

LETTER

# The thickening effect of interfacial surfactant in the drag-out coating problem

Prabir Daripa<sup>1</sup> and G Paşa<sup>2</sup>

<sup>1</sup> Department of Mathematics, Texas A&M University, College Station, TX-77843, USA

<sup>2</sup> Institute of Mathematics ‘Simion Stoilow’ of Romanian Academy, Bucharest, RO-70700, Romania

E-mail: [prabir.daripa@math.tamu.edu](mailto:prabir.daripa@math.tamu.edu) and [Gelu.Pasa@imar.ro](mailto:Gelu.Pasa@imar.ro)

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**Abstract.** In experiments involving dip coating flows on an infinite flat substrate which is withdrawn from an infinite liquid bath, the thin film deposited far up on the plate usually thickens in the presence of insoluble interfacial surfactant. Using perturbation analysis within the lubrication approximation we prove that the film thickens in the presence of interfacial surfactant for low capillary numbers if surface tension away from the transition and meniscus regions increases in the direction of withdrawal of the plate, a condition that should truly emerge from the solution of the full problem. Thus, we essentially show that fine scale properties of the interfacial dynamics and the dynamics in the bulk of the fluid near the transition and meniscus regions are, in fact, not important. We show that it is only the surface tension gradient far away from the transition and meniscus regions that matters. This result is arrived at by first deriving upper and lower bounds on the film thickness in terms of Marangoni and capillary numbers. An estimate based on these results and interfacial surfactant dynamics also yields a qualitative profile of the interfacial surfactant concentration that results in an increase in film thickness.

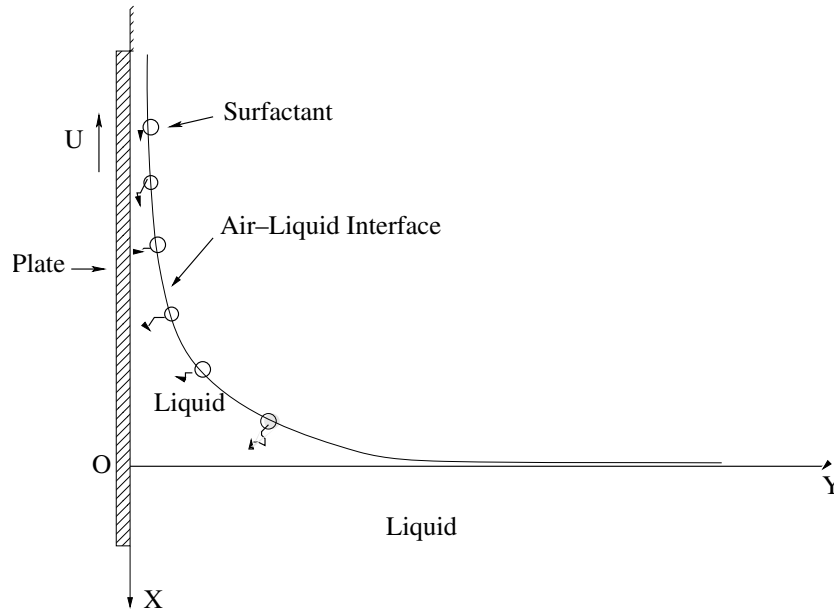
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In coating, thin liquid films are applied on a solid surface. Thin liquid films are used for many reasons in various applications, e.g., they find uses in manufacture of photographic films, aesthetic coatings, protective coatings, adhesives, magnetic tapes, coating of CD-ROM surfaces [1], to name just a few. Uses of thin films are also ubiquitous in Nature, e.g., they appear as membranes, as linings of mammalian lungs [2] and as tear films in the eye [3]. Because of such diverse and useful roles of thin liquid films in so many applications, coating is applied to geometries of various shapes such as planar plates [4]–[11], cylindrical exteriors as in coating on a roller or a fibre [11]–[13], interiors of tubes [6], [14]–[16], and discs [1]. Coating in general has been a subject whose various aspects have been extensively studied; many of these are discussed in the comprehensive book by Kistler and Schweizer [17]. Towards this end, review articles on general coating flows [18, 19] and on fibre coating [20] should also be cited.

