, has a real part that may become positive. A simple analysis of (37) for small k yields a growth rate of $O(k)$ for $2M<3A$, while the growth rate becomes $O(k^2)$ for $2M>3A$. For $2M=3A$, the root is proportional to $k^{4/3}$ for small k.

Several conclusions appear from expression (38) among which the most important is that the Marangoni effect does not affect the cutoff wave number k_c. In other words, the domain of unstable wave numbers in the case of a free film is the same whether or not the film contains any surfactant. This can be seen in Fig. 2 where we have plotted the curve $\omega=\omega_3=f(k)$ for different values of M. The orders of magnitude for the parameters M, T, and A have been chosen in order to be coherent with the hypotheses made to obtain the model. An increase of M results in a decrease of the fastest growth rate $\omega_{\max}$ which can be interpreted as the inverse of the rupture time of the free film. This means that the film will be more stable as we increase the concentration Γ_0 of surfactants in the film or the rate $(-\partial\sigma/\partial\Gamma)$ in order to increase the Marangoni number [Eq. (8)]. If we increase the tension T, the cutoff wave number k_c decreases [Eq. (38)]. The film is

TABLE I. Parameters for thin liquid films (aqueous).

Parameter	Symbol	Best estimate
Film viscosity	μ	$\approx 10^{-2}$ g/(cm s)
Film density	ρ	≈ 1 g/cm^3
Kinematic viscosity	ν	$\approx 10^{-2}$ cm^2/s
Equilibrium film thickness	h_0	10^{-6}–10^{-5} cm
Hamaker constant	A_H	10^{-14}–10^{-12} erg
Surface diffusion coefficient	D_S	10^{-5}–10^{-4} cm^2/s
Equilibrium surface tension	σ_0	1–30 dyn/cm
Equilibrium surfactants concentration	Γ_0	10^{-12}–10^{-10} mol/cm^2
Variation surface tension	$(-\partial\sigma/\partial\Gamma)$ at Γ_0	10^{9}–10^{11} erg/mol
Dimensionless Hamaker constant	$A=A_H/h_0\rho\nu^2$	10^{-5}–10^{-2}
Dimensionless surface tension	$T=\sigma_0 h_0/\rho\nu^2$	10^{-2}–3
Dimensionless Marangoni number	$M=(-\partial\sigma/\partial\Gamma)\Gamma_0 h_0/\rho\nu^2$	10^{-5}–1
Dimensionless Schmidt number	$S_c=\nu/D_s$	10–10^3

thus more stable as the domain of possible unstable wave numbers shrinks. In parallel, $\omega_{\max}$ decreases, i.e., the rupture time of the film will be longer which is in agreement with the fact that films with a higher interfacial tension are more stable. Increasing van der Waals interaction (A increasing) will have exactly the opposite influence because it increases k_c and $\omega_{\max}$ as can be intuitively expected.

The linear stability analysis of a free film provides thus qualitative understanding of the influence of the physical parameters of the problem on both the domain of unstable wave numbers and the rupture time. The linear analysis cannot, however, give any information on the dynamics of the rupture which depends strongly on the nonlinear interactions of the disturbances. This behavior can only be understood by solving the nonlinear model of the free film.

IV. NUMERICAL RESULTS

Equations (33) have been solved numerically using finite difference methods.[25] Forward differences in space are used to obtain the successive derivatives with respect to x up to an error of order Δx^4 where $\Delta x=0.2$ is the size of the spatial mesh. An explicit scheme is applied for the time derivative. The difference equations obtained are then solved iteratively. Table I summarizes the typical values of the various system parameters and an estimate of the corresponding dimensionless parameters used in the paper. The two extreme values for the equilibrium surfactants concentration Γ_0 correspond, respectively, to a gaseous and a condensed monolayer.

The cutoff wave number k_c gives the smallest unstable wavelength $\lambda_c=2\pi/k_c$ such that all wavelengths greater than λ_c are unstable. We choose parameter values in Table I which are consistent with the orders of magnitude of the development. If $M=0.025$, $A=0.05$, $T=3$, and $S_c=10$ as in most of our simulations, then $\lambda_c=19.9$. To follow the dynamics of the film we draw $h(x,t)$, $\Gamma(x,t)$ and $u(x,t)$ at several successive times separated by Δt, starting from the initial condition at time t_0 till the final rupture at time t_f. We define the rupture time of the film as the time for which $h\leqslant 0$ at any lateral location of the system. Let us remark that when h vanishes, the nonlinear model loses its applicability as the evolution equation for the tangential velocity (33c) becomes singular and consequently the numerical integration fails down. Hence, the final curve t_f of $h(x,t)$ and $\Gamma(x,t)$ may show a spiky short-scale behavior due to the numerical instability. In that regard, the final curve t_f of $u(x,t)$ will not be drawn when looking at the tangential velocity of the fluid because, at rupture time, u tends to infinity at the locations of rupture. We will indicate the last time preceding rupture at which $u(x,t)$ is drawn. More sophisticated numerical methods[26] using variable time steps and nonuniform mesh sizes in space could be used in the vicinity of the rupture point in order to focus on the dynamics of the rupture itself. However, we have checked in our simulations that, as long as $h(x,t)>0$, the integral of $h(x,t)$ over the length of the system is conserved throughout the evolution. This criterion indicates that our model describes the dynamics of the system until fairly close to the rupture and that the definition of the rupture time we introduced is accurate enough to study the influence of insoluble surfactants on rupture times.

