A Theory of Entrainment for Angular Withdrawal of Flat Supports

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Consider the entrainment of wetting liquids by continuous, steady state withdrawal at an angle as shown in Figure 1. In particular, consider the prediction of film thickness h_0 in the constant thickness region as a function of angle α and speed U_w, together with the influence of fluid properties (μ, σ, ρ). This problem has several applications in coating of sheets and drums (6).

One method of describing this problem is to integrate a simplified form of the Navier-Stokes equation for thin films, which is given by Deryagin and Levi (1) as

$$\sigma \frac{d^3h}{dx^3} - \rho g \sin\alpha + \mu \frac{\partial^2 u}{\partial y^2} = 0 \qquad (1)$$

where h is the meniscus film thickness, u the fluid velocity parallel to the plate, x is measured upward along the plate, and y perpendicular to the plate. The assumptions implied are a constant surface tension, one-dimensional flow in the thin film, and a negligible film thickness gradient ($dh/dx << 1$) in the thin film.

Equation (1) is a three-force equation which has not been solved for angular withdrawal. However, the two special cases of the equation which are relevant to flow have been solved; they are given by the following two-force equations:

$$\sigma \frac{d^3h}{dx^3} + \mu \frac{\partial^2 u}{\partial y^2} = 0 \qquad (2)$$

$$-\rho g \sin\alpha + \mu \frac{\partial^2 u}{\partial y^2} = 0 \qquad (3)$$

Equation (2) neglects the effect of gravity and represents a plug flow profile, and Equation (3) is a viscogravitational model of the flow. Both two-force descriptions have been solved by Deryagin and Levi (1). The resulting predictions of film thickness include the plug flow theory

$$h_0 = \frac{0.944}{(1-\cos\alpha)^{1/2}} \left(\frac{U_w \mu}{\sigma}\right)^{2/3} \left(\frac{\sigma}{\rho g}\right)^{1/2} \qquad (4)$$

and the viscogravitational theory

$$h_0 = \left(\frac{U_w \mu}{\rho g \sin\alpha}\right)^{1/2} \qquad (5)$$

Data taken at a constant angle of 90 deg. (7, 8) indicate that the exponent on speed is neither one-half nor two-thirds (but somewhere intermediate), so that neither Equation (4) nor (5) properly predict the entrainment that is observed experimentally.

The purpose of this communication is to develop an angular withdrawal theory for film thickness which is general for a wide range of speed. The complex influence of the liquid-gas interfacial tension on film thickness is included in analytical form, together with viscous and gravitational forces.

DERIVATION OF THE DYNAMIC EQUATION (7)

Equation (1) can be integrated at constant x to give an expression for the volume flow rate V for a support of width b:

$$\frac{V}{b} = \int u dy = U_w h - \left(\rho g \sin\alpha - \sigma \frac{d^3h}{dx^3}\right) \frac{h^3}{3\mu}$$

$$= U_w h_0 - \frac{\rho g \sin\alpha \, h_0^3}{3\mu} \qquad (6)$$

The last term in Equation (6) is the familiar expression for steady flow of a film down an upward moving plate. By substituting the nondimensional coordinates $L = h/h_0$ and $R = -x/h_0$ (thus changing the x direction to downward), Equation (6) becomes

$$L^3 L''' = 3\left(\frac{U_w \mu}{\sigma}\right)(L-1) - h_0^2 \left(\frac{\rho g}{\sigma}\right) \sin\alpha \, (L^3 - 1)$$

