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Falling films and the Marangoni effect

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The instability of a falling liquid film of an aqueous surfactant solution along a vertical slope with surfactant adsorption-desorption at its open surface originating surface stresses (Marangoni effect) is investigated. The diffusion of surfactant to the film surface from the bulk and desorption of surfactant to the gas phase are taken into account. The Navier-Stokes and Fick equations are reduced to a system of simpler hence, analytically and numerically, more tractable nonlinear evolution equations albeit with nine dimensionless parameters. The linear stability analysis yields a dispersion equation that is numerically solved and eigenvalues are obtained for various values of significant dimensionless parameters. A very rich picture of instabilities appears. In addition to the earlier known (Kapitza) hydrodynamic mode there are up to four new (Marangoni-driven) diffusion modes. Two modes travel with the liquid velocity on the film surface and the other two travel on their own downstream and upstream, respectively. One diffusion mode could be identified, in the reference frame moving with the liquid on the film surface, as a monotonic instability mode hence leading to a patterned film surface. All other modes are oscillatory ones. Resonance of modes is also predicted for suitable combinations of the parameters of the problem. The mode observed depends upon the surface stress (in terms of a dimensionless Marangoni number), the particular choice of the adsorption-desorption kinetics, and the surface tension state equation at the open surface of the film.

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I. INTRODUCTION

Surface tension gradients due to mass or heat transfer along or across a liquid-gas or a liquid-liquid interface generate surface stresses (thermocapillary or solutocapillary Marangoni effect) that either create flow, alter an existing one, or trigger instability eventually leading to flow motions, steady or otherwise [1–38]. Most publications dealing with the role of the Marangoni effect in hydrodynamic problems have been devoted to study the instability of initially motionless liquid layers or drops under conditions of stationary heating or mass diffusion. Here we shall consider the problem that arises when the Marangoni effect influences the hydrodynamic modes in an already existing flow in a vertically falling liquid film with deformable open outer surface. Thus we consider the surface tension gradient-driven extension of the problem long ago experimentally studied by the Kapitzas [39,40] with theory provided by Shkadov [41,42]; see also Refs. [43–62]. We confine our analysis only to the solutal Marangoni effect, when there is mass transfer of a surface active solute (hereafter called surfactant) in the vertically falling film. Sternling and Scriven [2] pointed out the importance of the solutal Marangoni effect in determining whether and under what conditions instabilities may develop at the interface separating two fluids of different material and transport properties (see also Refs. [16,17,20]). On the other hand the stabilizing effect of surfactants on growing waves in falling films has been observed in experiments and predicted by theory [3,5,8,63].

A theoretical analysis of the stabilizing effect of soluble and insoluble surfactants on growing waves in falling films has been carried out by Lin [8]. More recently the eigenvalues of the stability problem for vertical film flows with diffusion and evaporation of surfactant (in fact desorption of surfactant from liquid to the gas phase) was done by Ji and Setterwall [24]. These authors found in addition to the (Kapitza) hydrodynamic mode a weak diffusion instability mode. This analysis was extended to the flow with mass and heat transfer in a later publication [28]. A similar problem concerning the thermocapillary instability of a flowing film down an inclined plane was investigated for small wave numbers by Lin [11]. Kelly, Davis, and Goussis [14] and Goussis and Kelly [18] extended the theory to account for finite wave numbers. They obtained two thermocapillary (diffusion) modes of instability in addition to the hydrodynamic mode. Here we further extend their linear stability analysis to account for surfactant adsorption-desorption. As already shown by Ji and Setterwall [24] the stability analysis of the falling film implies several parameters even for very slow adsorption and desorption processes. Thus it is a very complicated task to obtain the full spectrum of eigenvalues. To avoid this difficulty we shall make use of a method introduced in Refs. [41,42] that has been shown useful in a variety of problems [33,64–71]. This method reduces the problem to a system of time-dependent one-dimensional differential equations and it allows to study instability for small and moderately large wave numbers. Palmer and Berg [10] have analyzed a rather general case of mass transfer at an interface (see also Ref. [19]). The following quantities were introduced: bulk concentration of a surface active solute (surfactant), $c(x,y,t)$, bulk concentration in the fluid sublayer (macroscopically near the interface), $\overline{c}(x,t)$, surface excess concentration in the adsorbed layer on the interface, $\Gamma(x,t)$, and mass flux of surfactant from the bulk liquid to the

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interface, $j(x,t)$. At the quasisteady state these quantities were assumed to be connected by the following adsorption-desorption kinetics:

$$\overline{c} - k_d\Gamma = j, \tag{1}$$

where only linear adsorption and desorption processes with rate constants k_a and k_d are considered. There are two limiting cases: fast and slow adsorption-desorption kinetics. For fast enough kinetics a local adsorption-desorption equilibrium could be introduced. As it follows from Eq. (1), equilibrium in the system with adsorption-desorption corresponds to $j=0$. There is local equilibrium of the surface excess solute with the solute in the adjacent subphase and hence the (local) equilibrium values of $\overline{c}$ and Γ are connected by the relation

$$\Gamma = k_a k_d^{-1}\overline{c} \tag{2}$$

which formally corresponds to the (ideal) Gibbs adsorption isotherm for very dilute solutions.

Deviations from equilibrium of the system with surfactant may be due to various reasons, namely, initial nonequilibrium conditions, intense adsorption and desorption of surfactant, chemical reaction at the interface, etc. With diffusion to the interface we have $j \neq 0$ [19,72]. The mass transfer process is determined by the values of $k_a, k_d, \overline{c}$, and Γ. If every term on the left-hand side (lhs) of Eq. (1) exceeds greatly the diffusion flux j, then the mass transfer process could be treated as locally in equilibrium (then j is a small difference between two large values on the lhs). In this case, the relation (2) at local equilibrium between $\overline{c}$ and Γ, which are functions of space and time, is fulfilled and the adsorption and desorption processes are controlled by bulk diffusion.

For simple surfactant molecules and moderately dense solutions the Langmuir adsorption isotherm is

$$\Gamma = \Gamma^{\infty}\frac{\overline{c}}{a+\overline{c}} \tag{3}$$

and the corresponding equation of state for the surface tension is the Szyszkowsky equation

$$\sigma - \sigma_0 = -RT\Gamma^{\infty}\ln\left(1+\frac{\overline{c}}{a}\right), \tag{4}$$

where Γ^{∞} corresponds to a complete coverage, the surface excess saturation or maximum realizable of surface excess concentration, and a is constant for a given surfactant (adsorption coefficient) [19]. From Eq. (4) follows the relation

$$\Gamma = \left(-\frac{1}{RT}\frac{d\sigma}{d\overline{c}}\right)\overline{c}. \tag{5}$$

Note that for small deviations from an initial equilibrium state

$$-\frac{1}{RT}\frac{d\sigma}{d\overline{c}} \equiv L = \text{const}.$$

Then Eq. (5) takes the form of the Gibbs equation (2),

$$\Gamma = L\overline{c}. \tag{6}$$

For a more general adsorption-desorption kinetics one needs to apply the nonequilibrium relation (1) with, e.g., the equilibrium Langmuir adsorption isotherm (3). Alternatively one could use nonlinear kinetics rather than Eq. (1). For instance, Boyadjiev and Beschkov [73] have used the relation

$$k_a\left(1-\frac{\Gamma}{\Gamma^{\infty}}\right)\overline{c} - k_d\Gamma = j. \tag{7}$$

More general forms of nonlinear relations have been discussed in the literature [27,74] but we shall not use them here in view of the additional complexity they add to the already very complex problem we have with many parameters involved.

The local equilibrium linear approximation (2) for systems with surfactants has been widely exploited to investigate various nonequilibrium mass transfer problems. Ward and Tardai [75] have investigated the time-dependent problem for one-dimensional solutal systems, with nonequilibrium adsorption-desorption caused by the initial condition $\Gamma=0$. They used the Langmuir isotherm (3) to close the mathematical formulation. However, deviations from the local equilibrium conditions for small Γ values could be significant. Nonequilibrium conditions also arise at the initial parts of the falling film or for the jet flowing out of the orifice. The surface excess concentration Γ increases from the initial value $\Gamma=0$ as the distance from the flow orifice grows. Defay and Petre [76], Balbaert *et al.* [77], and Bechtel *et al.* [78] have used one-dimensional unsteady formulations together with the time-space analogy to obtain the dynamic surface tension theoretically for these flows and to compare theoretical results with experiments. In an initially motionless liquid layer the deviations from equilibrium are connected with desorption to air or adsorption of surfactant on the interface. For $j \neq 0$, Brian [9] investigated the hydrodynamic instability of a motionless layer of solute under the assumption of local equilibrium (2). He only considered small deviations from the initial equilibrium state (see also Refs. [25,26]).

The second limiting case of Palmer and Berg's [10] analysis refers to very slow adsorption and desorption processes so that k_a and k_d are practically zero, and j vanishes. The mass transfer in the sublayer near the interface is kinetically frozen, so the surface excess concentration Γ is effectively unchanged, hence

$$\Gamma \equiv \Gamma_0 = \text{const}. \tag{8}$$

Ji and Setterwall [24,28] have applied Eq. (8) to study the stability of a falling film of solute with the Marangoni effect. They computed Γ_0 using Eq. (2), although this relation in fact corresponds to the case of fast adsorption-desorption kinetics.

Besides the simplification in the solution procedure both approximations (2) and (8) have the advantage that the Marangoni stress calculations are made simpler as the functional dependence $\sigma=\sigma(\overline{c})$ is appropriate for both cases. The situation is not so clear when the nonequilibrium adsorption-desorption kinetics is governed by Eq. (1) or Eq. (7). There is the choice between one of the three possibilities: $\sigma(\overline{c})$, $\sigma(\Gamma)$, or $\sigma(\overline{c},\Gamma)$. The latter case is the general one and, formally, solves the difficulty, but due to lack of experimental data this relationship is not so useful. The first two possibilities have been used in most publications. Palmer and Berg [10] used the relation $\sigma(\overline{c})$ in most of their computations, although they started considering $\sigma(\Gamma)$. Hennenberg *et al.* [20] used $\sigma(\Gamma)$ in their discussion of the stability of a motionless horizontal liquid layer with surfactant adsorption barrier. Ryabitzkiy [29] has also done a similar study. Feinermann *et al.* [79] investigated the complicated problem of filling the adsorbed layer with molecular chains of two types. They had to introduce two surface excess concentrations Γ_1 and Γ_2. At the same time the dependence $\sigma(\overline{c})$ was considered to compare theoretical and experimental results. In view of all these earlier studies here both functional possibilities or surface equations of state, $\sigma=(\overline{c})$ and $\sigma(\Gamma)$, are considered separately one after the other, and results are compared at the end.

