STUDIA UNIV BABEŞ-BOLYAI, MATHEMATICA, XXXVIII, 2, 1993

EFFECTS OF SURFACTANTS ON AN UNDERFORMABLE DROP INITIALLY AT REST

I. STAN*, C.I. GHEORGHIU** and Z. KÁSA*

Dedicated to Professor P Szilágyi on his 60th anniversary

Received November 19, 1993
AMS subject classification 76D07, 76D45, 76T05

REZUMAT. - Efectul surfactanţilor asupra unei picături nedeformabile iniţial în repaus. Curgerea pe suprafaţa unei picături şi mişcarea de translaţie a acesteia, datorate unor gradienţi de tensiune superficială ce apar pe suprafaţa ei, sunt investigate teoretic pentru o picătură nedeformabilă, iniţial în repaus
Repartiţia surfactantului pe suprafaţa picăturii este dată prin legi particulare
Din punct de vedere matematic se rezolvă sistemul Stokes-Oseen printr-o metodă de separare a variabilelor şi se face un studiu asimptotic al forţei (componentelor normală şi tangenţială) ce acţionează asupra picăturii

Abstract. The surface flow and the translational motion of a drop caused by interfacial tension gradients are theoretically investigated in the case of an undeformable drop, initially at rest (or at zero gravity) The interfacial tension gradients are induced by injecting the drop with surfactant The spreading of the surfactant on the interface is described by a particular law A covering degree of the drop by the surfactant it is found out beginning with which the drop undergoes an upward translational motion

Introduction A viscous liquid drop immersed in an immiscible liquid undergoes complicated motions, when interfacial tension gradients arise on its surface The theoretical

---

* "Babeş-Bolyai" University, Faculty of Mathematics and Computer Science, 3400 Cluj-Napoca, Romania

** Institute of Mathematics, P O Box 68, 3400 Cluj-Napoca, Romania

model reported here considers that

- the drop is underformale and initially at rest,

- an interfacial tension gradient is established by injecting a droplet of surfactant in a well-determined point on its surface,

- a real surface flow - Marangoni fow - arises on the drop surface, with a distinct front, which advances continously,

- from all possible motions, induced by the surface tension gradients (translation, rotation, oscillations, waves on its surface, deformation, fission, etc) we shall take into account only the translational motion of the drop,

- the translational velocity varies with the covering degree of the drop by the surfactant;

- no surfactant transfer, inside or outside the drop is considered

1. Governing equations. It will be considered an undeformable drop Ω_1 (density ρ_1) immersed into an immiscible liquid Ω_2 (density ρ_2) If the two liquids, have the same density $\rho = \rho_1 = \rho_2$, the drop is called free and is motionless The two liquids inside and outside the drop (see Fig 1) are Newtonian, incompressible and viscous having the viscosities μ_1 and μ_2 On the physical and chemical aspects of the problem see our previous works [2,8]

On the assumption of undeformability we note the following In the experiments reported in our works [2, 8] the condition is fulfilled that surface tension at the interface between drop and ambient liquid is strong enough to keep it approximately spherical against any deforming effect of viscous forces This condition (see for example Batchelor [1]) reads $\frac{\sigma}{a} \gg \frac{\mu_1 U}{a}$, and expresses that stress due to surface tension should be large, compared with the normal