By using a nondimensional speed (capillary number $N_{Ca} \equiv U_w \mu/\sigma$) and a nondimensional thickness $D_0 \equiv h_0(\rho g/\sigma)^{1/2}$, the differential equation becomes

$$L^3 L''' = 3N_{Ca}(L-1) - D_0^2 \sin\alpha \, (L^3 - 1) \qquad (7)$$

with

$$L = 1, \quad L' = 0, \quad L'' = 0 \quad \text{at} \quad R = 0 \qquad (8)$$

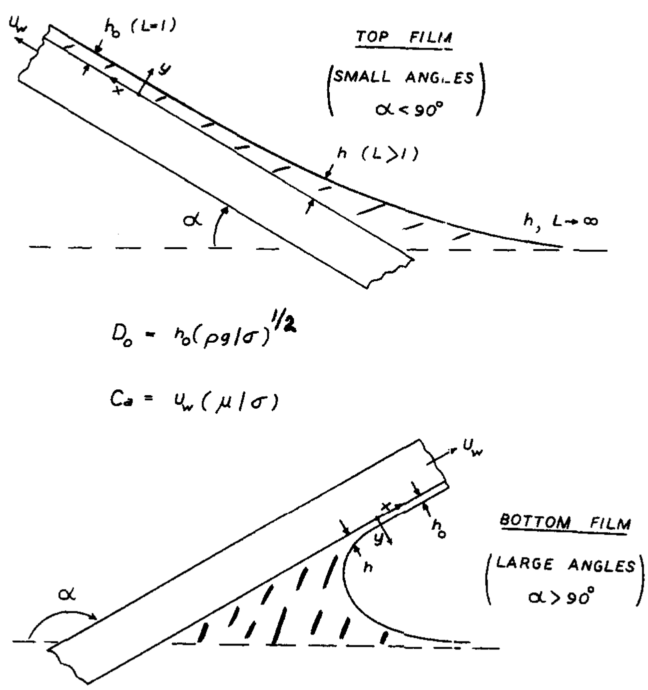

Fig. 1. Sketch of angular withdrawal.

Here the nondimensional parameters D_0, N_{Ca}, and α are constants for purposes of integration (thickness, speed, and angle).

Equation (7) is equivalent to that given by Deryagin and Levi (*1*), but they did not give a solution to this general equation.

VERTICAL WITHDRAWAL, A PREVIOUS SOLUTION

White and Tallmadge (*8*) solved Equation (7) for the case where $\alpha = 90$ deg. For this case, Equation (7) is

$$L^3 L''' = 3N_{Ca}(L - 1) - D_0^2 (L^3 - 1) \qquad (9)$$

To obtain a convergent solution for an estimate of curvature, they invoked (again) the assumption of a thin film. Specifically they took $L = 1 + E$, where E is a small number, and substituted to obtain

$$L^3 E''' = 3E(N_{Ca} - D_0^2) + 0(E^2)$$

By neglecting higher-order terms and by returning to L, Equation (9) simplifies to

$$L^3 L''' = (L - 1)\ (3)\ (N_{Ca} - D_0^2) \qquad (10)$$

In effect, the right side of Equation (9) was approximated for thin menisci by $(L - 1)\ (3)\ (N_{Ca} - D_0^2)$. By approximating the curvature at moderate L by that for $L \to \infty$ (the numerical values are nearly identical) the resulting limiting curvature C_{DL} was found to be

$$C_{DL} = 0.642\ (3)^{2/3} (N_{Ca} - D_0^2)^{2/3} \qquad (11)$$

Matching C_{DL} with the Landau-Levich (*2, 3*) boundary condition of capillary statics, $C_{SL} = D_0 \sqrt{2}$, is sufficient to give the following three-force withdrawal theory:

$$N_{Ca} = 1.09\ D_0^{3/2} + D_0^2 \qquad (12)$$

Equation (12) has been verified within experimental error for the entire range of available data, including a 20,000 fold range of N_{Ca} (*8*). Thus the value for the matching curvature C_{SL} in the lower part of the meniscus is a reasonable one, not only for low speeds but also for all speeds tested to date. The term C_{SL} is approximated by the precisely known curvature at the top of the static meniscus.