In Sec. II we state the mathematical problem. Sections III and IV are devoted to a description of the reduced evolution and stability problems, respectively. In Sec. V we present the results obtained and we discuss the various unstable modes found for positive and negative values of the Marangoni number, and two different adsorption-desorption kinetics and surface tension equations of state. In Sec. VI we provide a summary of results and conclusions.

II. MATHEMATICAL FORMULATION

We consider a falling liquid (e.g., an aqueous solution) with flow and diffusion connected together by the adsorption-desorption of surfactant on the open deformable surface.

Let x,y,z be the orthogonal coordinate system with origin located on the rigid solid wall. The axis x is directed along the wall, positive down in the direction of gravity. The film flow of the aqueous solution is described by the Navier-Stokes equations, and for the bulk concentration of surfactant, c, we use Fick's equation

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0,$$

$$\frac{dv}{dt}=-\frac{1}{\rho}\frac{\partial p}{\partial y}+\nu\triangle v,$$

$$\frac{du}{dt}=-\frac{1}{\rho}\frac{\partial p}{\partial x}+\nu\triangle u+g,$$

$$\frac{dc}{dt}=D\triangle c \tag{9}$$

together with the following boundary conditions on the rigid wall,

$$y=0,\quad u=0,\quad v=0,\quad \frac{\partial c}{\partial y}=0, \tag{10}$$

and on the film open surface

$$y=h(x,t),\quad \frac{\partial h}{\partial t}+u\frac{\partial h}{\partial x}=v,$$

$$p=p_a+2\mu\frac{1}{b^2}\left[(1-b^2)\frac{\partial v}{\partial y}-\frac{\partial h}{\partial x}\left(\frac{\partial v}{\partial x}+\frac{\partial u}{\partial y}\right)\right]-\sigma\frac{1}{b^3}\frac{\partial^2 h}{\partial x^2},$$

$$\mu(1-b^2)\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right)+2\mu\left(\frac{\partial v}{\partial y}-\frac{\partial u}{\partial x}\right)\frac{\partial h}{\partial x}-b\frac{\partial \sigma}{\partial x}=0, \tag{11}$$

$$\frac{\partial \Gamma}{\partial t}+\frac{1}{b}\frac{\partial}{\partial x}\left[\frac{\Gamma}{b}\left(u+v\frac{\partial h}{\partial x}\right)\right]-D_s\frac{1}{b}\frac{\partial}{\partial x}\left(\frac{1}{b}\frac{\partial \Gamma}{\partial x}\right)+\frac{k_g}{m}\overline{c}=j,$$

$$j=-D\frac{1}{b}\left(\frac{\partial c}{\partial y}-\frac{\partial h}{\partial x}\frac{\partial c}{\partial x}\right),$$

$$b=\left[1+\left(\frac{\partial h}{\partial x}\right)^2\right]^{1/2}. \tag{12}$$

Note that in Eq. (9) d/dt is the material derivative. Δ denotes here the Laplacian. In view of the long wavelength approximation to be used here a term due to the expansion of the curved interface [80] is omitted in Eq. (12). In Eq. (11) p_a denotes the outside air or gas pressure.

In the initial section of the film a uniform distribution of surfactant concentration is assumed,

$$x=x_0,\quad c=c_*=\text{const}. \tag{13}$$

Equations (9)–(13) have been employed by Palmer and Berg [10] and by Hennenberg *et al.* [20]. Equation (12) also appears in the formulation for the falling film done in Ref. [24] with, however, $\Gamma=\text{const}$. The last term on the left-hand side of Eq. (12) accounts for the desorption of the surfactant from the liquid phase into the gas phase; k_g is the gas phase mass transfer coefficient of the surfactant, m is the ratio of the concentration in the liquid phase to the concentration in the gas phase at equilibrium. Two assumptions when deriving this boundary equation are that the concentration of the surfactant in the gas phase far from interface is zero and that there is equilibrium at the interface between the concentration in the gas phase and the concentration in the liquid film. To obtain $(\partial\sigma/\partial x)$ an equation of state for σ must be specified thus leading to a closed mathematical formulation. As already mentioned, two relationships $\sigma(\overline{c})$ and $\sigma(\Gamma)$ will be used here.

Let us consider that the surface tension σ is a linear function of the bulk surfactant concentration on the free surface, $\overline{c}(x,t)$,

$$\sigma=\sigma_*+\frac{d\sigma}{d\overline{c}}(\overline{c}-c_*). \tag{14}$$

To state the problem in dimensionless form we introduce suitable scales and hence

$$x,y,h,t \to \frac{1}{n_*}lx, \quad ly, \quad lh, \quad \frac{l}{n_* U_*}t,$$

$$u,v,c,\Gamma \to U_* u, \quad n_* U_* v, c_*(1+c), \quad \Gamma_*(1+\Gamma). \tag{15}$$

Dimensional quantities stand on the left sides of Eq. (15) and their corresponding dimensionless values are contained on the right sides. The scales l, U_*, c_*, Γ_* together with a stretching or contracting parameter n_* are yet to be prescribed.

After introducing Eq. (15) in Eqs. (9)–(13), the dimensionless formulation of the problem yields the corresponding equations. The following ten dimensionless parameters have been introduced:

$$\mathrm{Re} = \frac{U_* l}{\nu}, \quad \mathrm{Pe} = \frac{U_* l}{D}, \quad \mathrm{We} = \frac{\rho l U_*^2}{\sigma}, \quad \mathrm{Fr} = \frac{U_*^2}{gl},$$

$$\mathrm{Ma} = -\frac{d\sigma}{d\overline{c}}\frac{c_*}{\mu U_*}, \quad \mathrm{G} = \frac{\Gamma_* U_*}{c_* D}, \quad \mathrm{Bi} = \frac{k_g l}{mD},$$

$$\mathrm{Di} = \frac{D_s \Gamma_*}{D l c_*}, \quad \pi_1 = \frac{k_a l}{D}, \quad \pi_2 = \frac{k_d \Gamma_* l}{c_* D}. \tag{16}$$

Re, Pe, We, Fr, Ma, and Bi stand for Reynolds, Peclet, Weber, Froude, Marangoni, and Biot numbers (recall that here Bi refers to mass transfer only and it plays a similar role to the usual Bi number in heat transfer) [13,15,37,38]. G gives an indication of the relative value of the surface excess concentration to the bulk concentration. Di refers to diffusion.

We shall consider film flows when the capillary forces are of the same order as the viscous and the gravitational ones. Let us introduce for these flows the relations

$$\frac{n_*^2}{\mathrm{We}} = \frac{3}{n_* \mathrm{Re}} = \frac{1}{n_* \mathrm{Fr}} = \frac{1}{5\delta}. \tag{17}$$

From Eq. (17) the three quantities l, n_*, and δ are found,

$$n_* = \gamma^{-1/3}(3\ \mathrm{Re})^{2/9}, \quad \delta = \frac{1}{45}\gamma^{-1/3}(3\ \mathrm{Re})^{11/9},$$

$$\gamma = \frac{\sigma}{\rho}(\nu^4 g)^{-1/3}, \quad l = \left(\frac{3\nu^2}{g}\right)^{1/3}\mathrm{Re}^{1/3}. \tag{18}$$

The parameter n_* which plays a crucial role in the procedure of simplification of the Navier-Stokes and Fick equations, Eqs. (9)–(12), can be expressed in terms of the capillary or crispation number Ca,

$$\mathrm{Ca} = \frac{\mu U_*}{\sigma} = \frac{\mathrm{We}}{\mathrm{Re}} \tag{19}$$

and thus $n_* = (3\ \mathrm{Ca})^{1/3}$. The relevance of the above introduced quantities and approximations can be seen by considering a water film $\gamma = 2850$ for a sequence of Re values. The conditions $n_*^2 \ll 1$ and $n_*^2 \mathrm{We}^{-1} \sim 1$ are fulfilled for Re values, $30 > \mathrm{Re} > 5$, or for δ values, $0.4 > \delta > 0.043$. Noteworthy is that the Kapitzas in their pioneering experiments on wavy film flows worked precisely in such interval of Re numbers [40].

To investigate the multiparameter problem Eqs. (9)–(13) let us make use of a simplifying method [41,42]. Let us also, as already noted, consider that $n_*^2 \ll 1$. For wavy motions this condition means that the wavelength is larger than the film thickness. Thus for a wave number α we have the condition $n_* \alpha \ll 1$. We intend now to omit those terms in Eqs. (9)–(13), which have an order $o(n_*^2)$ and which are negligible for $n_*^2 \ll 1$. For example, from Eq. (12) it follows $b = (1 + n_*^2 h_x^2)^{1/2}$, where $h_x = o(1)$ in accordance with the choice of the factor n_*. Then the cumbersome boundary conditions (11) and (12) could be simplified by taking $b = 1$ to order $o(n_*^2)$. At the same time we retain the products $n_*\mathrm{Re}$, $n_*\mathrm{Ma}$, $n_*\mathrm{Fr}$, $n_*^2\mathrm{We}^{-1}$, and $n_*^2\mathrm{Di}$, which could have order unity or even higher, i.e., of the order of $n_*\mathrm{Pe}$ and $n_* G$ in accordance with the magnitudes of the full dimensionless parameters. Thus we can consider values of G, Re, Pe, Ma, Fr, We, and Di in a broad range.

After omitting all terms in Eqs. (9)–(12) of order n_*^2, the boundary layer approximation, with self-induced pressure, is obtained. Such an approximation includes hydrodynamic and diffusion parts which are connected by the Marangoni stress due to the boundary condition for tangential forces in Eq. (11),

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{\partial p}{\partial x} + \frac{1}{n_* \mathrm{Re}}\frac{\partial^2 u}{\partial y^2} + \frac{1}{n_* \mathrm{Fr}},$$

$$\frac{\partial p}{\partial y} = 0,$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \tag{20}$$

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} = \frac{1}{n_* \mathrm{Pe}}\frac{\partial^2 c}{\partial y^2},$$

$$y = h(x,t), \quad \frac{\partial h}{\partial t} + u\frac{\partial h}{\partial x} = v, \tag{21}$$

$$p = -\frac{n_*^2}{\mathrm{We}}\left(1 - \frac{\mathrm{Ma}\mathrm{We}}{\mathrm{Re}}\overline{c}\right)\frac{\partial^2 h}{\partial x^2},$$

$$\frac{\partial u}{\partial y} = -n_* \mathrm{Ma}\frac{\partial \overline{c}}{\partial x}, \tag{22}$$

$$\frac{\partial c}{\partial y} + \mathrm{Bi}(1+\overline{c}) + n_* G\left(\frac{\partial \Gamma}{\partial t} + \frac{\partial u(1+\Gamma)}{\partial x}\right) - n_*^2 \mathrm{Di}\frac{\partial^2 \Gamma}{\partial x^2} = 0,$$

$$-\frac{\partial c}{\partial y} = \pi_1(1+\overline{c}) - \pi_2(1+\Gamma) \tag{23}$$

together with the boundary conditions (10) and initial conditions

$$x=0, \quad h=1, \quad c=0.$$

If rather the relation $\sigma=\sigma(\Gamma)$ instead of $\sigma=\sigma(\overline{c})$ is considered then in Eq. (22) the term $\mathrm{Ma}_1\Gamma_x$ appears instead of $\mathrm{Ma}\overline{c_x}$ with $\mathrm{Ma}_1=-(d\sigma/d\Gamma)(\Gamma_*/\mu U_*)$.