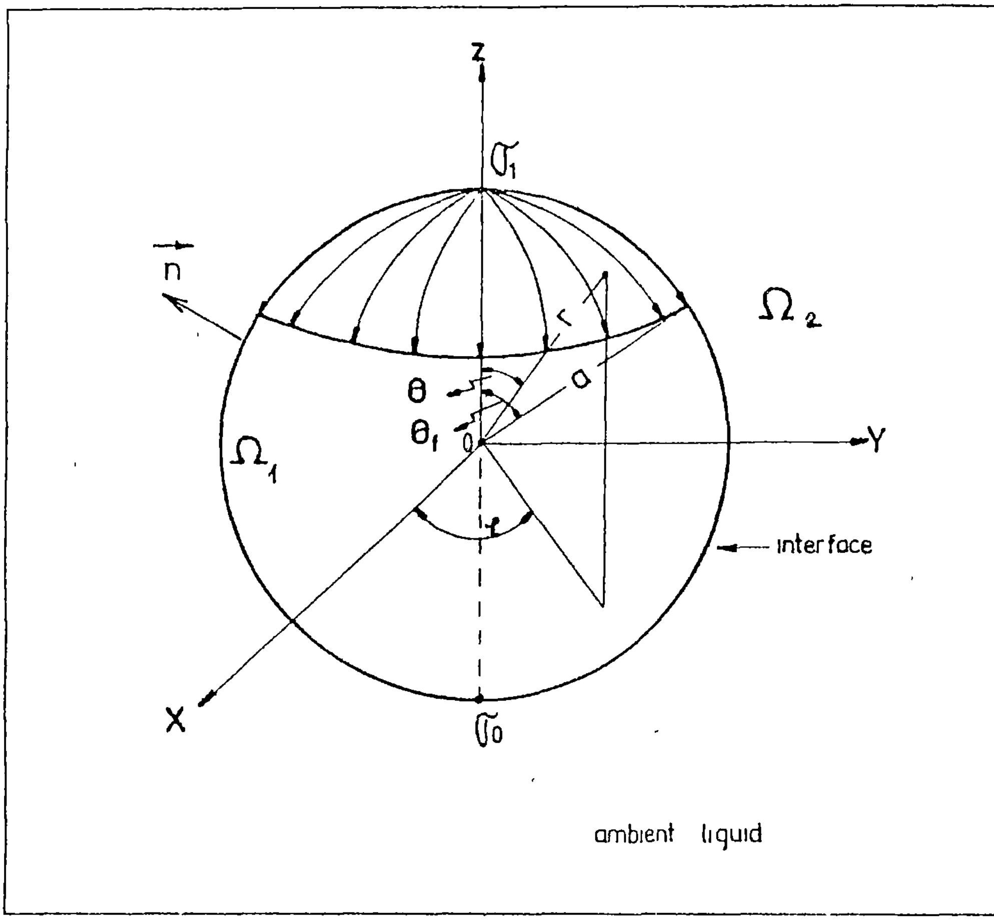

Fig 1

stress due to motion

We must notice that this condition don't contradict the assertion from [2], "the drop behaves like a rigid sphere for small interfacial tension gradient and large viscosity of the drop" First of all the smallness of the term $\frac{\mu_1 U}{a}$ is given essentially by μ_2 from $U(\mu_2 < \mu_1)$. Moreover, we know only by a qualitative point of view that for large interfacial tension gradients and reduced viscosity of the drop, it becomes strongly deformed and phenomena of oscillation or possibly fission may arise

Due to the viscous interface the more viscous fluid from the drop drives the less viscous ambient fluid In [4], the authors state this fact in a suggestive way "high viscosity liquids are the victims of the laziness of the high viscosity liquids because they are easy to pust around"

Because the drop is initially at rest, we don't possess a characteristic velocity U, so we can take that $U = \mu_2/a\rho$, which permits to consider the Reynolds number $\mathrm{Re}_2 = 1$ in the system of equations describing the flow of the ambient fluid (exterior flow) We shall call this velocity "viscous" velocity Taking that into account as a characteristic one for the flow inside the drop, we'll obtain

$$Re_1 = \frac{\mu_2}{\mu_1}$$

With the two values of viscosity taken from [8], the Reynolds number corresponding to the drop phase ranges between 1/80 and 1/40

This observations suggested us to couple Oseen's and Stokes' equations, the first one for the ambient liquid and the second for the drop liquid Taking Cartesian axes fixed relative to the drop and (r, θ, φ) spherical polar coordinates, with origin at the centre of the drop, we denote by Ω_1 the interior of the sphere of radius a centered at origin, and by Ω_2 the complementary space of $\bar{\Omega}_1$ in R^3 (see Fig 1) The dimensions of Ω_2 are extremely large compared with the radius a of Ω_1

Using subscripts 1 and 2 related to quantities associated with the drop phase and ambient fluid (liquid) respectively, we denote by $q_i = (q_{r,i}, q_{\theta,i}) = (u_i, v_i)$, $i = 1, 2$ the components of velocity, by $p_{r\theta}$, p_{rr} the tangential and normal components at stress tensor respectively, and by σ the interfacial tension, $\sigma = \sigma(\theta)$