APPROXIMATE SOLUTION OF EQUATION (7)

The general solution of Equation (7) for any withdrawal angle will now be derived by using the thin meniscus approximation (*8*). By approximating the right side for thin menisci, Equation (7) becomes

$$L^3 L''' = (L - 1)\ (3)\ (N_{Ca} - D_0^2 \sin\alpha) \qquad (13)$$

and thus

$$C_{DL} \doteq 0.642\ (3)^{2/3} (N_{Ca} - D_0^2 \sin\alpha)^{2/3} \qquad (14)$$

The top curvature for an angular, static meniscus in an infinite bath is given by Deryagin and Levi (*1*) as $[(1 - \cos\alpha)(2\rho g/\sigma)]^{1/2}$. Thus the curvature for the lower meniscus is

$$C_{SL} \doteq D_0\ [2(1 - \cos\alpha)]^{1/2} \qquad (15)$$

Matching curvatures leads to (*5*)

$$N_{Ca} = 1.09 D_0^{3/2} (1 - \cos\alpha)^{3/4} + D_0^2 \sin\alpha \qquad (16)$$

Equation (16) is the desired new theory. It is an approximate solution of general validity to Equation (7) and is the first solution to the three-force Equation (1). It predicts not only the proper effect of speed observed in vertical withdrawal (*8*), but it also predicts that the effect of angle is more complex than that implied by earlier special case theories [Equations (4) and (5)]. Note that the angle appears as a nonlinear combination of sin and cos functions in Equation (16).

DISCUSSION OF THE THEORY

For an angle of $\alpha = 90$ deg., Equation (16) reduces as expected to the verified theory of vertical withdrawal, as given by Equation (12).

At low speeds (and thus small thicknesses), the D_0^2 term becomes negligible with respect to the $D_0^{3/2}$ term, and Equation (16) reduces to

$$N_{Ca} = 1.09 D_0^{3/2}\ (1 - \cos\alpha)^{3/4} \qquad (17)$$

At higher speeds (and thus larger thicknesses), but subject to upper speed limits due to waves and turbulence, the $D_0^{3/2}$ term becomes negligible with respect to the D_0^2 term, and Equation (16) reduces to

$$N_{Ca} = D_0^2 \sin\alpha \qquad (18)$$

Since Equations (17) and (18) are equivalent to Equations (4) and (5), respectively, of Deryagin and Levi (*1*), we see that the two-force, plug flow theory (for negligible gravitational effects) is a low speed theory. Furthermore, the two-force, viscogravity theory (for negligible surface tension effects) is a moderate or medium speed theory. The limited applicability of viscogravity or medium speed theories has been discussed elsewhere (*4, 6*).

Deryagin and Levi report that they found approximate agreement of the plug flow theory with data. However, neither the film thicknesses nor the conditions were reported for any run. Furthermore, no indication of the range of angles was given (*1*). Thus no independent or quantitative tests of their data can be made. The only conclusion that can be drawn is that the plug flow theory is a good approximation for h_0 entrainment under some limited but unknown conditions of angle and capillary number. It is clear that a well-defined test of the angular withdrawal equations is needed, especially for a wide range of angles and capillary numbers.

In summary, a theory of nonvertical withdrawal has been developed for a wide range of speeds. The theory simplifies to previously available special case theories. An alternative method of deriving surface tension theories of withdrawal are compared with the curvature method in the Appendix.

ACKNOWLEDGMENT

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NOTATION

C = curvature, $L'' = d^2L/dR^2$
C_{DL} = upper region limiting curvature
C_{SL} = lower region limiting curvature
D_0 = nondimensional film thickness, constant region, $h_0(\rho g/\sigma)^{1/2}$
E = small number, $E << 1$
g = gravitational acceleration, cm./sec.^{2}
h = meniscus thickness, cm.
h_0 = film thickness, constant thickness region, cm.
L = h/h_0
L' = dL/dR, $L'' = d^2L/dR^2$, etc.
N_{Ca} = capillary number, $\mu U_w/\sigma$
R = $-x/h_0$
u = local field velocity, cm./sec.
U_w = plate withdrawal speed, cm./sec.

x = coordinate parallel to the plate, cm.
y = coordinate perpendicular to the plate, cm.
α = withdrawal angle, Figure 1
μ = viscosity, poise
ρ = density, g./ml.
σ = surface tension, dyne/cm.

