



UNIVERSITY OF GENOA
ADVANCED FLUID DYNAMICS

Flows with Surfactants

Final Report

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1 Introduction

The word fluid is used to describe common liquids and gases that continually deforms under an applied shear stress. If we consider the presence of more fluids, their molecules can be mixed or separated from surfaces that refer to fluid interfaces.

In order to account for the presence of interfaces, it is important to understand which physical and chemical phenomena have to be introduced in the continuum description of fluids. These phenomena occurring on the separation surface between two different phases, result fundamental in physics, chemistry, biology and technology.

Microscopically, liquids are made up of molecules, including forces (cohesion forces), mainly of electrical origin. A molecule inside the liquid is attracted to all the other molecules surrounding it, but a molecule close to the free surface suffers a direct force towards the inside of the liquid (figure 1). Moreover the cohesive force between the molecules provides a tangential force to the surface. Thus, the surface of a liquid acts as an elastic membrane that wraps and compresses the liquid below. Surface tension expresses the force with which surface molecules attract each other.

Therefore it is interesting to understand how surface tension and other interface properties can be modified and controlled by changing the chemical properties of the fluids, adding for example molecules different from those of the liquid.

It is well known that *surfactants* are often added to liquids in order to decrease the surface tension and achieve a desired effect. In fact, for these chemicals, the equilibrium configuration is when nearly all the molecules in the interfacial region are actually at the interface itself, resulting in a dramatic change of the value of the surface tension compared to that of pure liquid. These agents are formed by molecules that have a hydrophilic head and a hydrophobic tail which leads a portion of them on the surface of the fluid forming the monomolecular layer (figure 1).

The purpose of this study is to understand how microscale fluid flow can be efficiently induced and controlled by changing the properties of interfaces.

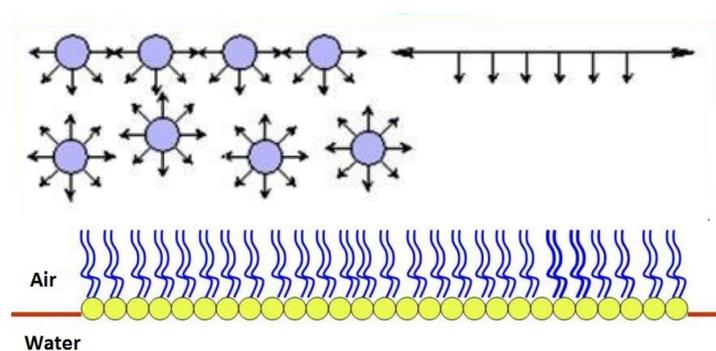


Figure 1: Diagram of the attraction forces between the molecules of a liquid (up); At the interface the surfactant molecules form a monomolecular layer with the polar heads oriented to the aqueous solution (bottom).

2 Formulation of the problem

We can consider the chemical behaviour of the surfactant molecules, which tend to accumulate at the interface forming a monolayer, as a film that is not expected to remain uniform under small forces.

In fact, we expect that a variation in the surfactant concentration will generate a shear stress and thus a liquid flow, which could deform the interface.

2.1 Two-dimensional lubrication-type model

The configuration that provides a good interface reproduction is a long and thin domain, whose profile will be changing in time. Ajaev (2012) developed a two-dimensional lubrication-type model of evolution of a layer of initially uniform thickness d in which the flow is driven by a nonuniform surfactant concentration in the limit of small capillary numbers (figure 2). The problem of interest is different from the classical lubrication theory of Reynolds since only one boundary is a solid surface, while the other one is a deforming fluid interface.

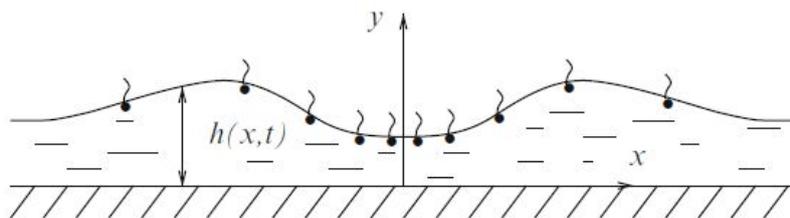


Figure 2: A snapshot of a liquid-air interface deforming under the effect of surfactants.

