EFFECT OF VARIABLE SURFACE TENSION
IN LANDAU-LEVICH PROBLEM

GELU PAŞA

We study the effect of a variable surface tension in the Landau-Levich problem, concerning the thickness of the fluid layer adhering on a plate withdrawn from a pool filled with a viscous liquid, in the range of very small capillary numbers. A thickening effect was observed, when the surface tension on the air-fluid interface is variable, compared to the case of a constant surface tension studied by Landau and Levich (1942). In some previous papers a thickening factor of order $4^{2/3}$ was obtained. In this paper, we obtain a thickening factor of order $4^{2/3}(1 - N\Gamma)$ where N is the derivative of the variable surface tension in terms of the *reduced surfactant concentration* Γ, computed at the value of Γ on the liquid pool surface – see formula $(2)_2$ in Introduction.

AMS 2010 Subject Classification: 76D07, 76D08, 76D45, 76B45.

Key words: variable surface tension, thin film flows, Landau-Levich problem.

1. INTRODUCTION

We consider a plate which is pushed out from a pool filled with an incompressible fluid of viscosity μ and density ρ. A thin layer of fluid is adhering on the plate. The *air-fluid interface*, the velocity and pressure of the fluid, the surface tension and the surfactant concentration on the air-fluid interface are denoted by

$$h(x), u, p, \sigma, \Gamma_1.$$

The reduced surfactant concentration Γ is given below in formula $(2)_2$, related to the surfactant concentration on the pool surface and Γ_1.

The Ox axis is down, in the gravity direction. The Oy axis is horizontal, then $x = 0$ is denoting the pool surface. In this coordinate system, the plate is moving upward with the velocity $(-U)$.

An important parameter is the capillary number $Ca = \mu U/\sigma_0$ where $\sigma_0 = \sigma(\Gamma_0)$ is the surface tension on $x = 0$ and Γ_0 is the surfactant concentration on $x = 0$. The thickness of the thin fluid layer adhering far on the top of the plate is denoted by b.

A large literature exists, concerning the calculation of film thickness b. One of the first results was given in the seminal paper of Landau and Levich (1942), where a matching procedure with the static meniscus was used to obtain the value of b in the case of constant surface tension σ_0 on the fluid-air interface. The flow was divided in three regions – see Fig. 1: a region AB very close to the horizontal surface of the pool, the static meniscus BC (an intermediate region where the lubrication approximation will be used) and the constant thickness region CD far up on the plate.

This problem is quite similar (from a mathematical point of view) with the flow of a gas-bubble in a horizontal thin tube filled with a viscous fluid, studied by Bretherton (1961). In this last paper, a disagreement between experimental and theoretical results concerning the values of b was observed. For small Ca, the experimental values were larger, compared with the theoretical results. Bretherton supposed that this disagreement is due to the traces of variable surfactant concentration existing on the bubble surface. Later, this disagreement was observed also in the Landau-Levich problem.

Wilson (1982) studied the Landau-Levich problem and gave a rigorous justification of the matching procedure used by Landau and Levich in 1942.
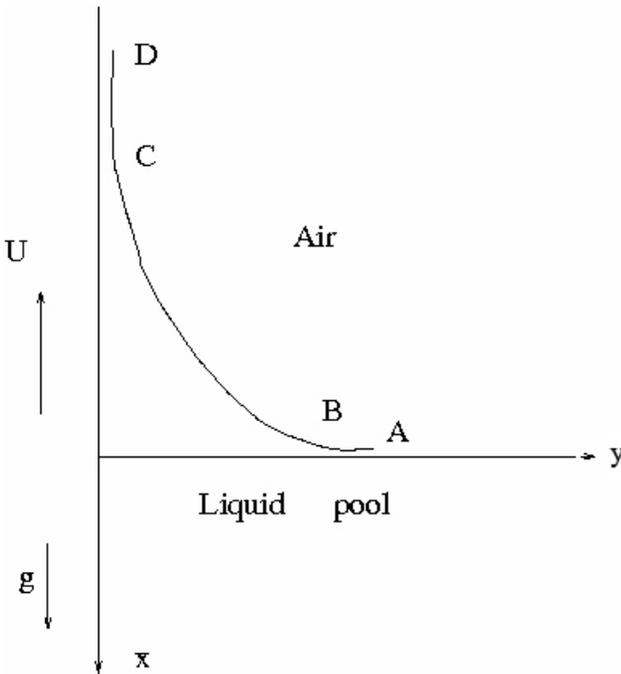

Fig. 1. Matching regions in Landau-Levich problem.

