

# THE PRIMARY INSTABILITY OF FALLING FILMS IN THE PRESENCE OF SOLUBLE SURFACTANTS

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**Keywords:** Liquid film flow, linear stability, Galerkin finite-element method.

**Abstract.** *We investigate the linear stability of a film flowing down a solid substrate in the presence of soluble surfactants. The Navier-Stokes equations for the liquid motion are considered, together with advection-diffusion equations for the concentrations of the species involved, which include monomers and micelles in the bulk and monomers adsorbed at the liquid-air interface. The adsorption-desorption kinetics of the surfactant at the interface is explicitly accounted for. An Orr-Sommerfeld eigenvalue problem is formulated, and solved analytically in the limit of long-wave disturbances and numerically for arbitrary wavelength using a finite element method. An extensive parametric study is performed to reveal the role of surfactant solubility and adsorption-desorption kinetics. The results quantify the stabilizing effect of soluble surfactants due to the presence of Marangoni stresses, and indicate that moderately soluble surfactants may be more effective than insoluble ones. Disturbances of finite wavelength are stabilized by more than an order of magnitude, and their detailed behavior depends in a non-monotonic way on the amount of surfactant and on its solubility and kinetics. The above predictions provide insights for the interpretation of recent experimental findings on the primary instability and on the ensuing unstable dynamics of liquid films doped with soluble surfactants.*

## 1 INTRODUCTION

The formation of waves in thin films flowing down inclined surfaces has attracted the interest of many researchers in the past because of their importance in a broad range of engineering applications. Extensive reviews on the rich dynamics of this system and main developments on the field are given in Craster and Matar<sup>[1]</sup>.

It is well known that interfacial instabilities can be significantly affected by the presence of surface-active materials (surfactants). Wave formation in falling films is no exception and this has been known since the ancient times. The first attempts to investigate the mechanisms that are responsible for the stabilization of the flow were made by Benjamin<sup>[2]</sup> and Whitaker<sup>[3]</sup>. Despite the significant differences between the two approaches, in the case of an insoluble surfactant the analytical prediction was found to be exactly the same, providing a unambiguous confirmation that the elasticity is the mechanism responsible for the stabilization of the flow. The asymptotic analysis for large values of the elasticity parameter by Anshus and Acrivos<sup>[4]</sup> confirmed the findings of the previous works about the existence of a critical Reynolds number and also showed that the presence of surfactants results in the decrease of the growth rate and increase of the wave length of the most unstable mode.

The effect of insoluble surfactants on the linear stability of a film flowing down a corrugated wall in the limit of vanishing Reynolds number was examined by Pozrikidis<sup>[5]</sup>. Subsequently, Blyth and Pozrikidis<sup>[6]</sup> presented a numerical solution of the Orr-Sommerfeld eigenvalue problem for finite Reynolds numbers of a film laden with insoluble surfactant flowing on an inclined plane and demonstrated the occurrence of the usual interfacial mode along with a new mode associated to the spatial variation of the surfactant concentration. The same problem was also studied by Pereira and Kalliadasis<sup>[7]</sup>, who presented a systematic analysis of the Orr-Sommerfeld problem of the full Navier-Stokes and concentration equations and also investigated the non-linear dynamics in the unstable regime.

Despite the large number of studies on the role of surfactants on film flows and the fact that this is a very old problem, it appears from the above review that the effects of surfactant solubility and adsorption/desorption kinetics on the primary instability and on the unstable dynamics have not yet been adequately addressed. In addition, there is recent experimental activity that points to a non-trivial influence of these parameters. For example, Georgantaki et al<sup>[8]</sup> performed a series of experiments to study the effect of soluble surfactants on inclined film flows. They have used aqueous solutions of Isopropanol (IP) and Sodium Dodecyl Sulfate (SDS) and found that these two agents exhibit a remarkably different influence on the flow. More specifically, it was

shown that, in the case of IP solutions, the inlet disturbances turned into solitary humps preceded with capillary ripples, as would be expected for a clean fluid with similar surface tension as the IP solution. On the contrary, when SDS solutions were used, the dominant structures were sinusoidal travelling waves of small amplitude. These structures were found to be extremely stable for a wide range of frequencies and up to high Reynolds numbers. Also, with respect to the primary instability, the same authors observed a strong stabilization of water films by the addition of SDS, whereas previous results with IP solutions<sup>[9]</sup> had shown no difference in the critical Reynolds number from that of other clear liquids with the same Kapitza number. The mechanisms that are responsible for the so different behaviours of the two surfactants are unknown, and it was speculated that these behaviors may be interpreted as an effect of the different solubility and/or sorption kinetics of the two agents.