Even though coating involves application of thin liquid films, the problem in itself is far from trivial because of the complexity of physical phenomena associated with thin film flows in coating. These flows mostly involve one or more free boundaries along which waves can travel and steepen under certain conditions for high flow rates causing rupture of thin films, entrapment of air bubbles, and exposure of substrates to the ambient gas, all of which are usually undesirable in most coating processes. Moreover, in many coating problems there are application-specific design requirements on thin films. For example, it is desirable in many coating processes that the thin films be of certain thickness under prevailing operating conditions of the coating processes. Therefore, it is of interest to determine the dependence of thickness of these thin films on various parameters of the problem. One such problem that has been extensively studied in recent years is the determination of the effect of surfactants on the film thickness in a variety of settings including what is now known as the Landau–Levich–Derjaguin problem.

The problem of depositing a thin film on a flat plate by withdrawing it from a liquid bath has come to be known as the Landau–Levich–Derjaguin (LLD for short) problem in the literature, even though there have been others before Landau and Levich [5], such as Morey [4], who have used the above drag-out process for coating purposes. The seminal theoretical work of Landau and Levich [5] on this drag-out problem, now recognized as the method of matched asymptotic expansion, uses the lubrication approximation for low capillary number and then solves governing equations by matching the thin film region far away from the bath with the static meniscus (near the horizontal liquid bath) through a ‘transition’ region (see figure 1) in between. During this matching process, a numerical method is used to obtain the film thickness  $h_{\text{LLD}} = 0.945l_c Ca^{2/3}$  far away from the meniscus. Here  $l_c = \sqrt{\gamma/\rho g}$  is the capillary length and  $Ca = U\mu/\gamma$  is the capillary number where  $U$  is the speed of the plate,  $(\mu, \rho) = (\text{viscosity, density})$  of the fluid,  $\gamma$  is the surface tension and  $g$  is the gravity. Later, this same problem was studied by Wilson [11] within the same lubrication approximation using by then well developed perturbation theory, thus justifying the matching procedure used by Landau and Levich [5]. Wilson [11] also generalized the result for the case of thin films deposited on rotating cylinders.

Almost two decades after the work of Landau and Levich [5], White and Tallmadge [9] integrated a simplified form of the Navier–Stokes equations for flow in thin films given by Levich [21] and obtained a numerical estimate of the film thickness as a function of the capillary number. A new theoretical treatment, significantly different from previous theories, of the same physical problem was later presented by Spiers *et al* [10], who



**Figure 1.** Sketch of the drag-out coating problem with coordinates.

required numerical integration to obtain an estimate of the film thickness as a function of the capillary number. All these estimates are found to agree favourably well with each other and with experimental results, though it is claimed by Spiers *et al* [10] that their estimates agree better than others [5, 9] with experimental data for  $Ca \leq 2$ .

The thickness of thin films in these coating processes is a subject of significant interest as this is a design requirement in many applications, as mentioned above. One way to control this thickness is to add surfactant in the solution. In recent years, there have been extensive experimental and analytical-cum-numerical studies in examining the effect of surfactant (either in the bulk or on the interface) on the film thickness on substrates of various geometries such as inner walls of circular tubes [15, 26], fibre [20, 22, 23], and flat plate [24, 25]. All of these works unequivocally show a thickening effect of surfactant on the thin film.

