

NUMERICAL SOLUTION OF THE DIP COATING PROCESS WITH INSOLUBLE SURFACTANTS: LANGMUIR OR A LINEAR APPROXIMATION FOR SURFACE TENSION?

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Abstract— In this work the dip coating process when an insoluble surfactant is adsorbed at the interface is numerically studied. The work centers in the applicability of the linear approximation usually employed to model the relationship between surface tension and the concentration of the surface active agent. Reported solutions show that film thicknesses predicted with a linear model can differ significantly from those computed with a more reliable equation of state.

Keywords— dip coating, insoluble surfactant, surface equation, finite elements.

I. INTRODUCTION

When a flat plate is vertically pulled out of a liquid bath with a constant speed, a uniform liquid film is deposited on the solid. The first theoretical analysis of this process—known as dip coating—was carried out by Landau and Levich (1942), and Derjaguin (1943) who reported an approximate expression for the film thickness valid at low coating speeds. Thenceforth, a large number of works have been published to incorporate the effects of gravity, inertia and Marangoni stresses.

Experiments as well as numerical and approximate analysis of the process usually report that the film thickens in the presence of a surfactant. The particular situation in which the surface active agent can be regarded as insoluble was considered by Park (1991) and more recently by Campana *et al.* (2011).

Park studied the problem in the limit of very small capillary number (i.e. very low coating velocities) using the method of matched asymptotic expansions. He considered two cases, one in which the interfacial distribution of surfactant has small gradients and the other one in which the concentration itself is small. The former may be associated with the deposition of Langmuir Blodgett films (Petty, 1996) and the latter with surface contamination. Results of this asymptotic analysis show that the film thickness is affected by the surfactant within a range of capillary number that depends on the magnitude of the elasticity parameter (see the definition below Eq. 6). Within that range, the thickening factor (i.e. the ratio between the thickness of the contaminated system and the Landau-Levich one for a uniformly distributed surfactant) is a non monotonic function of that parameter: at the lower and upper ends it is equal to one and in between it is equal to $4^{2/3}$.

Campana *et al.* (2011) numerically solved the full hydrodynamic problem. This study not only corroborates the predictions of Park's asymptotic analysis but also extends those results by incorporating the influence of inertia and gravity forces. An interesting finding is the non monotonic behavior exhibited by the film thickness as the substrate speed increases, a behavior that is not detected when inertia is not considered. The authors also describe the evolution of the flow patterns when the coating speed is increased and the Landau-Levich result is recovered.

One of the hypotheses proposed in the above works assumes a linear equation of state to model the dependence of surface tension on the concentration of adsorbed surfactant, an assumption that is reasonable only if the interfacial concentration of surfactant and/or its variation along the free surface are small.

In this paper we numerically study the influence of the equation of state used to model surface tension on the dip coating process. To this end we compute solutions when the adsorption of the surfactant corresponds to a Langmuir isotherm and compare them with the predictions of the corresponding linear model to determine the conditions under which the film thickness predictions of the linear model are reasonable. In order to explore the influence on the results of the concentration of surfactant about which the linearization process is carried out, we selected two values: one corresponds to the concentration of solute far away from the substrate and the other one is the concentration of solute carried out by the film.

II. MODEL FORMULATION

A. Governing equations and boundary conditions

A flat plate is vertically pulled out of a pool of liquid with constant speed U . The bath has infinite depth and semi-infinite horizontal dimensions; we assume that the liquid is Newtonian and incompressible with viscosity (μ) and density (ρ). The air in contact with the liquid is regarded as inviscid and its pressure is arbitrarily set equal to zero. An insoluble surfactant is adsorbed at the gas/liquid interface whose concentration is kept constant and equal to $\hat{\Gamma}(s=0)$; since the solute distribution depends on surface convection and surface diffusion the concentration of surfactant may present spatial variations which in turn give rise to gradients of the surface

