Analysis of Spin Coating for Non-Ideal Conditions

L. W. Schwartz

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

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Spin coating is a technique that uses centrifugal force to apply a uniform liquid coating layer to silicon wafers, LCD displays, eyeglass blanks, etc. For a perfectly horizontal substrate and a perfectly wetting Newtonian liquid, the governing equations accept a simple spatially- uniform coating whose thickness decreases with time; this is usually the desired solution. The process is subject to various instabilities and flows with liquid fingers can result, as observed experimentally and modeled numerically by our group. Here we will extend our work to include generalized Newtonian rheology, curved substrates, and gross misalignment of the initial coating deposition.

The lubrication approximation can be invoked to find an unsteady evolution equation for simulation of spin coating. 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. For a Newtonian coating, the equation is

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

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," and centrifugal force. Π is taken to be

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

where B prescribes the static or equilibrium contact angle θ_e and h^* is a "slip thickness" that is required because of the impossibility of moving a contact line without violating the no-slip condition. A number of solutions to spin coating problems, showing fingering patterns and good agreement with experiment, can be found in Schwartz & Roy [Physics of Fluids, 2004].

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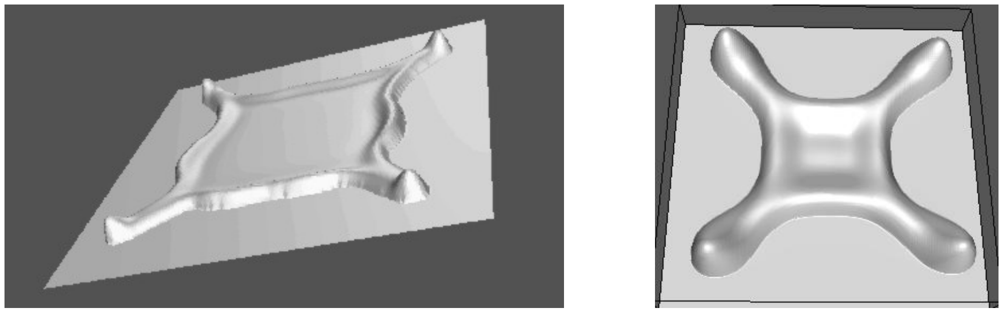

Figure 1: Rendered pictures of a Newtonian finger pattern compared with a strongly shear thinning case.

Many coatings are not simple liquids and exhibit non-Newtonian behavior where the viscosity depends on the stress experienced by each fluid element. An Ellis model can incorporate this effect. The Ellis viscosity law is

$$\mu = \frac{\mu^*}{1 + \left(\frac{\tau}{\tau_{1/2}}\right)^\alpha} \tag{2}$$

For an Ellis liquid, the quantity $h^3/(3\mu)$ that appears in each term on the right of Eqn. 1 is replaced by the "fluidity"

$$F \equiv \frac{h^3}{3\mu^*}\left[1 + K\left(\frac{r}{R_0}\right)^\alpha \left(\frac{h}{h_0}\right)^\alpha\right], \qquad K = \frac{3}{3+\alpha}\left(\frac{\rho\omega^2 R_0 h_0}{\tau_{1/2}}\right)^\alpha \tag{3}$$

where only the dominant stress component, due to rotation, is considered. R_0 and h_0 are the base radius and central height of the initial, assumed paraboloidal, drop. They are found from the given drop volume and static contact angle.

Figure 1 compares the Newtonian finger pattern with a strong shear thinning case. Parameter values are α = 1, K = 5. Unlike the Newtonian case which shows a large uniform coated region and small fingers, the Ellis case shows a very small flattened area near the center and large bulbous fingers.

Figure 2 shows four frames each from a coating experiment and the corresponding simulation, with gross misalignment of the initial drop. In both cases, the results have been "de-rotated." A droplet placed off-center will drift outward; by virtue of the nonlinearity in the equations, this asymmetry will also lead to early fingering.

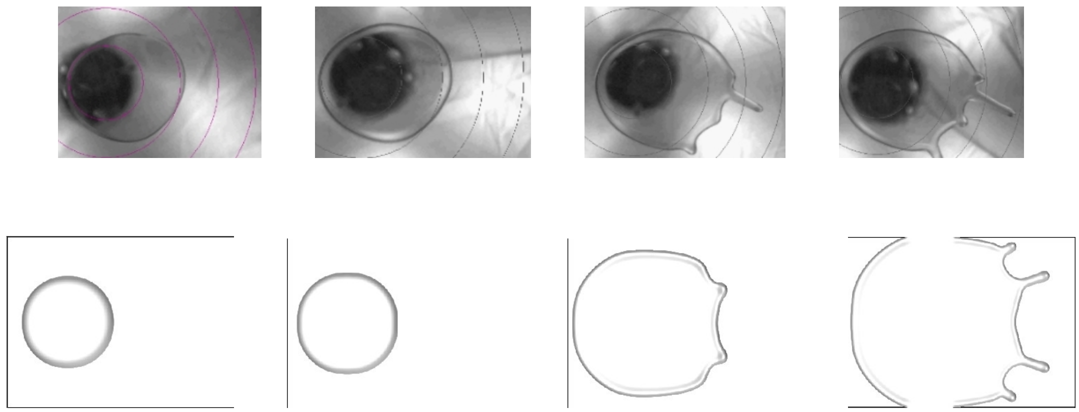

Figure 2: Early fingering caused by gross misalignment of initial drop in spin coating; experiment and simulation. Newtonian liquid is assumed in the simulation.