The equations governing the flow considered quasisteady (even steady in Ω_1) and axisymmetric are

$$\mu_1 \nabla^2 q_1 = \nabla p_1 \qquad \text{in } \Omega_1 \tag{1}$$

$$U \frac{\partial q_2}{\partial z} = -\frac{1}{p} \nabla p_2 + \frac{\mu_2}{\rho} \nabla^2 q_2 \qquad \text{in } \Omega_2 \tag{2}$$

$$\nabla q_i = 0 \qquad \text{in } \Omega_2 \cup \Omega_2 \ (i = 1,2) \tag{3}$$

The following boundary conditions are considered

$$|q_2| \to 0, \qquad r \to \infty \tag{4}$$

$$|q_1| \text{ is bounded}, \qquad r = 0 \tag{5}$$

$$q_1 = q_2 \qquad r = a \tag{6}$$

$$(p_{r\theta})_1 = (p_{r\theta})_2 + \frac{1}{a}\frac{\partial \sigma}{\partial \theta} \qquad r = a \tag{7}$$

$$(p_{rr})_1 = (p_{rr})_2 + \frac{2\sigma}{a} \qquad r = a \tag{8}$$

Since the liquid is at rest at infinity we must take condition (4) and because inside the velocity must be bounded - condition (5) The condition (6) expresses the mutual impenetrability of the interface ($r = a$) as well as the continuity of tangential velocity to the surface of the drop This last condition follows from assumption that two immiscible liquids can not slip over each other because of viscosity

In addition to these kinematic conditions there are two boundary dynamic conditions (7) and (8) The first one represents the continuity of tangential stress on crossing the surface of drop at any point We added there the term $\frac{1}{a}\frac{\partial \sigma}{\partial \theta}$ to express the Marangoni spreading of the surfactant Indeed, if we consider that the surface tension of the drop is σ_0 and if in the intersection point of the positive Oz axis (Fig 1) with the drop, the interfacial tension is lowered to $\sigma_1 (\sigma_1 < \sigma_0)$ by injecting a small quantity of a surfactant, an interfacial tension difference $\sigma_0 - \sigma_1$ appears This interfacial tension diffference produces the spreading of the surfactant on the surface We shall note by θ_f the angle characterising the position of the front of the invaded region In this region $0<\theta\leq\theta_f$ and the surface tension varies at $\sigma_1\leq\sigma(\theta)\leq\sigma_0$

The second dynamic condition (8) underlines that at the interface between immiscible viscous fluids in motion, the difference between the normal stress at any point of interface on the convex side and that on the concave side is the quantity which equals the stress due to the surface $2\sigma/a$, the normal being drawn from the concave to the convex side (the outward normal, Fig 1)

As for the pressure we have the following conditions $p_2 - \pi_2 \to 0$, $r \to \infty$ and $p_1 - \pi_1$ is finite everywhere within the drop π_1 and π_2 are respectively hydrostatic pressures within the drop and in ambient fluid When the drop is suspended at rest in an immiscible liquid ($p_1 = \pi_1$, $p_2 = \pi_2$) they satisfy the well known Laplace's equation

$$\pi_1 - \pi_2 = \frac{2\sigma_0}{a}$$

After the start of flow p_1 and p_2 represent from the physical point of view perturbations from π_1 respectively π_2 and they are harmonic functions in Ω_1 respectively Ω_2

Following [7], for example, we introduce stream functions Ψ_1 and Ψ_2 in order to satisfy the equations of continuity (3) by

$$q_{r\,i} = u_i = -\frac{1}{r^2 \sin\theta}\frac{\partial\Psi_i}{\partial\theta}, \quad i = 1,2$$

$$q_{\theta\,i} = v_i = \frac{1}{r\sin\theta}\frac{\partial\Psi_i}{\partial r}, \quad i = 1,2$$

The system (1)-(8) will now be written in dimensionless form We introduce as a length scale the radius a, as a velocity scale the characteristic velocity $U = \mu_2/a\rho$ and as interfacial tension scale the value σ_0 With these we have the following dimensionless quantities

$$\bar{r} = \frac{r}{a}, \quad \bar{u}_i = \frac{u_i}{U}, \quad \bar{v}_i = \frac{v_i}{U}, \quad i = 1,2, \quad \bar{p} = \frac{p}{\rho U^2}, \quad \bar{\sigma} = \frac{\sigma}{\sigma_0}$$

