Modeling and Simulation of Dynamic Wetting

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We present a mathematical model for the slow three-dimensional motion of a liquid coating on a substrate with wetting and de-wetting edges. Equilibrium contact angle θ_e is considered to be a material property of the liquid-substrate system. Substrate chemical heterogeneity, or physical roughness may also be an important determinant of edge motion. Conversely, dynamic contact angle information is not required by the model. It is predicted as part of the solution. Calculated results are compared with experimental observation.

The lubrication approximation can be invoked to find an unsteady evolution equation for a number of coating flow problems. Provided that the inclination of liquid boundaries, Reynolds number $\rho U h/\mu$, and capillary number $\mu U/\sigma$ are all sufficiently small, quantitative accuracy can be maintained. A representative equation is

$$h_t = -\nabla \cdot \frac{\sigma h^3}{3\mu}\left(\nabla\nabla^2 h - \frac{\rho g}{\sigma}\nabla h + (1/\sigma)\,\nabla\Pi\right) - \frac{h^2}{2\mu}\,\nabla\cdot\tau - \frac{\rho\omega^2}{3\mu}\,\nabla\cdot(rh^3\mathbf{e_r}) \qquad (1)$$

Here h is the liquid film thickness, t is time and ∇ is a two-dimensional operator in the substrate coordinates. The terms on the right represent the effects of surface tension, gravity, "disjoining pressure," shear stress, and centrifugal force. Not all terms need be present in any given problem, and there are sometimes other effects that require inclusion. Π may take on a number of functional forms. However the associated local energy density, given by $\Pi = de/dh$, should have a local minimum for $h = h^*$. h^* is a "slip thickness" that is required because of the impossibility of moving a contact line without violating the no-slip condition. One choice is

$$\Pi = B\left[\left(\frac{h^*}{h}\right)^n - \left(\frac{h^*}{h}\right)^m\right], \quad (n > m > 1)$$

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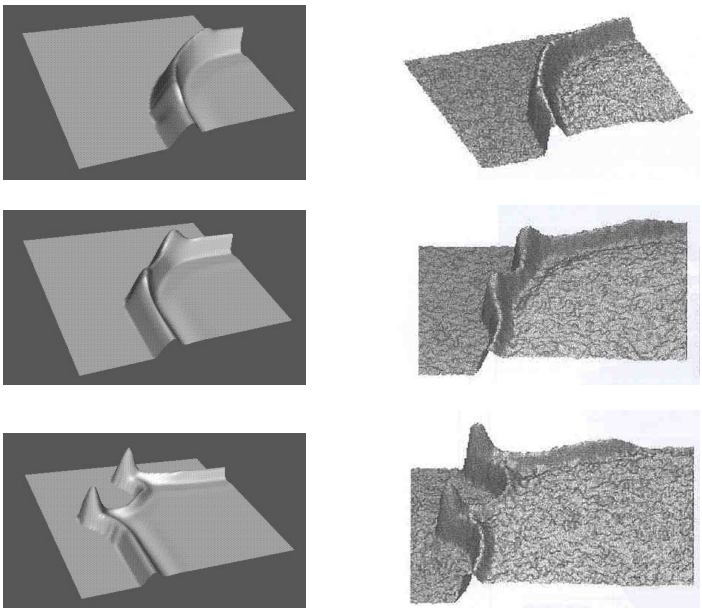

Figure 1: A comparison of simulation results for spincoating (left) with experimental pictures (right, courtesy Philips). Both show the development of the characteristic "wall and tower" structure. The center of rotation is near the lower right corner for each picture. The interval between frames is about 0.1 sec. Only one-quarter of an assumed four-fold symmetric pattern is calculated in the simulation. [Schwartz & Roy, Phys. Fluids 2004.]

where B prescribes θ_e, or can prescribe $\theta_e(x, y)$ for a heterogeneous substrate.

The evolution equation (1) is equivalent to the energy equation

$$\dot{E}_\mu = -\frac{d}{dt} E_{stored} \tag{2}$$

where E_{stored} includes integrated interfacial and other potential energy components. There is also a principle that, in slow motion, the system will take the "path of least resistance," subject to specific problem constraints. This is the cause of a variety of pattern-forming instabilities. The four figures show frames from simulations, compared with experimental pictures.

We believe it is remarkable that such a relatively simple theory can predict a wide variety of complicated results. Thus, according to "Occam's Razor," [†] this model should be preferred. Conversely, some workers use, *ab initio*, an algorithm of the form

$$U = f(\theta_d; \theta_e) \tag{3}$$

[†]Mediaeval philosopher William of Occam stated that "one should not increase, beyond what is necessary, the number of entities required to explain anything."