Two types of boundary conditions may be considered according to the physical situation of interest. Periodical boundary conditions (PBC) can be used to understand the behavior of an ideal infinite film corresponding to the more realistic case of a film of length L much greater than the thickness h. PBC apply also for instance to the case of a soap bubble the radius of which is large enough to neglect curvature effects. On the other hand, fixed boundary conditions (FBC) allow to study films of finite length, as obtained experimentally in engineering devices.[5] Moreover, FBC are immediately relevant if we want to compare the behavior of a free film with that of a film on a solid substrate (see Sec. V).

For PBC, three different dynamical regimes can be distinguished.

(i) If the wavelength of the initial disturbance λ_i and *a fortiori* the length of the film L are both greater than λ_c, the film is unstable and will rupture simultaneously at all the locations of the minima of the perturbation (Fig. 3). The nonlinear coupling between h, Γ and u induces a flow of the

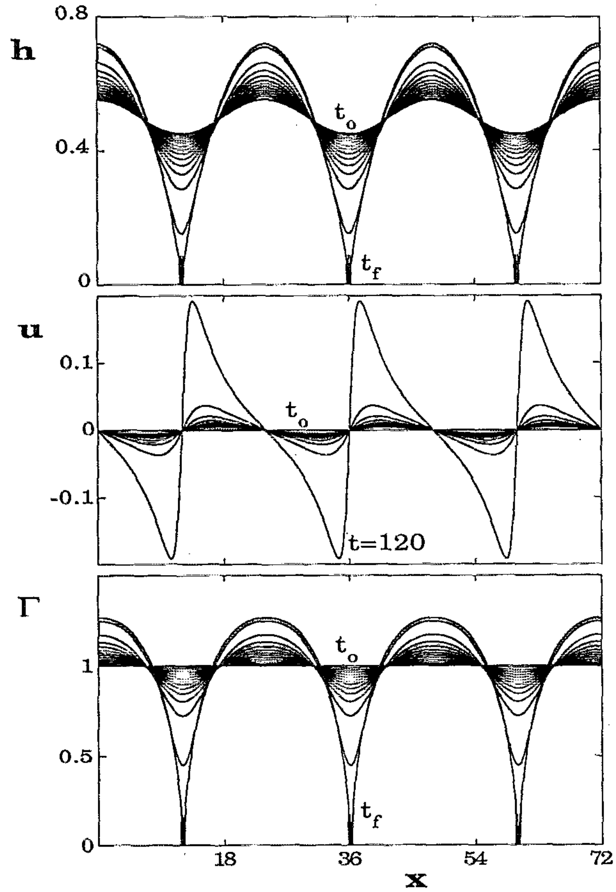

FIG. 3. Rupture of a free film with PBC. $A=0.05$, $T=3$, $M=0.025$, $S_c=10$, and, hence, $\lambda_c=19.9$. The length L of the system equals 72. We impose as initial condition a slight periodic disturbance on the stationary value of the thickness h while the other variables are set to their stationary states: $(h,\Gamma,u)=(0.5+0.05\cos[k_m x],1,0)$ with $m=6$ ($\lambda_i=24$). The initial disturbance (curve t_0) is amplified leading to the rupture of the film when h reaches zero. The curves plotted show successive situations distant in time by an interval $\Delta t=10$ while the curve indexed by t_f shows the situation at the rupture time=121. The spiky short-scale behavior of h and Γ at the rupture time is due to a numerical instability. Rupture occurs simultaneously at the location of each minimum of the perturbation. The curves $u(x,t)$ show the evolution of the tangential velocity of the fluid in the film. Starting from a film at rest ($u=0$ anywhere at t_0), the instability occurs because the fluid flows away from the location of the minima of the thickness. The plot of $\Gamma(x,t)$, i.e., of the concentration of the surfactants show that the surfactants concentrate in the region between the zones of rupture.

fluid in the film such that the fluid flows away from the minima of thickness h toward its maxima. Positive (negative) u corresponds by convention to fluid flowing to the right (left). In addition, the surfactants follow the movement of the fluid to escape the regions where the thickness of the film shrinks. Ultimately, the thickness h reaches zero at all the minima where the concentration of surfactants also tends toward zero. Rupture of the film occurs thus in the case of PBC via flow of the fluid outside all the regions of initially low thickness. We have checked numerically the influence of the various parameters M, T, and A on the rupture time. The predictions of the linear stability analysis are fully recovered, i.e., the film will rupture more slowly if one either adds surfactants (M increasing) or chooses a fluid with higher interfacial tension T or lower van der Waals attraction A (see Table II).

TABLE II. Rupture times for a free film with PBC and different values of the parameters. $L=72$, $Sc=10$, and the initial condition is as in Fig. 3.

