Modeling Dynamic Contact Line Motion for Partially-Wetting Systems

L. W. Schwartz

Department of Mechanical Engineering
University of Delaware, Newark, DE 19716

Presented at the 15th International Coating Science and Technology Symposium, September 13-15, 2010, St. Paul, MN*

Unsteady numerical modeling of the Landau-Levich plate withdrawal problem is presented. A disjoining-conjoining term is included in the evolution equation to simulate a lack of perfect wetting. Depending on the speed of withdrawal and the equilibrium contact angle, computed results show that various regimes are possible, as can be commonly observed in industrial practice. For very slow withdrawal, the meniscus will meet the plate at close to the static contact angle and the withdrawn plate will be dry. There is a somewhat faster range of speeds for which the calculated dynamic (receding) contact angle will be reduced from the static value, while the plate still remains dry. The extent of this ”hysteresis” region depends on the degree of imperfection of the substrate. Physically rough and chemically comtaminated substrates are both considered. At higher speeds, the plate will be withdrawn with a wet coating layer whose thickness is close to the Landau-Levich prediction. Depending on the nature of the intermolecular forces, the liquid layer may subsequently break up into discrete droplets before it dries.

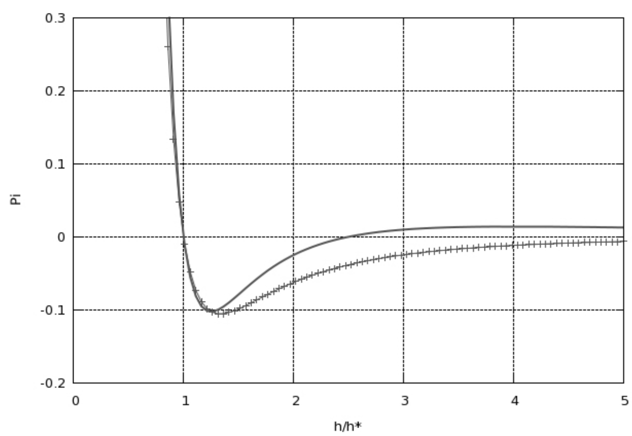
We explore effects of finite contact angle on the bath withdrawal problem. Here, for simplicity, only two-dimensional simulations are presented. For liquids with good wetting properties, e.g. machine oil on steel, minor imperfections in the substrate will not change flow behavior in dip coating. For poor-wetting liquids, that is liquids that want to“ball up,” imperfections will have a strong effect on flow.

We consider a substrate moving upward, out of a liquid bath, at constant speed U (in the $+x$ direction). An evolution equation for the wetting film thickness $h(x, y, t)$ is

$$h_t = -Uh_x - \frac{\sigma}{3\mu}\nabla \cdot \left[h^3 \left(\nabla\nabla^2 h\right)\right] + \frac{\sigma}{3\mu}\nabla \cdot \left[F(x, y)\Pi\right] \ . \quad (1)$$

Had gravity drainage back into the bath been considered as well, a term $\frac{\rho g}{3\mu}(h^3)_x$ would need to be appended on the right side of (1). For a plate that is being withdrawn continuously, gravity drainage is less important than the effects retained. The first of the three terms on the right of (1) is the time rate of change of the coating thickness due to the plate motion at speed U. The next term represents the effect of surface tension σ. The last term represents so-called “disjoining pressure” which contains wettability, or static-contact-angle, information. The function $F(x, y)$ allows for the

*Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.