Our interest here is in gaining a better theoretical understanding of the effect of interfacial surfactant on the film thickness in the LLD problem, which has been previously studied by Groenveld [24] and Park [25]. White and Tallmadge [9, 27] had observed experimentally film thickness significantly higher than the estimate of Landau and Levich [5]. Groenveld [24] speculated that this excess in the thickness of the film is perhaps due to the effect of impurities on the interface of the film. Later this problem was re-investigated by a combination of analytical and numerical methods by Park [25], surprisingly without any reference to the work of Groenveld [24]. In particular, Park [25] considered the drag-out problem with an insoluble surfactant on the surface of the liquid bath. Using an asymptotic analysis of this LLD problem within the lubrication approximation, Park [25] obtained simple equations for the case of small capillary and Marangoni numbers which were then solved numerically using Runge-Kutta and 'shooting' methods. In this way, it was found that the presence of Marangoni forces increases the film thickness. It is worth mentioning here that, at variance with this

huge body of work on the thickening effect of insoluble surfactants on thin films, there is an interesting paper of very recent origin [28] where numerical findings with *soluble* surfactants support film thinning instead of film thickening. The complexity of the equations governing the full problem even when only interfacial insoluble surfactant is present (with no surfactant in the bulk) defy a proof of the thickening effect based on the full problem.

In this letter, using perturbation analysis within the lubrication approximation we prove that the film thickens in the presence of interfacial surfactant for low capillary numbers if the surface tension away from the transition and meniscus regions decreases in the direction of withdrawal of the plate, a condition that should truly emerge from the solution of the full problem. Thus, we essentially show that fine scale properties of the interfacial dynamics and the dynamics in the bulk of the fluid near the transition and meniscus regions are, in fact, not important. We show that it is only the surface tension gradient (equivalently the Marangoni number and the gradient of the interfacial surfactant concentration) far away from the transition and meniscus regions that matters. This result is arrived at by first deriving upper and lower bound results on the film thickness which have been justified as being consistent with the above mentioned analytical-cum-numerical and experimental results. An estimate based on these results and interfacial surfactant dynamics yields a qualitative profile of the surfactant concentration along the interface in the far field.

Here and below all dimensional variables are denoted with an overbar and dimensionless variables without an overbar. Consider a vertical flat plate being pulled out from a horizontal bath of an incompressible fluid. The  $\bar{x}$  axis is downward in the direction of the force of gravity with the  $\bar{y}$  axis perpendicular to the plate as shown in figure 1. The plate velocity  $(\bar{U}, 0)$  is vertically upward and its equation is taken to be  $\bar{y} = 0$ . The equation of the free surface of the liquid bath far from the plate is  $\bar{x} = 0$ . The film thickness at finite (negative)  $\bar{x}$  on the plate is denoted by  $\bar{h}$  and the (constant) film thickness far up on the plate is denoted by  $\bar{H}_c (=h_{\text{LLD}})$  for the clean case and  $\bar{H}_s$  for the case with surfactant. We denote by  $\bar{u}$  the velocity component in the  $\bar{x}$  direction, by  $\bar{p}$  the pressure, and by  $\bar{y} = \bar{h}(\bar{x})$  the free surface of the liquid film for  $\bar{x} < 0$ . The surfactant concentration on the free surface is denoted by  $\Gamma$  and  $\gamma(\Gamma)$  denotes surface tension which depends on  $\Gamma$ . The  $\Gamma_\infty$  and  $\gamma_\infty$  are the corresponding values far up on the plate for the surfactant case,  $\gamma_c = \gamma(\Gamma = 0)$  denotes the constant surface tension for the clean case. Note that  $\gamma_\infty = \gamma_c$  if  $\Gamma_\infty = 0$ .

We consider first the ‘clean case’: the LLD problem defined earlier. We use the following lubrication model for the flow in the thin film far from the meniscus:

$$\nu \bar{u}_{\bar{y}\bar{y}} = \frac{1}{\rho} \bar{p}_{\bar{x}} - g, \quad \text{and} \quad \bar{p}_{\bar{y}} = 0, \quad \text{for } \bar{x} < 0, \quad 0 < \bar{y} < \bar{h}. \quad (1)$$

$$\bar{p} = -\gamma_c \bar{h}_{\bar{x}\bar{x}}, \quad \text{and} \quad \bar{u}_{\bar{y}} = 0, \quad \text{on } \bar{y} = \bar{h}(\bar{x}). \quad (2)$$