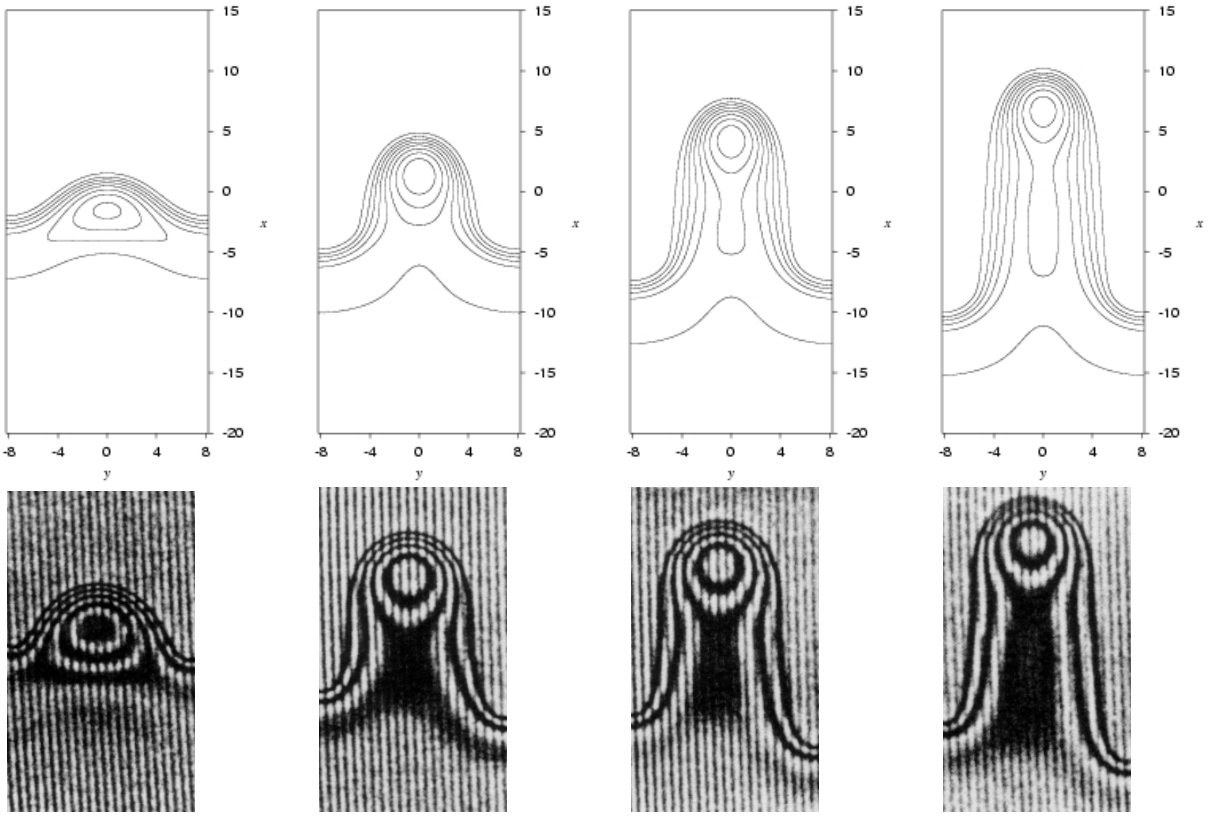

Figure 2: Thermal gradient causes fingering rise on a vertical metal plate in a liquid bath. Interferometric pictures from Cazabat *et al*, Adv. Coll. Interf. Sci., 1992. Model calculations from Eres *et al*, Phys. Fluids, 2000.