tension ($\hat{\sigma}$). Finally, we assume that inertia forces are negligible. Within this context, the flow is governed by Stokes and continuity equations which in the coordinate system adopted (see Fig. 1) and in dimensionless form read

$$0 = -\frac{1}{Ca} p_x + u_{xx} + u_{yy} - \frac{1}{Ca}, \quad (1)$$

$$0 = -\frac{1}{Ca} p_y + v_{xx} + v_{yy}, \quad (2)$$

$$u_x + v_y = 0. \quad (3)$$

Selected scales for velocities, lengths, and pressure are U , $l_c = (\hat{\sigma}_0/\rho g)^{1/2}$, and $\hat{\sigma}_0/l_c$, respectively. In the above expressions, $Ca = \mu U/\hat{\sigma}_0$ is the Capillary number, $\hat{\sigma}_0$ being the surface tension of the corresponding clean system.

The boundary conditions imposed to solve Eqs. (1) – (3) are

- i) On the solid plate $u=1$ and $v=0$.
- ii) At the film exit boundary, located far away from $x=0$, the flow is unidirectional and the film thickness is uniform and equal to h_0 . Thus, at $x=x_F$, $0 \leq y \leq h_0$ $u_x=v_x=0$, and $u_y=1/Ca$ ($y-h_0$).
- iii) Along the bottom surface of the computational domain ($x=-H/l_c$) the flow does not change in the x direction; therefore, u_x and v_x are both set equal to zero. Also, a uniform pressure is weakly imposed along this boundary; this pressure is equal to the pressure at the lowest right corner of the domain and is obtained by introducing an additional equation in the computational code that sets the slope of the free surface equal to zero at $(0, y_F)$.
- iv) At $y=y_F$, $0 \leq x \leq -H/l_c$ the flow does not depend on y ; thus, we set $u_y=v_y=0$ there. Also, at that distance from the moving plate, the free surface is flat.
- v) On the liquid air interface, stresses must be continuous. Considering that the gas phase is inviscid and assuming that the free surface viscosity is negligible, the expression for the traction vector is as follows:

$$-\frac{1}{Ca} p \mathbf{n} + \mathbf{n} \cdot [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] = \frac{1}{Ca} \frac{d(\sigma \mathbf{t})}{ds}, \quad (4)$$

where s is the arc length along the interface measured from $(0, y_F)$ to (x_F, h_0) , \mathbf{n} and \mathbf{t} are the normal and tangent unit vectors to the free surface, and σ is the local value of the surface tension measured in units of $\hat{\sigma}_0$.

In addition, since the gas/liquid interface is a material surface, the usual form of the kinematic condition is imposed, that is

$$\mathbf{v} \cdot \mathbf{n} = 0. \quad (5)$$

In order to account for variations of surface tension with the concentration of surfactant, we adopt Langmuir equation, that is

$$\sigma = 1 + \beta [\ln(1 - \alpha \Gamma)]. \quad (6)$$

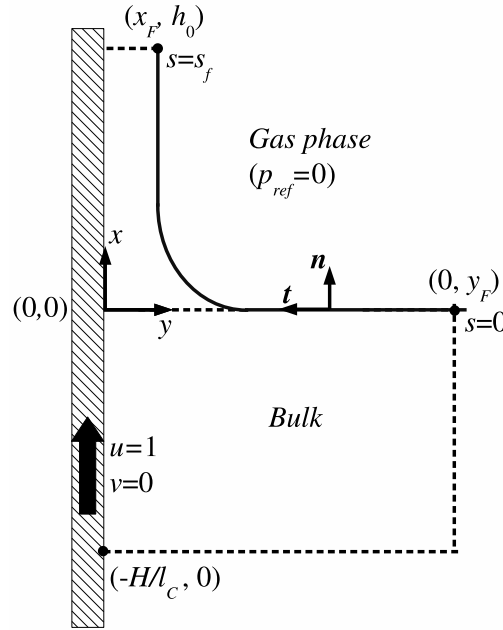


Fig. 1. Sketch of the flow domain and coordinate system adopted.