Also we have for dimensionless stream functions

$$\bar{\Psi}_i = \frac{\Psi_i}{Ua^2}, \quad i = 1,2$$

In dimensionless form and using $\bar{\Psi}_i$ variables, the equations (1)-(3) become (where the superscript '-' is dropped)

$$E^4\Psi_1 = 0 \qquad \text{in } \Omega_1 \tag{9}$$

$$\left(E^2 - Re_2\frac{\partial}{\partial z}\right)E^2\Psi_2 = 0 \quad \text{in } \Omega_2 \tag{10}$$

where

$$E^2(\cdot) = \frac{\partial^2(\cdot)}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial(\cdot)}{\partial\theta}\right)$$

Now let us consider in turn boundary conditions (4)-(8) To ensure the asymptotic condition (4) we take

$$\Psi_2 = o(r^2) \quad r \to \infty \tag{11}$$

while (6) gives

$$\frac{\partial\Psi_1}{\partial\theta} = \frac{\partial\Psi_2}{\partial\theta}, \quad r = 1 \tag{12}$$

$$\frac{\partial\Psi_1}{\partial r} = \frac{\partial\Psi_2}{\partial r}, \quad r = 1 \tag{13}$$

The condition (11) shows the free streaming relative to the centre of mass of the drop

It should be noted that the assumption that drop remains spherical in shape as it translates means that

$$u_1 = u_2 = 0, \quad r = 1 \tag{14}$$

may be replaced by

$$\Psi_1 = \Psi_2 = 0, \quad r = 1 \tag{15}$$

The dynamic condition (7) may be rewritten succesively

$$\mu_1 r\frac{\partial}{\partial r}\left(\frac{v_1}{r}\right) + \frac{\mu_1}{r}\frac{\partial u_1}{\partial\theta} = \mu_2 r\frac{\partial}{\partial r}\left(\frac{v_2}{r}\right) + \frac{\mu_2}{r}\frac{\partial u_2}{\partial\theta} + \frac{1}{a}\frac{\partial\sigma}{\partial\theta} \qquad r = a$$

or, by virtute of (14), in dimensionless form, reduces to

$$\frac{1}{Re_1} r \frac{\partial}{\partial r}\left(\frac{1}{r^2}\frac{\partial \Psi_1}{\partial r}\right) = r \frac{\partial}{\partial r}\left(\frac{1}{r^2}\frac{\partial \Psi_2}{\partial r}\right) + Ca \cdot \frac{1-\sigma_1/\sigma_0}{1-\cos\theta_f}\sin^2\theta, \quad r = 1 \tag{16}$$

Here θ_f stands for the angle under which the front of surfactant convers the drop, $0 < \theta_f \le \pi$, $0 \le \theta \le \theta_f$, the function $\sigma(\theta)$ is defined by

$$\sigma(\theta) = \frac{\sigma_0 - \sigma_1}{1-\cos\theta_f}(1-\cos\theta) + \sigma_1, \quad \sigma(0) = \sigma_1, \quad \sigma(\theta_f) = \sigma_0,$$

so $\partial\sigma/\partial\theta = \sin\theta \cdot (\sigma_0 - \sigma_1)/(1-\cos\theta_f)$, and the dimensionless number Ca is a measure for the relative importance of capillary forces to viscous forces $Ca = \sigma_0 / U\mu_2$ To unify the notations we have to observe that for proposed "viscous" velocity $Ca = 1/Oh^2$, $Oh = \mu_2 / \sqrt{\sigma_0 a \rho}$, being the Ohnesorge number [3] and more $Ca = 1/We$, where We is the Weber number [9]

To be scrupulous, we mention that, as is well known, the surface tension σ usually depends on the scalar fields in the system (e g the electrical field, the temperature field) as well as on the concentration of foreign materials on the surface [6] In the present paper we focus on the variation due to the foreign material given by $\sigma(\theta)$, in fact σ depending not only on θ but on θ_f, σ_0 and σ_1

The normal stress condition (8) gives

$$p_1 - 2\mu_1 \frac{\partial u_1}{\partial r} = p_2 - 2\mu_2 \frac{\partial u_2}{\partial r} + \frac{2\sigma}{a}, \qquad r = a$$

which by (14) in dimensionless form, reads

$$p_1 + \frac{2}{Re_1 r^2 \sin\theta} \cdot \frac{\partial \Psi_1}{\partial r\,\partial\theta} = p_2 + \frac{2}{r^2 \sin\theta} \cdot \frac{\partial^2 \Psi_2}{\partial r\,\partial\theta} + 2\,Ca \cdot \sigma, \quad r = 1 \tag{17}$$

