We consider the deposition of a film of viscous liquid on a flat plate being withdrawn from a bath, experimentally and theoretically. For any plate speed \( U \), there is a range of “thick” film solutions whose thickness scales like \( U^{1/2} \) for small \( U \). These solutions are realized for a partially wetting liquid, while for a perfectly wetting liquid the classical Landau-Levich-Derjaguin film is observed, whose thickness scales like \( U^{2/3} \). The thick film is distinguished from the Landau-Levich-Derjaguin film by a dip in its spatial profile at the transition to the bath. We calculate the phase diagram for the existence of stationary film solutions as well as the film profiles and find excellent agreement with experiment.

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When a solid object is pulled out of a liquid reservoir, a thin layer of liquid is entrained by viscous drag (Fig. 1). This principle is used widely in coating technology, where it is known as dip coating, because it is one of the simplest ways to deposit a thin film of liquid on a substrate [1]. According to the pioneering work of Landau and Levich [2] and Derjaguin [3] (LLD), a film of unique thickness \( h_{\text{LLD}} \) is selected by the speed of withdrawal \( U \). The LLD solution has remained the basis of coating theory for more than 60 years, having been generalized to include the effects of inertia [4,5], deposition on curved substrates [6], and non-Newtonian fluids [7]. The relative size of viscous drag and capillary retention in the film is measured by the capillary number \( \text{Ca} = U \eta / \gamma \), where \( \eta \) is the viscosity and \( \gamma \) the surface tension. At the foot of the film, LLD introduced the requirement that the film be matched smoothly to a static capillary meniscus (see Fig. 1), whose size is controlled by the capillary length \( \ell_c = \sqrt{\gamma \rho g} \). In the limit of small \( \text{Ca} \), this matching yields \( h_{\text{LLD}} = 0.946 \ell_c \text{Ca}^{2/3} \), which gives the small-\( \text{Ca} \) behavior of the LLD line in the phase diagram; cf. Fig. 2.

In this Letter, we show that at a given speed there exists another, thicker film in addition to the LLD film (cf. Figs. 1 and 2). These new solutions do not match smoothly to the bath but exhibit a bump at the foot of the film [cf. Fig. 1(c)]. As we will explain in more detail below, experimentally the thick solutions are most easily produced for partially wetting fluids just above the critical plate speed \( \text{Ca}_f \) at which a film begins to be deposited [8]. Our theoretical analysis, however, is for the long-time limit only, in which the plate is covered completely by a film. Any solution is therefore characterized by a pair \( (h_f, \text{Ca}) \), where \( h_f \) is the thickness expressed in terms of the capillary length \( \ell_c \), as shown in Fig. 2.

A striking feature of the new solutions is that they cover a continuous range of thickness \( h_f \) (Fig. 2, gray area). Each of these solutions entrains a different amount of liquid flux \( q \), representing the volume of liquid withdrawn from the bath per unit time and unit plate length. Clearly, this flux is limited by the flow through the narrow dimple. Below, we compute the maximum possible flux through the dimple and show how this provides a lower bound on \( h_f \) (Fig. 2). For larger \( h_f \), draining due to gravity becomes increasingly important, so at the upper bound (Fig. 2, dashed line) the flux vanishes. Above the dashed line, no solutions are possible, unless the film is alimented from above.

FIG. 1 (color online). Fluid films being deposited on a plate withdrawn from a bath of viscous liquid; symbols are experimental measurements of the film profile at successive times. (a) Schematic of the experiment. (b) The fluid wets the plate and deposits a LLD film \( \text{Ca} = 9.27 \times 10^{-2} \); the solid line is the classical LLD solution, which predicts a thickness of \( 57 \mu m \). (c) The plate is treated such that the fluid wets partially and deposits a thick film \( \text{Ca} = 8.05 \times 10^{-2} \); the solid line is the result of our theory fitted to the experimental thickness of \( 198 \mu m \).
FIG. 2 (color online). Phase diagram of stationary solutions in the parameter space \((h_f, Ca)\), where \(h_f\) is the film thickness expressed in \(\ell_c\). The dimple solutions exist in the light gray region, but only those in the dark region actually entrain liquid from the bath. The dotted line shows the Landau-Levich solution. The open symbols are for a partial wetting situation and the full symbols for complete wetting; error bars are below the size of the symbols. The two round symbols correspond to the two measurements shown in Fig. 1. The arrows show the experimental path as the speed is slowly increased starting from the dashed (red) line.

In our theoretical analysis we rescale all lengths by the capillary length \(\ell_c\). The interface profile is analyzed using the lubrication equation \([9]\) for free surface flows \([10]\):

\[
\kappa' - 1 + \frac{3}{h^2} \left( Ca - \frac{q}{h} \right) = 0. \tag{1}
\]

Here \(h(z)\) is the interface thickness, \(\kappa\) the interface curvature, and \(q\) the flow rate. The three terms correspond to the capillary pressure, gravity, and viscous effects, respectively. For steady solutions, considered here, \(q\) is constant along the plate. Film solutions become asymptotically flat (\(\kappa = 0\)), so that the flux can be related to the film thickness \(h_f\) as

\[
q = h_f \left( Ca - \frac{h_f^3}{3} \right). \tag{2}
\]

Crucially, \(q\) exhibits a nonmonotonic dependence on \(h_f\), owing to gravitational draining [Fig. 3(b)]. For small \(h_f\), the fluid velocity is uniform across the layer and equals the plate velocity, yielding a (dimensionless) flux \(h_f Ca\). For larger thickness, gravity induces draining inside the film, which can even reverse the direction of liquid transport: \(q < 0\) corresponds to transport from the film into the reservoir. As a consequence, the same flow rate \(q\) can be supported by two very different thicknesses of the film. This is why, physically, the thin “dimple” region can be matched to the much thicker film (Fig. 3).