A	T	M	Rupture time
0.05	3	0	97
0.05	3	0.025	121
0.05	3	0.050	163
0.05	3	0.075	228
0.05	3	0.100	316
0.050	3	0.025	121
0.075	3	0.025	53
0.100	3	0.025	36
0.125	3	0.025	28
0.05	0.5	0.025	55
0.05	1	0.025	61
0.05	2	0.025	80
0.05	3	0.025	121

As an example, see, also, Fig. 4 where $h_{\min}$, the minimum of thickness on the domain $(0,L)$, is plotted as a function of time for different values of T. Decreasing T clearly shortens the rupture time of the film. Moreover, these curves show that rupture happens very abruptly after a certain induction period, emphasizing the role of nonlinearities of the problem in accelerating the rupture time as compared to the rupture time predicted by a linear analysis. Figure 4 is in good qualitative agreement with the behavior predicted by an analytical nonlinear theory[20] for a system without any surfactants near the bifurcation point $T=T_c$.

It is also interesting to follow the evolution of the pressure profile $P_0(x,t)$ given by expression (28). Using Eqs. (26)–(28) and rewriting the pressure in term of the original variables, we visualize in Fig. 5 the evolution of the pressure $p(x,t)$ for the same dynamical regime as in Fig. 3. Positive pressure p corresponds to regions of maximum thickness (the terms $-2B_x$ and $-Th_{xx}$ are positive), while negative pressure corresponds to regions of minimum thickness. The pressure in this problem is an adiabatic variable, which is eliminated in the final set (33) of NEE. The fluid motion and

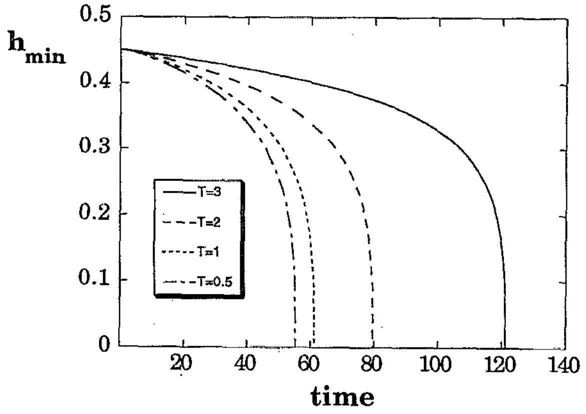

FIG. 4. Minimum of thickness $h_{\min}$ on the domain $[0,L]$ plotted as a function of time for different values of T: 0.5; 1; 2; 3 with $A=0.05$; $M=0.025$ and $S_c=10$ on a system $L=72$ using initial condition of Fig. 3.

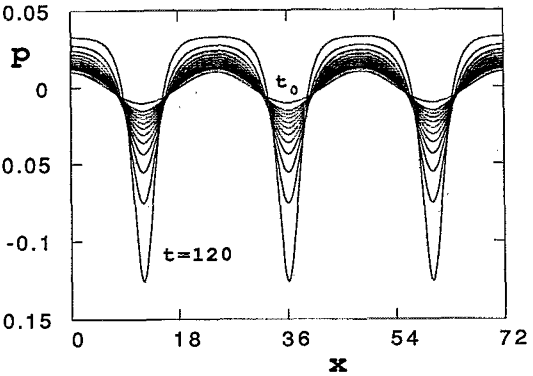

FIG. 5. Variation of the pressure $p(x,t)=-2u_x-Th_{xx}$ at successive times using PBC and the same initial conditions and parameters A, T, and M, as in Fig. 3. The pressure is positive in regions of maximum thickness while the pressure is negative in regions of minimum thickness.

surface deformation are essentially due to the interplay between van der Waals, capillary and Marangoni forces.

(ii) For fixed values of parameters, the behavior of the film depends also on the length L of the film corresponding to the maximum periodicity allowed and on the wavelength of the initial disturbance λ_i. If $L>\lambda_c$ but $\lambda_i<\lambda_c$, the initial wavelength is stable. In that case, a change of wavelength toward a longer and unstable one occurs, followed then by the rupture of the film (Fig. 6). The fluid and the surfactants again leave the region where the thickness of the film shrinks leading finally to rupture.

(iii) Last, if $L<\lambda_c$, the film is stable as any disturbance that might appear in the system has a stable wavelength ($\lambda_i<\lambda_c$ *a fortiori*). The initial perturbance disappears as the surfactants transitorily fill the depletion zones of h while the fluid moves from the regions of maximum thickness toward those of minimum thickness. The dynamics of this stabilizing procedure is thus exactly opposite to the one of rupture.

Three different dynamics (immediate rupture, rupture after a change of wavelength or stability) may thus be observed for a same set of parameters depending on the length of the system and the wavelength of the initial disturbance. These size related effects captured by numerical integration of the model and easily understood in terms of the linear stability analysis are reminiscent of the experimental observation that, in addition to curvature effects, small soap bubbles are genuinely more stable than bigger ones.