Some explanations of the above "thickening"phenomenon were given by Ratulowski and Chang (1989, 1990) and Park (1991), due to a variable surface tension on the air-fluid interface $h(x)$. Here a maximum thickening factor of order $4^{2/3}$ was obtained, compared with the case $\sigma = \sigma_0 = constant$, by using the scaling method introduced by Homsy and Park (1984).

Daripa and Pasa (2009, 2010) proved the thickening effect of surfactant, by using asymptotic methods and a direct integration of the flow equations, but they did not obtained the effective thickening factor.

In this paper, we give an estimate of b in terms of the problem data, when the surface tension is variable, function of the surfactant concentration on the air-fluid interface. When $(\Gamma_0 - \Gamma_1)$ is small, the surface tension σ is given by the following approximate formula

$$(1) \qquad \sigma = \sigma(\Gamma_1) = \sigma_0[1 + \frac{\Gamma_0}{\sigma_0}\frac{d\sigma}{d\Gamma_1}(\Gamma_0)\frac{\Gamma_1 - \Gamma_0}{\Gamma_0}] = \sigma_0(1 + N\Gamma),$$

$$(2) \qquad N = \frac{\Gamma_0}{\sigma_0}\frac{d\sigma}{d\Gamma_1}(\Gamma_0) = \frac{1}{\sigma_0}\frac{d\sigma}{d\Gamma}(\Gamma = 0) < 0, \quad \Gamma = [\Gamma_1(x) - \Gamma_0]/\Gamma_0,$$

where Γ *is the reduced surfactant concentration.* Γ_1 is the (variable) surfactant concentration in the points far from the liquid pool. We suppose that the surfactant is insoluble and the surfactant transport is due only to the surface diffusion process.

We obtain the thickening factor

$$(3) \qquad\qquad 4^{2/3}[1 - N\Gamma(C)],$$

given in the formula (49).

The new element, compared with Ratulowski and Chang (1990) and Park (1991) is the factor $[1 - N\Gamma(C)]$. We do not use the scaling procedure, but the direct integration of the flow equations and the flux method, described in Section 2.

Our main result is to compare the thickness of the adhering film far-up on the plate in the two cases – with constant and variable surface tension on the air-liquid interface. For this we do not need the exact values of the film thickness in the two cases.

The paper is laid out as follows. In Section 2 we give the value of b for a constant surface tension. The effect of a variable surface tension is described in Section 3, where we obtain the new thickening factor, starting with the full equations system which governs the flow, including also the diffusion equation for the surfactant. We conclude in Section 4.

2. **CONSTANT SURFACE TENSION**

Recall formula (2). In this section, we consider $N = 0$, $\quad \sigma = \sigma_0$.

a) A first empiric result can be obtained by equating the Gravity and Viscous forces in the thin fluid-layer adhering on the plate:

$$b\rho g \approx \mu u_y, \quad u_y \approx U/b \Rightarrow b^2 \approx O(\mu U/\rho g).$$

Therefore by using the capillary number $Ca = \mu U/\sigma_0$ we get the formula

(4) $$b \approx Ca^{1/2}d, \quad d^2 = \sigma_0/\rho g.$$

b) A second empiric result can be obtained by using lubrication equations (5) in the region BC and the Laplace's law (6) (the air pressure is considered zero)

(5) $$\mu u_{yy} = p_x - \rho g; \quad 0 = p_y;$$

(6) $$p = -\sigma_0 h_{xx}$$

We introduce the following dimensionless quantities:

(7) $$x^*, y^*, h^* = \frac{x}{d}, \frac{y}{d}, \frac{h}{d}, \quad u^* = \frac{u}{U}; \quad p^* = \frac{pd}{\sigma_0}, \quad \Gamma^* = \Gamma,$$

where $d^2 = \sigma_0/(\rho g)$ and the flow equations (5)–(6) become:

(8) $$Ca\, u^*_{y^*y^*} = p^*_{x^*} - 1, \quad p^* = -h^*_{x^*x^*}.$$

The thickness in the region BC is denoted by ϵ and the length of this region is denoted by l. From the first equation (8) we have

$$Ca \cdot O(u^*) \approx [O(p^*_{x^*}) - 1]\epsilon^2, \quad l[Ca \cdot O(u^*) + \epsilon^2] \approx \epsilon^2 O(p^*).$$

The second equation (8) is giving

$$l^2 \cdot O(p^*) \approx \epsilon.$$

Consider $O(p^*)$, $O(u^*) \approx 1$, then from the above two relations we get

(9) $$l(Ca + \epsilon^2) \approx \epsilon^2, \quad l^2 \approx \epsilon.$$

We use the hypothesis

(10) $$l\epsilon^2 << 1,$$

then from relations (9), (10) we obtain

(11) $$lCa \approx \epsilon^2, \quad l^2 Ca^2 \approx \epsilon^4, \quad Ca^2 \approx \epsilon^3 \Rightarrow \epsilon \approx Ca^{2/3}.$$

Near point C we use the approximation $\epsilon \approx b$ and obtain $b \approx Ca^{2/3}$.

The above *law* $b \approx Ca^{2/3}$ was first obtained by Landau and Levich (1942), who supposed $Ca << 1$. We also consider this assumption, then our condition (10) which is giving $Ca^{5/3} << 1$, is verified if $Ca << 1$. In experiments capillary numbers $Ca \approx 10^{-6}$ were considered, then we have $Ca^{2/3} \approx 10^{-4}$ and $Ca^{1/3} \approx 10^{-2}$.

c) We use now the lubrication approximation in BC and the corresponding boundary conditions for the velocity, in dimensional quantities:

$$(12) \qquad \mu u_{yy} = p_x - \rho g, \quad 0 = p_y, \quad for \quad 0 < y < h(x);$$

$$u_y = 0, \, p = -\sigma h_{xx}, \quad on \quad y = h(x);$$
$$u = -U \quad on \quad y = 0.$$

We use the dimensionless quantities (7) and from the last three above equations it follows

$$(13) \qquad Ca u^*_{y^*y^*} = p^*_{x^*} - 1; \quad 0 = p^*_{y^*};$$

$$u^*_{y^*} = 0, \, p^* = -h^*_{x^*x^*} \quad on \quad y^* = h^*(x^*); \quad u^* = -1 \quad on \quad y^* = 0.$$

The corresponding velocity and the surface velocity, denoted by u^* and u^{*s}, are given by

$$(14) \qquad u^* = \frac{p^*_{x^*} - 1}{Ca}(y^{*2}/2 - y^*h^*) - 1, \quad u^{*s} = \frac{p^*_{x^*} - 1}{2Ca}(-h^{*2}) - 1 < 0.$$

Far up on the plate we have $p^*_{x^*} = 0, h^* \approx b/d$, therefore from the last relation we obtain the estimate

$$(15) \qquad h^{*2} \leq 2Ca \Rightarrow b \leq Ca^{1/2}d\sqrt{2},$$

which is in agreement with the above value (4).

d) We use now the incompressibility condition, by equating the flux of liquid (flowing in the layer between the plate and the free surface) at a point $x \in BC$, denoted by $F(x)$, with the very small flux far up on the plate, denoted by $F(-\infty)$. We omit the * in this subsection d) where we use dimensionless quantities. From (14) we have

$$F(x) = \int_0^{h(x)} u\,dy = \frac{p_x - 1}{3Ca}(-h^3) - h, \quad F(-\infty) = \frac{b^3}{3Ca} - b,$$

therefore we get the equation of the free surface

$$(16) \qquad F(x) = F(-\infty) \Rightarrow \frac{h^3}{3Ca}(h_{xxx} + 1) = (h - b) + \frac{b^3}{3Ca}.$$