The conditions (5) and (11) show that suitable forms Ψ_1 and Ψ_2 are ([7], [10], [9])

$$\Psi_1 = \left(Ar^2 + Br^4\right)\sin^2\theta, \qquad r \le 1 \tag{18}$$

$$\Psi_2 = C(1+\cos\theta)\left\{1 - \exp\left[-\frac{r}{2}(1-\cos\theta)\right]\right\} + \frac{D}{r}\sin^2\theta \quad r \ge 1 \tag{19}$$

Thus there are four constants A, B, C, D to be determined, but five conditions (equations) to be satisfied (15), (13), (16), (17) It must be remembered that, the additional boundary conditions (15), imposed to keep the drop underformable, have replaced the boundary condition (12), and they are not one of the conditions (6)-(8) imposed purely by the kinematics and dynamics of the problem

2. Results and discussions We must observe the fact that in imposing the condition of the tangential stress on the surface of drop, we cannot satisfy the equation (16) exactly (the first term on the right hand side), but it can be satiesfied to $O(1)$ in Re_1 It means that the coupling between exterior flow (the solution of Ossen's equation) and interior flow (the solution of Stokes'equation) is realized only approximativelly A similar observation is valid for the boundary condition $\Psi_2 = 0$ and for the right hand side of (13).

So, on solving the equations given by (15), (13), (16) we obtain

$$A = -\frac{Ca \cdot h(\sigma,\theta_f)}{13/2 + 6/Re_1}, \quad B = -A, \quad C = -2A, \quad D = A \tag{20}$$

where for the sake of brevity, we have noted $\frac{1-\sigma_1/\sigma_0}{1-\cos\theta_f} = h(\sigma,\theta_f)$

For some values of parameters Re_1, θ_f, Ca etc we give in Fig 2 the streamlines for the flow within the drop (Ψ_1 = const ≤ 0) and in the ambient liquid (Ψ_2 = const ≥ 0)

We observe that because of the aproximativelly imposed boundary conditions (see above), the exterior streamlines present a detachment ($\Psi_2 = 0$ for $r > 1$) from the surface of drop As concern the interior streamlines is observad that they "start" only for a $\theta > 0$, which depends on the constants taken into account This fact is explained by the finite dimension of the surfactant droplet, injected in the north pole of the drop

The expressions of tangential velocities on the surface of drop as limits of interior and exterior flows respectively are

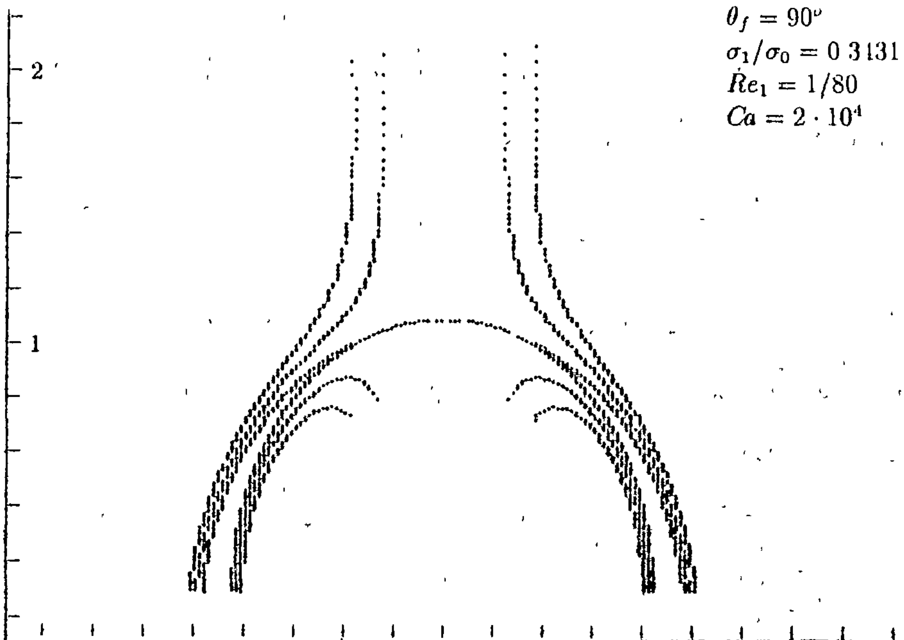

Fig 2

$$v_1 = -2A\sin\theta, \qquad 0 < \theta \le \theta_f \tag{21}$$

$$v_2 = -A\sin\theta\left\{\exp\left[\frac{1}{2}(\cos\theta - 1)\right] + 1\right\}, \quad 0 < \theta \le \theta_f \tag{22}$$