The scope of our study is to reveal these mechanisms and to this end we examine in detail the linear stability of a film laden with a non-volatile, soluble surfactant flowing down an inclined plane. We perform a systematic analysis of the Orr-Sommerfeld eigenvalue problem of the full Navier-Stokes and concentration equations, taking into account mass exchange by diffusion and convection between the bulk and the interfaces, as well as the effect of sorption kinetics along the liquid-air interface and along the substrate. The paper is organized as follows. In section 2 we formulate the problem and describe the details of our model. The linear stability analysis is performed in section 3, and consists of an analytical solution in the limit of disturbances with very small wavenumber and a numerical solution for arbitrary wavenumbers. The results are presented and discussed in this section, and are followed by the conclusions.

## 2 PROBLEM FORMULATION

### 2.1 Fluid mechanics

We consider the dynamics of liquid films flowing along an infinite planar wall, inclined at an angle  $\alpha$  with the horizontal plane. The film is laden with a soluble, non-volatile surfactant which may adsorb at the liquid-air interface altering the surface tension. The fluid is Newtonian with density  $\rho$ , viscosity  $\mu$  and surface tension  $\sigma$ ; the density and viscosity are considered constant whereas the surface tension depends on the interfacial concentration of the surfactant.

In order to model two-dimensional dynamics, we use a Cartesian coordinate system  $(x, z)$ , with  $x$  pointing in the streamwise and  $z$  in the cross-stream direction. The velocity field is  $\underline{u} = (u, w)$ , where  $u$  and  $w$  are the velocity components in the streamwise and the cross-stream direction. The liquid-air interface is located at  $z = h(x, t)$  and the liquid-solid interface at  $z = 0$ . The flow is incompressible and governed by the momentum and mass conservation equations given below:

$$\rho(\underline{u}_t + \underline{u} \cdot \nabla \underline{u}) = \nabla P - \mu \nabla^2 \underline{u} - \rho \underline{g} \quad (1)$$

$$\nabla \cdot \underline{u} = 0 \quad (2)$$

Solutions of (1) and (2) are obtained subject to the following boundary conditions: Along the free surface, the velocity field satisfies the local force balance between normal and viscous stresses in the liquid. Taking the components of this force balance tangential and normal to the free surface we obtain

$$\underline{n} \cdot \underline{\tau} \cdot \underline{t} = \underline{t} \cdot \nabla_s \sigma \quad (3a)$$

$$\underline{n} \cdot \underline{\tau} \cdot \underline{n} = 2\kappa \sigma \quad (3b)$$

where  $\underline{n}$  and  $\underline{t}$  denote respectively the outward unit normal and unit tangential vectors on the interface,  $\underline{\tau}$  is the total stress tensor and  $2\kappa$  is the mean curvature of the interface. In addition, along the moving interface we impose the kinematic boundary condition, and at the liquid-solid interface the usual no-slip and no-penetration conditions.

### 2.2 Mass transfer

To account for the presence of soluble surfactants, we utilize the surfactant kinetic model of Edmonstone et al<sup>[10]</sup> that allows for two surfactant species in the bulk (monomers and micelle aggregates) and one at each interface. The interaction between the bulk concentration of monomer,  $c$ , and the concentration of adsorbed monomer at the interface,  $c_a$ , is denoted by the following kinetic law,

$$S_a + c \leftrightarrow c_a \quad (4)$$

where  $S_a$  is the fraction of the interface area that is not covered with monomer, and is defined as in terms of the concentration,  $c_{a\infty}$ , at close packing, as  $S_a = 1 - c_a/c_{a\infty}$ . Note that the above "reaction" is

characterized by rate constants  $k_1, k_2$ , which determine the fluxes between phases. For example, the bulk and the gas-liquid interface exchange monomers by a flux  $J_{ba}$ , according to the expression

$$J_{ba} = k_1 c|_{z=h} S_a - k_2 c_a = -D(\underline{n} \cdot \nabla c)|_{z=h} \quad (5)$$

The evolution of monomer concentrations at the gas-liquid interface and in the bulk is described by standard convection-diffusion equations, taking into account the motion of the interface. Finally, to complete the description, we choose the Sheludko equation<sup>[11]</sup> as the constitutive relation to describe the dependence of the interfacial tension on surfactant concentration. This model is nonlinear and asymptotes to a minimal surface tension, which makes it appropriate for use at high surfactant concentrations.