We introduce the function $\delta(x)$ as follows:

$$\delta(x) = h(x)/b - 1 > 0, \quad \delta << 1, \quad \delta(-\infty) = 0$$

then we have $h_{xxx} = b\delta_{xxx}$ and the equation (16) is giving

$$\frac{b^3(\delta+1)^3}{3Ca}(b\delta_{xxx}+1) = b\delta + \frac{b^3}{3Ca}.$$

We consider the approximations $(1+\delta)^3 \approx 1+3\delta$, $(1+3\delta)^{-1} \approx (1-3\delta)$, we divide with b in the above relation and get

$$\frac{b^2}{3Ca}(b\delta_{xxx}+1) = \delta(1-3\delta) + \frac{b^2}{3Ca}(1-3\delta).$$

We neglect δ^2 in the last above relation and obtain

$$\frac{b^3}{3Ca}\delta_{xxx} + \delta(\frac{b^2}{Ca}-1) = 0.$$

This last equation has oscillating solutions, but we are interested in the solutions which verify the decay condition at $x = -\infty$, then we need $1 - b^2/Ca > 0$. Then in fact (recall we used the dimensionless quantities) we obtain $b^* < Ca^{1/2}$ and for the dimensional thickness b we obtain the estimate

(17) $$b < Ca^{1/2}d,$$

which can be considered as an improvement of (4).

e) We use the flux method, we put $h = b + \epsilon$, $\epsilon << 1$, we neglect $b^2\epsilon$, $b\epsilon^3$, ϵ^3 and from (16) we obtain:

(18) $$h_{xxx} = 3Ca\frac{h-b}{h^3}.$$

The following transformation was introduced by Bretherton (1961)

(19) $$h = b\eta, \quad x = \frac{b}{(3Ca)^{1/3}}z$$

and we obtain the equation of the free surface:

(20) $$\eta_{zzz} = (\eta-1)/\eta^3.$$

The equation (20) was first given by Landau and Levich (1942) and obtained again by Bretherton (1961). In the region $\eta \approx 1$, near the point C in the region BC (see Figure 1), from (20) we get

(21) $$\eta_{zzz} = 0, \quad \eta_{zz} = K_1,$$

where K_1 is a constant. Returning back to h, x we obtain

(22) $$b = \frac{(3Ca)^{2/3}K_1}{h_{xx}(C)}.$$

The above relation will be used for comparison with the thickness obtained when a variable surface tension exists on the free surface $h(x)$.

3. VARIABLE SURFACE TENSION

In this section, we consider a variable surface tension $\sigma(x)$ on the free surface, given by formula (2). We introduce the *Marangoni* number $M = -N$, then (2) becomes

$$\sigma = \sigma_0(1 - M\Gamma), \quad M = -N. \tag{23}$$

In dimensional quantities, we have two *new* equations, compared with the case of the constant surface tension σ_0:

$$p = -\sigma(x)h_{xx}, \quad \mu u_y = \sigma_x. \tag{24}$$

We still use the notations

$$b, \quad h$$

for the thickness of the fluid-layer adhering far up on the plate and for the free surface air-fluid, in the variable surface tension case. Only in the last part of this section, we compare with the corresponding values in the constant surface tension case, denoted by

$$b_C, \quad h_C.$$

In dimensionless quantities [*], equations (24) are (recall $\Gamma^* = \Gamma$)

$$p^* = -(1 - M\Gamma^*)h^*_{Sx^*x^*}, \quad Ca\, u^*_{y^*} = -M\Gamma^*_{x^*}. \tag{25}$$

