

## NONLINEAR DYNAMICS AND STABILITY OF THIN FILMS WITH INSOLUBLE SURFACTANTS

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**ABSTRACT.** In the present work the dynamics of a surfactant coated free film, laterally bounded by a solid frame, is studied by means of an evolutionary system consisting of three coupled non-linear Partial Differential Equations (PDE) for the film thickness, lateral velocity and insoluble surfactant concentration. A linear stability analysis is implemented numerically by the method of the differential Gauss elimination. It is found that the film is more stable with the increase of the surfactant concentration (related to the Marangoni number) with respect to antisymmetrical disturbances applied to its shape at different combinations of the Reynolds number, the Weber number, the Hamaker constant and the wetting angle. These results are approximately confirmed by the results of the non-linear stability analysis, from which the evolution of the film thickness, lateral velocity and surfactant concentration is found.

**KEY WORDS:** free thin film, insoluble surfactant, van-der-Waals force, linear stability, non-linear stability.

### 1. Introduction

The spreading of surfactants (surface-active agents) on thin viscous films is important for many industrial and biomedical processes, such as coating flow technology, micro-fluidics, surfactant replacement therapy, in which surfactants spread on thin pulmonary airway linings, film drainage in emulsions and foams, etc. [1]–[6]. The surfactant gradients along the film interfaces affect the local surface tension and cause tangential stresses, so-called Marangoni stresses, that produce fluid motions and deformations of the film. Thus, the surfactant concentration is coupled with the film motion and is distributed

on the film interfaces as well as in the film bulk, if the surfactant is soluble. However, if the surfactant is insoluble, its presence is restricted only on the film interfaces and usually retards the film flow by rigidifying its interfaces [2]. As the thin liquid films exhibit hydrodynamic instability under the action of the van der Waals attraction forces, leading to film rupture, the surfactants presence can compete with the van der Waals attractions and has a stabilizing effect on the rupture instability [5]. Therefore, the surfactants can be used to control the film shape. For example, the soaps and detergents are surfactants lowering the interfacial surface tension.

Two generic types of thin films exist depending on their geometry: free films, bounded by two free surfaces separating the liquid from a passive gas or another liquid (observed at coalescence of drops, in cell membranes, on thin frames pulled from a bulk phase, for example, from melt); supported films spread on solid substrates. The insoluble surfactant role on the stability of both types of films, when the van-der-Waals disjoining pressure is accounted, is investigated by De Wit et al. in [5]. There, the linear and non-linear stability analysis is performed in the framework of the long-wavelength model for different combinations of the problem parameters. The films are supposed to be infinitely or semi-infinitely long. It has been shown that in the case of the free film three coupled non-linear Partial Differential Equations (PDE) (for the film thickness, lateral velocity and surfactant concentration) are required, while for the supported film – a pair of PDE (for the film thickness and surfactant concentration). These equations describe the evolution of a squeezing mode, correspondent to symmetric thickness fluctuations, usually leading to film rupture. The linear stability is analytically studied and the non-linear - numerically. The same problems have been investigated in [6] by means of a weakly nonlinear analysis in the vicinity of a steady bifurcation point. The obtained rupture times are compared with the numerical results of De Wit et al. [5].

The case of a surfactant-free film, laterally bounded by a solid frame, has been studied in [7]-[11]. The linear stability analysis without or with the presence of the van-der-Waals disjoining pressure has been considered in [9] and [10]. A non-linear stability analysis has been performed for different wetting angles with the lateral solid frame in [11]. There, it has been shown that: the film rupture can be caused either by the non-existence of a static film shape or by the instability of an existing static shape; the static film shapes are always stable (at smaller wetting angle than  $\pi/2$ ) when subjected to symmetrical disturbances, but can be unstable if asymmetrical disturbances are imposed on them.

In the present work, we extend the latter studies including insoluble surfactants on the film interfaces. This means that the evolutionary system consists of three coupled non-linear equations for the film thickness, lateral velocity and surfactant concentration. A linear stability analysis is implemented numerically by the method of the differential Gauss elimination. It is found that the film will be more stable with the increase of the surfactant concentration (related to the solutal Marangoni number) with respect to antisymmetrical disturbances, imposed on the film static shape, at different combinations of the Reynolds number, the Weber number, the Hamaker constant and the wetting angle. These results are confirmed approximately by the results of the non-linear stability analysis. From the latter analysis, the evolution of the film thickness, lateral velocity and surfactant concentration are found. It is interesting to note that the surfactant concentration profile follows the film thickness one. This means that the surfactants follow the fluid flow leaving the regions where the thickness of the film decreases and tends to zero, i.e., where the film ruptures.

The paper structure is the following. The governing equations of the film dynamics and the insoluble surfactant distribution on the film surfaces are presented in Section 2. Their solutions, correspondent to static state or to rupture, are considered in Section 3. Both the linear and non-linear stability analysis are given in Section 4. Section 5 is devoted to the final conclusion.