The effects of the respective sizes of L, λ_i, and λ_c are recovered in a free film with FBC. In a long system such that $\lambda_i>\lambda_c$, the behavior will nevertheless differ depending whether the initial condition will be symmetrical or not with respect to the middle $L/2$ of the film. In a symmetrical system, the film will rupture at the two minima adjacent to the edges (Fig. 7) whereas in an asymmetrical system, rupture occurs only near one edge (Fig. 8). In both cases, all parameters were exactly the same as in the situation of Fig. 3 for which PBC had been imposed. We see thus clearly that for FBC, the edges favor a rupture of the film in their vicinity contrary to PBC where the film breaks at each location of a minimum of the initial disturbance. The influence on the rupture time of the different physical parameters M, T, and A goes the same way for both cases.

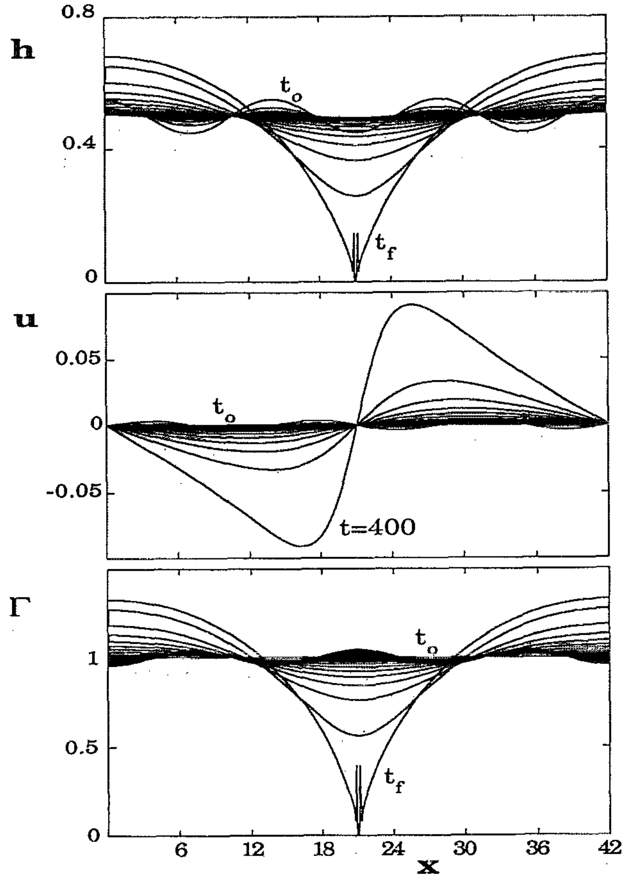

FIG. 6. Rupture of a free film with PBC when the wavelength of the initial disturbance λ_i is smaller than the critical wavelength λ_c but $L>\lambda_c$. All the parameters are the same as in Fig. 3 except $L=42$, $m=6$ (hence $\lambda_i=14$), and $\Delta t=20$. A change of wavelength toward a larger and unstable one occurs, leading finally to the rupture at $t_f=407$.

V. COMPARISON WITH FILMS ON A SOLID SUBSTRATE

For the case of a film on a solid substrate, the basic equations (1)–(11) are the same as for the case of a free film but only for the upper free surface $h_+(x,t)=h(x,t)$. It is now more natural to take the lower rigid surface at $z=0$. The geometry of the film is drawn on Fig. 9. Since the lower surface $h(x,t)$ is rigid, Eq. (13) is replaced by a no-slip condition:

$$u=v=0 \quad \text{at the lower surface } z=0. \tag{39}$$

This change in the boundary conditions profoundly affects the velocity field in the film. Indeed, for the same scaling (14) of the dependent and independent variables in a small parameter ϵ and the same expansion (24) we have now at leading order