Appendix Only

β = Equation (A1)
B = Equation (A3)
B_D = B in dynamic equation
B_S = B in static equation
B_{DL} = Equation (A5)
B_{SL} = Equation (A6)
H = (h/h_0)
H' = dH/dR
H'' = d^2H/dR^2
H''' = d^3H/dR^3, Equation (A2)
I_L = integral, Equation (A14)
I_R = integral, Equation (A15)
R = $(x/h_0)\ (3N_{Ca})^{1/3}$
R^* = arbitrary point in R

LITERATURE CITED

1. Deryagin, B. V., and S. M. Levi, "Film Coating Theory," Chapt. 2, 5, Focal Press, New York (1964).
2. Landau, L., and V. G. Levich, *Acta Phys. Chem. USSR*, **20**, 6 (1945).
3. Levich, V. G., "Physicochemical Hydrodynamics," Chapt. 12, Prentice Hall, Englewood Cliffs, N. J. (1962).
4. Tallmadge, J. A., *Ind. Eng. Chem. Fundamentals*, **8**, 109 (1968).
5. ———, paper presented at Am. Inst. Chem. Engrs. National Meeting, Portland, Ore. (Aug. 1969).
6. ———, and Chaim Gutfinger, *Ind. Engr. Chem.*, **59**, No. 11, 18 (1967). Corrections in **60**, No. 2, 74 (1968).
7. Van Rossum, J. J., *Appl. Sci. Res.*, **A7**, 121 (1958).
8. White, D. A., and J. A. Tallmadge, *Chem. Eng. Sci.*, **20**, 33 (1965).

APPENDIX

One purpose of this appendix is to determine (and at the end list) the differences between the B match method described by Deryagin and Levi (*1*) and the C match of Landau and Levich (*3*) and others. To do this, the two methods will be compared, apparently for the first time. The other purposes of this appendix are to show how the Deryagin plug flow theory was actually derived and to state why the C method was selected over the B method for the derivation of Equation (16).

The β and H''' parameters used by Deryagin and Levi (*1*) may be defined as

$$\beta \equiv \frac{D_0^2 \sin\alpha}{N_{Ca}} = h_0^2 \left(\frac{\rho g}{\mu U_w} \right) \sin\alpha \qquad \text{(A1)}$$

$$H''' \equiv \frac{L'''}{3N_{Ca}} = \frac{d^3(h/h_0)}{d(x/h_0)^3} \left(\frac{\sigma}{3\mu U_w} \right) \qquad \text{(A2)}$$

The B parameter was defined (for reasons suggested below) as

$$B \equiv \frac{1}{2} (H'')^2 + \beta H' \qquad \text{(A3)}$$

Note that B includes the flow properties of speed (U_w) and viscosity (μ) contained in the capillary number.

The B match method involves matching B values by

$$B_{SL} = B_{DL} \qquad \text{(A4)}$$

where

$$B_{SL} \doteq \lim_{R \to 0} B \text{ (static meniscus)} = \lim_{R \to 0} B_S \qquad \text{(A5)}$$

$$B_{DL} \doteq \lim_{R \to \infty} B \text{ (dynamic meniscus)} = \lim_{R \to \infty} B_D \qquad \text{(A6)}$$

The plug flow theory for angular withdrawal was originally derived by Deryagin and co-workers (*1*) for $\beta = 0$ using the B match method. To compare properties of the B match method with the C match method, the reported derivation (*1*) of the plug flow theory is briefly summarized below.

One probable reason for selecting B was based on the equation for static meniscus near the top which is

$$\frac{\sigma}{2\rho g} \left(\frac{d^2h}{dx^2} \right)^2 + \sin\alpha \left(\frac{dh}{dx} \right) = 1 - \cos\alpha \qquad \text{(A7)}$$

In nondimensional form, Equation (A7) became

$$\frac{1}{2} (H'')^2 + \beta H' = \frac{(1 - \cos\alpha)\, \beta}{(\sin\alpha)(3N_{Ca})^{1/3}} \qquad \text{(A8)}$$

Note that a flow parameter (N_{Ca}) has been introduced into the static meniscus equation by the change in variables.