From Eqs. (17) and (19) we obtain

$$\mathrm{Ma}\frac{\mathrm{We}}{\mathrm{Re}}=\frac{1}{3}n_*^3\mathrm{Ma}.$$

For $n_*^2 \ll 1$ this product is small, of order $o(n_*^2)$ for $\mathrm{Ma} \leqslant 10$. Thus $\mathrm{Ma}(\mathrm{We}/\mathrm{Re})$ in Eq. (22) could be omitted for all δ values under consideration. Due to Eq. (17) only the parameter δ enters the formulation Eqs. (20)–(23) instead of Re, Fr, and We. Then the formulation given applies for any liquid provided $\gamma \gg 1$.

III. THE REDUCED EVOLUTION EQUATIONS

To investigate the solutions of the differential equations with boundary and initial conditions, Eqs. (20)–(23), the Galerkin method is applied in coordinate y. For the spectral representation of the unknown functions a system of polynomials is used as a basis set. For the coefficients of spectral representations which are functions of x and t, a system of one-dimensional time-dependent differential equations follows from the Galerkin method. Direct numerical integration of the initial problem [Eqs. (20)–(23)] for $\mathrm{Ma}=0$ by Demekhin *et al.* [69] and experimental measurements by Alekseenko *et al.* [54] have shown that the velocity profile in coordinate y for the wavy film flow could be approximated by the simplest polynomial satisfying the boundary conditions. Thus for the spectral representation of u it is enough to take into account only the first term. Here we take advantage of their results and use them, as a working approximation, also for velocity profiles in wavy film flows with concentration profiles c, when $\mathrm{Ma}\neq 0$.

The small parameter $\varepsilon=(n_*\mathrm{Pe})^{-1/2}$ in Eq. (21) estimates the diffusion boundary layer near the outer open surface of the liquid film. Let us introduce the stretched coordinate near the surface $y=h(x,t)$,

$$y=h-\varepsilon\zeta. \tag{24}$$

For the concentration field $c(x,y,t)$ inside the diffusion boundary layer the following boundary conditions can be used:

$$\zeta=0, \quad c=\overline{c}(x,t),$$

$$\zeta=\Delta(x,t), \quad c=0, \quad \frac{\partial c}{\partial \zeta}=0. \tag{25}$$

The simplest polynomial representation of $c(x,y,t)$ which satisfies the boundary conditions (25) is

$$c=\overline{c}\left(1-\frac{\zeta}{\Delta}\right)^2. \tag{26}$$

Note that in Eq. (25), $\Delta(x,t)$ accounts for the thickness of the diffusion boundary layer, hence from Eqs. (24) and (25) follows $c=0$ for $h-\varepsilon\Delta > y > 0$.

The velocity field $u(x,y,t)$ is assumed to be represented according to boundary conditions (10) and (22) as follows:

$$u=\overline{u}(2\eta-\eta^2)+Mh(\eta-\eta^2)\overline{c_x}, \quad y=\eta h, \quad \overline{c_x}=\frac{\partial \overline{c}}{\partial x}, \tag{27}$$

where we have rescaled the Marangoni number, $M=n_*\mathrm{Ma}$.

By inserting Eqs. (26) and (27) in Eqs. (20) and by integrating the resulting expressions from $y=0$ to $y=h$, the equations for h, $\overline{u}$, $\overline{c}$, $\overline{\Gamma}$, and Δ as functions of (x,t) are obtained. With the help of Eq. (17) we have

$$\frac{\partial h}{\partial t}+\frac{\partial q}{\partial x}=0,$$

$$\frac{\partial q}{\partial t}+\frac{\partial Q}{\partial x}=\frac{1}{5\delta}\left(h\frac{\partial^3 h}{\partial x^3}+h-\frac{2}{3h}(\overline{u}+Mh\,\overline{c_x})\right),$$

$$\frac{\partial \varphi}{\partial t}+\frac{\partial}{\partial x}[(A\overline{u}+BMh\,\overline{c_x})\varphi]=2\frac{\overline{c}}{\Delta},$$

$$n_*G\left(\frac{\partial \Gamma}{\partial t}+\frac{\partial}{\partial x}(\overline{u}\Gamma)+\frac{\partial \overline{u}}{\partial x}-n_*^2\mathrm{Di}\frac{\partial^2\Gamma}{\partial x^2}\right)+\mathrm{Bi}(1+\overline{c})=-2\frac{\overline{c}}{\varepsilon\Delta},$$

$$\pi_1(1+\overline{c})-\pi_2(1+\Gamma)=-2\frac{\overline{c}}{\varepsilon\Delta}, \tag{28}$$

where

$$q=\int_0^h u\,dy=\frac{2}{3}\overline{u}h+\frac{1}{6}Mh^2\overline{c_x},$$

$$Q=\int_0^h u^2dy=\frac{8}{15}\overline{u}^2h+\frac{7}{30}Mh^2\overline{uc_x}+\frac{1}{30}h(Mh\,\overline{c_x})^2,$$

$$\varphi=\int_0^\Delta c\,d\zeta=\frac{1}{3}\overline{c}\Delta \tag{29}$$

with

$$A=1-\frac{1}{10}\left(\frac{h_1}{h}\right)^2, \quad B=\frac{1}{4}\frac{h_1}{h}-\frac{1}{10}\left(\frac{h_1}{h}\right)^2 h_1=\varepsilon\Delta.$$

In what follows we shall take approximate values

$$A=1, \quad B=\frac{1}{4}\frac{h_1}{h}$$

and for the thickness of the diffusion boundary layer $(h_1/h) \ll 1$. The system of equations (28) and (29) must be solved with the initial conditions

$$x=0,\ \overline{c}=0,\ \Gamma=0,\ \varphi=0,\ \Delta=0. \tag{30}$$

The first two conditions (30) together with Eq. (13) imply that the dimensional quantities $\overline{c}$ and Γ at the point $x=0$ are taken as reference values, $c_* = \overline{c}(0,t)$ and $\Gamma_* = \Gamma(0,t)$, respectively.

In the system (28) for surface tension, gravity, and viscous forces stand the terms $hh_{xxx}, h, -(2/3\ h)(\overline{u} + Mh\ \overline{c_x})$, respectively. As expected, for $\mathrm{Ma}=0$, Eqs. (28) reduce to the original result obtained in Refs. [41,42] for wavy film flows in the absence of surfactants. For $Mh\overline{c_x} = \tau$, where τ is prescribed, we recover the equations derived by Esmail and Shkadov [81]. Most of the Kapitzas [39,40] experiments and more recent experimental observations on regular wave film flows have been explained theoretically on the basis of periodic solutions of the nonlinear system (28) for $\mathrm{Ma}=0$. A detailed comparison of theory and experiments concerning wavy films has been recently provided by Shkadov and Sisoev [71].

The base state of the flow with surfactant mass transfer is expressed by the stationary solution of Eq. (28),

$$h_0 = 1,\ \overline{u_0} = \frac{3}{2},\ \overline{c_0},\ \Gamma_0. \tag{31}$$

Using the stretched variables, $x_1 = \varepsilon^2 x$ and $\varphi_1 = \varepsilon\varphi$, the system (28) becomes

$$\overline{u}\frac{\partial \varphi_1}{\partial x_1} - \frac{1}{2}\varepsilon^2 M \frac{\partial}{\partial x_1}\left(\frac{\overline{c}\varphi_1}{s}\overline{c_x}\right) = -s,$$

$$s = \mathrm{Bi}(1+\overline{c}) + \varepsilon^2 n_* G\overline{u}\frac{\partial \Gamma}{\partial x_1} - \varepsilon^4 n_*^2 \mathrm{Di}\frac{\partial^2\Gamma}{\partial x_1^2},$$

$$s = \pi_1(1+\overline{c}) - \pi_2(1+\Gamma),$$

$$\varphi = -\frac{2}{3}\frac{\overline{c^2}}{s}. \tag{32}$$

Neglecting the terms of order ε^2, from Eq. (32) follows that

$$\frac{d}{dx_1}\left(\frac{\overline{c^2}}{1+\overline{c}}\right) = \mathrm{Bi}^2(1+\overline{c}),$$

$$\pi_1(1+\overline{c}) - \pi_2(1+\Gamma) = \mathrm{Bi}(1+\overline{c}),$$

$$s = \mathrm{Bi}(1+\overline{c}). \tag{33}$$

The differential equation (33) with the initial condition (30) has a solution in closed form,

$$\ln(1+\overline{c}) + \frac{1}{2}\left(\frac{1}{1+\overline{c}}\right)^2 = \frac{1}{2} + \mathrm{Bi}x_1. \tag{34}$$

From the second equation, Eq. (33), we obtain

$$\pi_1 - \pi_2 = \mathrm{Bi}, \quad \Gamma = \overline{c}. \tag{35}$$

Now the concentrations $\overline{c}$ and Γ for the stationary diffusion conditions can be calculated from Eqs. (34) and (35) for every x_1 value, if the value of the parameter Bi is specified. From Eq. (33) follows that the desorption of surfactant to the gas phase is the only reason for the adsorption-desorption to deviate from the equilibrium state corresponding to $\mathrm{Bi}=0$. Thus we deal with the evolution and subsequent effects of the surfactant transfer from the equilibrium conditions at the initial section $x=0$. To estimate the accuracy of the approximate solution (34), comparison of Eq. (34) with the exact solution of the stationary diffusion problem given by Ji and Setterwall [24] can be done. For $\mathrm{Pe}=10^6, \mathrm{Bi}=10$, and $\overline{c_0} = -0.25$ the exact solution gives $x = 1000l$ and $h_1 = 0.09$ [h_1 is obtained only approximately from the graphical dependence $c(y)$]. The appropriate values from Eq. (34) are $x=1012l$ and $h_1 = 0.0666$.