Park (1991) considered the following *scalings*, by using the empiric estimates of l, b, given in point b) of the previous section:

$$(26) \quad \overline{x} = \frac{x^*}{Ca^{1/3}}, \; \overline{y} = \frac{y^*}{Ca^{2/3}}, \; \overline{h} = \frac{h^*}{Ca^{2/3}}, \; \overline{p} = p^*, \; \overline{u} = u^*, \; \overline{\Gamma} = \Gamma^*/(Ca)^{2/3},$$

that means surfactant values are of order $(Ca)^{2/3}$. Equations (13), (25) and the above scalings (26) are giving:

$$Ca\overline{u}_{\overline{yy}}/Ca^{4/3} = \overline{p}_{\overline{x}}/Ca^{1/3} - 1 \Rightarrow$$

$$\overline{u}_{\overline{yy}} = \overline{p}_{\overline{x}} - Ca^{1/3}, \tag{27}$$

$$\overline{p} = -(1 - MCa^{2/3}\overline{\Gamma})Ca^{2/3}\overline{h}_{\overline{xx}}/Ca^{2/3} \Rightarrow \overline{p} = -\overline{h}_{\overline{xx}}, \tag{28}$$

$$Ca \cdot \overline{u}_{\overline{y}}/Ca^{2/3} = -MCa^{2/3}\overline{\Gamma}_{\overline{x}}/Ca^{1/3} \Rightarrow \overline{u}_{\overline{y}} = -M\overline{\Gamma}_{\overline{x}}. \tag{29}$$

However, the relation [24] of Park(1991) is $\overline{u}_{\overline{yy}} = \overline{p}_{\overline{x}}$, therefore the term $Ca^{1/3}$ was neglected, compared with (27). The range $Ca \approx 10^{-6}$ was used in experiments. In Section 2, points b), e), we obtained $b_C \approx Ca^{2/3}$. Therefore we can't neglect that the value $Ca^{1/3}$ and the correct scaled form of equation (13) is relation (27).

In equation (28) we neglected the term $MCa^{4/3}\overline{\Gamma}\overline{h_{xx}}$ due to our hypothesis $Ca << 1$; the variable surface tension is not appearing in the Laplace's law (28).

A maximum multiplication factor of order $4^{2/3}$ due to the variable surface tension effect was obtained by Ratulowski and Chang (1990) and by Park (1991).

In this section, we do not use the above scalings and the surface tension will appear in the Laplace's law. As a consequence, the new factor of the form $(1 - N\Gamma)$ will appear as the thickening effect of surfactant, proved below.

We use a direct integration method of the flow equations. We get an improvement of the maximum thickening factor $4^{2/3}$, given by Park (1991) and Ratulowski and Chang (1990) and obtain an explicit formula in terms of the surfactant concentration and Marangoni number M defined by relation (23).

We consider the full dimensional equations system, including also the diffusion equation for the (insoluble) surfactant on the air-liquid interface:

$$(30) \qquad \mu u_{yy} = p_x - \rho g, \quad 0 = p_y,$$

$$(31)$$
$$\mu\, u_y = \sigma_x, \quad p = -\sigma h_{xx} \text{ on the free surface } y = h(x); \quad u = U \text{ on } y = 0;$$

$$(32) \qquad (\Gamma_1)_t + \nabla_s \cdot (\Gamma_1 \mathbf{u}^s) = D_s \Delta_s \Gamma_1 + J \text{ on } y = h(x),$$

where J is the flux of surfactant from the pool to the surface, $D_s > 0$ is the surface diffusion coefficient and the surface gradient ∇_s, the surface velocity $\mathbf{u}^s$ and the surface laplacian Δ_s will be given below. As we supposed that the surfactant is insoluble, we have $J = 0$. The surfactant transport is due only to the surface diffusion process.

The first point is to prove that the surfactant concentration is an increasing function in terms of x.

The free surface is given by

$$F(x, y) = y - h(x) = 0$$

therefore the corresponding normalized normal and tangent are:

$$\mathbf{n} = \frac{(-h_x, 1)}{(1 + h_x^2)^{1/2}}, \quad \mathbf{t} = \frac{(1, h_x)}{(1 + h_x^2)^{1/2}}$$

The *Surface gradient* ∇_s is given by

$$(\nabla_s)_1 = \frac{\partial}{\partial x} - n_1 (\mathbf{n} \cdot \nabla) = \frac{\partial}{\partial x} - \frac{-h_x}{1 + h_x^2}\left(-h_x \frac{\partial}{\partial x} + 1\frac{\partial}{\partial y}\right),$$