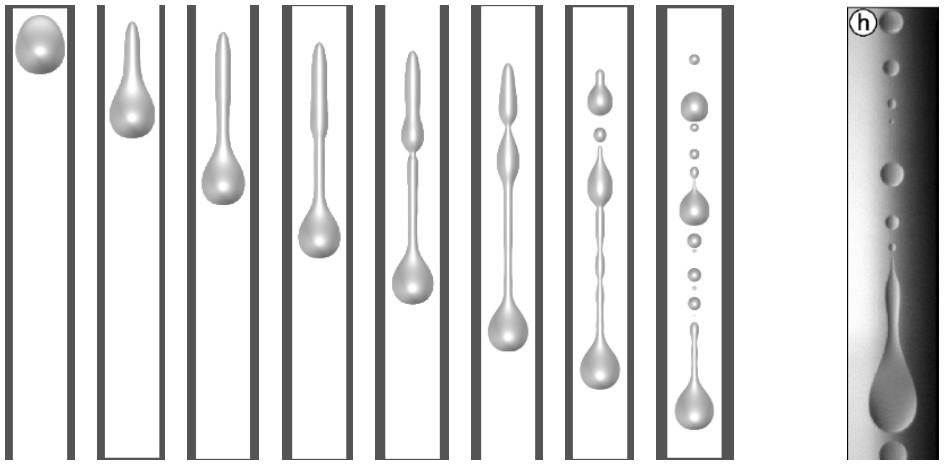

Figure 3: A draining drop on a window pane showing the complicated break-up pattern. Simulation: Schwartz *et al*, Physica D, 2005, Experiment: Podgorski *et al*, Phys. Rev. Lett., 2001. Interestingly, these apparently complicated patterns are really highly structured. A simplified theory yields a single control parameter

$$G_p = \frac{2\rho g}{\sigma}\left(\frac{4V}{\pi}\right)^{2/3}\frac{1}{\theta_e^{5/3}}$$

where V is the drop volume.

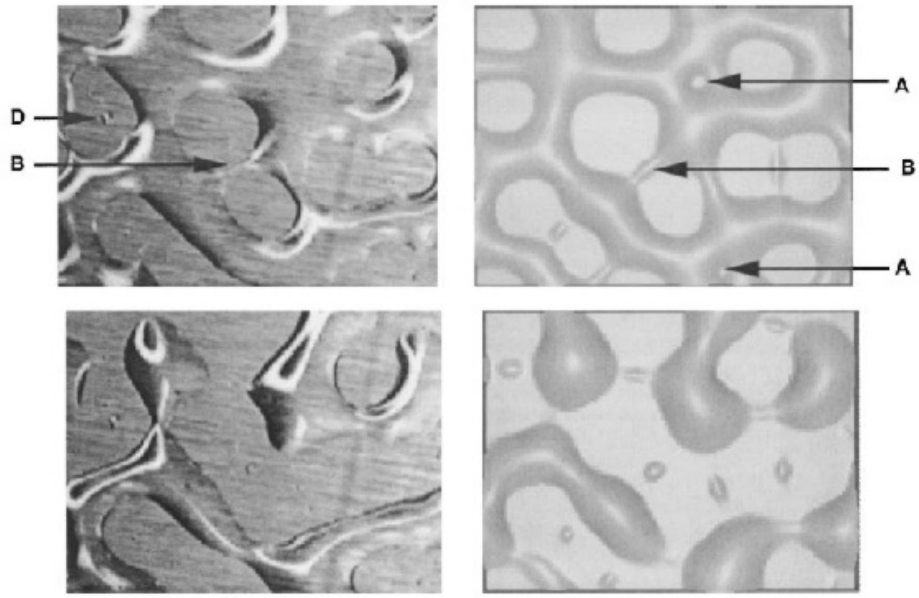

Figure 4: Break up of an originally continuous, liquid film, similar to a water film on a waxed car. Experimental micrographs and simulation from Schwartz *et al*, (JCIS 2001). The detailed patterning is caused by a few easily observed substrate defects.

where U is the local normal speed at the wetting line and θ_d is the dynamic contact angle. While it is usually true that $\theta_d > \theta_e$ when $U > 0$ and $\theta_d < \theta_e$ when $U < 0$, it can be argued that no such local relationship should be a postulate of a physical model of wetting, for a variety of reasons:
(i) Consider two *forced* spreading processes: spin coating driven by centrifugal force and metered gravitational flow of a uniform coating layer onto an inclined wall. In either case, the speed of frontal advance is essentially determined by forces that are remote from the moving front, e.g. drop volume and spin speed in the first case, and volumetric flow rate and gravity in the second. Equation (3) can be made dimensionally correct only by specifying length and time scales. These scales will depend on the remote driving mechanisms which are quite different in the two cases.
(ii) The equations of fluid mechanics that govern the motion of coating liquids are *elliptic* in character. Thus the dynamic angle at any point will be influenced by motions, boundaries, etc. that are remote from that point.
(iii) Even the static contact angle requires careful definition. The equilibrium contact angle θ_e must be determined from, say, a sessile axisymmetric droplet on a uniform horizontal substrate. Equation (3) implies that the static angle must be unique if the droplet is not moving. This is not true for a droplet that is held stationary on a dirty or cracked window. The minimum energy configuration will have many contact angle values on the same substrate.