This model considers a deforming layer under the action of small stresses, where the fluid flow is the result of the dependence of the surface tension. The surface tension under isothermal conditions can be expressed as a function of surfactant interfacial concentration (Γ^*) if this quantity is small, through the linear equation:

$$\sigma = \sigma_0 - \gamma_\Gamma \Gamma^* \quad (1)$$

where σ_0 is the value of the surface tension of pure water and γ_Γ is a constant which depends on the properties of the surfactant.

As the flow of liquid directed from the regions of higher concentration to the regions of lower concentration develops ($\gamma_\Gamma > 0$), the interface will deform and the film will gradually be depleted near $x = 0$, resulting in interface shapes such as the one illustrated in figure 2.

The Navier-Stokes and continuity equations for the two-dimensional flow in the film are

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right), \quad (2)$$

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \nu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) - g, \quad (3)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0. \quad (4)$$

In order to simplify the governing equations some assumptions were introduced:

- with L_x the characteristic length scale of the flow in x -direction, the ratio of the scales $\varepsilon = d/L_x$ is small and therefore the second derivatives with respect to x in (2) and in (3) can be neglected.
- With U the characteristic value of u the horizontal velocity component, then v is of the order of εU so that the continuity equation and the standard boundary condition ($u = v = 0$ in $y = 0$) guarantee a constant film thickness.
- A small Reynolds number is considered in order to neglect the non-linear terms in (2) and the term $\mu \frac{\partial^2 v}{\partial y^2}$ in (3).
- The gravity is considered negligible.

The problem formulated involves dimensional parameters, thus it is convenient that the actual solution of the problem is out to depend only on fewer dimensionless combinations of the dimensional quantities as described below

$$(y^*, h^*) = \frac{(y, h)}{d}, \quad x^* = \frac{x}{L_x}, \quad t^* = \frac{t}{L_x/U}, \quad u^* = \frac{u}{U}, \quad v^* = \frac{v}{\varepsilon U}, \quad p^* = \frac{p - p_0}{P}, \quad \Gamma = \frac{\Gamma^*}{\Gamma_0}; \quad (5)$$

where the choice of $P = \sigma_0 d/L_x^2$ reflects the fact that pressure gradients in the film appear because of the deformation of the interface and are therefore directly related to curvature (see section 2.1.1), and Γ_0 is the maximum initial surfactant concentration.

The governing equations (2)-(4) take the following nondimensional form where all variables will be assumed nondimensional unless noted otherwise:

$$\frac{\partial p}{\partial x} = \varepsilon^{-3} Ca \frac{\partial^2 u}{\partial y^2}, \quad (6)$$

$$\frac{\partial p}{\partial y} = 0, \quad (7)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0. \quad (8)$$

2.1.1 Scales for the Cartesian coordinates

The characteristic velocity U is used in the definition of the capillary number,

$$Ca = \frac{\mu U}{\sigma_0}, \quad (9)$$

which measures the importance of viscous effects relative to surface tension and is typically small, so that an asymptotic approximation can be developed in the limit $Ca \rightarrow 0$.

However the capillary number in (6) multiplies a large parameter ε^{-3} . This implies that it is necessary to consider both surface tension and viscous effects. To achieve this goal it is necessary that $\varepsilon^{-3}Ca = 1$ and thus $\varepsilon = \frac{1}{Ca^{-1/3}}$.

Recall the assumption $\varepsilon = \frac{d}{L_x}$ we can define $L_x = dCa^{-1/3}$ as the scale for the Cartesian coordinate x , and banally d as the scale of the y coordinate.

For the same reason t is the time variable scaled by $\frac{Ca^{-1/3}d}{U}$. Accordingly the (6) takes the simple form

$$\frac{\partial p}{\partial x} = \frac{\partial^2 u}{\partial y^2}. \quad (10)$$

As regards the boundary conditions at the air-liquid interface, defined by a time-dependent thickness of the film $y = h(x, t)$, in the limit $Ca \rightarrow 0$ are:

$$\frac{\partial h}{\partial t} + u \frac{\partial h}{\partial x} - v = 0 \quad (11)$$

$$p = -\frac{\partial^2 h}{\partial x^2} \quad (12)$$

$$\mu \frac{\partial u}{\partial y} = \frac{\partial \sigma}{\partial x}, \quad (13)$$

where (11) is the kinematic condition which relates the rate of change of the interface height and the components of the local flow velocity, while the other two conditions reflect the balances of normal and tangential components of the stress. In particular the tangential stress condition has to include a contribution due to the surfactant, thus substituting the nondimensional surfactant concentration Γ^* in the equation (1) we can estimate the derivative:

$$\frac{|d\sigma|}{|dx|} = -\frac{\gamma_\Gamma \Gamma_0 \Gamma_x}{L_x} = -\frac{\gamma_\Gamma \Gamma_0 Ca^{1/3}}{d} \Gamma_x. \quad (14)$$