In the above expression, Γ is the dimensionless surfactant concentration measured in units of $\hat{\Gamma}(s=0)$, $\alpha = \hat{\Gamma}(s=0)/\hat{\Gamma}_\infty$ is the ratio between the reference and the saturation concentration of the surfactant, $\beta = R T \hat{\Gamma}_\infty/\hat{\sigma}_0$ is the elasticity parameter of the surfactant, R being the ideal gas constant and T the temperature.

As we have already mentioned, the local concentration of surfactant results from the competition between surface convection and surface diffusion; consequently, the surface mass balance of solute is as follows (Stone, 1990)

$$\nabla_s \cdot (\Gamma \mathbf{v}^s) - \frac{1}{Pe_s} \nabla_s^2 \Gamma = j_n, \quad (7)$$

where ∇_s is the surface gradient operator, \mathbf{v}^s is the surface velocity, $Pe_s = U l_c/D_s$ is the surface Péclet number, D_s being the surface diffusion coefficient of the surfactant, and j_n is the mass flux of solute between the bulk and the interface; since we are considering an insoluble surfactant, $j_n=0$.

Finally, the following boundary conditions are imposed at the ends of the free surface:

$$\Gamma = 1, \frac{dx^{FS}}{ds} = 0, \text{ at } s=0, \quad (8-a)$$

$$\frac{d\Gamma}{ds} = 0, \frac{dy^{FS}}{ds} = 0, \text{ at } s=s_f. \quad (8-b)$$

In Eq. (8), x^{FS} and y^{FS} stand for the x - and y - coordinates of the free surface, respectively.

B. Numerical solution

The governing equations (1) – (3) and their boundary conditions are discretized by a standard Galerkin/finite-element formulation, and the location of the free surface is traced by means of spines.

The flow domain is tessellated into a structured mesh of quadrilateral elements and each element is isoparametrically mapped onto a unit square. Mixed interpolation is used: quadratic functions are used to interpolate the velocity components u and v , and linear basis functions are used to approximate the pressure. The interfacial concentration of surfactant and the coefficients that locate the free surface are interpolated with the one-dimensional specialization of the biquadratic basis functions used to approximate the velocities.

The nonlinear set of ordinary differential equations obtained is simultaneously solved using a Newton loop; the convergence criterion adopted is that the norm of the difference between two consecutive approximations is equal to or smaller than 10^{-5} .

The finite element mesh was selected so that the film thickness is independent of further refinements with a tolerance not larger than 1%. A complete discussion of the numerical tests performed to check the accuracy of the solution is reported elsewhere (Campana *et al.*, 2010, 2011).

III. DISCUSSION AND RESULTS

The adsorption of a large number of surfactants corresponds to a Langmuir type isotherm (Rosen, 1988); this type of adsorption is valid under the following conditions:

- i) The adsorption is homogeneous;
- ii) both solute and solvent have equal molar surface area;
- iii) there are not solute-solute or solute-solvent interactions;
- iv) the adsorbed film is monomolecular.

However, most analytical and numerical investigations of the effects of an insoluble surfactant on the dip coating process (Park, 1991; Daripa and Paşa, 2009; Campana *et al.*, 2011), assume only small deviations from the reference concentration adopted, and thus a linear relation between interfacial tension and interfacial composition is used. Linearization of Eq. (6) about $\Gamma(s=0)$ yields,

$$\sigma = 1 + \beta[\ln(1-\alpha)] + \frac{\alpha\beta}{(1-\alpha)}(1-\Gamma), \quad (9)$$

Solutions presented in those works show that the interfacial distribution of solute monotonically diminishes along the free surface from $\Gamma=1$ at $s=0$ towards Γ_f at $s=s_f$, as expected; also, those studies establish that for a given value of the elasticity parameter, there is a capillary number at which Γ_f becomes negligible. Under these conditions, one should expect larger concentration gradients when the reference concentration is augmented; i.e. for larger α when β is fixed, and thus, the film thickness predictions might be sensitive to the equation of state used.