IV. STABILITY ANALYSIS

Let us now consider the response of the base state to infinitesimal disturbances. The base state corresponds to the diffusion boundary layer near the surface of the falling film. The linear or nonlinear behavior of the aqueous solution film with surfactant desorption to air is described by the Eqs. (28). For the base state we take Eqs. (31), (34), and (35) combined with

$$\overline{c_0} = \overline{c}(\varepsilon^2 x_0), \quad \Gamma_0 = \overline{c}(\varepsilon^2 x_0),$$

$$s_0 = \mathrm{Bi}(1+\overline{c_0}), \quad \varphi_0 = \frac{2}{3}\frac{\overline{c_0^2}}{s_0}. \tag{36}$$

For the hydrodynamic stability analysis the base states (31) and (36) are assumed to have no x dependence as $\overline{c}(\varepsilon^2 x_0)$ is a slowly varying function and hence x enters in Eq. (36) as a parameter.

Thus we assume that $\overline{c_0} = \mathrm{const}, \Gamma_0 = \mathrm{const}$ and then we proceed to investigate the stability of the base state (31) to infinitesimal disturbances. The stability analysis must be repeated for various sections $x = x_0$ as x grows from the initial section $x=0$. Thus we now introduce

$$\overline{u} = \overline{u_0} + u',\ h = 1 + h',\ \overline{c} = \overline{c_0} + c',\ \Gamma = \Gamma_0 + \Gamma',$$

$$s = s_0 + s',\ \varphi = \varphi_0 + \varphi'. \tag{37}$$

After linearizing Eq. (28) the equations for disturbances (37) are

$$\frac{\partial h'}{\partial t} + \frac{\partial q'}{\partial x} = 0,$$

$$5\delta\left(\frac{\partial q'}{\partial t} + \frac{\partial Q'}{\partial x}\right) = \frac{\partial^3 h'}{\partial x^3} + 2h' - \frac{2}{3}u' - \frac{2}{3}Mc'_x,$$

$$\frac{\partial \varphi'}{\partial t} + \overline{u_0}\frac{\partial \varphi'}{\partial x} + \varphi_0\frac{\partial u'}{\partial x} - \frac{1}{2}M\frac{\overline{c_0}\varphi_0}{s_0}\frac{\partial^2 c'}{\partial x^2} = -s',$$

$$\frac{1}{\varepsilon}s' = \mathrm{Bi}c' + n_* G\left(\frac{\partial \Gamma'}{\partial t} + (1+\Gamma_0)\frac{\partial u'}{\partial x} + \overline{u_0}\frac{\partial \Gamma'}{\partial x}\right) - n_*^2\mathrm{Di}\frac{\partial^2\Gamma'}{\partial x^2},$$

$$\frac{1}{\varepsilon}s' = \pi_1 c' - \pi_2 \Gamma', \tag{38}$$

where

$$q' = h' + \tfrac{2}{3}u' + \tfrac{1}{6}\, Mc'_x,$$

$$Q' = \tfrac{6}{5}\, h' + \tfrac{8}{5}\overline{u} + \tfrac{7}{20}Mc'_x.$$

For the solutions of Eq. (38), moving or stationary waves periodic in x (normal modes), we consider

$$(u', h', c', \Gamma') = (\tilde{u}, \tilde{h}, \tilde{c}, \tilde{\Gamma}) \exp\, i\alpha(x - \omega t), \tag{39}$$

where ω is a complex quantity ($\omega = \omega_r + i\omega_i$).

Using Eqs. (38) and (39) we get the following equations for the unknown amplitudes, $\tilde{u}, \tilde{h}, \tilde{c}, \tilde{\Gamma}$, and $\tilde{\varphi}_1$:

$$\tfrac{2}{3}\tilde{u} + (1 - \omega)\tilde{h} + \tfrac{1}{6}z\tilde{c} = 0,$$

$$\left(\frac{\theta}{\beta} - \omega + \frac{12}{5}\right)\tilde{u} - \frac{3}{2}\left(2\frac{\theta}{\beta} - \alpha^2\theta - \frac{6}{5} + \omega\right)\tilde{h} + z\left(\frac{\theta}{\beta} - \frac{1}{4}\omega + \frac{21}{40}\right)\tilde{c} = 0,$$

$$\beta\xi\tilde{\varphi}_1 - [B_1^2 + M_1\alpha^2(1 + \overline{c_0})]\tilde{c} - B_1 G_1\left(\beta\xi + \frac{d}{\mathrm{T}}\right)\tilde{\Gamma} + \beta(1 - B_1 G_1)(1 + \overline{c_0})\tilde{u} = 0,$$

$$\tilde{\varphi}_1 - \frac{2 + \overline{c_0}}{\overline{c_0}}\tilde{c} - \frac{G_1}{B_1}\left(\beta\xi + \frac{d}{T}\right)\tilde{\Gamma} + \frac{G_1}{B_1}(1 + \overline{c_0})\beta\tilde{u} = 0,$$

$$\tilde{c} - (1 + T\beta\xi + d)\tilde{\Gamma} - T\beta(1 + \overline{c_0})\tilde{u} = 0. \tag{40}$$

We have introduced in Eq. (40) the following quantities $\theta = 1/5\delta$, $\beta = i\alpha$, and $z = M\beta$. We also have

$$B_1 = \varepsilon V \mathrm{Bi},\ G_1 = \varepsilon n_* V G,\ D_1 = \varepsilon n_*{}^2 \mathrm{Di},$$

$$M_1 = -\frac{n_*\overline{c_0}\mathrm{Ma}}{2\mathrm{Bi}(1 + \overline{c_0})},\ \tilde{\varphi} = \gamma_2\tilde{\varphi}_1,$$

$$V = \sqrt{\frac{3}{2}\frac{1 + \overline{c_0}}{|\overline{c_0}|}},\ \gamma_1 = \frac{2 + \overline{c_0}}{\overline{c_0}}\gamma_2,\ \gamma_2 = -\frac{2}{3}\frac{\overline{c_0}^2}{\mathrm{Bi}(1 + \overline{c_0})^2},$$

$$T = \frac{n_* G}{\pi_2}, \quad d = TD_1\alpha^2. \tag{41}$$

Let us now assume that $\tilde{c}$ and $\tilde{u}$ obey the following relationship:

where the factor $\mathfrak{R}$ is to be obtained from the diffusion part of Eq. (40).

As the problem is homogeneous, the existence of nontrivial solution to Eq. (40) demands that the determinant of this system vanishes. From this condition the dispersion equation is obtained for $\xi = 1.5 - \omega$:

$$-\frac{2}{3}\beta\xi^2 + \left(\frac{2}{5}\beta - \frac{2}{3}\theta\right)\xi + \frac{1}{10}\beta - \theta + \frac{2}{3}\beta\alpha^2\theta + z\mathfrak{R}\left[-\frac{1}{6}\beta\xi^2 + \left(\frac{3}{20}\beta - \frac{2}{3}\theta\right)\xi + \frac{1}{6}\beta\alpha^2\theta\right] = 0. \tag{42}$$

From Eq. (40) the relation connecting $\tilde{c}$ and $\tilde{u}$ follows. The factor $\mathfrak{R}$ is

$$\mathfrak{R} = \frac{\Phi_{30} + \xi\Phi_{31} + \xi^2\Phi_{32}}{\Psi_{30} + \xi\Psi_{31} + \xi^2\Psi_{32}}. \tag{43}$$

Inserting Eq. (43) into Eq. (42) leads to the dispersion equation in the form of a fourth-order algebraic problem

$$\Phi_{10} + \xi\Phi_{11} + \xi^2\Phi_{12} + z(\Phi_{20} + \xi\Phi_{21} + \xi^2\Phi_{22})\frac{\Phi_{30} + \xi\Phi_{31} + \xi^2\Phi_{32}}{\Psi_{30} + \xi\Psi_{31} + \xi^2\Psi_{32}} = 0. \tag{44}$$

The dispersion equation (44) determines four eigenvalues ξ_k, depending on the wave number α, and on the dimensionless parameters $\mathrm{Bi}, G, T, \mathrm{Di}$, δ, n_*, $\overline{c_0}, \mathrm{Ma}$, and ε.

The coefficients Φ_{1k} and $\Phi_{2k}, k = 0, 1, 2$ in Eq. (44) are known from Eq. (42). The coefficients Φ_{3k} and Ψ_{3k} for the case $\sigma = \sigma(\overline{c})$ are

$$\Phi_{30} = (-B_1 G_1 + 1 + d)(1 + \overline{c_0})\beta,$$

$$\Phi_{31} = \left(\frac{G_1}{B_1} - \mathrm{T}\right)(1 + \overline{c_0})\alpha^2, \quad \Phi_{32} = 0,$$

$$\Psi_{30} = [B_1{}^2 + M_1(1 + \overline{c_0})\alpha^2](1 + d) + G_1 B_1\frac{d}{T},$$

$$\Psi_{31} = -\beta\left[\frac{2 + \overline{c_0}}{\overline{c_0}}(1 + d) - [B_1{}^2 + M_1(1 + \overline{c_0})\alpha^2]\mathrm{T} - G_1 B_1 - \frac{G_1}{B_1}\frac{d}{\mathrm{T}}\right],$$

$$\Psi_{32} = \alpha^2\left[\frac{2 + \overline{c_0}}{\overline{c_0}}\mathrm{T} - \frac{G_1}{B_1}\right]. \tag{45}$$

When the Marangoni number is set to zero, Eq. (42) reduces to the corresponding equation for a falling film with no Marangoni effect, as expected (see, e.g., Refs. [41,42,62]). From Eq. (42) the instability interval is determined, $0 < \alpha < \alpha_0$, with neutral curve

$$\alpha_0 = \sqrt{15\ \delta} \tag{46}$$

and with $\omega_r = 3$ as wave velocity of the neutral disturbance. Later on expecting no confusion in the reader we shall use C_r

rather than ω_r to denote wave velocity. The relations (46) for neutral disturbances together with the growth or amplification factor $(\alpha\omega_i)_{max}$ of the fastest growing disturbances have been compared with the direct numerical solutions of the full Navier-Stokes formulation [Eqs. (9)–(13)] and to the results of Ref. [69] for the boundary layer with self-induced pressure approximation [Eqs. (20)–(23)]. These three approaches give practically identical results for $0<\delta<0.5$. Such an agreement shows the utility of the approximations used to obtain the dispersion equation (44). Needless to say, the above given methodology for the derivation of the evolution equations and their spectral analysis could be extended almost verbatim to the instability of the film flow with heat transfer.