We suppose $\sigma_y \approx 0$, then we obtain

$$(33) \qquad (\nabla_s)_1 = \frac{\partial}{\partial x} - \frac{-h_x}{1 + h_x^2}\left(-h_x \frac{\partial}{\partial x}\right) = \frac{1}{1 + h_x^2} \cdot \frac{\partial}{\partial x},$$

(34) $$(\nabla_s)_2 = \frac{\partial}{\partial y} - n_2(\mathbf{n} \cdot \nabla) = \frac{h_x}{1 + h_x^2} \cdot \frac{\partial}{\partial x}$$

Therefore, the vectorial form is

$$\nabla_s = \frac{1}{1 + h_x^2}(\mathbf{i} \cdot \frac{\partial}{\partial x} + \mathbf{j} \cdot h_x \frac{\partial}{\partial x}),$$

where $\mathbf{i}$, $\mathbf{j}$ are the unit vectors.

The *Surface velocity* is defined by $\mathbf{u^s} = \mathbf{u} - \mathbf{n}(\mathbf{un})$:

$$\mathbf{u^s}_1 = \frac{u + h_x v}{(1 + h_x^2)}; \quad \mathbf{u^s}_2 = \frac{h_x u + h_x^2 v}{(1 + h_x^2)}.$$

We use this particular form of $\mathbf{u^s}_2$ and introduce the notation

$$\mathbf{u^s}_1 = u^s$$

therefore

$$(u^s)_1 = u^s = \frac{u + h_x v}{1 + h_x^2};$$
$$(u^s)_2 = \frac{h_x(u + h_x v)}{1 + h_x^2} = h_x u^s.$$

The relations (33)–(34) are giving:

$$\nabla_s \cdot \Gamma_1 \mathbf{u^s} = \frac{1}{1 + h_x^2}[(\Gamma_1 u_1^s)_x + h_x(\Gamma_1 u_2^s)_x] =$$

$$\frac{1}{1 + h_x^2}[(\Gamma_1 u^s)_x + h_x(\Gamma_1 h_x u^s)_x].$$

We define the *Surface Laplacian* by the expressions: $(\nabla_s) \cdot (\nabla_s)$;

$$(\nabla_s)_1(\nabla_s)_1 = \frac{1}{1 + h_x^2} \frac{\partial}{\partial x}(\frac{1}{1 + h_x^2} \frac{\partial}{\partial x});$$

$$(\nabla_s)_2(\nabla_s)_2 = \frac{h_x}{1 + h_x^2} \frac{\partial}{\partial x}(\frac{h_x}{1 + h_x^2} \frac{\partial}{\partial x}),$$

therefore

(35) $$\Delta_s = (\frac{1}{1 + h_x^2})\frac{\partial^2}{\partial x^2} - (\frac{h_x h_{xx}}{(1 + h_x^2)^2})\frac{\partial}{\partial x}.$$

We use the above formulas and equation (32)

(36) $$[(1 + \Gamma)u^s]_x + h_x[h_x(1 + \Gamma)u^s]_x = D_s\{\Gamma_{xx} - \frac{h_x h_{xx}\Gamma_x}{1 + h_x^2}\},$$

We have to find the sign of Γ_x. For this, we use equation (36), the hypothesis

$$\Gamma u^s \approx 0, \quad h_x[h_x(1 + \Gamma)u^s]_x \approx 0, \quad h_x h_{xx} \approx 0$$

and get

$$(u^s)_x = D_s\Gamma_{xx}.$$

Far up on the plate we have $u^s = -U$ then

$$u^s = D_s\Gamma_x - U.$$

We have $u^s > -U$ in the lubrication region BC, then

(37) $\Gamma_x > 0.$

The above property is very natural: recall the axis Ox is pointed down, directed toward the pool filled by the viscous liquid, then Γ is increasing.

Daripa and Paşa (2009) proved the thickening effect, by using relation (37) and an asymptotic expansion, but they did not obtained the thickening ratio.