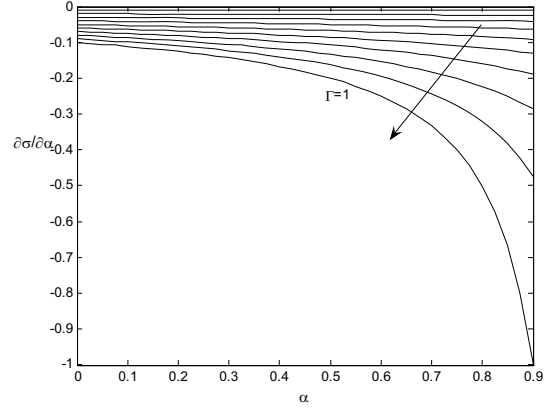


Fig. 2. Derivative of Eq. (6) with respect to α vs α for selected values of Γ and $\beta=0.10$. The arrow points in the direction of increasing Γ . Curves are drawn for Γ varying between 0 and 1 in steps of 0.1.

Both the full and the linear dimensionless approximation of Langmuir expression are written as function of $\alpha = \hat{\Gamma}(s=0)/\hat{\Gamma}_\infty$. In order to establish the dependence of Eq. (6) on this parameter we calculated $\partial\sigma/\partial\alpha$, and evaluated the resulting expression within the interval $0 < \alpha < 0.8$, for $\beta=0.1$, and selected values of Γ ; results are illustrated in Fig. 2.

It is easy to see that when α is small, the derivative of the interfacial tension varies slightly and almost linearly with the interfacial concentration of surfactant. A simple calculation shows that $\lim_{\alpha \rightarrow 0} (\partial\sigma/\partial\alpha) = \beta(1-\Gamma)$ for

both expressions and thus one would not expect significant deviations between the predictions of a model based on either Eq. (6) or Eq. (9). However, if α is larger than approximately 0.5 and $\beta=0.10$, $\partial\sigma/\partial\alpha$ strongly depends on the surface concentration; consequently, one could anticipate larger deviations between the predictions of both models provided that the interfacial concentration gradients are important.

To emphasize the above results we evaluated $\partial\sigma/\partial\Gamma$ as a function of Γ for the linear and non linear equations when α is set equal to 0.1, 0.5, and 0.8. Results are depicted in Fig. 3.

As expected, the two curves corresponding to the smallest α are nearly superimposed while those for $\alpha=0.8$ differ significantly. Therefore, when the distribution of surfactant along the interface is not uniform and α is not small, the Marangoni tractions $[T_{ns} = (1/Ca)(d\sigma/ds)]$ will depend significantly on the equation of state employed to model surface tension.

Based on the previous analysis, we can presume that the film thickness predictions of the dip coating process when a linear approximation is used to model the dependence of surface tension on surfactant concentration will be valid provided $\hat{\Gamma}(s=0) \ll \hat{\Gamma}_\infty$ (i.e. $\alpha \ll 1$), or the resulting interfacial distribution of solute is nearly uniform (i.e. very low coating speeds).

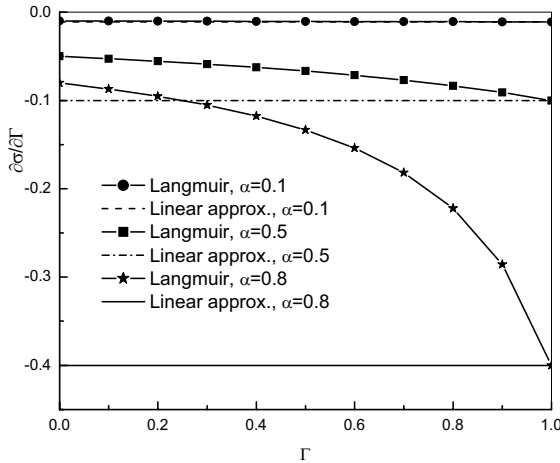


Fig. 3. Evolution of $\partial\sigma/\partial\Gamma$ vs. Γ for α equal 0.1, 0.5, and 0.8.