Demekhin *et al.* [70] have shown that Eqs. (38) give a very good approximation to the Orr-Sommerfeld formulation of the instability problem for prescribed τ and for low enough values of α.

V. NUMERICAL RESULTS: EIGENVALUES

Too many particular cases can be considered in view of the dispersion equation (44) which includes nine independent dimensionless groups. It is convenient to take the following quantities as free parameters

$$\text{Re},\ \text{Ma},\ \text{Pe},\ \gamma,\ \text{Bi},\ \text{G},\ \overline{c_0},\ T,\ D_1. \tag{47}$$

Then the values of δ and n_* implicit in the coefficients of Eq. (44) could be computed using Eq. (18). For every specified set of parameter values (47), the roots of equation can be obtained and hence the phase velocity $C_r(\alpha)$ and the corresponding growth rate $\alpha\omega_i(\alpha)$. If the parameter Ca is specified instead of γ, then the value of γ could be obtained using Eqs. (18) and (19).

Relations exist to assign numerical values to free parameters. For example, we have

$$\text{Pe} = \left(\frac{\nu}{D}\right)\text{Re}, \quad \text{G} = \frac{\Gamma_*}{c_* l}\text{Pe}.$$

A classification of parameters in view of their physical or mechanical significance is useful. The main parameter connecting the hydrodynamic and diffusion parts of the film flow problem with surfactant is the Marangoni number Ma. Both cases positive (Ma>0) and negative (Ma<0) Marangoni numbers have been considered. Considering both cases is not a matter of mere academic interest. Schwarz [7] studied two-phase systems Cyclohexanol/Water with diffusion substances Methanol, *n*-Propanol, *n*-Butanol, *n*-Amylol, and *n*-Hexanol in concentrations from 2% to 8%. These systems are characterized by $d\sigma/d\overline{c}<0$, Ma>0 (the first three) and by $d\sigma/d\overline{c}>0$, Ma<0 (the latter two). Other cases showing positive growth in the surface tension or a minimum in the surface tension which can be considered as anomalous behavior, $d\sigma/dc>0$ or $d\sigma/dT>0$, relative to that of pure water have been described by several authors [82–86]. For instance, the mixture 2-butoxyethanol-water has $d\sigma/dT>0$.

The most significant hydrodynamic parameters are Re and γ, or equivalently δ and γ. Their corresponding values determine the mean film thickness l, mean velocity U_*, flow rate lU_*, as well as the parameter n_*. The diffusion parameters $\overline{c_0}$ and Pe determine the local thickness of the diffusion boundary layer, h_1, and the smallness parameter ε. Two quantities T and D_1 characterize the mass transfer of surfactant by the adsorption-desorption and the intensity of dissipation by the surface diffusion. The intensity of the surfactant desorption to the gas phase is determined by the parameter Bi. Recall that G gives an indication of the typical value of surface excess concentration Γ_* relative to c_*.

For every prescribed set of parameter values (47) the eigenvalues $\omega(\alpha)$ could be computed for arbitrary $\alpha>0$ values. But we must keep in mind that the assumptions made for the long wave approximation introduce limitations on α. For the problem under consideration there exist indeed two length scales h and h_1. This distinction is significant for the understanding of our results. Indeed, due to the inequality $h_1 \ll h$, short waves in the h scale could be considered as long waves in the h_1 scale. In view of this a cutoff value for practical purposes, $\alpha<10$, is used in the numerical study that we describe below.

A few remarks about the parameter T are pertinent. Actually, the last equation (40) is the disturbed equation of the adsorption-desorption kinetics (1). This equation contains T, D_1, and $\overline{c_0}$ together with the wave number α. From Eqs. (16) and (41) we obtain

$$T = n_* \frac{U_*}{k_d l}, \quad TD_1 = n_*^2 \frac{D_i}{k_d l^2}. \tag{48}$$

From Eq. (48) follows that the parameter T characterizes the ratio of rates of the surface excess concentration, Γ, transfer by two processes: one is convective flow along the film surface, and the other is desorption inside the liquid bulk. For $T\rightarrow 0$ the case of diffusion controlled adsorption-desorption kinetics from Eq. (40) is obtained,

$$\Gamma = \overline{c}, \tag{49}$$

like Eq. (6) for the equilibrium Marangoni effect. Equation (49) corresponds to a fast desorption process leading to local kinetic equilibrium. In the opposite limiting situation $T\rightarrow\infty$, it follows from Eq. (40),

$$\widetilde{\Gamma} = \frac{1+\overline{c_0}}{\overline{u_0}-\omega-\beta D_1}\widetilde{u}. \tag{50}$$

Equation (50) corresponds to kinetically frozen desorption. Only for $1+\overline{c_0}=0$ it is possible to consider the surface excess concentration of surfactant, Γ, as constant and hence $\widetilde{\Gamma}=0$ for $j\neq 0$. Besides the limiting cases of fast desorption ($T=0$) and slow desorption ($T\rightarrow\infty$) the more general case $T\sim 1$ is also considered here. Note that the difference between Eqs. (1) and (7) may be important only when Γ_0/Γ^{∞} is not small. Yet the two approaches are equivalent at the linear stability level in spite of various coefficients appearing in Eq. (40).

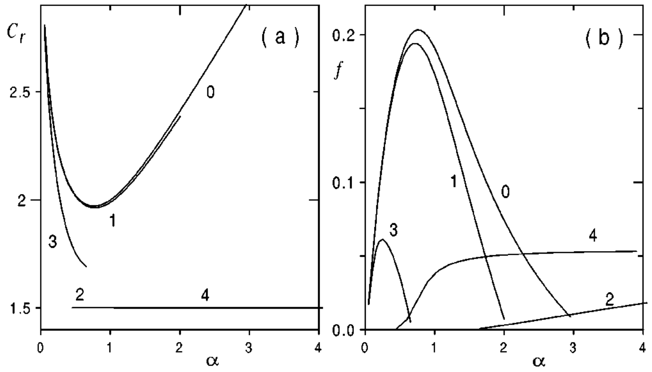

FIG. 1. (a) Phase velocity C_r and (b) growth rate $f = m\alpha\omega_i$, as functions of the wave number α for constant surface excess concentration Γ. $\mathrm{Bi}=10$, $\gamma=29.4$, $\mathrm{G}=1.33\times10^3$, $\mathrm{Pe}=0.66\times10^6$, $\mathrm{Re}=13.33$, $D_1=10^{-3}$, $\overline{c_0}=-0.25$; $\mathrm{Ma}=0$ (0), 0.015 (1,2), 1.5 (3,4); $m=1$ for (0,1,3), 10 for (2,4).

A. Constant surface excess concentration Γ

First of all we have cross-checked our method to obtain the eigenvalues given by the dispersion equation (44) by comparing our results with the exact numerical solutions of the Orr-Sommerfeld formulation given by Ji and Setterwall [24] for $\Gamma=\mathrm{const}$. Note that in this work we are dealing with a more general formulation of the instability problem as we include nonequilibrium surfactant adsorption-desorption kinetics. Besides, their particular case is somewhat artificial as it does not follow from the general formulation (49) as $T\to\infty$. Furthermore, when $T\to\infty$ the term $(1+\overline{c_0})$ in Eq. (49) must be set to zero. For $\Gamma_0=0$ and $\tilde{\Gamma}=0$ in Eq. (40) the coefficients Φ_{3k} and Ψ_{3k} in the dispersion equation (44) are

$$\Phi_{30}=\beta(1+\overline{c_0}-B_1G_1),\quad \Phi_{31}=\alpha^2\frac{G_1}{B_1},\quad \Phi_{32}=0,$$

$$\Psi_{30}=B_1{}^2,\quad \Psi_{31}=-\frac{2+\overline{c_0}}{\overline{c_0}}\beta,\quad \Psi_{32}=0. \tag{51}$$

The dispersion equation (44) with coefficients (51) is a third-order algebraic equation for this case. For $\mathrm{Ma}>0$ two of three roots yield unstable modes. For illustration and comparison we choose the following numerical values:

$$\mathrm{Re}=\frac{40}{3},\ \mathrm{Pe}=\frac{2}{3}10^6,\ \mathrm{Bi}=10,\ \overline{c_0}=-0.25.$$

This set of parameter values fits well a liquid metal with $\gamma=29.24$ and $\mathrm{Ca}=0.2$. The calculations of eigenvalues have been done for several values of Ma and α. In Fig. 1, typical curves for $C_r=C_r(\alpha)$ and $\alpha\omega_i=\alpha\omega_i(\alpha)$ are plotted. As the growth rate $\alpha\omega_i(\alpha)$ of various instability modes could differ by several orders, a normalized growth rate $f=m\alpha\omega_i(\alpha)$, where m is the appropriate scale used in figures. One of these growing modes (0,1,3) is easily identified as the (Kapitza) hydrodynamic mode of the falling film with small wave number and it is indeed the same when $\mathrm{Ma}=0$. The phase velocity C_r of this wave mode diminishes from $C_r=3$ as α grows from $\alpha=0$, takes a minimum value, and then increases. The growth rate $\alpha\omega_i$ is positive in the interval $0<\alpha<\alpha_*$ and has a maximum value $(\alpha\omega_i)_m$ inside this interval. Other growing modes (2,4), which are referred to as diffusion (Marangoni-driven) modes, appear only if $\mathrm{Ma}\neq0$. The term "diffusion" is applied to any mode which disappears as $\mathrm{Ma}\to0$. Diffusion modes in the case under consideration exist as solutions of the dispersion equation (44) for high enough wave numbers $\alpha>\alpha_{**}$, where α_{**} is to be determined by computations. The wave velocity of a diffusion mode is equal to 3/2 with great accuracy. Thus this wave moves with the velocity of the liquid on the film surface. This mode, which can be identified as a monotonic instability mode of the liquid open surface, leads to a patterned interface. The growth rate $\alpha\omega_i$ of this diffusive mode is two to three orders below that of the hydrodynamic mode and tends to its maximum value as α grows.

For $\alpha=1.355$, the eigenvalues are

$$\omega_1=1.313-0.106\,00i,\quad \omega_2=1.253-0.112\,50i,$$

$$\omega_1=0.999+0.000\,45i,\quad \omega_2=1.000+0.001\,67i.$$

The solutions of Eq. (44) are on the right side while the solutions obtained by Ji and Setterwall [24] of the full Orr-Sommerfeld formulation are on the left side. There is reasonable agreement between the results obtained using the two approaches.