$$-(p_0^*+W)_X+U_{0ZZ}=0, \tag{40a}$$

$$p_{0Z}^*=0, \tag{40b}$$

$$U_{0X}+V_{0Z}=0, \tag{40c}$$

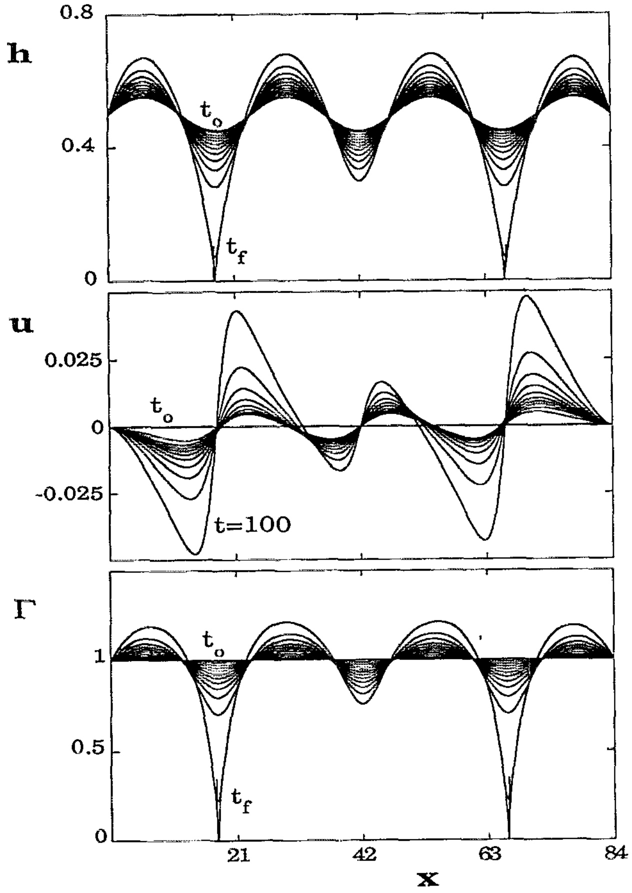

FIG. 7. Rupture of a free film with FBC. All parameters are the same as in Fig. 3 except $L=84$ and the initial condition is assigned to $(h,\Gamma,u)=(0.5+0.05\sin[k_m x],1,0)$ with $m=7$ ($\lambda_i=24$). The FBC favor rupture of the film near its edges and as the initial condition is symmetric with regard to the middle of the system, rupture occurs simultaneously at both edges at time $t_f=110$.

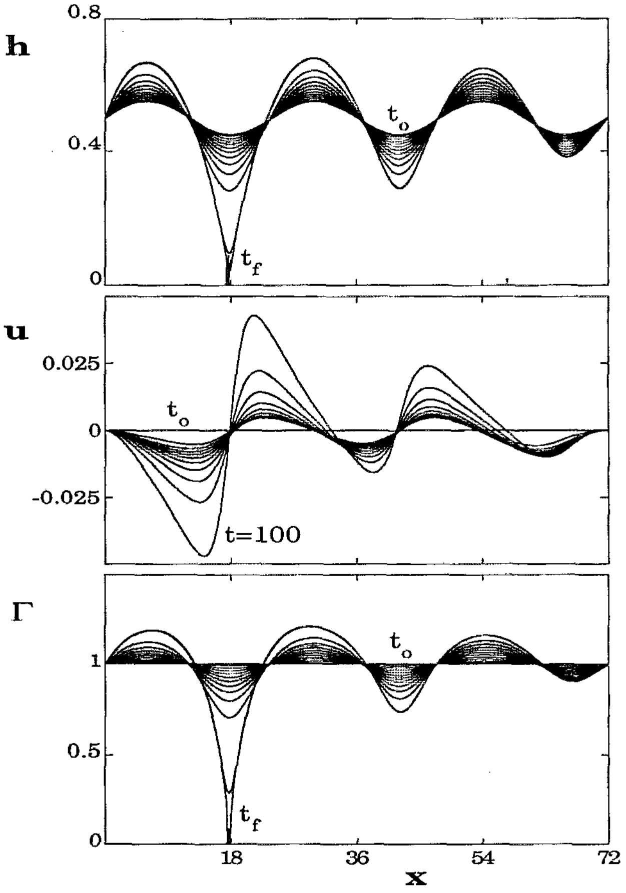

FIG. 8. Rupture of a free film with FBC and the same parameters as in Fig. 6 but $L=72$ and $m=6$. The film is thus asymmetrical with regard to the middle of the system, and rupture occurs only near one edge at $t_f=110$.

with $W=A/h^3$, and $A=O(1)$ defined as previously by (4b) and $p_0^* = \epsilon^2 P$. The velocity variables and derivatives are unit order as ϵ—>0. The choice of the scaling for the parameter A is dictated by the new condition (39) which allows one to determine directly the velocity field at zero order. This different scaling is justified by the fact that the gradient of pressure and the van der Waals forces are playing here a role at leading order allowing to solve completely the problem at this order. On the other hand, in the case of a free film, Eq. (31a) shows that the gradient of pressure and the van der Waals forces appear only at order one. Their consideration at order zero would lead to an inconsistency in the velocity field.

The boundary conditions read then at leading order:

$$-p_0^*=T^*H_{XX} \quad \text{at } Z=H, \tag{40d}$$

$$U_{0Z}=-M\Gamma_x \quad \text{at } Z=H, \tag{40e}$$

$$U_0=V_0=0 \quad \text{at } Z=0, \tag{40f}$$

$$H_\tau+H_X U_0=V_0 \quad \text{at } Z=H, \tag{40g}$$

$$\Gamma_\tau+(\Gamma u_0)_X=\Gamma_{XX}/S_C \quad \text{at } Z=H, \tag{40h}$$

where we assume $T^*=\epsilon^2 T=O(1)$ with the dimensionless parameter T defined as previously [Eq. (7)]. On the other hand, the Marangoni number M defined as previously [Eq. (8)] appears now at leading order $M=O(1)$.

Two remarks are in order here. First, this set of equations is similar to the set of equations used by Jensen and Grotberg,[17] who have taken directly the lubrication approximation for the flow inside the film. Second, the Marangoni effects due to the spatial gradients of the component $\sigma(\Gamma)$ arise here at the leading order. The gradient in Γ along the free surface induces a shear stress at the surface [see Eq. (40e)] and thus a Marangoni flow in the liquid film below

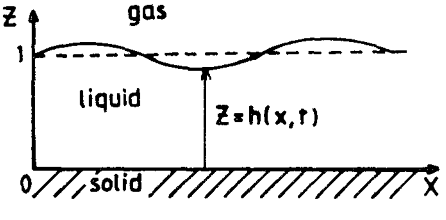

FIG. 9. Sketch of a film on a solid substrate. The free surface is described by the equation $z=h(x,t)$. The dashed line indicates its mean position at $h=1$.

and vice versa. It is thus expected that the presence of surfactants will influence more specifically the film dynamics than in the case of a free film.