Recall that the thickness of the thin film of fluid adhering on the plate in the variable surface tension is denoted by b and the free surface is denoted by h.

In the following, we obtain the thickening factor due to the surfactant effect, but we use the dimensional variables. The solution of (30)–(31) is given by

(38) $u = (1/\mu)(p_x - \rho g)(y^2/2 - yh) + (y/\mu)\sigma_x - U,$

(39) $u^s = (1/\mu)(p_x - \rho g)(-h^2/2) + (h/\mu)\sigma_x - U,$

where u^s is the *surface* velocity. We use the flux method, then the equation (38) of the velocity is giving the free surface equation below

(40) $(h^3/3\mu)(-p_x + \rho g) + (h^2/2\mu)\sigma_x - Uh = \rho g b^3/(3\mu) - Ub$

We multiply relation (39) with $h/2$, we subtract from (40) and get

(41) $$\frac{h^3}{12\mu U}(-p_x + \rho g) = \frac{2(h-b) - h(u^s/U + 1)}{2} + \frac{\rho g b^3}{3\mu U}.$$

The following transformation is considered

(42) $$h = b\eta, \quad x = \frac{b}{(12Ca)^{1/3}}z$$

and from relations (1), $(31)_2$ and (41) we get

(43) $$b((1 + N\Gamma)\eta_{zz})_z + \frac{b^3\rho g}{\sigma_0 12Ca} = \frac{2b(\eta - 1) - b\eta(u^s/U + 1)}{2\eta^3} + \frac{\rho g b^3}{\sigma_0\eta^3 3Ca}.$$

In points b), e) of Section 2 we obtained $b_C \approx Ca^{2/3}$. We use this result and suppose that, also in the variable surface tension case, the adhering film

thickness b is of order $Ca^{2/3}$. This assumption will be verified in formula (49) given below.

The terms containing b^3 in equation (43) can be neglected, if $b \approx Ca^{2/3}$. Indeed, in this case, the ratio b^3/Ca is of order $Ca << 1$ - see the last lines of point b) in Section 1.

Near point C in the region BC, *where $\eta \approx 1$ and $u^s \to -U$*, the relation (43) becomes

$$(44) \qquad ([1 + N\Gamma(C)]\eta_{zz})_z \approx \frac{\eta - 1}{\eta^3} \approx 0,$$

obtained with the transformation (42). From (44) we get

$$(45) \qquad [1 + N\Gamma(C)]\eta_{zz} \approx K2 = constant.$$

Recall the case $\sigma = \sigma_0$, but where h_C, b_C stand for the air-fluid intreface and film-thickness. The relation (21), where we use the subscript $_C$, becomes

$$(46) \qquad (\eta_C)_{zz} \approx K1 = constant$$

and was obtained with the transformation $h_C = b_C\eta_C, \quad x = \{b_C/(3Ca)^{1/3}\}z$ from relation (18).

It is natural to consider that $M \to 0$ is giving $\eta \to \eta_C$; moreover in this case we get $h_{xx}(C) \approx h_{Cxx}(C)$, where C is the upward point of the meniscus BC - see Fig. 1. Therefore, the last two formulas are giving

$$(47) \qquad K1 = K2 \Rightarrow [1 + N\Gamma(C)]\eta_{zz} = (\eta_C)_{zz}.$$

Returning to the dimensional quantities, relations (45)–(47) and the corresponding transformations (19) and (42) are giving

$$(48) \qquad [1 + N\Gamma(C)]\frac{b}{(12Ca)^{2/3}} = \frac{b_C}{(3Ca)^{2/3}}.$$

Recall $N < 0$ - see the relations (1)-(2). We use the approximation

$$\frac{1}{1 + N\Gamma(C)} \approx [1 - N\Gamma(C)]$$

which holds iff $N\Gamma(C) \approx 0$. Then we not only suppose a very small value of the surfactant concentration Γ, but a very small value of the product $N\Gamma(C)$. In this case, from (48) it follows

$$(49) \qquad b \approx 4^{2/3}[1 - N\Gamma(C)]b_C,$$

then the new "thickening" factor $4^{2/3}[1 - N\Gamma(C)]$ appears, as an effect of the variable surface tension.