## 2. Mathematical model

We consider a free thin film, symmetrical with respect to its central plane and laterally bounded by a solid rectangular frame. A Cartesian coordinate system  $(x, y, z)$ , connected with the film symmetry plane  $z = 0$ , is chosen. Only the simple case of one-dimensional film (in  $x$  direction) can be considered if the frame sides are taken as  $x = \pm a$ ,  $y = \pm b$  with  $a \ll b$ . The average film thickness  $\bar{h}$  is assumed to be much smaller than the frame side  $a$  and their ratio determines a small parameter  $\varepsilon = \frac{\bar{h}}{a} \ll 1$ . The free symmetrical surfaces are defined as  $z = \pm h'/2$ , where  $h'(x, t) = O(\varepsilon)$  represents the film shape. Further, the following characteristic scales are used:  $a$  for lateral length scale;  $U$  for lateral velocity scale;  $a/U$  for time scale and  $\varepsilon a$  for film thickness scale. The film liquid is supposed to be Newtonian viscous one with constant density  $\rho$  and dynamic viscosity  $\mu$ . The gravity force action is neglected, while the van-der-Waals force action is taken into account as a disjoining pressure. The film interfaces are coated with insoluble surfactants, which diffuse along them. Thus, the surface tension  $\sigma$  will change with the surfactant concentration  $\Gamma$ ,

that represents the Marangoni effect. The insoluble surfactants are assumed of low concentration, which means that their influence on the disjoining pressure in the film may be neglected, as well as on the interface rheology.

The dynamic system for the longitudinal velocity and the film thickness, obtained from the Navier-Stokes equations, the kinematic and dynamic boundary conditions (normal stress jump and zero shear stress for a surfactant-free film) on the interfaces have been derived in [7] and in [8] for the case of a general disjoining pressure. There is a jump of the tangential stress if insoluble surfactants are present on the film interfaces. As the tangential stress of the surrounding air is zero, it means that the tangential stress on the film interfaces,  $z = \pm h'/2$ , is non-zero and equals the surface gradient of the surface tension:

$$(1) \quad \mathbf{T} \cdot \mathbf{n} \cdot \mathbf{t} = (\nabla_s \sigma) \cdot \mathbf{t}$$

Here,  $\mathbf{T}$  is the stress tensor,  $\mathbf{n}$  and  $\mathbf{t}$  are unit vectors, outward normal and tangential to the interfaces, respectively, defined by  $\mathbf{n} = n^{-1}(-h'_x/2, \pm 1)$ ,  $\mathbf{t} = n^{-1}(1, \pm h'_x/2)$ , where  $n = [1 + (h'_x/2)^2]^{1/2}$  and  $\nabla_s = (\mathbf{I} - \mathbf{nn}) \cdot \nabla$  is the surface gradient with  $\mathbf{I}$  being the plane identity tensor.

For insoluble surfactants, the surfactant concentration  $\Gamma$  is independent of  $z$ , i.e.  $\Gamma(x, t)$ , which is attributed also to the surface tension  $\sigma$ , as it is related to the surfactant interfacial concentration by an equation of state. The simplest form of this equation, correspondent to dilute concentrations, is given by the linear relation (cf. [12]):  $\sigma = \sigma_0 + \Gamma \sigma_\Gamma|_{\Gamma=0}$ , where  $\sigma_0$  is the surface tension of a clean interface at  $\Gamma = 0$  and the subscript  $\Gamma$  signifies partial differentiation. Thus, the surface gradient of  $\sigma$  becomes:

$$(2) \quad (\nabla_s \sigma) \cdot \mathbf{t} = n^{-3} \frac{\partial \Gamma}{\partial x} \sigma_\Gamma|_{\Gamma=0}.$$

Further, an initial surfactant concentration  $\Gamma_0 = \text{const.}$  will be used as a characteristic scale for the surfactant concentration.

The surfactant evolution on the interfaces is obtained through a convective-diffusion equation. The time-dependent convective-diffusion equation for surfactant transport along a deforming interface has been presented by many authors (cf. [13]):

$$(3) \quad \frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{v}) = D_s \nabla_s^2 \Gamma,$$

where  $D_s$  is the surface diffusion coefficient of the surfactant and  $\mathbf{v}$  is the velocity vector.

We have to note that the dependence of  $\sigma$  on  $\Gamma$  enters the dynamic system only through the surface-tension gradient (Marangoni term) and it does not affect the capillary term. Such one-dimensional system together with the one-dimensional surfactant transport equation (3), when all of them are made dimensionless, is given here after:

$$(4) \quad \frac{\partial h}{\partial \tau} + \frac{\partial}{\partial x}(uh) = 0,$$

$$(5) \quad \frac{\partial u}{\partial \tau} + u \frac{\partial u}{\partial x} = \frac{\varepsilon}{We} \frac{\partial^3 h}{\partial x^3} + \frac{4}{Re} \frac{\partial}{\partial x} \left( h \frac{\partial u}{\partial x} \right) + \frac{A}{h^4} \frac{\partial h}{\partial x} - 2M \frac{\partial \gamma}{\partial x},$$

$$(6) \quad \frac{\partial \gamma}{\partial \tau} + \frac{\partial(\gamma u)}{\partial x} = \frac{1}{Pe_s} \frac{\partial^2 \gamma}{\partial x^2},$$

where  $\tau$  is the dimensionless time,  $x$  is the dimensionless longitudinal coordinate,  $u$  is the dimensionless longitudinal velocity,  $h$  is the dimensionless film thickness,  $\gamma$  is the dimensionless surfactant concentration,  $Re = \rho a U / \mu$  is the Reynolds number,  $We = Re Ca = 2 \rho a U^2 / \sigma_0$  is the Weber number,  $Ca$  is the capillary number,  $A = \frac{A_H}{2\pi \rho U^2 a^3 \varepsilon^3}$  is the dimensionless Hamaker constant with  $A_H$  the dimensional Hamaker constant,  $M = -\frac{2}{\varepsilon We} \frac{\Gamma_0}{\sigma_0} \sigma_{\Gamma}|_{\Gamma=0}$  is the solutal Marangoni number,  $Pe_s = Sc Re$  is the surface Peclet number and  $Sc = \frac{\mu}{\rho D_s}$  is the Schmidt number.