$$\bar{u} = -U, \quad \text{on } \bar{y} = 0. \quad (3)$$

In dimensionless variables:  $u = \bar{u}/U, x = \bar{x}/l_c, y = \bar{y}/l_c, p = \bar{p}l_c/\gamma_c, h = \bar{h}/l_c$ , the problem (1)–(3) becomes

$$Ca \cdot u_{yy} = p_x - 1, \quad \text{and} \quad p_y = 0, \quad \text{for } x < 0, \quad 0 < y < h(x). \quad (4)$$

$$p = -h_{xx}, \quad \text{and} \quad u_y = 0, \quad \text{on } y = h(x). \quad (5)$$

$$u = -1, \quad \text{on } y = 0. \quad (6)$$

An exact solution of the clean case problem defined by (4)–(6) for the velocity  $u$  in terms of the pressure  $p$  is easily seen to be

$$u(x, y) = \frac{p_x - 1}{2Ca}(y^2 - 2yh) - 1. \quad (7)$$

The above formula can be used to obtain an upper limit for the constant thickness  $H_c$  far up on the plate using an expression for the ‘surface’ velocity  $\mathbf{u}^s = (u^s, 0)$  for large negative values of  $x$ . Since  $\lim_{x \rightarrow -\infty} h(x) = H_c$ ,  $\lim_{x \rightarrow -\infty} p_x = -\lim_{x \rightarrow -\infty} h_{xxx} = 0$ , it follows from (7) that

$$u^s(-\infty) = \frac{H_c^2}{2Ca} - 1. \quad (8)$$

In the far field (i.e., as  $x \rightarrow -\infty$ ), the ‘surface’ velocity is *negative* (recall that the positive  $x$  axis is downward—see figure 1) since the fluid moves up together with the plate there, which is expected on physical grounds and is not an assumption. If there is any stagnation point on the interface, it should be far away from the far field, i.e., it should be in the meniscus or transition regions. In fact, such findings should emerge from the full solution of the problem (see [21, 29]) though we stress that we do not impose such assumptions. Then from relation (8), we obtain the upper bound  $H_{1c}^u$  for  $H_c$ . The subscript ‘1’ is used here to distinguish this bound from another (improved) bound which will carry a subscript ‘2’ as we will see below.

$$u^s < 0 \Rightarrow H_c < H_{1c}^u = \sqrt{2Ca}. \quad (9)$$

We shall show that an improved upper estimate can be obtained using the flux on the plate, denoted by  $Q$ :

$$Q(x) = \int_0^h u(x, y) dy = \frac{(-p_x + 1)h^3}{3Ca} - h. \quad (10)$$

The corresponding value of  $Q$  for large (negative) values of  $x$  is

$$Q(-\infty) = \frac{H_c^3}{3Ca} - H_c. \quad (11)$$

Due to the incompressibility of the fluid,  $Q(x) = Q(-\infty)$ , which, upon using the above two relations, leads to

$$\frac{h^3}{3Ca}(-p_x + 1) - h = \frac{H_c^3}{3Ca} - H_c. \quad (12)$$

Using (5)<sub>1</sub>, this equation can be rewritten as

$$\frac{h^3}{3Ca}(h_{xxx} + 1) - h = \frac{H_c^3}{3Ca} - H_c. \quad (13)$$

Consider  $\alpha = h/H_c$ ,  $\alpha(-\infty) = 1$ ; then from the last relation we obtain

$$\frac{H_c^3}{3Ca} \alpha_{xxx} + \frac{H_c^2}{3Ca} - \left\{ (\alpha - 1) + \frac{H_c^2}{3Ca} \right\} \frac{1}{\alpha^3} = 0. \quad (14)$$

Far up on the plate, the film thickness varies from  $H_c$  by a small amount and hence we can use for this regime the following approximations:  $\alpha = 1 + \delta$ ,  $\delta \ll 1$ . To leading order, we get from (14)

$$\frac{H_c^3}{3Ca} \delta_{xxx} - \delta \left\{ 1 - \frac{H_c^2}{Ca} \right\} = 0. \quad (15)$$