For some values of parameters in Fig 3 are plotted the velocities v_2 on the surface of the drop corresponding to θ_f on x axe The differences between the values of v_1 and v_2 for the same θ are due to the approximativelly imposed boundary conditions

For a given θ_f the velocity of front of surfactant become

$$v_f = -A\sin\theta_f\left\{\exp\left[\frac{1}{2}(\cos\theta_f - 1)\right] + 1\right\}$$

The pressure p_1 within the drop is

$$p_1 = 2\frac{A}{Re_1} r\cos\theta$$

so in the centre of mass of the drop acts only the hydrostatic pressure π_1

With the condition for normal stress (17), not used in the computation of spectrum of flow, and with p_1, we can determine the value of p_2 on the surface of the drop.

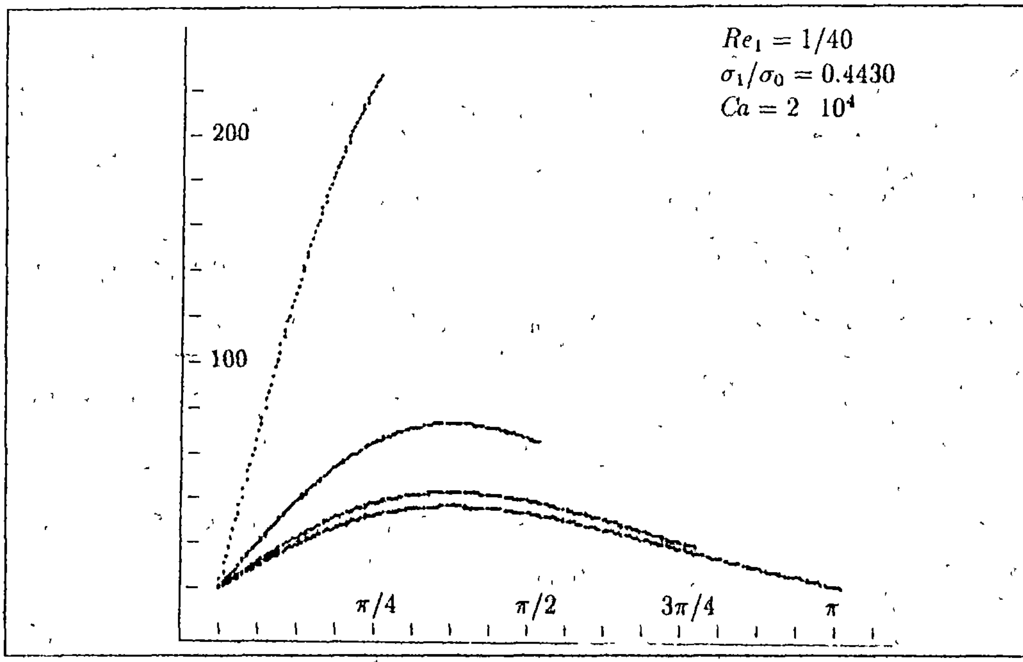

Fig 3

The force acting on the drop may be calculated from the general expression of force [6], which gives in this case

$$F = 2\pi a^2 \int_0^{\theta_f} \left[(p_{rr})_2 \cos\theta - (p_{r\theta})_2 \sin\theta \right] \sin\theta \cdot d\theta ,$$

where $(p_{rr})_2$ and $(p_{r\theta})_2$ are the normal and tangential components of the viscous stress tensor corresponding to the exterior flow We have respectively

$$(p_{rr})_2 = -p_2 + \frac{2}{Re_2} \cdot \frac{\partial u_2}{\partial r}$$

$$(p_{r\theta})_2 = \frac{1}{Re_1} \left(\frac{1}{r} \cdot \frac{\partial u_2}{\partial \theta} + \frac{\partial v_2}{\partial r} - \frac{v_2}{r} \right)$$

The normal component of force F per unit of area, has the following expression

$$F_n = 2\pi Ca\left[\frac{2}{3}(1-\lambda) - \frac{8Re_1}{13Re_1+12}\right]\left(1+\cos\theta_f+\cos^2\theta_f\right) + \\ +2\pi Ca\left(\lambda\cos\theta_f - 1\right)\left(1+\cos\theta_f\right), \quad \lambda = \frac{\sigma_1}{\sigma_0} \tag{23}$$