In the system (4)–(6), the terms of  $o(\varepsilon)$  have been neglected. This means that the dimensionless numbers are upper limited as:  $Re \leq \varepsilon^{-1}$ ,  $We \leq 1$  and  $Pe_s \leq \varepsilon^{-1}$ . If  $M \ll \varepsilon$  and/or  $A \ll \varepsilon$ , the film interfaces can be regarded as clean and/or the van-der-Waals forces action – as negligible. Usually, the water films of mean thickness of  $O(10^{-5}m)$  attached on frames with sides of  $O(10^{-2}m)$  enter into these restrictions.

The boundary conditions for  $h$ ,  $u$  and  $\gamma$  on the frame are the following:

- wetting condition for the film shape  $h$ :

$$(7) \quad \frac{\partial h}{\partial x}(\pm 1, \tau) = \pm \tan \alpha,$$

where  $\pi/2 - \arctan(0.5 \tan \alpha)$  is the wetting angle with the frame (Note, that for planar films  $\alpha = 0$ , as the wetting angles are right angles.);

- zero condition for the lateral velocity  $u$ :

$$(8) \quad u(\pm 1, \tau) = 0;$$

- uniform surfactant concentration on the the frame:

$$(9) \quad \frac{\partial \gamma}{\partial x}(\pm 1, \tau) = 0.$$

The mass conservation condition reads:

$$(10) \quad \int_{-1}^1 h dx = W,$$

where  $W = \text{const}$  is the initial film volume.

We give the initial conditions in a general form, as they will differ when studying separately the relaxation and the stability problem:

$$(11) \quad h(x, 0) = h_0(x), \quad u(x, 0) = u_0(x), \quad \gamma(x, 0) = \gamma_0(x).$$

The functions  $h_0(x)$ ,  $u_0(x)$  and  $\gamma_0(x)$  will be specified in the next sections.

### 3. Film dynamics

The unstationary coupled system (4)–(11) has no analytical solution and has been solved numerically by a finite difference scheme using the control volume method. The full description of the numerical model for the surfactant-free film case can be found in [7]. The numerical scheme in time is implicit and the three coupled equations are solved iteratively. A staggered grid is exploited in  $x$  direction, such that the grid points of the film shape function  $h$  and the concentration function  $\gamma$  are displaced in a half step with respect to the grid points of the velocity function  $u$ . The numerical calculations have been performed with steps  $\delta x = 0.01$  and  $\delta \tau = 10^{-5}$  or  $10^{-6}$ . The accuracy of the finite-difference scheme is  $O(\delta x + \delta \tau)$ . The calculations have been stopped when reaching  $h_{\min} = O(\delta x)$ , which corresponds to a film rupture or when the velocity becomes small enough,  $|u_{\max}| = 10^{-4}$ , to obtain the film static shape.

The static solution of (4)–(11), without the action of the disjoining pressure, is:

$$(12) \quad h_s(x) = 0.5(x^2 - 1/3) \tan \alpha + 0.5W, \quad u_s(x) \equiv 0, \quad \gamma_s(x) \equiv \text{const.}$$

The limit  $h_s(x) > 0$  gives a restriction of the wetting angle, if the film volume is fixed. For example, at  $W = 2$ , the upper limit of  $\alpha$  is:  $\alpha < 1.40565$ . However, no analytical solution can be found under the action of the disjoining pressure and the static solution can be obtained as a numerical solution of the dynamical problem (4)–(11) with constant initial conditions, for example:

$$(13) \quad h_0(x) = 1, \quad u_0(x) = 0, \quad \gamma_0(x) = 1.$$

Static shapes can be found only for some combinations of the problem parameters (for some values of  $B$  and  $\alpha$ , where  $B = \frac{WeA}{\varepsilon}$ ), as it is shown