### 2.3 Scaling and linearization

We non-dimensionalize lengths and velocities by the Nusslet film thickness  $H$  and velocity  $U$ , and the interfacial and bulk concentrations by the closely packed value,  $c_{a\infty}$ , and by the critical micelle concentration,  $c_{cmc}$ , respectively. As a result, the following dimensionless parameters appear:

$$\begin{aligned} Re = \frac{\chi}{2} \sin \alpha, \quad \chi = \frac{g H^3}{v^2}, \quad Ka = \frac{\sigma_c}{\rho g^{1/3} v^{4/3}}, \quad \Sigma = \frac{\sigma_c}{\sigma_m}, \quad Sc_i = \frac{v}{D_i}, \quad Pe_i = Re Sc_i \quad (i=a, b) \\ \beta_a = \frac{c_{a\infty}}{H c_{cmc}}, \quad k_a = \frac{k_2 H}{U}, \quad R_a = \frac{k_1 c_{cmc}}{k_2 c_{a\infty}}, \quad \zeta_a = \beta_a R_a = \frac{k_1}{H k_2} \end{aligned} \quad (6)$$

At this point, it is instructive to attach physical significance to the various dimensionless parameters just defined. Term  $\beta_a$  compares the maximum amount that can adsorb on the interface to the maximum amount that can reside in the bulk as monomer. Term  $R_a$  is a ratio of the maximum possible forward and backward reaction rate for the adsorption process. Term  $\zeta_a$  is the ratio of the kinetic constants of the forward and backward reaction for the interface-bulk interaction, and thus provides a direct measure of the surfactant solubility in the bulk liquid<sup>[11]</sup>. We note that most of the recent theoretical literature refers to insoluble surfactants, and thus  $\zeta_a \gg 1$  is a useful limit for comparisons.

Next, we select as base case the flow with a flat interface and spatially uniform surfactant concentrations  $c_0, c_{a0}$  in equilibrium. We perturb the flow around this base case, and linearize the equations assuming that the disturbances are small. Finally, we define flow perturbations in terms of a streamfunction and expand parameters in normal modes as follows,

$$\bar{\psi}(x, z, t) = \Psi(z) \exp(\lambda t + ikx) \quad (7)$$

resulting in an Orr-Sommerfeld-like equation in terms of the eigenvalue  $\lambda$ , backed by a set of boundary conditions. This eigenvalue system is solvable analytically in the long-wave limit by an expansion in the wavenumber,  $k$ , of the form

$$\Psi(z) = \Psi^0(z) \lambda^0 + \Psi^1(z) \lambda^1 ik + \Psi^2(z) \lambda^2 k^2 + O(k^3) \quad (8)$$

For arbitrary wavenumber, the set is solved numerically by a Galerkin finite-element method. The weak form of the equations is derived by applying the divergence theorem, and all the variables are approximated by the use of quadratic Lagrangian basis functions. The order of the equation is reduced to 2nd by the substitution  $\Psi_{zz} = \Phi$ .

## 3 RESULTS

### 3.1 Long-wave limit

The analytic solution for the critical conditions, derived in the long-wave limit, is as follows:

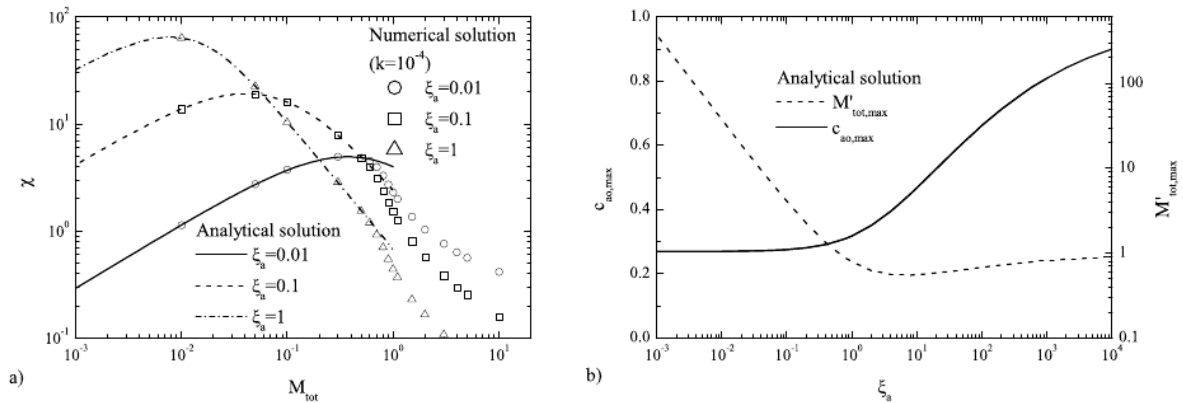
$$Re_c = \frac{5}{4} \cot \alpha + \frac{15}{4} Ma \frac{3 \zeta_a (c_{a0} - 1)^2}{3 \zeta_a (c_{a0} - 1)^2 + 4} \quad (8)$$

where  $Ma = E_0 \frac{Ka}{\chi^{2/3} \sin \alpha}$  and  $E_0 = \frac{3c_{a0}(\Sigma^{1/3} - 1)}{[1 + c_{a0}(\Sigma^{1/3} - 1)]^4}$  is the surface elasticity.

In the limit of an insoluble surfactant ( $\xi_a \gg 1$ ) the above equation reduces to

$$Re_c = \frac{5}{4} \cot \alpha + \frac{15}{4} Ma \quad (9)$$

in agreement with the expression given in the literature<sup>[7]</sup>. For a clear liquid,  $Ma = 0$ , both equations lead to the well known prediction for a Newtonian falling film. It is interesting to note that this prediction is also recovered in the limit of an interface saturated with a mildly soluble surfactant ( $c_{a0} \rightarrow 1$ ,  $\xi_a$  finite), as well as in the limit of a very soluble surfactant ( $\xi_a \ll 1$ ). The latter prediction is in agreement with recent experiments<sup>[9]</sup> with the highly soluble surfactant Isopropanol, which show a behavior reminiscent of a clear liquid with reduced surface tension.



**Figure 1.** a) Dependence of critical  $\chi$  on the total amount of surfactant,  $M_{tot}$ . b) Dependence of the interfacial concentration (and interfacial amount of surfactant) at maximum stability of the flow as function of surfactant solubility. The rest of the parameters are  $\alpha=90^\circ$ ,  $\beta_a=0,01$ ,  $R_a=1$ ,  $k_a=0,01$ ,  $Sc_a=100$ .