Using the condition that  $\delta(-\infty) = 0$ , the solution of this equation that approaches the thickness in the far field monotonically must be of the form  $\delta(x) \sim \exp(kx)$  with a *positive*  $k$  and hence the term within curly brackets in (15) must be positive. Thus, we obtain the following improved upper bound  $H_{2c}^u$  for  $H_c$ ; the subscript ‘2’ here distinguishes it from the previous upper bound  $H_{1c}^u$  which carries a subscript ‘1’:

$$H_c < H_{2c}^u = \sqrt{Ca}. \quad (16)$$

To this end, we mention that there is the possibility of another thicker solution which can support oscillations at the free surface and consistent with equation (15). Such solutions, though they have been found only recently (see [30]), are not of interest in this work. From (9) and (16), we obtain  $H_{2c}^u < H_{1c}^u$ . Thus (16) provides an improved upper bound. It is worth mentioning that a simple force balance between gravity and viscosity suggests a thickness of the order of  $H_{2c}^u$  whereas the more definitive approach given above shows that it is an upper bound.

The thickness (scaled by capillary length  $l_c$ ) of the film far up on the plate obtained in Landau and Levich [5] and Wilson (1982) (for the clean case) is  $H_{LLD} = 0.945 Ca^{2/3}$ . This and our upper bound result  $H_c < Ca^{1/2}$  given by (16) then yield  $0.945 Ca^{2/3} < Ca^{1/2}$ . This implies  $Ca < (1.058)^6 = 1.404$  which falls within the lubrication approximation regime (low  $Ca$ ).

Now, we consider the ‘surfactant case’: the free surface of the thin film in the LLD problem is now doped with insoluble surfactant. The surfactant concentration on the free surface of the film is denoted by  $\Gamma$  which is a function of  $x$  with the property that  $\Gamma = \Gamma_\infty$  as  $x \rightarrow -\infty$  which defines the concentration far up on the surface of the thin film. The surface tension  $\gamma(x) = \gamma(\Gamma(x))$  and we define  $\gamma_\infty = \gamma(\Gamma_\infty)$ , the surface tension far up on the thin film surface. To show the effect of surfactant on the film thickness, the surfactant concentration and its variation along the film surface are taken as small.

The boundary condition  $u_y = 0$  on  $y = h(x)$  for the previous case (i.e., the case with no surfactant) is replaced by the second condition (18) (see below) involving the derivative of the surface tension  $\gamma$ . In this case, the problem in non-dimensional variables is defined by (see also [26])

$$Ca \cdot u_{yy} = p_x - 1, \quad \text{and} \quad p_y = 0, \quad \text{for } x < 0, \quad 0 < y < h(x). \quad (17)$$

$$p = -h_{xx}, \quad \text{and} \quad Ca \cdot u_y = \gamma_x, \quad \text{on } y = h(x). \quad (18)$$

$$u = -1, \quad \text{on } y = 0, \quad (19)$$



where  $Ca = U\mu/\gamma_\infty$  and  $\gamma$  in (18) is normalized by  $\gamma_\infty$ . For proper and fair comparison of the film thickness in the presence of surfactant with that in the clean case, we will be interested in film whose profile decays monotonically to the far field thickness  $H_s$ . The exact solution of the problem defined by (17)–(19) is given by

$$u(x, y) = \frac{p_x - 1}{2Ca}(y^2 - 2hy) + \frac{\gamma_x}{Ca}y - 1. \quad (20)$$

From this we get the surface velocity  $u^s(x) = u(x, y = h(x))$  as

$$u_s = \frac{h^2}{2Ca}(-p_x + 1) + \frac{\gamma_x}{Ca}h - 1. \quad (21)$$

In the above equation, we consider  $x \rightarrow -\infty$  and since the surface velocity must be negative in the far field (for reasons mentioned after (8)), we obtain the same upper bound as in (9) for  $H_s$  assuming  $\gamma_x = 0$  as  $x \rightarrow -\infty$ .