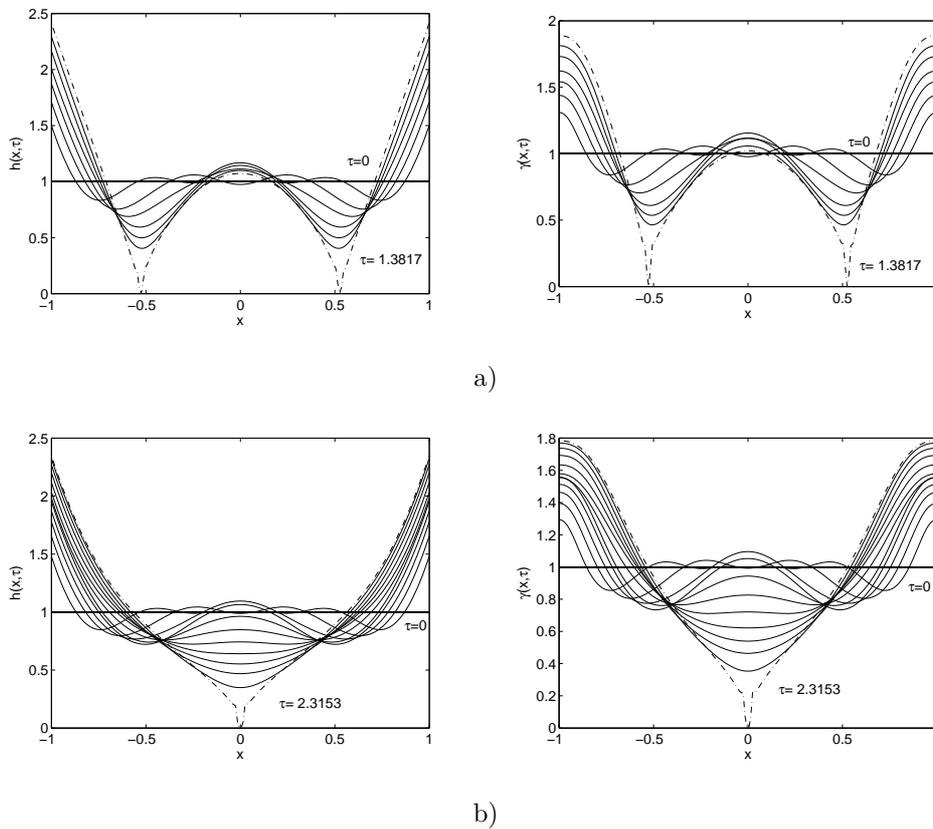


Fig. 1. Rupture of a thin film starting from a planar shape at  $\tau = 0$  at  $\alpha = 1.37$ ,  $Re = 100$ ,  $We = 1$ ,  $\varepsilon = 0.01$ ,  $A = 0.1$  ( $B = 10$ ) and  $Sc = 1$ : a)  $M = 0$ ; b)  $M = 0.1$ . (The plotted curves are at time interval  $\Delta\tau = 0.2$ . The final shapes are plotted as “dash-dotted” lines.)

in Fig. 2 of [11]. For example, at  $B \geq 9$ , the static film shapes exist only for  $\alpha = 0$ , while at  $B = 0.01$  – for  $0 \leq \alpha \leq 1.37$ . If the film shape is static for clean interfaces, it also remains static for surfactant coated interfaces at different values of the Marangoni number  $M$ . The static film shape is reached for the final time:  $\tau = 14.9$  at  $M = 0$ ;  $\tau = 16.24$  at  $M = 0.1$  and  $\tau = 24.62$  at  $M = 1$  for the case presented in Fig. 3a) of [11], at  $Re = 1$ ,  $We = 0.01$ ,  $\varepsilon = 0.01$ ,  $A = 0.01$  ( $B = 0.01$ ),  $Sc = 10$  and  $\alpha = 1.37$  (some values of  $Sc$  are given in [5] for water films). Different types of rupture have been observed at bigger values of  $B$  and  $Re$  following Fig. 3b), c), d) of [11]. The increase of  $M$  also increases the rupture time, but without reaching a static film shape. There is a competition between the Marangoni and viscous forces, which has a stronger effect near the film boundaries at bigger Reynolds numbers. However, the increase of the Marangoni number changes the locations of the film minima (rupture points) and sometimes changes the type of rupture: the “rim” rupture could become a “pimple” rupture. This effect is shown in Fig. 1 a), b) at  $Re = 100$ ,  $We = 1$ ,  $\varepsilon = 0.01$ ,  $A = 0.1$  ( $B = 10$ ),  $Sc = 1$  and  $\alpha = 1.37$  for both cases  $M = 0$  and  $M = 0.1$ . The rupture time is  $\tau = 1.38$  for  $M = 0$  and  $\tau = 2.31$  for  $M = 0.1$ . The surfactant mobility is decreased if the Schmidt number is decreased and the rupture time is higher. For example, for the case presented in Fig. 1 b) (when  $M = 0.1$ ), but at  $Sc = 0.1$ , the rupture time is  $\tau = 2.826$ . However, the rupture time at  $M = 0$  remains the same with the change of  $Sc$ , as the surfactant diffusion is separated from the film dynamics.

## 4. Stability analysis

### 4.1. Linear stability

As discussed in the previous chapter, the static state solutions are obtained numerically and they exist only for some combinations of the parameters  $\alpha$ ,  $B$ ,  $Re$ ,  $We$  and  $\varepsilon$ . The parameters connected with the surfactant presence,  $M$  and  $Sc$ , do not alter the static state existence. Here, we shall start with the linear stability of the static state solutions and further, in the next section, continue with their non-linear stability.

Small disturbances  $\tilde{h}(x, \tau)$ ,  $\tilde{u}(x, \tau)$  and  $\tilde{\gamma}(x, \tau)$  are imposed on the static state solutions:

$$(14) \quad h = h_s + \tilde{h}, \quad u = \tilde{u}, \quad \gamma = \text{const.} + \tilde{\gamma},$$

where the constant in the expression of  $\gamma$  is usually taken equal to 1 without loss of generality.