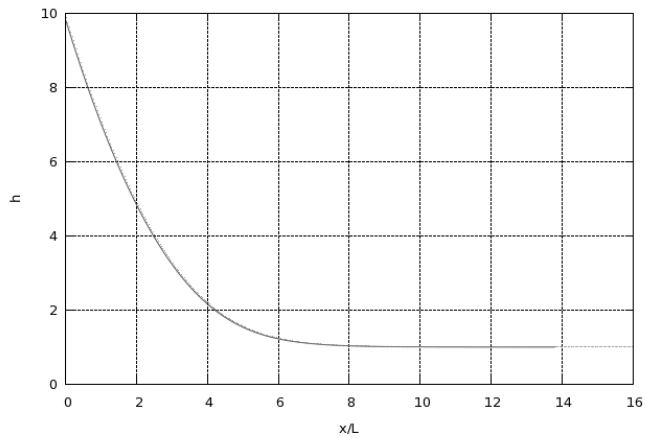


Figure 1 (left): Two disjoining pressure functions as explained in the text. Symbols correspond to $C = 0$ in equation (2) while the solid curve is for $C = 0.4$.
Figure 2 (right): To validate the unsteady time marching solution, we compare the long-time solution, after reaching steady-state, with the solution of Landau-Levich differential equation. The unsteady problem is solved as a two-point boundary value problem using an implicit time-marching method. The Landau-Levich equation is solved by a shooting method. The solutions are seen to be identical.

possibility that the contact angle may vary from place to place on the substrate which is the (x, y) plane. For a uniform substrate $F = 1$. Subscripts in equation (1) signify partial differentiation. The symbol ∇ is the gradient operator with respect to the substrate position coordinates x and y.

The characteristic thickness scale for disjoining pressure Π is h_* and we use the five-parameter model

$$\Pi(h; h_*) = B_1 \left[\left(\frac{h_*}{h}\right)^{N-1} - \left(\frac{h_*}{h}\right)^{M-1} \right] \left(\frac{h_*}{h} - C\right) \tag{2}$$

where $B_1 \geq 0,\ N > M > 1,\ h_* > 0,\ 0 \leq C < 1$. Mathematically, a repulsive pressure ($\Pi > 0$) is developed for $h < h_*$. h_* can be though of as a slip-layer thickness that allows contact line motion on a solid substrate without violating the no-slip condition. For $h > h_*$ the disjoining pressure is attractive ($\Pi < 0$). This makes it possible to assign a value to the equilibrium contact angle θ_e using energetic considerations. While the disjoining effect becomes negligible for $h >> h_*$, it can be preferable to make Π repulsive again in the large h limit. This can be accomplished by using a positive value of the constant C in Eqn (2). The two cases, $C = 0$ and $C > 0$, correspond to the two basic types of Π functions shown schematically in Teletzke et al (*Chem. Eng. Comm.* 1987). Sample disjoining pressure functions are shown in Fig. 1. Setting the parameter B_1 equal to zero will remove the disjoining effect entirely.

The model becomes more transparent if we assume a uniform substrate and take a specific set of values for the parameters. With $F = 1$, $C = 0$ and $(N, M) = (4, 3)$, equation (1) becomes

$$h_t = -Uh_x - \frac{\sigma}{3\mu}\nabla \cdot \left[h^3 \left(\nabla\nabla^2 h + 3\,\theta_e^2\,h_*^2\,\left[\frac{3}{h^4} - \frac{4h_*}{h^5}\right]\nabla h\right)\right]\,. \tag{3}$$

The relationship between B_1 and the equilibrium or static contact angle θ_e may be found in Schwartz (*Langmuir*, 1998). Some additional insight is gained by writing the equation in dimensionless form. Let the characteristic substrate length and time units be

$$L = h_0 \left(\frac{\sigma}{3\mu U}\right)^{1/3}\ , \quad T^* = L/U. \tag{4}$$

The characteristic coating thickness is h_0, the thickness predicted by Landau-Levich theory for a plate pulled out of a bath at speed U. (See Levich, V., *Physiochemical Hydrodynamics*, Prentice-Hall, 1962). Assuming perfect wetting, the result is

$$h_0 = 0.643 R_0 \left(\frac{3\mu U}{\sigma}\right)^{2/3} \quad \text{where} \;\; R_0 = \sqrt{\frac{\sigma}{2\rho g}}$$

is the radius of curvature of a static meniscus on a vertical plate. The steady-state solution satisfies a third-order nonlinear ordinary differential equation. It may be solved by a shooting method, as described by Tuck & Schwartz (*SIAM Review*, 1990).