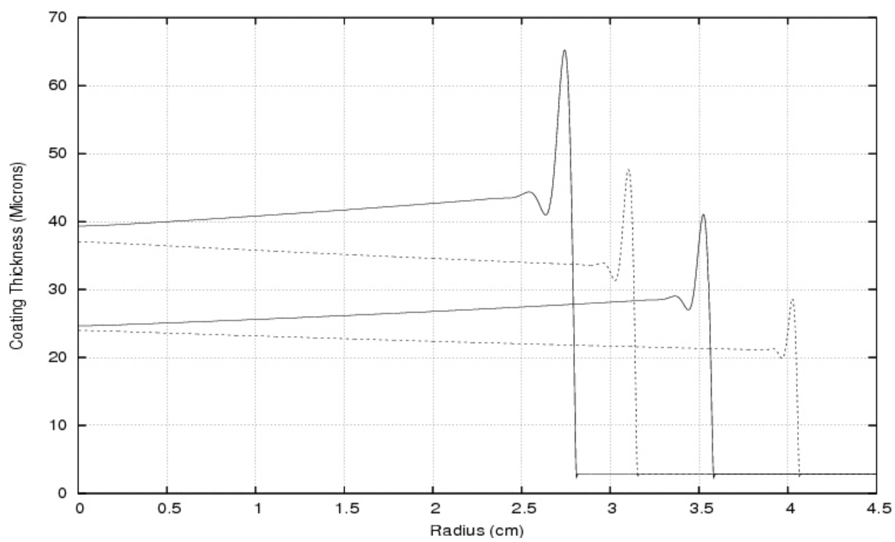

Figure 3: Calculated spin coating thickness profiles for optical lenses at two times. The rotation rate is 500 rpm, the viscosity is 2 centipoise, and the liquid volume is 0.1 ml. Results are shown for a a convex (solid) and a concave lens (dashed) at 0.4 sec and 1.0 seconds after the start of spinning. The lens radius of curvature is 16.5 cm, corresponding to an optical “strength” of 3 diopters.

For a convex optical lens, magnification is measured in diopters D which is given approximately by

$$D = \frac{n-1}{R_L}$$

where n is the index of refraction and R_L is the radius of curvature of the lens, measured in meters. Computed coating profiles for convex and concave lenses are compared in Fig. 3. Axisymmetric flow is assumed. The simulation considers only the dominant effect arising from the surface normal component of centrifugal force. One additional term is added to the evolution equation (1):

$$h_t \leftarrow \frac{1}{2}\frac{\rho\omega^2}{\mu r R_L}\frac{\partial}{\partial r}\left(h^3 r^3\right) \qquad (4).$$

It may be seen that spin coating at constant speed will not yield uniform thickness coatings for nonplanar substrates. For a lens blank of 3.5 cm radius and parameter values given in the figure caption, the difference between central and edge thicknesses is about 10 per cent. For a convex lens, the coating is thicker at the edge. For very thin coatings this nonuniformity can result in undesirable visible interference fringes. Results shown in the figure are largely independent of rotation rate and the physical properties of the coating.

In Fig. 3, the entire coating volume was deposited before the start of the spinning. It is possible to continue deposition after spinning starts. Fig. 4 shows a coating profile at 2 seconds after starting. A small quantity of the coating (5 %) was retained and deposited during the first second of spin. The profile (solid) is compared with the result when all the material is deposited before the start (dashed). The figure demonstrates that deposition history can affect the coating shape and that careful control may yield more uniform profiles.

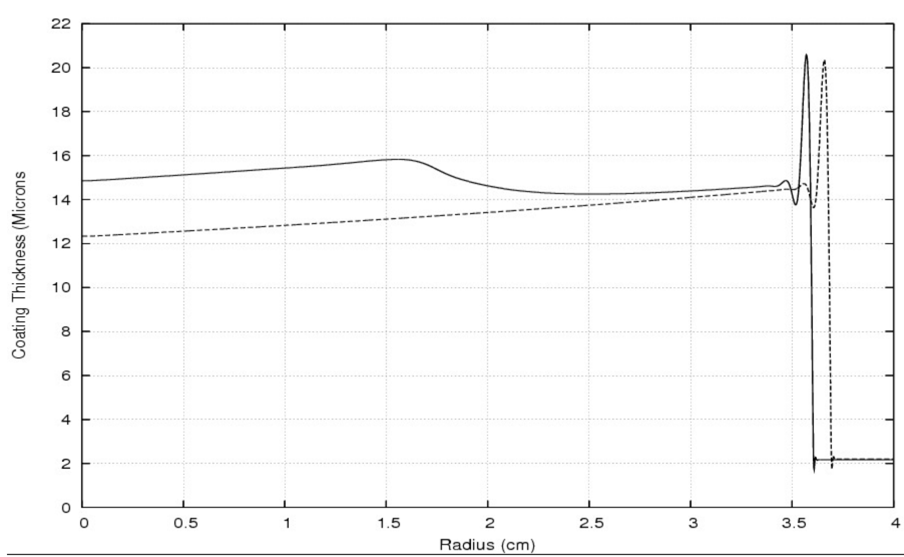

Figure 4: Two axisymmetric spin coating profiles. The dashed profile has 5 % of the coating deposited after the start of the motion. Liquid volume is 0.05 ml; the rotation rate is 700 rpm. Other parameter values are the same as for the previous case.