The disturbances  $\tilde{h}$ ,  $\tilde{u}$  and  $\tilde{\gamma}$  are sought as exponential functions in time with unknown growth rate  $\omega = \omega_r + i\omega_i$  and unknown distributions  $H(x)$ ,  $V(x)$  and  $G(x)$ :

$$(15) \quad \tilde{h} = H(x) \exp(\omega\tau), \quad \tilde{u} = V(x) \exp(\omega\tau), \quad \tilde{\gamma} = G(x) \exp(\omega\tau).$$

After inserting (14) with (15) in Eqs (4)–(6), neglecting the 2<sup>nd</sup> order disturbances and performing some manipulations with  $H = -\frac{(h_s V)'}{\omega}$ , the following characteristic system for  $\Omega = \frac{We}{\varepsilon Re} \omega$  is obtained:

$$(16) \quad (h_s V)^{IV} - \frac{4\Omega}{h_s} (h_s V')' + P\Omega^2 V + \frac{B}{h_s^4} (V h_s)'' - \frac{4B h_s'}{h_s^5} (V h_s)' + 2Ma\Omega G' = 0,$$

$$(17) \quad G'' - \Omega P S c G - P e_s V' = 0,$$

$$(18) \quad V(\pm 1) = 0,$$

$$(19) \quad (h_s V)''(\pm 1) = 0,$$

$$(20) \quad G'(\pm 1) = 0,$$

where  $P = \frac{\varepsilon Re^2}{We}$  and  $Ma = MRe$ .

The eigenvalue problem (16)–(20) at  $\alpha = 0$  transforms into a cubic equation for  $\Omega$ , which has one real solution (positive or negative depending on the parameters) and two complex conjugate solutions with a negative real part:

$$(21) \quad \Omega^3 + \frac{m^2}{P} \left( \frac{1}{Sc} + 4 \right) \Omega^2 + \frac{m^2}{P} \left( m^2 - B + \frac{4m^2}{PSc} + 2Ma \right) \Omega + \frac{m^4}{ScP^2} (m^2 - B) = 0,$$

where  $m = (2k_1 + 1)\pi/2$ , ( $k_1 = 0, 1, \dots$ ) corresponds to asymmetrical disturbances of the film shape and  $m = k_2\pi$ , ( $k_2 = 1, 2, \dots$ ) – to symmetrical disturbances.

The critical wave number  $m_c$ , at which  $\Omega = 0$ , depends only on  $B$ , as it has been found in the surfactant-free case by many authors [5], [14] and also found in our previous works [10], [11]:

$$(22) \quad m_c = \sqrt{B}.$$

Table 1. Values of the real root  $\Omega_r$  of (21)

Ma	0	0.01	0.05	0.1	0.5	1
$\Omega_r$	0.1314	0.1297	0.1233	0.1158	0.0746	0.0494

Thus, the surfactant presence does not influence the critical wave number, but it influences the values of the real root,  $\Omega_r$  of (21), which are given in Table 1, for example for  $P = 1$ ,  $B = 3$ ,  $Sc = 10$  and  $m = \pi/2$  (the latter corresponding to the eigenvalue with the greatest real part).

The eigenvalue problem (16)–(20) for  $\alpha > 0$  has no analytical solution, a numerical eigenvalue search is applied by the secant method and the differential Gauss elimination method [15]. These methods have been applied to the case of a surfactant-free film in [9] and in [10]. Here, we shall give only the changes of the Gauss elimination method, made to cope with the surfactant presence.

Following [9], new variables are introduced by:

$$(23) \quad \mathbf{v} = (v_1, v_2, v_3) = (h_s V', (h_s V)''' - \Omega V', G''),$$

$$(24) \quad \mathbf{w} = (w_1, w_2, w_3) = (h_s V, (h_s V)'' - \Omega V, G').$$

Then the 4<sup>th</sup> order system of Ordinary Differential Equations (ODE) (16) and the derivative of (17) (appropriate to compare with the analytical solution of (21) at  $\alpha = 0$ ) is transformed into a linear ODE system of 1<sup>st</sup> order:

$$(25) \quad \mathbf{v}' = \mathbf{K}\mathbf{v} + \mathbf{G}\mathbf{w},$$

$$(26) \quad \mathbf{w}' = \mathbf{D}\mathbf{v} + \mathbf{E}\mathbf{w},$$

where

$$\mathbf{G} = \begin{pmatrix} -\frac{h_s' - \Omega}{h_s} & 1 & 0 \\ -\frac{\Omega}{h_s^2} (3h_s'' - 3\Omega + P\Omega h_s + \frac{B}{h_s^3}) + \frac{4Bh_s'^2}{h_s^5} & \frac{3\Omega}{h_s} - \frac{B}{h_s^4} & -2Ma\Omega \\ Pe_s \left( \frac{\Omega - h_s'' + h_s'^2}{h_s^2} - \frac{h_s'^3}{h_s^3} \right) & \frac{Pe_s}{h_s} & PSc\Omega \end{pmatrix},$$

$$\mathbf{K} = \begin{pmatrix} -\frac{h_s'}{h_s} & 0 & 0 \\ -\frac{2\Omega h_s'}{h_s^2} + \frac{4Bh_s'}{h_s^5} & 0 & 0 \\ -\frac{2Pe_s h_s'}{h_s^2} & 0 & 0 \end{pmatrix}, \quad \mathbf{E} = \begin{pmatrix} \frac{h_s'}{h_s} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

and  $\mathbf{D} = \mathbf{I}$ , as  $\mathbf{I}$  is the identity matrix.