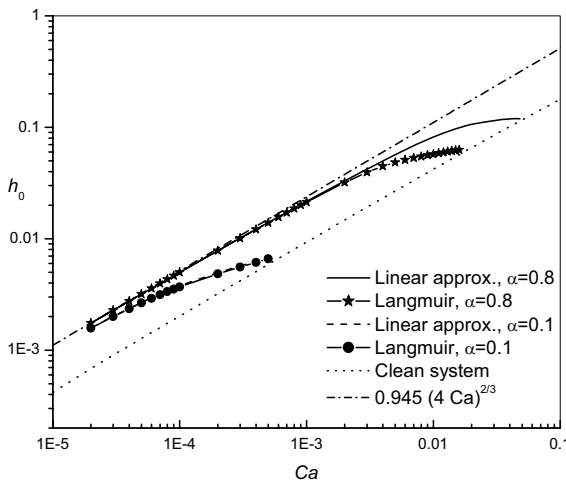


Fig. 4. Dimensionless film thickness as a function of Ca for the linear and nonlinear models, and two values of α . The lower and upper bounds are also depicted.

To verify the validity of our assumption, we carried out computations of the model described in Section I within an appropriate range of the capillary numbers when $\beta=0.1$, and α is equal either to 0.1 or 0.8. We also computed solutions when Eq. (6) is replaced by Eq. (9). Film thickness predictions as a function of Ca are reported in Fig. 4. Since the main objective of this work is to assess the effect of the equation of state, the computations were carried until the film thickness of the contaminated system was nearly equal to the film thickness of the corresponding clean system. Computed predictions beyond this point were presented by Campana *et al.* (2011).

The four curves depicted show the same trend. At low values of the capillary number, the film thickness is approximately equal to $4^{2/3}$ times that of the clean surface (dotted line in Fig. 4). As Ca is augmented, i.e. as the ratio between viscous and surface forces increases, h_0 approaches the value observed in the corresponding clean system (dash-dot line in Fig. 4). When $\alpha=0.1$, numerical predictions of h_0 are nearly independent of the equation of state used to compute surface tension

(the largest difference is $\sim 2.4\%$ when $Ca \approx 0.0005$); however, when that parameter is equal 0.8, films predicted by the linear approximation are in good agreement with those computed with Langmuir equation only if the capillary number is smaller than ~ 0.002 . Thence Eq. (9) produces thicker films than Eq. (6); thus the difference between the thicknesses of the coating layers is approximately equal to 56% for $Ca \approx 0.016$ (i. e. when the solutions of the non linear model approach the clean system solutions).

The thickening of the film detected when a surfactant is adsorbed at the interface is due to the non-zero value of the tangential component of the surface traction and to a reduction of the adverse pressure gradient that exists in the dynamic flow region. In fact, results previously reported (Campana *et al.*, 2011) show that when an insoluble surfactant is present in the system, the stagnation point that exists at the free surface of the corresponding clean system, moves toward the bulk phase; therefore, the interfacial concentration of solute monotonically diminishes from $s=0$ to $s=s_f$, and this gradient gives rise to Marangoni tractions which pull more liquid toward the film region. Also, the adsorption of the surface active agent induces changes in the interfacial shape: the dynamic region stretches and the free surface curvature diminishes; accordingly, the adverse pressure gradient is reduced and more liquid can be pulled toward the film.