A straightforward integration of Eqs. (40a) and (40b) using boundary conditions (40d)–(40f) leads to the following velocity field:

$$U_0=\Phi_X(-Z^2/2+ZH)-M\Gamma_X Z, \tag{41a}$$

$$V_0=\Phi_{XX}Z^3/6-(\Phi_X H-M\Gamma_X)_X Z^2/2, \tag{41b}$$

with

$$\Phi(x,t)=-A/H^3+T^*H_{XX}. \tag{41c}$$

It is easily seen that the tangential velocity U_0 is proportional to M. Furthermore, it varies along the normal axis Z and is zero at $Z=0$. The velocity profile for the tangential velocity is a superposition of a linear term in Z, proportional to the competition between the force due to the gradient of potential Φ_X and the Marangoni force, and a parabolic term in Z^2, proportional to the gradient of potential. This contrast with the expression of the tangential velocity for the free film case, which is independent of the Z axis. The velocity field is completely determined here at zero order due to the condition (40f).

Inserting these expressions in the kinematic condition (40g) and the surfactants conservation relation (40h), we get

$$H_\tau=(M\Gamma_X H^2/2-\Phi_X H^3/3)_X, \tag{42a}$$

$$\Gamma_\tau=\Gamma_{XX}/S_c+(M\Gamma_X\Gamma H-\Gamma\Phi_X H^2/2)_X. \tag{42b}$$

We end thus with a set of two NEE governing the position of the free surface and the surfactants concentration, instead of three NEE in the case of a free film. Rewriting these equations in terms of the original variables leads to

$$h_t=(M\Gamma_x h^2/2-\phi_x h^3/3)_x, \tag{43a}$$

$$\Gamma_t=\Gamma_{xx}/S_c+(M\Gamma_x\Gamma h-\Gamma\phi_x h^2/2)_x, \tag{43b}$$

with

$$\phi(x,t)=-A/h^3+Th_{xx}. \tag{43c}$$

A linear stability analysis of the homogeneous steady state (1,1) of model (43) with fixed boundary conditions leads to the following dispersion relation:

$$\omega^2+\omega\left(\frac{k^2}{3}\right)\left[k^2T-3A+3\left(\frac{1}{S_c}+M\right)\right]+(k^4/3)\left(\frac{1}{S_c}+\frac{M}{4}\right)(k^2T-3A)=0. \tag{44}$$

The critical wave number k_c for which $\omega=0$ reads

$$k_c^2=3A/T. \tag{45}$$

This critical wave number is similar to the expression found by Ruckenstein and Jain[2] for a film on a solid support and by Jensen and Grotberg[17] for a liquid film with spreading of insoluble surfactants. It shows that, at leading order, the range of unstable wavelengths remains unchanged if the Marangoni number is increased. Besides, when comparing the square of the critical wave number for the free film [Eq. (38)] and for the film on solid substrate [Eq. (45)], we observe that it is larger by a factor of 2 in the case of a free film, leading to a smaller critical wavelength for a free film than for a film on a solid substrate.

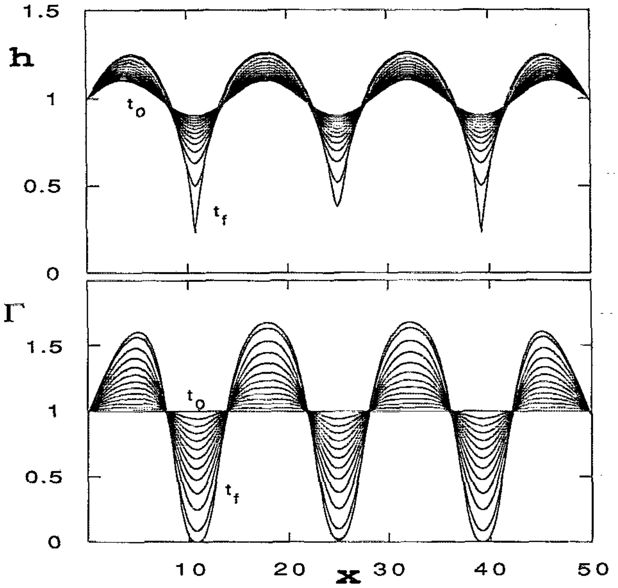

FIG. 10. Rupture of a film on a solid substrate with FBC when λ_i and $L>\lambda_c$. The parameters are $L=50$, $m=7$ (so that $\lambda_i=14.2$), and $A=5$, $T=30$ (hence $\lambda_c=8.9$), $M=0.1$, $S_c=10$. Periodic initial conditions are imposed for the thickness h, while the initial concentration is set to its stationary value: $(h,\Gamma)=(1+0.1\sin[k_m x],1)$. For symmetrical initial conditions, the film ruptures at the two minima adjacent to the edges at time $t_f=1.6$.