Only the half interval  $x \in [0, 1]$  is considered since the conditions (18)–(20) are homogeneous boundary conditions for  $\mathbf{w}$ . Then the boundary conditions (18)–(20) can be written as:

$$(27) \quad \mathbf{v}(0) = \mathbf{0},$$

$$(28) \quad \mathbf{w}(1) = \mathbf{0}.$$

The unknown vector  $\mathbf{v}$  is sought in the form:

$$(29) \quad \mathbf{v}(x) = \mathbf{A}(x)\mathbf{w}(x),$$

where  $\mathbf{A}(x) = \{A_{ij}(x)\}$ , with  $i, j = 1, 2, 3$ , is an unknown matrix, whose elements will be found after solving the differential equation:

$$(30) \quad \mathbf{A}' = \mathbf{G} - \mathbf{AE} + (\mathbf{K-AD})\mathbf{A}$$

with the homogeneous boundary condition:

$$(31) \quad \mathbf{A}(0) = \mathbf{0}.$$

The solution of (30), (31) represents the direct differential Gauss elimination. In a similar way, as shown in [9], the inverse differential Gauss elimination is constructed: starting at  $x = 1$  and directing towards  $x = 0$ . Both eliminations are matched at some inner point  $x_c \in (0, 1)$ , which leads to an eigenvalue condition (characteristic equation) containing the elements of the two matrices  $\mathbf{A}$  and  $\mathbf{B}$  (the inverse elimination matrix). The elements of both matrices are found numerically by the Runge-Kutta method. The eigenvalue is sought iteratively from the obtained condition (characteristic equation) via the secant method, which is fast converging. A brief description of this method is given in [9].

The eigenvalue analytical solution  $\Omega_r$ , presented in Table 1 for  $\alpha = 0$ , has been recovered by the presented numerical method of differential Gauss elimination with a relative error  $O(10^{-5})$ . The numerically found eigenvalues  $\Omega_r$  for the same case of  $P = 1$ ,  $B = 3$  and  $Sc = 10$  are presented in Fig. 2 as functions of  $\alpha$  and  $Ma$ . The maximum value of  $\alpha$  for a static shape existence, according to the static shape existence plot, Fig. 3 of [11] at  $P = 1$  and  $B = 3$ , is 0.8. It is clear from the linear stability analysis that for all values of  $Ma$ ,  $0 \leq Ma \leq 1$ , the film is unstable to asymmetrical disturbances, if  $0 \leq \alpha < 0.5$

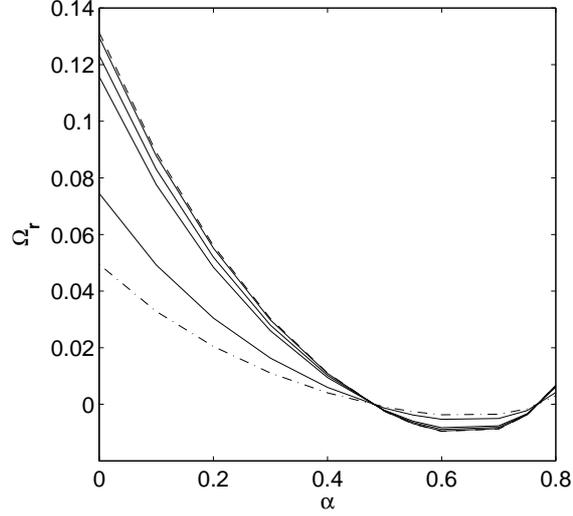


Fig. 2. Eigenvalues  $\Omega_r$  at  $P = 1$ ,  $B = 3$  and  $Sc = 10$  as functions of  $\alpha$  and  $Ma = 0$ ; 0.01; 0.05; 0.1; 0.5; 1. (The “dashed” line corresponds to  $Ma = 0$ , the “dash-dotted” line – to  $Ma = 1$  and  $Ma$  increases from up to down when  $\alpha < 0.48$ )

and  $0.75 < \alpha \leq 0.8$ . However, the bigger values of  $Ma$  create smaller positive  $\Omega_r$  and bigger negative  $\Omega_r$  in such a way, that  $\Omega_r \approx 0$  for all  $Ma$  corresponding to one and the same wetting angle,  $\alpha \approx 0.48$ . This means that always the bigger  $Ma$ , i.e., the higher surfactant concentration, will retard the relaxation (leading to a stable film shape) or the rupture process. For example, the static state, obtained numerically in the previous chapter for the case of  $Re = 1$ ,  $We = 0.01$ ,  $\varepsilon = 0.01$ ,  $A = 0.01$  ( $B = 0.01$ ),  $Sc = 10$  and  $\alpha = 1.37$ , is linearly stable, when subjected to asymmetrical disturbances. The eigenvalues are negative and presented in Table 2 for  $0 \leq Ma \leq 1$ :

Table 2. Eigenvalues for  $0 \leq Ma \leq 1$

Ma	0	0.01	0.05	0.1	0.5	1
$\Omega_r$	-0.0302	-0.0297	-0.0278	-0.0258	-0.0166	-0.0116

As discussed in [11], in the case of  $\alpha = 0$ , the film is unstable to asymmetrical disturbances, when  $m = \pi/2 \leq m_c$  (i.e. when  $B \geq 2.467$ ) and unstable to symmetrical disturbances, when  $m = \pi \leq m_c$  (i.e. when  $B \geq 9.8696$ ). Here, this assertion is also valid, despite of the surfactant presence. It has been established that there are no static shapes for  $\alpha > 0$  at  $B \geq 9$ ,

too. We shall study in the next subsection only the asymmetrical disturbances imposed on the static film shape using the numerical solution of the nonlinear model (4)–(11).