Starting with the general dimensional version of the tangential stress balance ($\mathbf{t} \cdot \mathbf{T} \cdot \mathbf{n} = \frac{\partial \sigma}{\partial x}$) and using the scales described above, we can obtain the left-hand side of the equation (13) which takes the form:

$$\frac{\mu U}{d} u_y = -\frac{\gamma_\Gamma \Gamma_0 Ca^{1/3}}{d} \Gamma_x. \quad (15)$$

The two sides of this equation are equal when $\frac{\mu U}{d} = \frac{\gamma_\Gamma \Gamma_0 Ca^{1/3}}{d}$, from which we define the characteristic velocity through the capillary number:

$$U = \frac{(\gamma_\Gamma \Gamma_0)^{3/2}}{\mu \sigma_0^{1/2}}, \quad (16)$$

and (13) takes the form

$$u_y = -\Gamma_x, \quad (17)$$

which includes the contribution of the surfactants.

Hence, we can obtain the velocity profile

$$u = -\frac{1}{2}h_{xxx}(y^2 - 2yh) - \Gamma_x y \quad (18)$$

integrating twice the equation (10) since the pressure is not a function of y as suggested by (7), and using (17) and the no-slip condition to find the constants of integration.

Substituting this profile into the standard integral mass balance $h_t + (\int_0^h u dy)_x$, we obtain the following evolution equation for the film thickness h :

$$h_t + \left(\frac{h^3}{3}h_{xxx} - \frac{h^2}{2}\Gamma_x\right)_x = 0. \quad (19)$$

2.2 The surfactant concentration

The surfactant concentration Γ in equation (19) is unknown then a second equation has to be determined to solve the problem.

Consider the sketch in figure 3 which represents a part of the interface at time t (solid line) and at the later time $t + \Delta T$ (dashed line) that is the new interface shape under action of surfactant diffusion. An arbitrary point A of the solid curve is distant from B of a small quantity Δs and the points C and D on the dashed line are chosen that the straight line segments AC and BD are locally normal to the solid line.

Under these premises we can define the segments

$$|AC| = V_n^A \Delta t, \quad |BD| = V_n^B \Delta t, \quad (20)$$

where V_n^A and V_n^B are the interface normal velocities at the points A and B , respectively. For small value of Δs we can use $V_n^A \approx V_n^B = V_n$ and we can approximate AB and CD by circular arcs of the radii k^{-1} and $k^{-1} + V_n \Delta t$, respectively, where k is the curvature.

As shown in figure 3 both arcs are centered at a point O ; if we define $\Delta\phi$ the angle between $A\hat{O}B$, then $\Delta s = k^{-1}\Delta\phi$ and the points C and D will be distant of the quantity

$$\Delta s' = (k^{-1} + V_n \Delta t)\Delta\phi = \Delta s(1 + kV_n \Delta t). \quad (21)$$

The surfactant mass balance condition is

$$\Gamma_C \Delta s' - \Gamma_A \Delta s = (j_a - j_b)\Delta t, \quad (22)$$

where Γ_C and Γ_A are the concentrations, j_A and j_B are the surfactant fluxes at the respective points. If the effects of chemical reactions and diffusion of surfactant along the interface are negligible, the fluxes j_A and j_B are determined by the amount of surfactant carried by the flow, so they can be expressed in terms of the values of the velocity along the interface, \hat{u}_A and \hat{u}_B , as follows:

$$j_A = \Gamma_A \hat{u}_A, \quad j_B = \Gamma_B \hat{u}_B. \quad (23)$$

Substituting in the surfactant mass balance condition the equations (21) and (23), taking the limit of $\Delta t \rightarrow 0$, $\Delta s \rightarrow 0$ and assuming that the arc length value corresponding to the point A is equal to s we obtain:

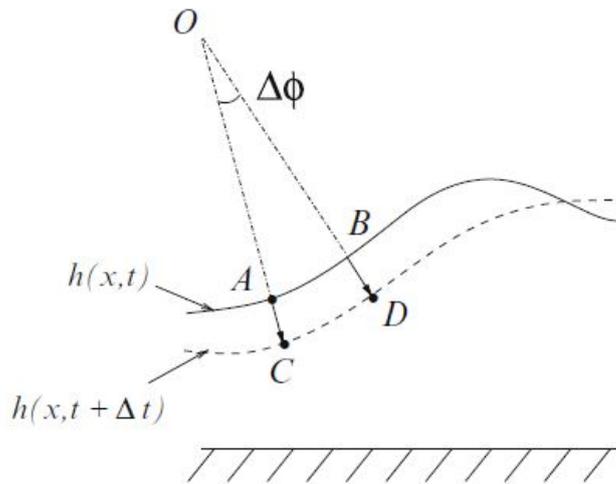


Figure 3: A snapshot of a liquid-air interface for the derivation of surfactant transport equation. The solid line represents the interface shape at a time t and the dashed line the new interface shape at a time $t + \Delta t$.

$$[\Gamma_t]_n + \Gamma(s, t)k(s, t)V_n(s, t) + (\Gamma(s, t)\hat{u}(s, t))_s = 0 \quad (24)$$

where $[\Gamma_t]_n$ defined as $[\Gamma_t]_n = \lim_{\Delta t \rightarrow 0} \frac{\Gamma_C - \Gamma_A}{\Delta t}$ (Wong et al. (1995)) is the time derivative of Γ in the direction normal to the interface at the point A .

In order to simplify the equation (24) some assumptions were introduced:

- consider an arbitrary point on the interface can be defined by its horizontal coordinate x or by the arc length variable s defined as the distance from the point corresponding to $x = 0$ and scaled by $d/Ca^{1/3}$ (see 2.1.1), thus we can write:

$$\frac{ds}{dx} = \sqrt{1 + Ca^{2/3}h_x^2}. \quad (25)$$

In the limit of $Ca \rightarrow 0$ the variable s can be replaced by x .

- The term proportional to the normal velocity V_n is asymptotically negligible.
- $[\Gamma_t]_n = [\Gamma(x, t)]_t$.

Therefore, we obtain:

$$\Gamma_t + (\Gamma\hat{u})_x = 0, \quad (26)$$

and using the velocity equation (18) and the definition $y = h(x, t)$, the equation for surfactant concentration $\Gamma(x, t)$ takes the form

$$\Gamma_t + [(\frac{1}{2}h^2h_{xxx} - h\Gamma_x)\Gamma]_x = 0. \quad (27)$$

In order to complete the equation, a term that represents the diffusion fluxes is added chosen to be proportional to the local derivative of the concentration, to the surfactant mass balance:

$$\Gamma_t - Pe_s^{-1}\Gamma_{xx} + \left[\left(\frac{1}{2}h^2h_{xxx} - h\Gamma_x\right)\Gamma\right]_x = 0. \quad (28)$$

This term is characterized by the surface Peclet number

$$Pe = \frac{Ud}{D_sCa^{1/3}}, \quad (29)$$

where D_s is the surfactant diffusion coefficient. The Peclet number for mass transport is comparable to the Reynolds number for momentum transport and in engineering applications it is often very large.

3 Numerical approach

By solving simultaneously (19) and (28) it is possible to determine the evolution of the thickness in time and space provided that proper boundary and initial conditions and the distribution of the surfactant.

For the numerical technique we consider a film thickness that is initially uniform and the surfactant distribution is chosen to be Gaussian to simulate a situation in which the surfactant is localized near $x = 0$:

$$h(x, 0) = 1, \quad \Gamma(x, 0) = \exp(-\alpha x^2). \quad (30)$$

Since the flow is generated due to the nonuniform surfactant concentration at the interface, the characteristic length scale of the flow in the horizontal direction $L_x = dCa^{-1/3}$ (see section 2.1) has to be of the same order of the characteristic length imposed by equation (30), namely $\alpha^{-1/2}$.

Because the derivative of the profile given by (30) is small for $x \gg \alpha^{-1/2}$ it is natural to expect that the deformation to be small as well for a sufficiently large x . The extent of the film in the snapshot shown in figure (2) is assumed to be infinite, so the computational domain size $[0, L]$ has to be sufficiently large so that the variations of $h(x, t)$ and $\Gamma(x, t)$ are negligible for $|x| > 1$.