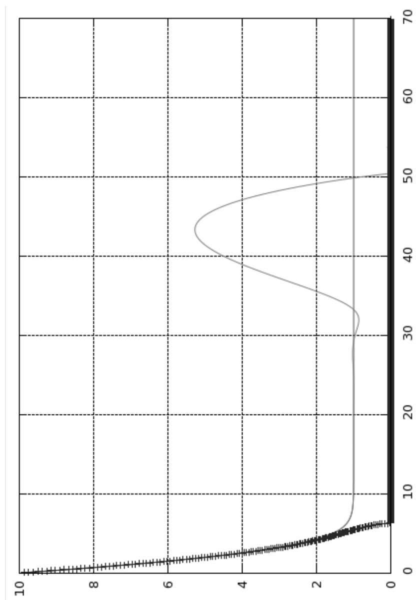
For an assumed two-dimensional flow, ∇ becomes simply $\partial/\partial x$, and the dimensionless form of equation (3), is then

$$h_t = -h_x - (h^3 h_{xxx})_x - K\left[h^3\left(\frac{3}{h^4} - \frac{4h_*}{h^5}\right)h_x\right]_x\ . \tag{5}$$

This equation is solved numerically subject to an essentially arbitrary initial condition; there are also two boundary conditions at each end of the computational domain. The layer thickness and slope are prescribed at the left or bath side. At the right, or thin film side, the slope and third derivative h_{xxx} are taken to be zero. The input constant K controls the equilibrium contact angle effect. This single dimensionless parameter, which is

$$K = \frac{h_*^2}{3^{1/3}}\,\left(\frac{\sigma}{\mu U}\right)^{4/3}\,\theta_e^2\ , \tag{6}$$

determines whether the contact angle is small enough, or the plate speed U is great enough, for the



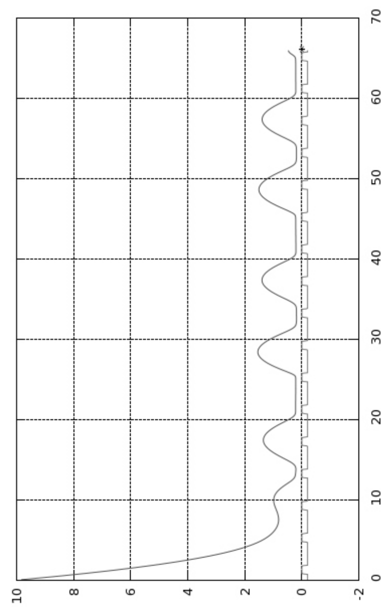


Figure 3(left): Demonstration of critical wetting condition for the pulled plate. The coefficient $K = 1.65\text{x}10^{-3}$ for the non-wetting case (symbols). Reducing K to $1.6\text{x}10^{-3}$ allows wetting. For that value, profiles are shown at t/T^* = 70 (large hump) and t/T^* = 200 (uniform coating).
Figure 4 (right): A corrugated or roughened plate is pulled from a bath. A frame from the unsteady solution. The film has broken into a pattern of drops.

moving plate to be successfully coated.

Figure 2 compares the steady shooting method solution with the long-time result of solving equation (5) with K = 0. They are seen to be identical, thus providing validation for the unsteady algorithm. The existence of a critical speed for coating is demonstrated in Figure 3. When K is larger than a critical value, the meniscus is only deformed by the moving plate; the liquid meniscus will slip along the plate and the withdrawn plate will not be wetted. For a slightly smaller K value, the liquid first forms a large "hump"; then the coating film is drawn upward until the hump passes out of the top of the computational window.

Non-planar substrates can also be treated by the model. The quantity h^3 is replaced by $(h - h_{ss})^3$ wherever it appears on the right of Equation (5). $h_{ss}(x)$ is the input function giving the shape of the substrate. A frame from a computation of a corrugated plate being drawn from a bath is shown in Figure 4. Here the contact angle is sufficiently small that the meniscus is pulled up the plate. However, because the contact angle is large enough, the drawn liquid film breaks up into a pattern of isolated droplets. A pattern of contamination, rather than roughness, can be modeled in a similar way. The function $F(x, y)$ in equation (1) can be used to simulate high-contact-angle "greasy" patches, for example. Generally speaking, contamination acts analogously to roughness.