**4.2. Non-linear stability**

The non-linear stability analysis is based on the numerical solution of the dynamical problem (4)–(11) with initial conditions:

$$(32) \quad h_0(x) = h_s(x) + 0.1 \sin(\pi/2x), \quad u_0(x) = 0, \quad \gamma_0(x) = 1.$$

The predictions of the linear stability analysis for the case shown in Fig. 2 are approximately confirmed by the non-linear analysis results. According to them, the static film shape is unstable to asymmetrical disturbances, if  $0 \leq \alpha < 0.6$  and  $0.7 < \alpha \leq 0.8$ , which means that the range of stability in  $\alpha$  is shortened. The film thickness rupture and the surfactant distribution is shown at  $Ma = 0.1$  in Fig. 3 a), b) and at asymmetrical initial disturbances for  $\alpha = 0.5$  and  $\alpha = 0.8$ , respectively. The rupture takes place in different points  $x$ : at  $x = -0.505$  for  $\alpha = 0.5$  and at  $x = -0.185$  for  $\alpha = 0.8$ . The rupture times for different  $Ma$  and  $\alpha = 0; 0.5; 0.8$  are given in Table 3.

Table 3. Rupture times for different  $Ma$  and  $\alpha = 0; 0.5; 0.8$

$Ma$	0	0.1	1
$\tau_{rupture}/$	6.48	6.81	11.44
$\tau_{rupture}/\alpha = 0$	60.59	68.92	155.26
$\tau_{rupture}/\alpha = 0.8$	52.86	59.15	123.2

It turns out that the surfactants retard the film rupture in correspondence with the linear analysis predictions. The plots of the surfactant concentration function  $\gamma(x, \tau)$  show that the surfactants concentrate far from the rupture region. However, they leave the rupture region very fast, depending on the Marangoni number,  $M$ . The only stable shapes are for  $0.6 \leq \alpha \leq 0.7$ , which also remain stable when changing  $M$ . The case of  $M = 0$  at  $\alpha = 0.6$  is presented in Fig. 6c) of [11]. It occurs that the return to the static shape is a very long process for all considered values of  $M$ , as the eigenvalue predicted by the linear theory is negative, but close to zero (see Fig. 2).

A detailed discussion on the general case of asymmetrical disturbances with shorter wavelengths, correspondent to  $m = 3/2\pi$  has been made in [11] for surfactant-free films. The film becomes unstable at  $\alpha = 0$  when the initial wavelength  $\lambda_d$  is bigger than the critical wavelength  $\lambda_c$  (correspondent to  $m_c$ ),  $\lambda_d = \frac{\pi}{m} > \lambda_c = \frac{\pi}{\sqrt{B}}$ , and when the film length  $L = 2$  is bigger than the critical

wavelength  $\lambda_c$ . This means that for  $\alpha = 0$  the rupture occurs at  $B > 22.21$ . However, this analysis is not applicable for films with smaller wetting angles than  $\pi$ , i.e., at  $\alpha > 0$ , as they do not possess any static shape at  $B > 9$ . In the opposite case, when the initial wavelength is smaller than the critical wavelength  $\lambda_d < \lambda_c$  (at  $B < 22.21$ ), the initial shorter stable wavelength is changed to a longer unstable wavelength for some combinations of the parameters  $B$  and  $\alpha$ . In the present work we shall not stop our attention on the shorter wavelength disturbances, but expect that the surfactants presence will not change qualitatively the upper mentioned results, as it has been noticed in [5].