$$H_s < H_{1c}^u = \sqrt{2Ca}. \quad (22)$$

Below we use the flux method as used for the ‘clean’ case. But we shall see that it is difficult to apply the method in a similar way. Instead, we will use some physical considerations and weak formulations to obtain a lower and a upper bound for the film thickness. We use (20) and get the fluxes  $Q(x)$  and  $Q(-\infty)$ :

$$Q(x) = \frac{h^3}{3Ca}(-p_x + 1) + \frac{h^2}{2} \frac{\gamma_x}{Ca} - h. \quad (23)$$

$$Q(-\infty) = \frac{H_s^3}{3Ca} - H_s, \quad (24)$$

because  $p_x \rightarrow 0$  and  $\gamma_x \rightarrow 0$  as  $x \rightarrow -\infty$ . From the incompressibility condition  $Q(x) = Q(-\infty)$ , we obtain the following equation for the film thickness  $h$ :

$$\frac{h^3}{3Ca}(h_{xxx} + 1) + \frac{h^2}{2} \frac{\gamma_x}{Ca} - h = \frac{H_s^3}{3Ca} - H_s, \quad (25)$$

subject to boundary conditions:  $h(-\infty) = H_s, h_x(-\infty) = 0, h_{xx}(-\infty) = 0$ . As before, consider  $\beta = h/H_s$ . Then from (25) we get

$$\frac{H_s^3}{3Ca}\beta_{xxx}\beta^3 + \frac{H_s^2}{3Ca}\beta^3 + \frac{H_s}{2} \frac{\gamma_x}{Ca}\beta^2 - \left\{ (\beta - 1) + \frac{H_s^2}{3Ca} \right\} = 0, \quad (26)$$

with boundary conditions  $\beta(-\infty) = 1, \beta_x(-\infty) = 0, \beta_{xx}(-\infty) = 0$ . Away from the transition region and far up on the plate, the film thickness  $\beta$  changes very slowly as it approaches the far field film thickness (normalized) of 1. Therefore we assume  $\beta = 1 + \delta; 0 < \delta \ll 1$ . Thus within the linearized approximation, we obtain the following problem for  $\delta$  to leading order:

$$a\delta_{xxx} + b\delta = f(x)(1 + 2\delta), \quad (27)$$

subject to the use of notation  $f(x) = -(H_s/2)(\gamma_x/Ca)$ ,  $a = (H_s^3/3Ca)$ ,  $b = ((H_s^2/Ca) - 1)$  above and the boundary conditions:  $\delta(-\infty) = 0, \delta_x(-\infty) = 0, \delta_{xx}(-\infty) = 0$ . Multiplying (27) by  $\delta$  and after some manipulation, we obtain

$$a(\delta\delta_{xx} - 0.5(\delta_x)^2)_x + b\delta^2 = f(x)\delta(1 + 2\delta). \quad (28)$$

Integrating this equation from  $-\infty$  to some finite value  $x_*$  and then using the conditions for  $\delta$ , we obtain

$$a (\delta(x_*)\delta_{xx}(x_*) - 0.5(\delta_x(x_*))^2) + b \int_{-\infty}^{x_*} \delta^2(x) dx = \int_{-\infty}^{x_*} f(x)\delta(x)(1 + 2\delta(x)) dx.$$

It is convenient to rewrite this equation as follows:

$$b = \frac{\int_{-\infty}^{x_*} f(x)\delta(x)(1 + 2\delta(x)) dx - a (\delta(x_*)\delta_{xx}(x_*) - 0.5(\delta_x(x_*))^2)}{\int_{-\infty}^{x_*} \delta^2(x) dx}. \quad (29)$$