Then, it might be interesting to analyze if the difference between the solutions of both Langmuir and linear models can be ascribed to differences in the strength of the mechanisms described. To that end, we evaluated the Marangoni tractions and the pressure gradient along the free surface for α equal to 0.1 and 0.8, and selected values of Ca , when either Eq. (6) or Eq. (9) is used to compute surface tension. Results reported in Fig. 5, show that differences in the pressure gradient along the dynamic meniscus between the linear and non linear models for $Ca=0.005$, $\alpha=0.1$, and $Ca=0.016$, $\alpha=0.8$ (i.e. at the point where differences in the film thickness predictions are the largest) are negligible. Therefore, differences in film thicknesses cannot be ascribed to differences in the adverse pressure gradient.

The curves depicted in Fig. 6, point out that differences in the maximum of the tangential component of the surface traction depend on the expression employed to evaluate surface tension. In fact, they are about 5.6% and 119% when $\alpha=0.1$ ($Ca=0.0005$) and $\alpha=0.8$ ($Ca \approx 0.016$), respectively.

Therefore, we can conclude that differences between the computed film thicknesses are mainly due to the differences detected in T_{ns} ; these differences could be anticipated from the derivatives of Eqs. (6), and (9) with respect to Γ ; i.e.

$$\left. \frac{\partial\sigma}{\partial\Gamma} \right|_{\text{Eq. (6)}} = \frac{-\beta\alpha}{(1-\alpha\Gamma)}, \quad (10\text{-a})$$

$$\left. \frac{\partial\sigma}{\partial\Gamma} \right|_{\text{Eq. (9)}} = \frac{-\beta\alpha}{(1-\alpha)}; \quad (10\text{-b})$$

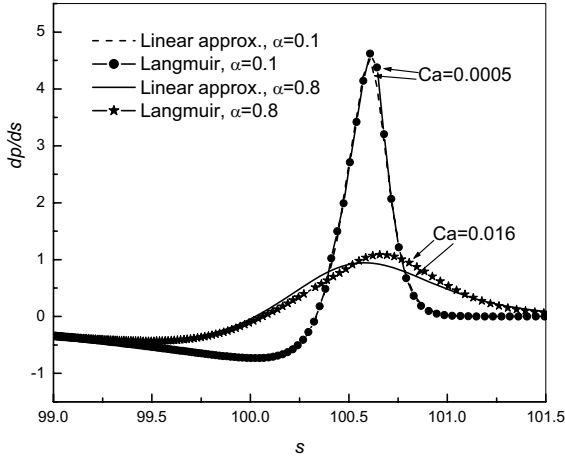


Fig. 5. Pressure gradient distribution along the dynamic meniscus for α equal to 0.1 and 0.8, and selected values of Ca .

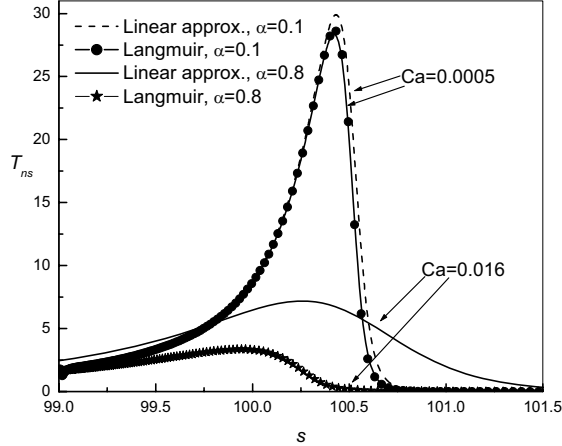


Fig. 6. Marangoni traction along the dynamic meniscus for α equal 0.1 and 0.8, and selected values of Ca .

Since $0 \leq \Gamma \leq 1$, the magnitude of (10-a) is smaller than or equal to (10-b) for all α, β . If α is a small quantity, $\partial\sigma/\partial\Gamma \approx -\beta\alpha$ for both equations, and in consequence the elastic effects will be similar when either Langmuir expression or its linear approximation is used (see Fig. 3). On the other hand, as α increases, the linear model predicts larger surface forces (see Fig. 6) than the non linear one; thus, larger viscous forces (i.e. a faster moving substrate) will be required to overcome the Marangoni stress when Eq. (6) is replaced by Eq. (9) in the numerical code. Actually, results reported in Fig. 4 show that in this case the contaminated system approaches the clean system solution at a larger Ca .