Thus the boundary conditions in $x = L$ are:

$$h(L, t) = 1, \quad h_x(L, t) = 0, \quad \Gamma(L, t) = \Gamma_x(L, t) = 0. \quad (31)$$

Based on (30), we expect the solution to be an even function of x , so we consider only positive values of x and impose symmetry conditions of the computational domain:

$$h_x(0, t) = h_{xxx}(0, t) = \Gamma_x(0, t) = \Gamma_{xxx}(0, t) = 0. \quad (32)$$

4 Results

The numerical solution allows one to find the interface shape as a function of time.

The goal of this work is to obtain a numerical solution of the equation system given by (19) and (28) with the conditions (30),(31) and (32).

Ajaev (2012) propose a MATLAB code for this problem and show as result a snapshots of the interface at different moments in time (4). Using the same code with the parameters recommended by the authors of this study ($Pe = 1000, \alpha = 100$), one does not get exactly the same condition shown in the figure (4) but the result represented in figure (5).

It is clear that the interface thickness is drastically vanished in the region localized near $x = 0$, while in figure (4) we can note a simple thinning film. Since the results appear to be discordant, I decided to evaluate how the interface deforms at shorter time than those proposed by Ajaev (2012). An example is shown in figure (6).

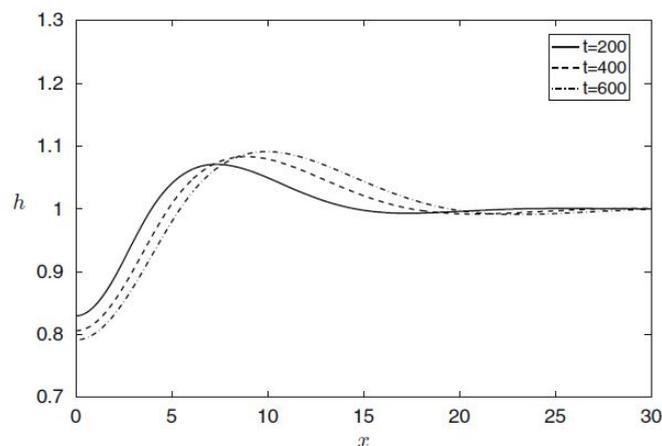


Figure 4: Interface shapes at different times found from the numerical solution shown by Ajaev (2012).

In this case we observe that the liquid film becomes thinner in the middle of the area with high concentration of surfactant and the flow pushes liquid away from there. In particular, a maximum deformation value of h is evident that increases in time, while this condition is not present at higher time value as shown in figure (5). Moreover the extent of the region of high-interface deformation is significantly wider than the length scale of the chosen initial concentration profile ($\alpha = 100 \rightarrow \alpha^{-1/2} = 0.1$).

In order to understand how the value of h in $x = 0$ may be different in my results from those of Ajaev (2012) I plot the initial value of the film thickness with respect to obtaining the result below shown in figure (7).

It is clear in figure (7) that the MATLAB code proposed by Ajaev (2012) can not provide the result shown in figure (4) because for a value of $t > 100$ the thickness h tends to zero.

Finally, by changing the Peclet number of even two orders of magnitude, the results remain qualitatively the same.

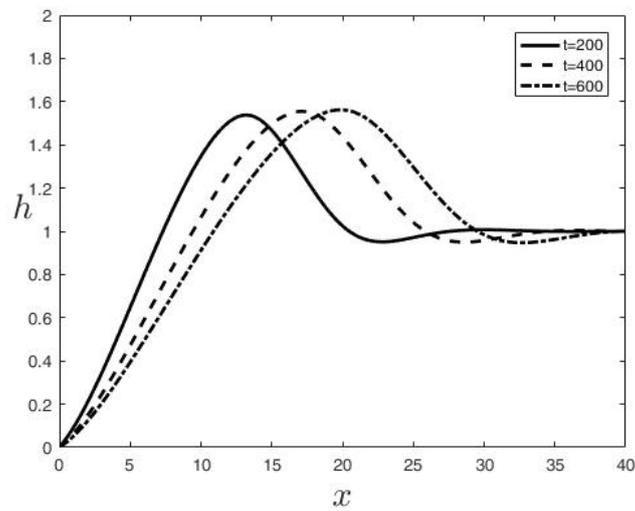


Figure 5: Interface shapes at different times found from the numerical solution proposed by Ajaev (2012) but different from those shown by the authors.