The eigensolutions have been obtained for various α and Ma values and $D_1=0.01$ and 0.0001. The structure of the spectrum, $\omega(\alpha)$ (Fig. 1), is valid for all values $\mathrm{Ma}>0$. The existence of hydrodynamic and diffusion Marangoni instability modes is the main feature of that spectrum. The influence of the surfactant and the Marangoni effect on the hydrodynamic instability model (1,3) can be seen in Fig. 1. The growth rate of the most unstable mode diminishes with Ma increasing.

If δ is small enough and Ma is sufficiently high the diffusion mode grows faster than the hydrodynamic mode grows. The critical value of the wave number α_* moves to zero and, as a result, the region of the long wave instability shrinks. The phase velocity of the hydrodynamic wave tends to diminish. The salient features of the surfactant influence on the hydrodynamic instability mode which follow from solutions of Eq. (44) agree with the results of Lin [8].

Results for the case $\Gamma=\mathrm{const}$ and $\mathrm{Ma}<0$ have been obtained. As seen in Fig. 2 there are three unstable modes according to the values of α, which can be identified by their phase velocities. The growth rate of the diffusion mode (2) with phase velocity $C_r=1.5$ does not appreciably vary when we change from $\mathrm{Ma}=1.5$ to $\mathrm{Ma}=-1.5$. There is a second particular diffusion mode (3) on the finite interval wave numbers whose phase velocity varies linearly in the vicinity of the point $C_r=1$ and $\alpha=0.5$. The third branch of solutions (1) begins at $\alpha=0$ as a hydrodynamic instability mode with phase velocity $C_r=3$, but then converts into a mode of explosive growth as α tends to the critical value α_k, i.e., $\alpha\omega_i\to\infty$ as $\alpha\to\alpha_k$.

Let us show that the appearance of an explosive growing mode is genuine of film flows for the case $\Gamma=\mathrm{const}$ and

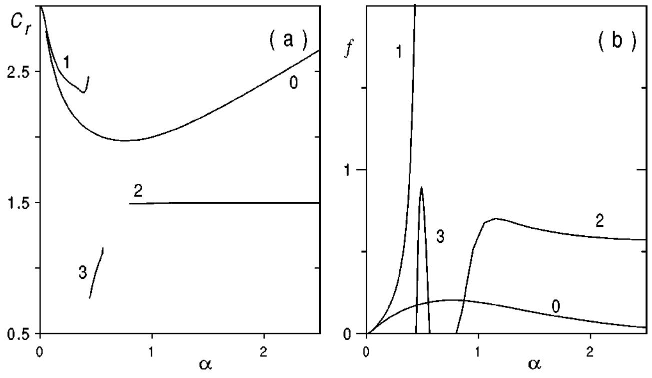

FIG. 2. Ma=−1.5(1,2,3); $m=1$ for (1), 10^2 for (2,3). Other parameters as in Fig. 1.

$\mathrm{Ma}<0$. By setting to zero the coefficient of ξ^3 in Eq. (44) we obtain

$$\Phi_{12}\Psi_{31} + z\Phi_{22}\Phi_{31} = 0. \qquad (52)$$

Using Eq. (18), from Eq. (52) follows

$$\alpha_k{}^2 = 4\frac{2+\overline{c_0}}{\overline{c_0}}\frac{\mathrm{Bi}}{n_*{}^2\mathrm{G}}\frac{1}{\mathrm{Ma}}. \qquad (53)$$

For the values given to the dimensionless parameters in Fig. 2, Eq. (53) becomes

$$\alpha_k^2 = -\frac{0.385}{\mathrm{Ma}} \qquad (54)$$

and Eq. (54) gives $\alpha_k \approx 0.507$. For the values in Fig. 3, Eq. (53) gives $\alpha_k=5.07$. Let us introduce the smallness parameter ε_1, so that $\omega=\varepsilon_1{}^{-1}\Omega$, $\varepsilon_1 \ll 1$, and $|\Omega|=o(1)$. Then from Eqs. (40) follows that

$$\tilde{h} = \varepsilon_1{}^2\check{h}, \quad (\tilde{\Gamma},\tilde{\varphi}) = \varepsilon_1(\check{\Gamma},\check{\varphi}), \quad \tilde{c} = \check{c}, \quad \tilde{u} = \check{u}, \qquad (55)$$

where all quantities $\check{h}$, $\check{\Gamma}$, $\check{\varphi}$, $\check{u}$, and $\check{c}$ have the same order. Neglecting terms $o(\varepsilon_1{}^2)$, from the first equation (40) we obtain

$$\check{u} + \tfrac{1}{4}i\mathrm{Ma}\ \alpha\check{c} = 0. \qquad (56)$$

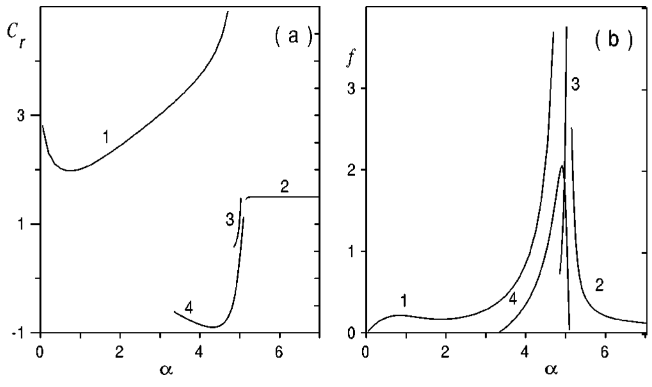

FIG. 3. Ma=−0.015(1,2,3,4); $m=1$ for (1,4), 10 for (2), 10^{-1} for (3). Other parameters as in Fig. 1.

The unstable mode actually represents a longitudinal or dilational wave since surface deformations are negligible as it is clear from Eq. (55). The disturbances u' and c' are phase shifted by $\varphi=\pi/2$ as it follows from Eq. (56). They can be expressed in the following way:

$$c' = |c|\exp[ix_1], \quad u' = \frac{1}{4}\alpha|\mathrm{Ma}\ c|\exp\left[i\left(x_1 - \frac{\pi}{2}\right)\right],$$

$$x_1 = \alpha(x - \omega t). \qquad (57)$$

As Eq. (57) shows the longitudinal oscillations u' carry surfactant away from the points where c' is minimal and bring it to the points where c' is maximal. Some sort of resonance takes place. Unbounded solutions appear at the critical wave number α_k, defined by Eq. (53). When $\mathrm{Ma}<0$ and $|\mathrm{Ma}|$ is small enough the critical wave number α_k of the explosive mode is outside the interval for hydrodynamic mode instability ($\alpha_k > \alpha_*$). When $|\mathrm{Ma}|$ grows, α_k approaches α_* (Figs. 2 and 3).

A transformation of the transverse hydrodynamic instability wave into the longitudinal Marangoni-driven wave under resonant conditions as α grows in Figs. 2 and 3 could be seen. The phase velocity C_r and growth rate $\alpha\omega_i$ increase with α approaching α_k so that the condition $|\omega| \gg 1$ is gradually attained. By virtue of Eq. (55) the amplitude of the film thickness oscillations $\tilde{h}$ diminishes and resonant conditions (56) and (57) for the wave under consideration occur. Such eigensolutions of Eq. (44) are a form of combined modes. A resonant interaction based on a frequency coalescence point for (transverse) capillary and (longitudinal) dilational Marangoni modes for insoluble surfactants has been described by Rednikov *et al.* [32,36]. This singular behavior for the growing coefficient sets limitations to the validity of the model $\Gamma=\mathrm{const}$ that, as earlier mentioned, is a somewhat artificial case. Accordingly, we proceed to examine the more realistic case, $\Gamma \neq \mathrm{const}$ for $\mathrm{Ma}<0$.

B. Soluble surfactant transfer accompanied by adsorption-desorption processes

Taking now adsorption and desorption into account we return to investigate the general case of the film flow with surfactant. It is worth noting that the method used leading to Eqs. (38) and then to the dispersion equation (44) is highly efficient for large γ values and for small Ca values. According to Eq. (19) the crucial parameter n_* is small for small Ca values. For water $\gamma=2850$ while $\gamma=29.241$ for a liquid metal, and $\mathrm{Ca}=0.0024$ instead of $\mathrm{Ca}=0.2$ in the discussed case. For our numerical study the following parameter values have been used:

$$\gamma = 2904, \quad \delta = 0.412, \quad n_* = 0.193.$$

These values fit well a water film flow with a soluble volatile surfactant. We shall sequentially consider the two earlier mentioned surface tension equations of state, $\sigma=\sigma(\overline{c})$ and $\sigma=\sigma(\Gamma)$.

Case (i): $\sigma=\sigma(\overline{c})$. For this case the coefficients Φ_{3k} and Ψ_{3k} of the dispersion equation (44) are obtained using Eq.

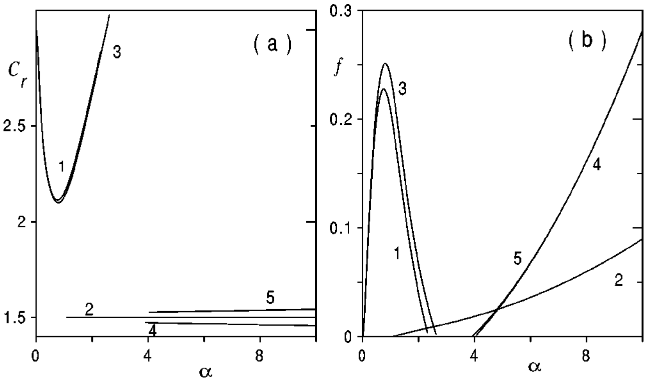

FIG. 4. (a) Phase velocity C_r and (b) growth rate $f=m\alpha\omega_i$ as function of the wave number α for adsorption-desorption controlled surfactant transfer with $\sigma=\sigma(\overline{c})$. Bi=10, $\gamma=2904$, G=2000, Pe $=10^6$, Re=32, $D_1=10^{-2}$, $\overline{c_0}=-0.25$; $T=5$: Ma=1 (1,2); Ma=−1 (3,4,5); $m=1$ for (1–5).

(45). The parameter T in Eq. (45) estimates the role of adsorption-desorption kinetics on the hydrodynamic instability. For finite values of T the mass rate transfer of the adsorbed surfactant concentration Γ by convective flow is of the same order as that by desorption inside the liquid bulk. From the dispersion equation (44) we obtain four eigenvalues $\xi_k=\overline{u_0}-\omega_k$ with corresponding rates for growing or decaying modes. The salient features of film flow instability obtained in numerical experiments with aqueous solutions for various Ma, T, and α values are depicted in Figs. 4–9. Results were obtained for positive (Ma>0) as well as for negative (Ma<0) Marangoni numbers with soluble surfactants.