The left-hand side of Equation (A8) was used to define the B parameter. Thus

$$B_S = \frac{(1 - \cos\alpha)\, \beta}{(\sin\alpha)(3N_{Ca})^{1/3}} = \frac{D_0^2\,(1 - \cos\alpha)}{(3N_{Ca})^{4/3}} \qquad \text{(A9)}$$

By taking the limiting value (at the top), the same function was obtained because (x/h_0) does not appear in Equation (A9).

$$B_{SL} = \lim_{R \to 0} B_S = \frac{D_0^2\,(1 - \cos\alpha)}{(3N_{Ca})^{4/3}} \qquad \text{(A10)}$$

One difference between the B_{SL} expression of Equation (A10) and the C_{SL} expression of Equation (15) is that flow quantities (N_{Ca}) have been introduced into B_{SL}.

Another probable reason for use of the B parameter is related to the Equation (13) dynamic meniscus equation, which was given by Deryagin as

$$H^3\,(H''' + \beta) = (H - 1) + \beta \qquad \text{(A11)}$$

Multiplying both sides of Equation (A11) by $H''\,dR$, Deryagin obtained

$$[H'''\ H'' + \beta H'']dR = \left[\frac{H - 1 + \beta}{H^3} \right] H''dR \qquad \text{(A12)}$$

or

$$\frac{1}{2} d\,[(H'')^2] + \beta d(H') = \left[\frac{H - 1 + \beta}{H^3} \right] H''dR \qquad \text{(A13)}$$

Integration of both sides of Equation (A13) from R of negative infinity $(-\infty)$ to an arbitrary point R^* led to two integrals, left (I_L) and right (I_R):

$$I_L = |B|_{-\infty}^{R^*} = B(R^*, \beta) \qquad \text{(A14)}$$

$$I_R = \int_{-\infty}^{R^*} \left[\frac{H - 1 + \beta}{H^3} \right] H''\,dR \qquad \text{(A15)}$$

Equating Equations (A14) and (A15), we get

$$B(R^*, \beta) = \int_{-\infty}^{R^*} \left[\frac{H - 1 + \beta}{H^3} \right] H''dR \qquad \text{(A16)}$$

Since the integrand of Equation (A16) vanishes as $R^* \to \infty$, then the limit of B exists for finite β, and

$$B_{DL}\,(\beta) = \lim_{R^* \to \infty} B(R^*, \beta) \qquad \text{(A17)}$$

Also, by definition

$$B_{DL}\,(\beta) = \lim_{H \to \infty} \left[\frac{1}{2} (H'')^2 + \beta(H') \right] \qquad \text{(A18)}$$

At this point, Deryagin assumed that $\beta = 0$. This is the same as neglecting gravity to obtain Equation (2) or assuming thickness and speeds (D_0 and N_{Ca}) are small. Thus

$$B_{DL} = \lim_{H \to \infty} \left[\frac{1}{2} (H'')^2 \right] = \int_{-\infty}^{+\infty} \frac{(H - 1)H''dR}{H^3} \qquad \text{(A19)}$$

where $H = 1$ for $R < 0$

By starting at the boundary condition of $H = 1$ at $R = 0$, as indicated by Equation (8), the value of B_{DL} is determined by numerical integration. Deryagin and Levi (*1*) report

$$B_{DL} = 0.204 \ldots \tag{A20}$$

Matching B_{DL} and B_{SL} by using Equations (A10) and (A20), we get

$$0.204\,(3N_{Ca})^{4/3} = D_0^2\,(1 - \cos\alpha) \tag{A21}$$

Rearrangement of Equation (A21) leads to the plug flow theory, which may be written as

$$N_{Ca} = \frac{D_0^{3/2}\,(1 - \cos\alpha)^{3/4}}{3(0.204)^{3/4}} \tag{A22}$$

There is a slight difference in constants between Equation (A22) and Equation (17) owing to the slight difference in results of numerical integration. The difference can be shown by evaluation of H''_{DL} from Equation (A19) and (A20). Thus

$$H''_{DL} = (2B_{DL})^{1/2} = (0.408)^{1/2} = 0.636$$

The comparable result used in Equations (12), (16), and (17) was the 0.642 value of White and Tallmadge (*8*). This 1% difference is not important for the discussion under consideration.