Using the asymptotic expansion of the function $1/(1+\varepsilon)$ when $\varepsilon \to 0_+$, for the coefficient A with $\varepsilon = Re_1$, we may have simply an asymptotic representation for F_n

Fischer, Hsiao and Wendland in [3] obtain an asymptotic representation for the force exerted on a rigid obstacle by the fluid This representation has the form $F = A_0 + A_1 Re + O(Re^2 \ln Re^{-1})$ as the Reynolds number $Re \to 0_+$ and is essentially different to ours by the factor $\ln Re^{-1}$

From (23) it is observed that the normal (and tangential) component of force acting on the drop, depends direct proportionally on Ca

As a final observation, we have to underline that the representation (23) hides the dependence of F_n on $Re_2 = 1$

The assumption that the drop is undeformable seem to be too restrictive.

Re / λ	1/20	1/40	1/60	1/80
1/20	165°	169°	171°	173°
1/10	167°	171°	173°	173°
35/102	169°	173°	174°	175°
3/5	173°	175°	176°	177°

Table 1

In fact there are some other effects (see Fig 6 from [2]), so we consider that the force corresponding to $F_n < 0$ is consumed for other type of movements except translation The propulsive (lifting) force, $F_n > 0$, responsible for the upward movement of the drop appears only when the covering of the drop with surfactant is greater than $\pi/2$ However this aspect is only in a qualitative agreement with our previous experimental data [8] From Table 1 results that the smaller the ratio λ is the smaller θ_f for which $F_n > 0$ will be. So, it is clear that, for $\lambda \to 0$ the obtained values of θ_f beginning with a lifting force appears, tends to those obtained experimentally A more clear judgement will be provided considering the shape of drop deformable and, of course, the flow unsteady

Concluding Remarks Perhaps, it would be of some interest to take for characteristic velocity U the experimantal values from our works [2] and [8] That might be the aim of a future work

However, the aspect of our results, the spectra of flows inside and outside of the drop, the existence of the lifting force, as well as the asymptotic representation of force exerted on the drop by ambient liquid due to the variation $\sigma - \sigma_1$, are in good qualitative accordance with experimental results The question of quantitative accordance remain open from both side theoretical and experimental It is very likely that the results presented in this paper would be improved if the differential system (1) - (8) were solved by a numerical method, e g. a spectral method This could also make the topic for a future work

An asymptotic analysis in the spirit of [5] in the assumption of deformability of the drop is almost finished There, all the quantities found in this work, stream functions, pressures, etc will play the role of the first approximations

However, it seems that only by the use of some nonlinear terms (all possible) in vicinities of the surface of the drop inside and outside [5] one could solve some discrepancies between theory and experiments

REFERENCES

1. G K Batchelor *An Introduction to Fluid Mechanics* Cambridge Univ Press, Cambridge, 1967
2. E Chifu, I Stan, Z Finta, and E.Gavrilă. *Marangoni-type surface flow on an undeformable drop* J.Colloid Interface Sci., 93(1): 140-150, 1983
3. T M.Fischer, G.C.Hsiao, and W L Wendland. *Singular perturbation for the exterior three-dimensional slow viscous flow problem* J Math. Anal Appl., 110 583-603, 1985
4. D.D.Joseph, K Nguyen, and G S.Beavers *Nonuniqueness and stability of the configuration of flow of immiscible fluids with different viscosities* J Fluid Mech., 143 319, 1984
5. S.Kaplun and P A.Lagerstrom. *Asymptotic expansions of Navier-Stokes solutions for small Reynolds numbers.* J Math. and Mechanics, 6 585-603, 1957
6. L.Landau and E.Lifschitz, *Mecanique de fluides*, Mir, Moscow, 1971
7. M.E.O'Neill and F Chorlton. *Viscous and Compressible Fluid Dynamics* Ellis Horwood, Chichester, West Sussex, 1989
8. I.Stan, E.Chifu, Z.Finta, and E Gavrilă. *Marangoni translational motion of a free drop initially at rest* Rev. Roumaine Chim., 34(2) 603-615, 1989
9. T.D.Taylor and A Acrivos. *On the deformation and of a falling viscous drop at low reynolds number* J.Fluid Mech., 18· 466 -476, 1964
10. M Van Dyke *Perturbation Methods in Fluid Mechanics* Academic Press, 1964