Equations (43) have been solved numerically using also finite difference methods but with an implicit scheme.[19] FBC conditions will be considered here, and we recall some results in order to compare with the corresponding situation for FBC for the free film. The chosen parameters are different now and correspond to the order of magnitude used to obtain the system of two NEE, i.e., we take $A=O(1)$, $T=O(1/\epsilon^2)$. This clearly implies that the order of magnitude of the van der Waals forces must be higher for the film on solid substrate than for the free film in order to induce rupture instability.

The same regimes as in the case of the free film are recovered, i.e., three different behaviors can be distinguished depending on the relative size of L, λ_i, and λ_c. As an example, see Fig. 10. The dynamics of the film on a solid support being described by only two variables, the mechanism for the rupture stabilized by surfactants can be understood more easily than for free films and is the following: for an initial periodic disturbance of the film's thickness with a uniform distribution of surfactants, the potential $\phi(x,t)$ begins to rise beneath the depressions and falls at the elevations [see Eq. (42)]. So flows are generated in the film away from the depressions towards elevations, as shown by the value of the tangential velocity [see Eq. (41a)]. This flow produces gradients of surface tension and hence shear stresses that oppose the flow, following the tangential condition (40e). The concentration of surfactants is then high at the elevations (low surface tension) and nearly zero at the depressions (higher surface tension). In Fig. 10, we have taken a small value of the Marangoni number ($M=0.1$) in order to compare with the case of a free film. For $M=1$, the tangential velocity induces a shear stress sufficiently large to accumulate rapidly the surfactants near the edges.[19]

Despite the similarity of the dynamical behavior for the case of film on solid substrate and the case of free film at small Marangoni number, there appears significant differences between the order of magnitude of the rupture times. Indeed in the case of films on a solid substrate, the dimensionless rupture times are of the order one, which is about two orders of magnitude lower than in the case of a free film. This is explained by the fact that the van der Waals forces needed to induce the rupture are larger in the case of a film on a substrate.

VI. DISCUSSION

The main purpose of this paper was to study the role of insoluble surfactants on the stability of free-liquid films, taking into account the influence of van der Waals attraction and surface tension. We have shown that the nonlinear dynamics of such a free film with insoluble surfactants can be described by a simple model of three NEE for the evolution of the film thickness, the surfactants concentration and the tangential velocity of the fluid in the film. This fact was not clearly recognized in two preliminary studies devoted to the same problem by Prevost and Gallez[23] and by Sharma and Ruckenstein.[27] The previous model of Erneux and Davies[20] of two NEE for the evolution of a free film devoided of surfactants is naturally recovered as a special case.

A preliminary linear analysis of the model allows us to obtain the critical wave number of the problem, which depends on the van der Waals attraction and surface tension. This value corresponds to a steady bifurcation point, independent of the Marangoni forces. However, the physical role of the surfactant appears already: increasing the Marangoni number decreases the growth rate of the perturbation, and increases thus the time of rupture of the film.

Numerical integration of the NEE shows that for both periodic and fixed boundary conditions, three different dynamical regimes related to size effects can be observed: rupture instability, rupture after change of wavelength and stability. As concerns the rupture instability, we have carried out a parametric study for the role of van der Waals forces, surface tension and Marangoni forces, which confirms the results of the linear analysis. It has been shown that the surfactant monolayer has a stabilizing effect on the growth of the instability. Moreover, the flow dynamics in a rupture case indicates that the surfactants will flow away from the depressions of the thickness of the film to concentrate at its elevations. The boundary conditions influence also the dynamics in the sense that in large systems, PBC allow the film to rupture at all the minima while FBC distinguish between symmetrical or asymmetrical initial conditions, and the rupture is favored in the vicinity of the edges.

We have compared these results to those previously obtained for the stability of liquid films on solid substrate.[19] It was clearly shown that the velocity field is quite different in the two cases, due to the different boundary conditions imposed on the two surfaces. In the case of a free film, the SQ mode condition imposes zero normal velocity at the center of the film and no variation along z axis of the tangential velocity. In the case of a film on a solid substrate, the no-slip condition at the rigid boundary is simply zero normal and tangential velocity. This difference leads to another simple model for the dynamics of a film on a solid substrate, involving only two NEE for the evolution of the film thickness and surfactants concentration. This result will clearly reject the assumption often stated,[13,26] that the dynamics of a free film can be approximated by the dynamics of film of half thickness on a solid substrate.