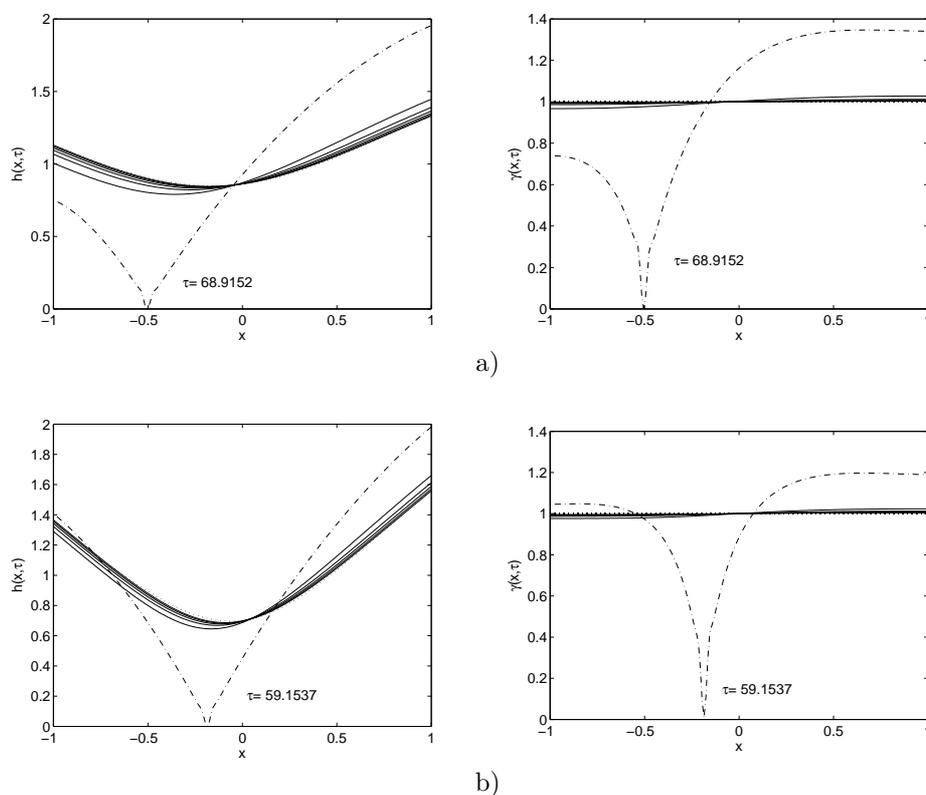


Fig. 3. Rupture of a free film at  $Re = 1$ ,  $We = 0.01$ ,  $\varepsilon = 0.01$ ,  $A = 3$  ( $B = 3$ ),  $Sc = 10$ ,  $M = Ma = 0.1$  after applying the initial disturbance  $h(x, 0) = h_s(x) + 0.1 \sin(\pi/2x)$  on its static shape  $h_s(x)$  and at: a)  $\alpha = 0.5$ ;  $\alpha = 0.8$ . (The final states are plotted as “dash-dotted” lines, the initially disturbed states – as “dotted” lines. The plotted curves are at time interval  $\Delta\tau = 10$ .)

## 5. Conclusions

The present paper is devoted to the influence of insoluble surfactants, spread along the interfaces of a free thin film laterally bounded by a frame, on the film dynamics and stability, when the van-der-Waals attractive disjoining pressure is taken into account.

An evolutionary system consisting of three coupled non-linear PDE for the film thickness, lateral velocity and insoluble surfactant concentration has been derived. In the general case of the problem parameters, its solution has been obtained numerically. The surfactant concentration (related to the solutal Marangoni number) augments the final time for both states since the film relaxation leads to two different final states: static film shape and film rupture. For the obtained static shapes, a linear stability analysis is implemented numerically by the method of the differential Gauss elimination. It is found that the film is more stable with the increase of the Marangoni number with respect to antisymmetrical disturbances at different combinations of the Reynolds number, the Weber number, the Hamaker constant and the wetting angle. These results are confirmed approximately by the results of the non-linear stability analysis, from which the evolution of the film thickness, lateral velocity and surfactant concentration are found. The importance of the wetting angle is confirmed, the film can be stable or unstable depending on the competition between the wetting with the lateral boundary (frame), the surface tension and the van-der-Waals attraction. The addition of surfactants in the film does not change the stability of the film, that is the film rests stable or unstable. The surfactants only affect its relaxation or rupture time.

## REFERENCES

- [1] ORON, A., S. H. DAVIS, S. G. BANKOFF. Long-scale Evolution of Thin Liquid Films. *Rev. Mod. Phys.*, **69** (1997), 931–980.
- [2] CRASTER, R. V., O. K. MATAR. Dynamics and Stability of Thin Liquid Films. *Rev. Mod. Phys.*, **81** (2009), 1131–1198.
- [3] WARNER, M. R. E., R. V. CRASTER, O. K. MATAR. Unstable van der Waals Driven Line Rupture in Marangoni Driven Thin Viscous Films. *Phys. Fluids*, **14** (2002), 1642–1654.
- [4] CHESTERS, A. K., I. B. BAZHLEKOV. Effect of Insoluble Surfactants on Drainage and Rupture of a Film between Drops Interacting under a Constant Force. *Journal of Colloid and Interface Science*, **230** (2000), 229–243.

- [5] DE WIT, A., D. GALLEZ, C. I. CHRISTOV. Nonlinear Evolution Equations for Thin Films with Insoluble Surfactants. *Phys. Fluids*, **6** (1994), No. 10, 3256–3266.
- [6] RUBINSTEIN, B. Y., A. M. LESHANSKY. Dynamics of Thin Liquid Films with Nonsoluble Surfactants: Weakly Nonlinear Analysis. *Langmuir*, **16** (2000), 2049–2051.
- [7] POPOVA, L., G. GROMYKO, S. TABAKOVA. Numerical Solution of a Nonlinear One-Dimensional System of Differential Equations Describing the Motion of a Free Thin Film. *Differential Equations*, **39** (2003), No. 7, 1037–1043.
- [8] TABAKOVA, S., K. DANOV. Effect of Disjoining Pressure on Dynamics and Relaxation of Liquid Films with Mobile Interfaces. *Journal Colloid and Interface Science*, **336** (2009), 273–284.
- [9] TABAKOVA, S., S. RADEV. On the Stability of a Free Viscous Film, *AIP Conference Proceedings*, **1067** (2008), 166–173.
- [10] TABAKOVA, S., S. RADEV. Linear Stability of a Free Viscous Film under the van-der-Waals Force Action. *Journal of Theoretical and Applied Mechanics, BAS*, **40** (2010), No. 1, 23–32.
- [11] TABAKOVA, S. Dynamics and Stability of Free Thin Films, *AIP Conference Proceedings* **1301** (2010), 531–542.
- [12] WARNER, M. R. E., R. V. CRASTER, O. K. MATAR. Fingering Phenomena Associated with Insoluble Surfactant Spreading on Thin Liquid Films. *J. Fluid Mech.*, **510** (2004), 169–200.
- [13] ZAPRYANOV, Z. D., S. S. TABAKOVA. Dynamics of Bubbles, Drops and Rigid Particles. Dordrecht, Kluwer Acad. Publ., 1998.
- [14] ERNEUX, T., S. H. DAVIS. Nonlinear Rupture of Free Films. *Phys. Fluids A* **5** (1993), No. 5, 1117–1122.
- [15] GOLDSHTIK, M.A., V. N. SHTERN. Hydrodynamic Stability and Turbulence, Novosibirsk, Nauka, 1977 (in Russian).