Comparison of the B value method with C value method indicates that:

1. The B value places flow parameters into the static term, whereas the C value does not.
2. The B value does not have a direct physical significance, whereas the C value signifies the curvature.
3. The B value is a complicated function of H'', whereas C is simply equal to L''.
4. The B value method appears to be longer and less direct.
5. The C value provides for an analytical but approximate expression for the effect of D_0 (or β).
6. The B value provides for an exact but numerical expression for the effect of D_0 without approximation.

The only apparent advantage of the B method is noted in reason 6. The C value method was selected for use in deriving Equation (16) mainly because an analytical solution (reason 5) was desired, but also in order to present the simpler and more direct derivation (reasons 1 and 4).

Zeroth-Order Reactions in Heterogeneous Catalysis

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The simultaneous zeroth-order reaction and diffusion in porous catalyst appeared in the classical paper of Wheeler (*1*). Successive influence of volume change on catalyst effectiveness has been discussed by Weekman and Gorring (*2*); selectivity under diffusion limitation has been reported by Van de Vusse (*3*), and effectiveness functions have been used to describe selectivity and poisoning (*4*). The zeroth-order reactions are special cases of power law kinetics (*5, 6*) and particular types of the Langmuir-Hinshelwood reactions, the treatment of which, in presence of diffusion limitation, has been given by Roberts and Satterfield (*7*).

In the cited references the diffusion during reaction is characterized by an experimentally determined diffusivity, or a simple pore structure is assumed (single-pore model). This model (*8, 9*) has been extended by Mingle and Smith (*10*) and Carberry (*11, 12*) to a more complex model (macro-micropore model) representing catalyst pills containing macropores created via pelletting of porous microspheres. The last may be visualized by a cylindrical pore (macropore) from which micropores branch along the length and at right angle to the macropore; Knudsen diffusion and molecular diffusion may be considered prevailing in the micropores and in the macropore, respectively. The macro-micropore effectiveness factor has been derived for isothermal irreversible and reversible first-order reactions (*10, 11*) and irreversible second-order reactions (*13*). In the last case, a generalized Thiele modulus has been introduced by which the functions effectiveness factor vs. Thiele modulus follow one another very closely.

The present paper pertains to the problem of reaction and diffusion for a zeroth-order kinetic law in the macro-micropore model. The derivations that follow are based upon the following assumptions:

1. The catalyst pellet is at uniform temperature.
2. The irreversible zeroth-order reaction occurs without volume change.
3. Significant reaction occurs only in the micropores; that is, the surface of the macropore is assumed entirely covered by micropores.

CATALYTIC EFFECTIVENESS

The controlling regime for zeroth-order reactions may be assumed as chemical if the effectiveness factor η_0 is unity; it happens for values of the micropore diffusion-reaction/modulus along the macropore length that

$$\mu \equiv \left[\frac{2\,K_0 C^{-1}}{r\,D}\right]^{1/2} \quad l < \sqrt{2}.$$

On the other hand, the strong pore diffusion regime occurs when the reactant concentration drops to zero at the micropore and macropore end. In these conditions, because the micropore effectiveness factor is $\sqrt{2}/\mu$, and the number of micropores per unit area of macropore wall is $1/\pi r^2$, a balance over the macropore gives

$$\frac{d^2y}{d\rho^2} = 2\sqrt{2}\; m_0\; \theta^2\; y^{1/2} \tag{1}$$

or

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