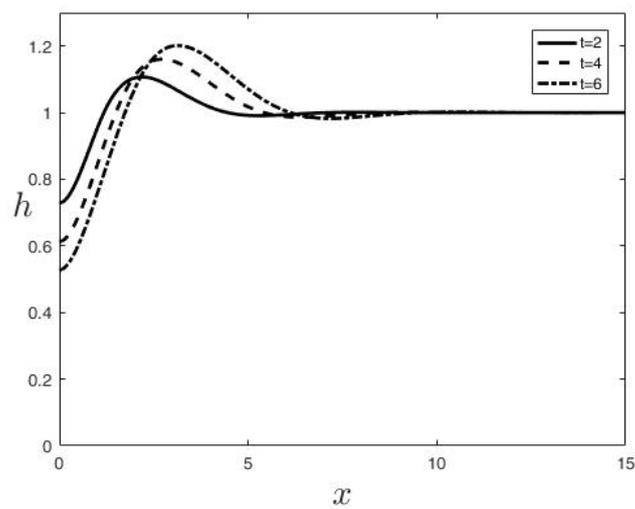


Figure 6: Interface shapes found in the range of time $0 \leq t \leq 10$.

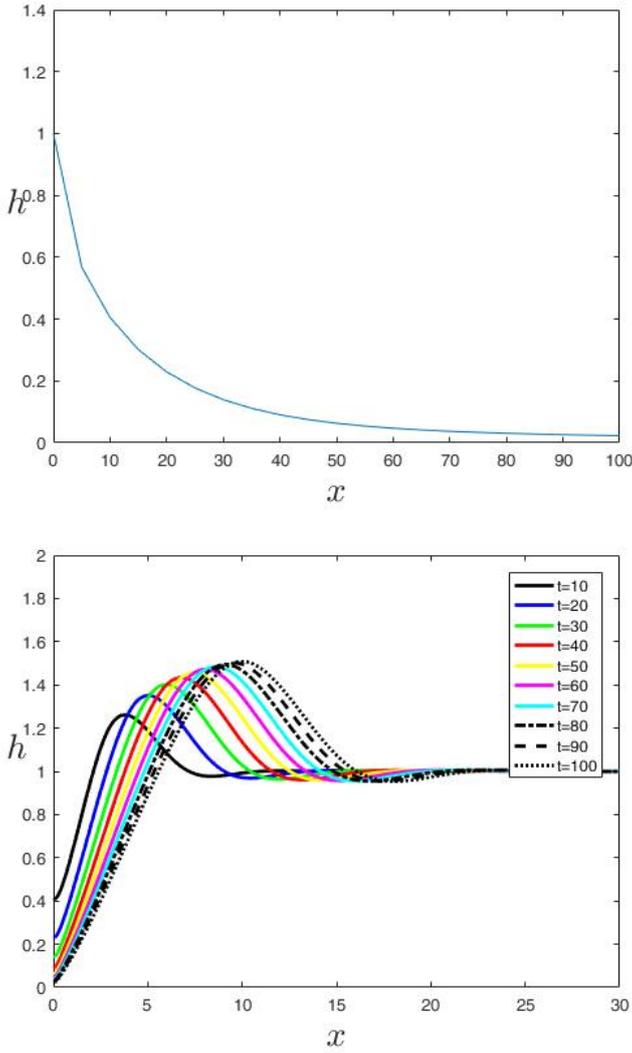


Figure 7: Evolution of the film thickness vs time in $x = 0$ (up); interface shapes found in the range of time $10 \leq t \leq 100$ (bottom).

5 Conclusions

(Ajaev, 2012) developed a two dimensional lubrication-type model in order to study the evolution of a layer under action of a nonuniform surfactant concentration. Through the adimensionalization of the Navier-Stokes and continuity equations with the appropriate boundary and initial conditions, we obtain the analytical system consisting of two equations (19) and (28): the first describes the evolution of the film thickness, the second one is the equation of the surfctant concentration.

This study includes a MATLAB code for the numerical finite difference solution of the analytic system proposed. The authors shown as result the interface shape at different times demonstrating that the region characterized by a higher concentration of surfactant (near $x = 0$ imposed by the initial condition (30)) is thinner due to the decrease of the surface tension.

Using the same code developed by the authors with the parameters that they are proposed, the result obtained is not equal. In fact the formation of the depression near $x = 0$ is obtained only for at times in the range of $0 \leq t \leq 10$ while the authors study the problem at very high value of time.

Moreover the extent of the region of the layer deformation due to the flow driven by the nonuniform surfactant concentration is wider than the length scale of the initial concentration. This result is obtained also by the authors but in their case the deformation results developed more quickly.

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