Since the term  $(\delta(x_*)\delta_{xx}(x_*) - 0.5(\delta_x(x_*))^2)$  in the numerator above is second order in perturbation, to leading order this can be neglected. Moreover, since  $\delta(x) \ll 1$ , we can neglect this in comparison to 1 in the numerator. Then the above relation becomes

$$b = \frac{\int_{-\infty}^{x_*} f(x)\delta(x) dx}{\int_{-\infty}^{x_*} \delta^2(x) dx}. \quad (30)$$

Since  $f(x) = -(H_s/2)(\gamma_x/Ca) > 0$ , assuming  $\gamma_x < 0$  and  $\delta(x) > 0$ , since  $h \rightarrow H_s$  as  $x \rightarrow \infty$ , the numerator above is positive and so is the denominator. Therefore  $b = ((H_s^2/Ca) - 1) > 0$ , from which we conclude that

$$H_s > H_s^l = \sqrt{Ca}. \quad (31)$$

Note that the strict upper bound given in (16) for the film thickness in the ‘clean’ case is equal to the strict lower bound given in (31) for the film thickness in the surfactant case. This proves the thickening effect of surfactant.

In the surfactant case, Park [25] obtained  $H = 0.945 \times 4^{2/3} Ca^{2/3}$ . This and the strict lower bound result  $H_s > Ca^{1/2}$  (see (31)) then give the following regime of validity of the results:  $Ca > 5.4786 \times 10^{-3}$ . It is interesting to recall that a good agreement between experimental and theoretical results was obtained in [15] also for  $Ca > 10^{-3}$ .

The strict upper bound (31) can be used in the following way to estimate the leading order dependence of  $h$  on  $\gamma$  in the asymptotic limit. Equation (25) can be rewritten as

$$\frac{h^3 - H_s^3}{3Ca} = (h - H_s) - \frac{\gamma_x h^2}{2Ca} - \frac{h^3 h_{xxx}}{3Ca}, \quad (32)$$

or equivalently in the form

$$h^2 + h H_s + H_s^2 = 3Ca - \frac{3h^2 \gamma_x}{2(h - H_s)} - \frac{h^3 h_{xxx}}{(h - H_s)}. \quad (33)$$

Since the thickness  $h(x)$  usually approaches  $H_s$  exponentially fast as  $x \rightarrow -\infty$ , the last term in the above equation drops out and we have

$$\lim_{h \rightarrow H_s} (h^2 + h H_s + H_s^2) = \lim_{h \rightarrow H_s} \left\{ 3Ca - \frac{3h^2 \gamma_x}{2(h - H_s)} \right\}. \quad (34)$$

Then in the limit we obtain the bound given in (31), i.e.,  $H_s > H_s^l = \sqrt{Ca}$ , provided  $-\gamma_x = O(h - H_s)$ , as  $h \rightarrow H_s$ ; thereby we obtain dependence of  $h$  on  $\gamma_x$  for large negative values of  $x$ .



In our deliberation above, we have avoided the use of the Marangoni number which however enters through the relation of  $\gamma_x$  (gradient of surface tension) and the Marangoni number  $M$  as follows. Within the linear approximation for small variation of  $\Gamma$  from  $\Gamma_\infty$  along the interface, we can write  $\gamma - \gamma_\infty = -M(\Gamma - \Gamma_\infty)$ , where  $M = -d\gamma/d\Gamma|_{\Gamma_\infty} > 0$  is the Marangoni number and  $\gamma_\infty = \gamma(\Gamma_\infty)$ . Then it follows that  $\gamma_x = -M\Gamma_x$ . Then  $\gamma_x < 0$  implies  $\Gamma_x > 0$ . The interfacial surfactant dynamics in the far field governed by  $q\Gamma_x = D_s\Gamma_{xx}$  (given in dimensional form here) then implies  $\Gamma_{xx} < 0$ . Thus the far field surfactant concentration profile is defined by  $\Gamma_{xx} < 0$  and  $\Gamma_x > 0$  from which one can easily draw the qualitative shape of the profile  $\Gamma(x)$  in the far field.

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