4. **CONCLUSIONS**

In this paper, we improved the value of the thickening factor due to the surfactant effects in the Landau-Levich problem, by using the flux method and the surface velocity expression, without the scaling procedure. The new element is the factor $[1 - N\Gamma(C)]$ appearing in formula (49), where N, Γ are given in relations (2) and C is the upward point of the meniscus BC. This factor appears because, without the scaling procedure used in Park(1991), the variable surface tension is still appearing in Laplace's law. On the other hand, without scaling procedure, we do not need only a very small surfactant concentration Γ, but also a very small product $M\Gamma$, as is mentioned at the end of Section 3.

In the papers of Ratulowski and Cang (1990) and Park (1991), the thickening factor $4^{2/3}$ is a *maximum* or a *limit thickening* effect. We have $N < 0$. Moreover, we proved $\Gamma_x > 0$ – see equation (37) – then Γ is increasing and we get $\Gamma(C) < \Gamma(B)$ (recall the Ox axis is downward) because our analysis holds only in the meniscus region. However, it is natural to consider that $\Gamma(B) < \Gamma(x = 0)$ and we have $\Gamma(0) = 0$ – recall the formula $(2)_2$. Therefore we can consider $[1 - N\Gamma(C)] < 1$ and our thickening factor is in agreement with the results obtained in both the above cited papers.

We mention here the paper of Krechetnikov and Homsy (2006) where a numeric method is used to integrate the full system of governing equations in the Landau-Levich problem, including the *dynamic meniscus*; here is pointed out that a pure hydrodynamic model of the surfactant effect is not enough for understanding this phenomenon. In our paper, we supposed a monotonic constitutive relation between the surface tension and surfactant concentration – see relations (1) and (2). It seems that some fluids for which this assumption is not verified do exist. In this case, the results of Krechetnikov and Homsy (2006) suggest that it is possible to have a thinning effect due to a variable surface tension on the fluid-air interface.

REFERENCES

[1] F.P. Bretherton, *The motion of long bubbles in tubes.* J. Fluid Mech. **10** (1961), 166–188.
[2] P. Daripa and G. Paşa, *Surfactant effect on the motion of long bubbles in horizontal capillary tubes.* J. Stat. Mech. **Article Number L02002** (2010), 10 pages, DOI: 10.1088/1742-5468/2010/02/L02002
[3] P. Daripa and G. Paşa, *The thickening effect of interfacial surfactant in the drag-out coating problem.* J. Stat. Mech. **Article Number L07002** (2009), 10 pages, DOI: 10.1088/1742-5468/2009/07/L07002
[4] G.M. Homsy and C.W. Park, *Two-phase displacement in Hele-Shaw cells: theory.* J. Fluid Mech. **139** (1984), 291–308.

[5] R. Krechetnikov and G.M. Homsy, *Surfactant effects in Landau-Levich problem.* J. Fluid Mech. **559** (2006), 429–450.

[6] D. Landau and V.G. Levich, *Dragging of a liquid by a moving plate.* Acta Physicochim. **17** (1942), 42–54.

[7] V.G. Levich, *Physicochemical hydrodynamics.* Prentice Hall, Englewood Cliffs, New Jersey, 1962.

[8] C.W. Park, *Effects of insoluble surfactant in dip coating.* J. Colloid Interface Sci. **146** (1991), 382–394.

[9] J. Ratulowski and H. Chang, *Transport of gas bubbles in capillaries.* Phys. Fluids A. **1** (1989), 1642–1655.

[10] J. Ratulowski and H. Chang, *Marangoni effects of trace impurities on the motion of long gas bubbles in capillaries.* J. Fluid Mech. **210**(1990), 303–328.

[11] S.D.R. Wilson, *The drag-out problem in film coating theory.* J. Engrg. Math. **16** (1982), 209–221.

Romanian Academy,
"Simion Stoilow" Institute of Mathematics,
Calea Grivitei 21, 017400 Bucharest,
Romania
Gelu.Pasa@imar.ro