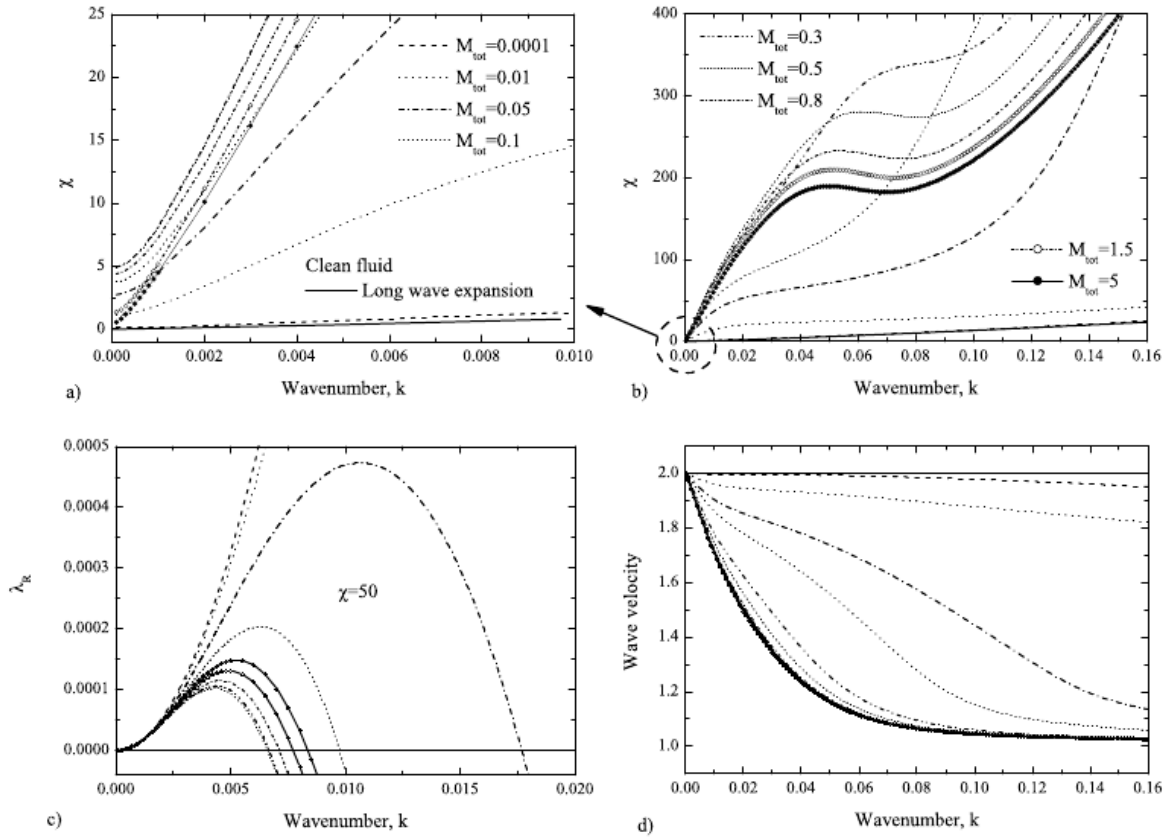
We start by considering the critical conditions, which correspond to the onset of long-wave disturbances. A question of evident interest is the effect on stability of the total amount of surfactant contained per unit area of the channel. To this end, we present in figure 1a the critical  $\chi$  as a function of  $M_{tot}$ , for three different values of the solubility parameter. The lines in this figure depict the analytical solution, while the points depict the numerical solution taking also into account the presence of micelles for large surfactant concentrations.

It is notable that the dependence on  $M_{tot}$  is not monotonic, exhibiting maximum stabilization at an intermediate value below the cmc. For very small, as well as for large values of  $M_{tot}$ , the critical  $\chi$  approaches the limit of the clean fluid. This is somewhat counter-intuitive because one would expect that the more surfactant is present in the system the more stable the system would be. However, we should keep in mind that it is not the amount of surfactant that stabilizes the flow, but actually the Marangoni stresses, which are related to the elasticity of the interface. When the surfactant exhibits significant solubility, the behavior is further complicated because of two competing effects: With increasing amount of surfactant, the dimensionless elasticity grows. At the same time, the growth in bulk concentration provides higher driving force for mass transfer with the interface, leading to the attenuation of surface tension gradients. As a result, when the adsorbed surfactant at the liquid-air interface approaches saturation, surface tension gradients decrease and therefore the Marangoni effects become less significant.

The parametric variation of the curves in figure 1a with  $\xi_a$  motivates investigation of two complementary issues: how does the location and how does the magnitude of the maximum in the critical conditions depend on surfactant solubility. Thus, in the following we study  $M'_{tot,max}$  and  $c_{a0,max}$  as function of  $\xi_a$ . The variation in the location of the maximum with surfactant solubility is shown in figure 1b. The solid line in figure 1b, depicts the interfacial surfactant concentration for maximum  $\chi$ . For an insoluble surfactant the flow is most stable for a nearly saturated interface. On the other hand, with increasing surfactant solubility,  $c_{a0,max}$  decreases monotonically, and for highly soluble surfactant it reaches a plateau. This is explained by the previous argument relating increased solubility to the ability of the flow to attenuate surface tension gradients.

### 3.2 Disturbances of arbitrary wavelength

Having analyzed the limit  $k \rightarrow 0$ , we now focus on the behavior of disturbances of finite wavelength. Results are derived by numerical integration of the Orr-Sommerfeld equation by a standard Galerkin finite element method. Figures 2a,b show the critical modified Reynolds number,  $\chi_c$ , as function of disturbance wavenumber for different amounts of surfactant. Figure 2a is a magnification of figure 2b at small values of  $\chi$  and  $k$ . It is evident that the addition of a small amount of surfactant results in drastic stabilization of practically all disturbances of finite length. This is still valid even for wavelengths three orders of magnitude larger than the liquid film thickness. Though the primary instability is a long-wave one, the above behavior will have serious consequences in the non-linear evolution of the flow. In particular, it is expected that higher harmonics will grow far more reluctantly than in the clear liquid, and the transition to solitary waves will be delayed, leaving a broad regime with sinusoidal or nearly sinusoidal traveling waves. This prediction is in agreement with recent data, which showed that the free surface is dominated by small-amplitude sinusoidal waves over a very wide range of flow rates and inlet disturbance frequencies.