Some perspectives remain open in the framework of this paper. First, it would be interesting to describe the traveling wave solutions which appear naturally as solutions of the linear set of equations for a steady-state with nonzero lateral velocity. Second, an investigation of the nonlinear problem in the vicinity of the steady bifurcation point in the presence of surfactants would shed new light on the behavior of the film near the rupture and allow comparison with the present numerical results. Third, it would be possible to extend the model in both geometries to interfaces with more general rheological behavior. In fact, if the interface possess surface viscosity, an additional term will appear in the constitutive equation for the surface. As already pointed out by Erneux and Davis,[20] the result of Williams and Davis[11] for a film without surfactants would appear if $\mu_s/\mu \rightarrow 0$ while the Prevost and Gallez[14] result for tangential immobile surface would emerge for $\mu_s/\mu \rightarrow \infty$. Eventually, different source terms could be taken into account for the change of surfactants concentration (surface chemical reactions with fixed or mobile sites, adsorption–desorption of soluble surfactants...). In that sense, the present paper should provide a useful basis to understand the interplay between the reaction–diffusion terms and the convective terms in the film dynamics.

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[1] R. K. Jain and E. Ruckenstein, "Stability of stagnant viscous films on a solid substrate," J. Colloid Interface Sci. **54**, 108 (1976).
[2] E. Ruckenstein and R. Jain, "Spontaneous rupture of thin liquid films," J. Chem. Soc. Faraday Trans. II **70**, 132 (1974).
[3] M. Prevost and D. Gallez, "Role of repulsive hydration forces on the stability of aqueous films. Application to vesicle fusion," J. Chem. Soc. Far. Trans. II **79**, 961 (1984).
[4] D. Gallez and W. T. Coakley, "Interfacial instability at cell membranes," Progr. Biophys. Mol. Biol. **48**, 155 (1986).
[5] A. Sheludko, "Thin liquid films," Adv. Colloid Interface Sci. **1**, 391 (1967).
[6] J. G. H. Joosten, "Spectral analysis of light scattered by liquid films," J. Chem. Phys. **80**, 2363, 2383 (1984).
[7] C. Y. Young and N. A. Clark, "Dynamics of freely suspended lyotropic films: An inelastic light scattering study of thermal surface fluctuations," J. Chem. Phys. **74**, 4171 (1981).

[8]B. U. Felderhof, "Dynamics of free liquid films," J. Chem. Phys. **49**, 44 (1968).

[9]E. H. Lucassen-Reynders and J. Lucassen, "Properties of capillary waves," Adv. Colloid Interface Sci. **2**, 247 (1969).

[10]R. J. Gummerman and G. M. Homsy, "The stability of radially bounded thin films," Chem. Eng. Commun. **2**, 27 (1975).

[11]M. B. Williams and S. H. Davis, "Nonlinear theory of film rupture," J. Colloid Interface Sci. **90**, 220 (1982).

[12]J. P. Burelbach, S. G. Bankoff, and S. H. Davis, "Nonlinear stability of evaporating/condensing liquid films," J. Fluid Mech. **195**, 463 (1988).

[13]D. Hatziavramidis, "Stability of thin evaporating/condensing films in the presence of surfactants," J. Multiphase Flow **18**, 517 (1992).

[14]M. Prevost and D. Gallez, "Nonlinear rupture of thin free liquid films," J. Chem. Phys. **84**, 4043 (1986).

[15]D. Gallez, N. M. Costa Pinto, and P. M. Bisch, "Nonlinear dynamics and rupture of lipid bilayers," J. Colloid Interface Sci. **160**, 141 (1993).

[16]Z. Dagan and L. M. Pismen, "Marangoni waves induced by a multistable chemical reaction on thin liquid films," J. Colloid Interface Sci. **99**, 215 (1984).

[17]O. E. Jensen and J. B. Grotberg, "Insoluble surfactant spreading on a thin viscous film: shock evolution and film rupture," J. Fluid Mech. **240**, 259 (1992).

[18]O. E. Jensen and J. B. Grotberg, "The spreading of heat or soluble surfactant along a thin liquid film," Phys. Fluids A **5**, 58 (1993).

[19]D. Gallez, "Nonlinear stability analysis for animal cell adhesion to solid support," Colloids Surf. B: Biointerfaces **2**, 273 (1994).

[20]T. Erneux and S. H. Davis, "Nonlinear rupture of free films," Phys. Fluids A **5**, 1117 (1993).

[21]C. V. Sternling and L. E. Scriven, "Interfacial turbulence: hydrodynamic instability and the Marangoni effect," AIChE J. **5**, 514 (1959).

[22]C. Maldarelli, R. K. Jain, I. B. Ivanov, and E. Ruckenstein, "Stability of symmetric and unsymmetric thin liquid films to short and long wavelength perturbations," J. Colloid Interface Sci. **78**, 118 (1980).

[23]M. Prevost and D. Gallez, "Nonlinear stability of thin free liquid films: rupture and Marangoni effects," AIChE Symp. Ser. **252**, 123 (1986).

[24]H. A. Stone, "A simple derivation of the time-dependent convective–diffusion equation for surfactant transport along a deforming interface," Phys. Fluids A **2**, 11 (1990).

[25]W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1989).

[26]P. Constantin, T. F. Dupont, R. E. Goldstein, L. P. Kadanoff, and M. J. Shelley, "Droplet breakup in a model of Hele–Shaw cell," Phys. Rev. E **47**, 4169 (1993).

[27]A. Sharma and E. Ruckenstein, "Rupture of thin free liquid films with insoluble surfactants: nonlinear aspects," AIChE Symp. Ser. **252**, 130 (1986).