For every value of the Marangoni number, one hydrodynamic instability (Kapitza) mode exists together with one to three growing, unstable diffusion (Marangoni) modes. For Ma=1 in addition to the hydrodynamic mode (1), only one diffusion mode (2) with $\alpha_{**}\approx 1$ on Fig. 4 could be seen. Note that on the wave number interval $\alpha_{**}<\alpha<10$ the diffusion modes have a growth rate of the same order than the hydrodynamic mode. Figure 4 shows, for small negative Marangoni numbers (e.g., Ma=−1), three unstable modes, namely, the hydrodynamic mode (3) and two diffusion modes (4,5). The influence of the Marangoni effect on hydrodynamic waves is rather weak for this value of the Marangoni number. The curves $C_r(\alpha)$ and $\alpha\omega_i(\alpha)$ are practically the same for Ma=0 and Ma=±1. A pair of diffusion modes exists in the interval $\alpha>\alpha_{**}$ ($\alpha_{**}\approx 4$). For one of them the wave phase velocity is slightly above the value $C_r=1.5$, while for the other (2,3) it is slightly below this value and both are growing.

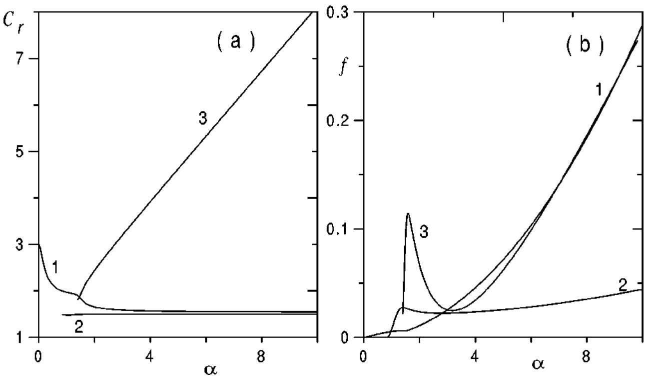

FIG. 5. Ma=−10, $T=1.0$ (1,2,3); $m=10^{-2}$ for (1), 1 for (2,3). Other parameters as in Fig. 4.

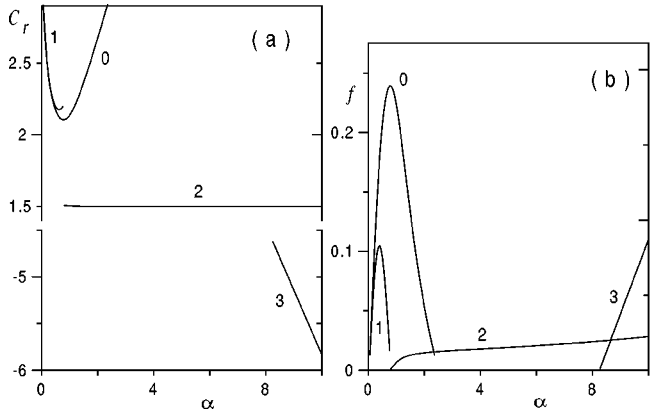

FIG. 6. Ma=0 (0); Ma=10, $T=0.5$ (1,2,3); $m=1$ for (0,1,2,3). Other parameters as in Fig. 4.

A drastic modification of the instability curves $C_r(\alpha)$ and $\alpha\omega_i(\alpha)$ with increasing (absolute) values of the Marangoni number is shown in Fig. 5. New instability modes for Ma $=-10$ and $T=1.0$ are observed. There exists a slow diffusion mode (2) at $\alpha>\alpha_{**}$ ($\alpha_{**}\approx 1$) which moves with the liquid on the film surface ($C_r=1.5$). Its growth rate $\alpha\omega_i$ is about that of the similar mode (2) in Fig. 4. Another diffusion mode (3) appears at $\alpha>\alpha_n$ ($\alpha_n\approx 1.5$) which has very different nature. The corresponding disturbances represent fast waves with phase velocity $C_r(\alpha)$ linearly growing when α increases. For example, the phase velocity varies from $C_r\approx 2$ to $C_r\approx 8$ as α increases from $\alpha=2$ to $\alpha=10$. The growth rate of the fast diffusion mode (3) is about one order higher than that of the slow diffusion mode (2).

The salient effect of the Marangoni number on the instability of film flow in Fig. 5 is the appearance of a strong

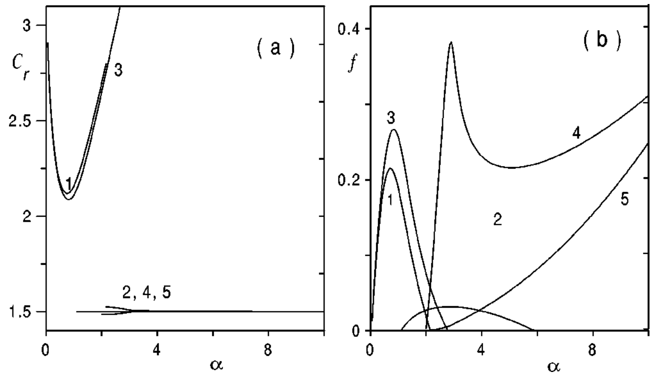

FIG. 7. (a) Phase velocity C_r and (b) growth rate $f=m\alpha\omega_i$ as function of the wave number α for adsorption-desorption controlled surfactant transfer with $\sigma=\sigma(\Gamma)$. Bi=10, $\gamma=2904$, G=2000, Pe $=10^6$, Re=32, $D_1=10^{-2}$, $\overline{c_0}=-0.25$; $T=5$: Ma=1 (1,2), Ma=−1 (3,4,5); $m=1$ for (1,3), 10 for (4), 10^2 for (2), 10^{-1} for (5).

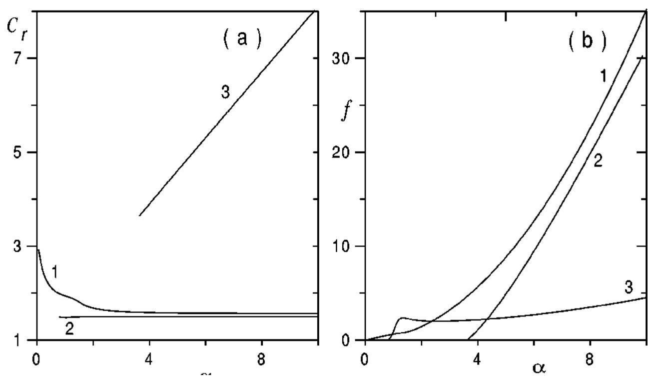

FIG. 8. Ma=−10, T=0.5 (1,2,3); m=1 for (1), 10^2 for (2,3). Other parameters as in Fig. 7.

combined hydrodynamic-diffusion (Kapitza-Marangoni) mode (1) with growth rate two orders higher relative to the case of low Ma values. This strong combined mode begins at $\alpha=0$ as an ordinary hydrodynamic mode with phase velocity $C_r=3$ and then diminishes to $C_r\approx 2$ as α grows to $\alpha\approx 1.5$. But then instead of growing, C_r falls down to $C_r\approx 1.5$ with subsequent asymptotic behavior $C_r\rightarrow 1.5$ for α growing as it occurs for the diffusion mode. Such transverse hydrodynamic wave gets over to a longitudinal wave due to $|\omega|\gg 1$ as shown above. In the vicinity of $\alpha\approx 1.5$ this instability mode exhibits features of both transverse and longitudinal waves. A jump from $T=1$ to $T=0.5$ does not appreciably change the picture of instability modes. Transverse and longitudinal waves for a horizontal initially resting film in the presence of an adsorption barrier were discussed by Hennenberg *et al.* [20].

In Fig. 6 the curves $C_r(\alpha)$ and $\alpha\omega_i(\alpha)$ from eigensolutions of Eq. (44) for Ma=10 and T=0.5 are shown. Three instability modes can be distinguished noting their phase velocity. The first two modes were discussed for negative values of the Marangoni number, namely, a hydrodynamic mode (1) with phase velocity $3>C_r>2$ in the interval $0<\alpha<\alpha_*$ and a diffusion mode (2) with phase velocity $C_r\approx 1.5$ in the interval $\alpha>\alpha_{**}$. A strong damping effect of the Marangoni number Ma>0 on the hydrodynamic waves (0) is shown in Fig. 6. The maximum growth rate is equal to one-half and the boundary value of the wave number α_* is one-third of the corresponding value for Ma=0. Accordingly, the Marangoni effect generates the diffusion mode which exists for $\alpha>\alpha_{**}$ ($\alpha_{**}\approx 0.7$) and for which the growth rate $\alpha\omega_i$ is the same order as that of the hydrodynamic mode. It should be noted that for Ma>0 the hydrodynamic and the diffusion modes do not interact to form a combined mode at variance with the earlier discussed case for Ma<0.

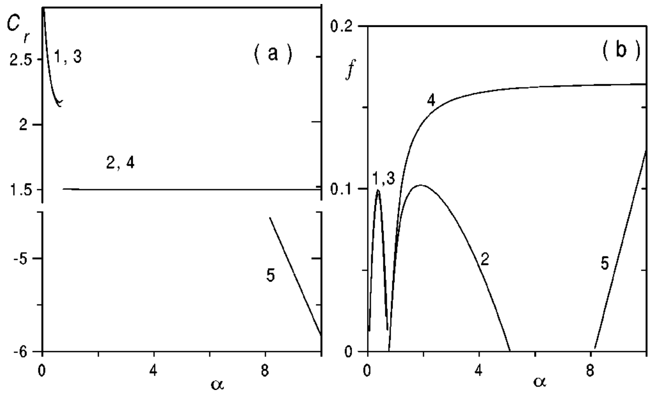

FIG. 9. Ma=10: T=1 (1,2,5), T=0 (3,4,5); m=1 for (1,3,5), 10 for (2,4). Other parameters as in Fig. 7.

The third unstable mode (3) at $\alpha>\alpha_n$ in Fig. 6 is unusual because its phase velocity is negative. Accordingly, the corresponding wave moves upstream. These waves have short lengths ($\alpha_n\approx 8.5$), are fast moving ($|C_r|>5$), and grow fast [$\alpha\omega_i$ is of the same order as for the hydrodynamic mode (1)]. As $|\omega|\gg 1$ these waves are longitudinal ones in accordance with results described earlier.