**Figure 2.** a) Neutral curves for different values of  $M_{tot}$ ; comparison with analytical solution for a clean fluid. b) Zoom of figure 2a for  $0 < k < 0.01$ . c) Dispersion curves for different values of  $M_{tot}$  and for  $\chi = 50$ . d) Wave velocity of the most unstable mode at critical  $\chi$  as a function of the wavenumber,  $k$ . The rest of the parameters remain the same as in figure 1.

In the small wavenumber range, and with increasing amount of surfactant, the neutral curves in figures 2a,b tend to accumulate around a rough asymptote. The variation at higher wavenumbers is more complex, and eventually becomes non-monotonic. More specifically, an inflection point appears, which above  $M_{tot}=0.3$  leads to a local maximum in  $\chi$ . Further increase in the amount of surfactant renders higher wavenumbers progressively less stable. Figure 2c presents the dispersion curves for the same values of  $M_{tot}$  as in figure 2a,b. The non-monotonic effect of  $M_{tot}$  that was discussed in fig. 1 is also apparent here. For a given value of  $\chi=50$ , the growth rate of the disturbances (and in particular the most dangerous one) decreases for small values of  $M_{tot}$ , reaches a minimum around  $M_{tot}=0.5$  and increases again for large values of  $M_{tot}$ . Similar is also the behaviour of the wavenumber of the most dangerous mode and the cut-off wavenumber.

Finally, in figure 2d we present the wave velocity of the marginally unstable mode at neutral stability as a function of the wavenumber and for different amounts of surfactant. In agreement with previous studies<sup>[12]</sup>, we find that the wave velocity decreases in the presence of surfactant. It is also shown that wave velocity decreases with increase of the wavenumber and that it reaches an asymptotic value for very high surfactant concentrations. It is notable though that the variation with  $M_{tot}$  is now strictly monotonic. Therefore, the wave velocity appears

to depend directly on the surface concentration of the soluble surfactant, and not on the surface elasticity, as determined by the combination of stretching and diffusion/convection.

It is worth noting that the abrupt decrease of the wave velocity for high values of  $M_{tot}$  may also provide an explanation for the non-monotonic neutral curves that appear in fig. 2b. As the wave moves from the left to the right, it continuously sweeps surfactant by convection, thus inducing surface tension gradients that stabilize the flow. With the decrease of the wave velocity, as the wavenumber increases, less surfactant will be swept by the wave and the induced gradient will decrease. On the other hand, the surface tension gradient becomes more intense for high wavenumbers because the variation of the concentration takes place in smaller space. The interplay between these two actions can be responsible for the non-monotonic dependence of the critical  $\chi$  on the wavenumber.

### 3.3 Adsorption kinetics

Next, we consider the role of sorption kinetics at the liquid-air interface, which is potentially of central importance, and which has typically been neglected in simplified treatments of the problem. Thus, in figure 3 we examine the parametric effect of  $k_a$  on the curves of neutral stability for the reference case of figure 1. It is expected that for long-wave perturbations ( $k \ll 1$ ) the kinetics will not be very important because there will always be enough time for the different species to reach equilibrium around the interface. Indeed, as it can be seen in figure 3, for  $k = 0$  the critical  $\chi$  is the same for all values of  $k_a$ . This result is in direct agreement with the analytical expression that has been derived in the limit of  $k \rightarrow 0$ , where there is no dependence of the critical  $Re$  on the value of  $k_a$ .