All the studies of the dip coating process establish that the behavior of the system is mainly determined by the dynamic meniscus; for instance, the film thickness as well as the amount of surfactant that leaves the system depend on the characteristic presented by the flow in that region. Eq. (9) results from the linearization of Langmuir equation about the value of the surface tension at $s=0$, i.e. a place far away from the dynamic meniscus. Then, one could argue that the predictions of the

full and approximate models could be closer if Eq. (6) were made linear about $\sigma(s=s_f)$. To verify if it is indeed the case, we carried out numerical computations for $\alpha=0.8$ and the following linearized expression for surface tension,

$$\sigma = 1 + \beta \ln(1 - \alpha \Gamma_{film}) + \frac{\alpha \beta}{1 - \alpha \Gamma_{film}} (\Gamma_{film} - \Gamma), \quad (11)$$

where $\Gamma_{film} = \Gamma(s=s_f)$. The resulting film thicknesses as well as those obtained with Langmuir equation for the same value of α as a function of Ca are illustrated in Fig. 7.

We observe that the film thickness is now underestimated by the linear model. It is easy to see that the magnitude of $\left. \frac{\partial\sigma}{\partial\Gamma} \right|_{Eq(11)} = \frac{-\alpha\beta}{(1-\alpha\Gamma_{film})}$ is even smaller

than the values given by Eq. (10-a); therefore, for the same distribution of surfactant, Marangoni tractions computed with Eq (11) will be smaller than those computed with Eq (6). The difference between both derivatives becomes larger as the concentration at $s=s_f$ diminishes, i.e. as the coating speed increases; therefore, viscous forces will counterbalance surface forces at a smaller value of Ca and the clean system solutions will be approached faster. The largest difference between the thicknesses computed when Eq. (6) is replaced by Eq. (11) in the numerical code is equal to 46%.

From the above discussion, it is apparent that a reliable prediction of the film thickness when the interfacial distribution of the surfactant is not uniform must consider a realistic equation of state for the surface tension.

III. CONCLUSION

In this work we analyze the condition at which the commonly employed linear relationship between surface tension and interfacial concentration of surfactant is valid. To that end, a numerical code previously developed (Campana *et al.*, 2010, 2011) to study the dip coating process, has been adapted to include Langmuir equation of state as well as the two linear expressions that result when the linearization process is carried out

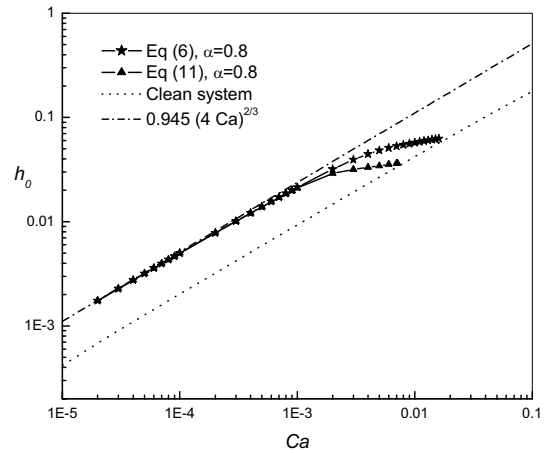


Fig. 7. h_0 vs. Ca for $\alpha=0.8$.

about two selected concentrations of surfactant.

The numerical experiments carried out show that the linear approximations are suitable to predict the film thickness when the interfacial distribution of surfactant is nearly uniform and/or the maximum concentration adsorbed is far from the saturation value. In fact, results presented in this work show that the film thickness can largely be either underestimated or overestimated when a linear equation of state is adopted.

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