The fast surface waves at $\alpha>\alpha_n$ deserve to be discussed in more details. From the dispersion equation (44), to order $o(1/\alpha^2)$ we obtain

$$\omega-\frac{3}{2}=\alpha b+A_0+A_1\frac{1}{\alpha},\quad b=\pm\sqrt{\theta},\ \theta=\frac{1}{5\delta}. \tag{58}$$

For the purely hydrodynamic instability case, Ma=0, the coefficients A_0 and A_1 are

$$A_0=-\frac{3}{10},\quad A_1=-\frac{3}{25}\frac{1}{b}-\frac{1}{2}\theta i. \tag{59}$$

Relations (58) and (59) determine two waves moving up and down the main flow with corresponding phase velocities $C_r=\frac{3}{2}+\alpha b$. These waves are slightly damped since $\omega_i=-\frac{1}{2}\theta<0$.

The inclusion of the Marangoni effect in the dispersion equation (44) makes these fast waves to grow. For Ma≠0, we obtain from Eq. (44) $A_0=A_r+iA_i$, where $\operatorname{sgn}A_i=\operatorname{sgn}N$,

$$N=-n_*b\mathrm{Ma}\left(T\frac{2+\overline{c_0}}{\overline{c_0}}-\frac{G_1}{B_1}\right)\left(T-\frac{G_1}{B_1}\right)(1+\overline{c_0}).$$

Two waves determined by the eigenvalues (58) now will grow if $A_i>0$, since $\omega_i=A_i+o(1/\alpha)$. For all cases in Figs. 5–9 the instability condition $A_i>0$ is fulfilled if bMa<0. Thus we have a fast upstream growing wave when Ma>0 and $b=-\sqrt{\theta}$, while it is a downstream wave with Ma<0 and $b=+\sqrt{\theta}$.

The resonance mechanism of amplification is seen from Eq. (57) derived for $|\omega|\gg 1$. According to Eq. (57) the velocity perturbation u' changes the concentration c' by transferring surfactant from points of minimal c' values to points of maximal c' values. Then the perturbations of surfactant concentration amplify the velocity perturbation thanks to the Marangoni effect. Thus the fast wave disturbances are surface longitudinal convective-concentration waves accompanied by very small liquid surface deformations. The wavelength correlates with the smallest of the two characteristic lengths, diffusion boundary layer thickness h_1, and film thickness h. Wave numbers $\overline{\alpha}$ based on h_1 are one order of magnitude lower, namely $\overline{\alpha}\approx 1$ instead of $\alpha\approx 10$ because $h\approx 0,1h_1$, as noted earlier.

Case (ii): $\sigma=\sigma(\Gamma)$. Let us examine now the role of the functional relation $\sigma=\sigma(\Gamma)$ for the surface tension. Instead of $z\tilde{c}$ we must have $z_1\tilde{\Gamma}$ in the amplitude equations (38) with

$$z_1 = n_* \mathrm{Ma}\beta, M_1 = -\frac{d\sigma}{d\Gamma}\frac{\Gamma_*}{\mu U_*}. \qquad (60)$$

For the coefficients Φ_{3k} in Eq. (43) we obtain from Eq. (40) the following expressions:

$$\Phi_{30} = \beta\{1 - B_1 G_1 - T[B_1{}^2 + M_1(1+\overline{c_0})\alpha^2]\}(1+\overline{c_0}),$$

$$\Phi_{31} = \left(\frac{G_1}{B_1} - \frac{2+\overline{c_0}}{\overline{c_0}}\mathrm{T}\right)(1+\overline{c_0})\alpha^2, \quad \Phi_{32} = 0. \qquad (61)$$

Equation (44), with coefficients Φ_{3k} from Eq. (61) and Ψ_{3k} from Eq. (45), determines four eigenvalues ω. The picture of instabilities for the case $\sigma=\sigma(\Gamma)$ resembles that for $\sigma=\sigma(\overline{c})$ though less diverse. In Fig. 7, for low Ma (absolute) values (Ma $=\pm 1$, $T=5$) two instability modes could be seen for Ma $=1$; namely, a hydrodynamic mode (1) and the diffusion mode (2) with phase velocity $C_r \approx 1.5$. There are three instability modes (3,4,5) for Ma $=-1$. This picture is essentially the same as that of Fig. 4, but there are two differences: on the one hand, the stabilizing effect of the negative Marangoni number, Ma <0, on the diffusion mode (4) is stronger, and, on the other hand, the only slow diffusion mode (2) at Ma >0 exists on the finite interval α.

In Fig. 8 the curves $C_r(\alpha)$ and $\alpha\omega_i(\alpha)$ for Ma $=-10$ and $T=0.5$ are shown. We see a combined hydrodynamic-Marangoni-driven mode (1) at $\alpha \geqslant 0$. Near the beginning of the curve, the phase velocity changes from $C_r \approx 3$ at $\alpha=0$, as it must be for a hydrodynamic mode, then diminishes and tends to $C_r=1.5$ with α growing as for the base diffusion mode. The growth rate of this combined mode monotonically grows with α increasing and reaches the high value of $(\alpha\omega_i)=30$ at $\alpha=8$. It could be compared with $(\alpha\omega_i)=20$ in Fig. 5, for the case $\sigma=\sigma(\overline{c})$. According to results earlier given the disturbances defining this combined mode are long transverse waves for small α and for high α short longitudinal waves moving with the liquid on the film surface. The second instability mode (2) is represented by the fast short length waves at $\alpha > \alpha_n$ ($\alpha_n \approx 4$). The corresponding fast wave mode (3) in Fig. 5 for the other surface tension model is shown for wave numbers $\alpha_n \geqslant 1.5$. The third mode (3) in Fig. 8 is the Marangoni-driven slow diffusion mode with phase velocity $C_r \approx 1.5$.

The numerical results for positive values of the Marangoni number (Ma $=10$, $T=0,1$) are shown in Fig. 9. We see the hydrodynamic modes (1,3) which are attenuated to a large degree by the Marangoni effect. The maximal value of its growth rate $(\alpha\omega_i)_m=0.095$ is less than half that for Ma $=0$. Accordingly, the short length diffusion mode (4) is very weak with $(\alpha\omega_i)_m \approx 0.016$ for $\alpha=9$. It could be compared with $(\alpha\omega_i)=0.025$ in Fig. 6 for a solutal system with $\sigma=\sigma(\overline{c})$. Note the absolutely unstable wave (5) with negative phase velocity shown in Fig. 9 for the case $\sigma=\sigma(\Gamma)$ with $T=0,1$.

VI. SUMMARY AND CONCLUSIONS

The linear stability analysis of a falling film flow of an aqueous surfactant solution endowed with mass transfer and surfactant adsorption-desorption processes has been investigated. Hence we have dealt with a two-phase, three-component system liquid-air where mass transfer of a volatile surfactant occurs through the interface from the liquid into gas. Changes of the solute component concentration along the interface induce changes of the surface tension and, eventually, generate surface stresses (Marangoni effect) leading to interfacial instability and flow changes. Two model equations relating the surface tension σ to the surfactant concentrations $\sigma(\overline{c})$ and $\sigma(\Gamma)$ have been examined. The mathematical formulation of the interaction of the mass transfer process with hydrodynamics includes the Navier-Stokes and Fick diffusion equations together with the equations for the adsorption-desorption kinetics on the film surface. The nondimensional form of the corresponding nonlinear boundary value problem contains nine independent parameters, including Reynolds (Re), Marangoni (Ma), Peclet (Pe), Weber (We), and Biot (Bi) numbers, excess of surfactant concentration in a sublayer (G), local surfactant concentration on the film surface ($\overline{c_o}$) co-efficient for desorption intensity (T), and surface diffusion (D_1). An approximate nonlinear system of the Galerkin type not containing coordinates normal to the interface was derived. In the linear approximation the model equations have been used for systematic computations of eigenvalues. The full Navier-Stokes formulation has also been used for cross-checking methodology and accuracy estimates.

For Ma $=0$ hence in the absence of Marangoni stress with, however, mass diffusion included, there exists only one hydrodynamic mode in the finite interval of wave number values $0 \leqslant \alpha \leqslant \alpha_0$. This is the Kapitza mode. Thus, the mass transfer process alone does not significantly influence the flow of an aqueous solution. Inclusion of Ma $\neq 0$ in the dispersion equation results in damping of hydrodynamically unstable waves and in the appearance of new Marangoni-driven (diffusion) modes. Contrary to the hydrodynamic long wave, the diffusion waves obey the condition $\alpha > \alpha_{**}$ and must be considered as short relative to the other one. A lower cutoff α_{**} has been determined by numerical calculations, while an upper one is not formally considered in our mathematical model. All Marangoni-driven modes could be classified according to their phase velocity C_r. For every positive value of the Marangoni number, Ma >0, there exists a slow mode which has phase velocity $C_r \approx 1.5$. In the coordinate system moving with the liquid on the film surface these waves are practically stationary. This mode can be considered weak, because its growth rate $\alpha\omega_i$ is two orders of magnitude lower than the corresponding growth rate of the hydrodynamic mode. For negative values of the Marangoni number, Ma <0, there exist two additional modes. One of them approaches the hydrodynamic mode as $|\mathrm{Ma}|$ grows and a combined (Kapitza-Marangoni) mode appears. The corresponding eigenvalues exist for wave numbers $\alpha \geqslant 0$. This mode begins as a transverse hydrodynamic long wave with phase velocity $C_r=3$ at $\alpha=0$, then as α increases transforms into a longitudinal Marangoni-driven short wave with phase velocity $C_r \approx 1.5$. The main property of the combined mode is its very high growth rate which is two orders of magnitude higher than that of the slow diffusion mode. The third type of Marangoni-driven instability is a fast wave diffusion mode. Its corresponding phase velocity is positive and grows as α increases to values $C_r \approx 10$ in the interval of wave numbers $\alpha_n < \alpha < 10$. For the fourth diffusion mode $(\mathrm{Ma} > 0, \alpha > \alpha_n)$ the phase velocity is negative. These short length upstream moving waves could generate absolute instability. All four types of instability modes arising from the influence of the Marangoni effect appear for both surface tension models, $\sigma(\overline{c})$ and $\sigma(\Gamma)$, but their corresponding Ma and T values are different.

The role of two surfactant transfer kinetics has been studied. The first is the model with the adsorbed surface excess concentration artificially set constant, but with diffusion taken into account. The second is the more complete model with an adsorption-desorption barrier, with surfactant diffusion to the bulk liquid and desorption to the adjacent gas or air. Numerical results for both models show significant differences on the eigenvalues and their corresponding instability behavior. Only for low positive values of the Marangoni number, $\mathrm{Ma} > 0$, both models provide about the same results. The more complete model is better suited to obtain results amenable to experimental observation. The change from one to the other of the surface tension equations of state with surfactant concentration has weak effect on the instability picture and the results of numerical computations of eigenvalues are about the same.

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