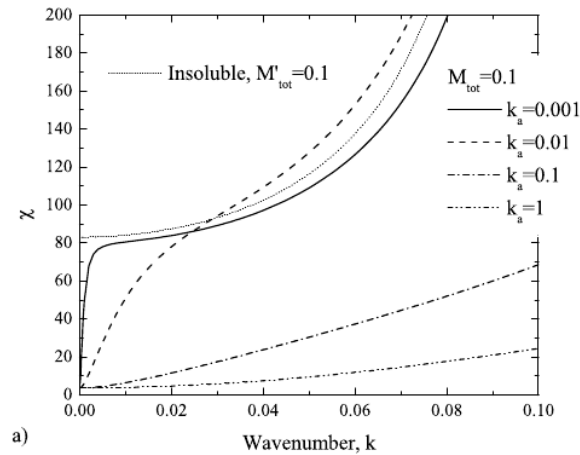


Figure 3. Neutral curves for different values of  $k_a$ . The rest of the parameters remain the same as in figure 1.

However, we see that, for disturbances with larger wavenumbers, this is clearly not the case. In particular, we plot in figure 3 the result for an insoluble surfactant, and observe that, for the lowest value of  $k_a$  shown, the neutral curve for the soluble surfactant follows it very closely, for all wavenumbers except for a very narrow range around zero. We should note at this point that to enable such a comparison between a soluble and an insoluble surfactant we have selected two cases with similar levels of interfacial concentration,  $c_{a0}$ . The similarity between the case of a soluble and an insoluble surfactant for large wavenumbers may be readily understood by considering that, when the kinetics are relatively slow and the disturbances have short wavelength, there will not be enough time for the species to approach equilibrium, and the system will behave as though the monomers that have been adsorbed at the liquid-air interface are isolated from the monomers in the bulk.

It is concluded, based on the above, that for small values of the kinetic parameter  $k_a$  there is strong selection of wavelengths that are unstable, and, on the contrary, when the kinetics are fast enough a wide range of wavelengths becomes unstable almost simultaneously, i.e. for similar values of  $Re$ . This behavior is expected to have significant implications on the non-linear dynamics of the flow. For example, assuming that  $k_a=0,001$  and that the flow rate is such that  $\chi=70$ , we conclude from figure 3, that, a long-wave disturbance in the narrow unstable range will grow remaining roughly sinusoidal, because higher harmonics are stable and will die away. On the contrary, if  $k_a=0,1$  there is a wide unstable range and therefore the initial long-wave disturbance will interact with its superharmonics and end up in the formation of solitary humps. The persistence of near-sinusoidal waves recently reported in the presence of soluble surfactant SDS<sup>[8]</sup>, is plausibly explained by this mechanism.

## 4 CONCLUSIONS

We investigated the linear stability of a film flowing down a solid substrate in the presence of a soluble surfactant. We used a detailed surfactant model, which considers monomers and micelles in the bulk, and monomers adsorbed with Langmuir kinetics at the gas/liquid and the solid/liquid interfaces. The Navier-Stokes equations for the liquid motion and the advection-diffusion equations for surfactant concentrations were linearized around the base flow, resulting in an Orr-Sommerfeld eigenvalue problem that was solved analytically in the limit of long-wave disturbances, and numerically for arbitrary wavelength using a finite element method.

The instability was shown to be a long-wave one, and the derived analytic solution indicated that, among all the model parameters, critical conditions depend only on the solubility of the surfactant and on its interfacial concentration. An interesting finding was that, for a given total amount of surfactant, a moderately soluble one may produce stronger stabilization than the insoluble one. Optimum conditions were also found to vary with solubility, the insoluble surfactant maximizing its performance at the tightest interfacial packing, whereas the soluble one at a fraction of it. These observations were explained by the competing effect of mass exchange between the interface and the bulk, which short-circuits surface tension gradients, and thus attenuates Marangoni stresses.

Disturbances of finite wavelength were considered in detail, because (though they are not the most dangerous ones) they have a strong bearing on nonlinear dynamics. It was found that small amounts of surfactant drastically stabilize the entire spectrum of nonzero wavenumbers, and that the effect maximizes at intermediate amounts and then drops again. This non-monotonic variation was related to the observed strong decline of the phase speed of finite-wavelength waves towards an asymptotic value of one, with the increase in the amount of surfactant. The adsorption/desorption kinetics was also shown to have a strong influence on the dynamics of finite wavelengths, with very slow kinetics leading to a virtually frozen interface and an insoluble-like behavior.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support by the General Secretariat of Research and Technology of Greece under the Action Supporting Postdoctoral Researchers (Grant No: PE8(906)), co-funded by the European Social Fund and National Resources.

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