The interface structure in the dimple region results from a balance between viscosity and surface tension. To describe the profile near the dimple position \(z_d\), we therefore look for a similarity solution of (1):

\[
h = Ca^{2/3} H(\xi), \quad \xi = (z - z_d)/Ca^{1/3}. \tag{3}\]

Following LLD, this solution has the additional property that the curvature \(H'\) remains finite in the limit of small \(Ca\), which we are analyzing. This ensures that (3) can be matched to the capillary meniscus of the bath, which has a constant curvature of \(\sqrt{2}\) \([11]\), so the boundary condition in the limit \(\xi \to -\infty\) is \(H'_{\infty} = \sqrt{2}\). Defining \(Q = \frac{q}{Ca^{-5/3}}\), one obtains the equation for the dimple:

\[
H''' + \frac{3}{H^2} \left( 1 - \frac{Q}{H} \right) = 0. \tag{4}\]

So far, (4) is the same as for the LLD solution, but the boundary condition toward the flat film region will be less restrictive, so we are able to produce additional solutions. In that region, the curvature becomes small, giving the condition \(H''_{\infty} = 0\). In the following discussion, we will justify this condition in more detail.

Figure 4 shows that there is a one-parameter family of solutions \(H(\xi)\), each corresponding to a different value of \(Q\) and forming a dimple that matches the thick film to the static bath. The case \(Q = 0\) can be solved analytically \([12]\), while the others have been obtained numerically. We identified a maximum value \(Q_{\text{max}} \approx 1.376\), above which the boundary conditions can no longer be satisfied. Note that the LLD film is a particular solution of (4) for which \(H\) approaches a constant value rather than shooting back upwards (dotted line).

The final step is to relate the flux through the dimple to the film thickness \(h_f\) at a large distance from the reservoir. Just before \(q(h_f)\) changes sign, it becomes small enough to match the flux in the dimple (cf. Fig. 3). For a small enough capillary number, (2) can be solved to give
Experimental methods.—In our experiment, a silicon wafer is withdrawn vertically from a bath of silicone oil (viscosity \( \eta = 4.95 \text{ Pa s} \), surface tension \( \gamma = 0.0203 \text{ N m}^{-1} \), density \( \rho = 970 \text{ kg m}^{-3} \), and molecular size 70 nm) by a step motor. The silicon wafer is totally wetted by the silicone oil. When coated with the fluorinated surfactant FC725, partial wetting conditions are obtained. Depending on the protocol, the contact angle lies between 48° and 55°, with an hysteresis of 5°. The film thickness \( h_f \) is measured by spectrometry. A reflection probe made of a tight bundle of six illumination fibers around one read fiber is placed at 5 mm from the plate. It is connected to a tungsten halogen light source and to a diffraction-grating spectrometer resolving visible and near-infrared wavelengths. The relative resolution, limited by the entrance slit and the size of the photosensitive elements, is around 0.25 nm. A 3648-element linear CCD-array detector measures the intensity as a function of the wavelength \( \lambda \), averaged over 4 s. Defects of the CCD are calibrated in the absence of film and corrected to improve the signal-to-noise ratio. Once a film is present, the spectrum contains oscillations of the form \( \cos(4\pi n h_f/\lambda) \), where \( n = 1.4034 \) is the refractive index of silicone oil. By fitting the spectrum, the thickness \( h_f \) can be measured to within 0.2% up to a thickness of 240 \( \mu \text{m} \) (cf. Fig. 5).

The spatial profile of the entrained film is measured by placing a 200 \( \mu \text{m} \) wire at a distance \( d = 14 \pm 1 \text{ mm} \) from the silicon wafer. The mirror image of the wire (reflected in the silicon plate) is distorted by refraction through the liquid-vapor interface of local slope \( h' \), making the system equivalent to a wire placed at a distance \( d \) behind a prism of (small) angle \( 2h' \). At small angles, the rays are thus deflected by an angle \( 2(n-1)h' \) in the direction of steepest slope, independent of the incident angle. Hence the mirror image of the wire is vertically displaced by a distance \( 2(n-1)dh' \). The wire is imaged with a 2048 \( \times \) 2048 CCD camera, fitted with a 60 mm macro lens. The position of the wire image is determined by image intercorrelation, achieving subpixel resolution.

We have calibrated the relation between the displacement and the local interface slope by two independent methods. First, we have replaced the oil film by optical glass prisms \( (n = 1.52) \) of angle 1°, 2°, 3°, and 4°. We obtain a resolution of 950 \( \pm \) 30 pixels per unit slope (16.5 pixels/degree), once the index difference between oil and glass is taken into account. Second, using the step motor, we have determined an image resolution of 11.7 \( \mu \text{m/pixel} \), which leads to 970 \( \pm \) 70 pixels per unit slope. In summary, the displacement of the image of the wire gives the local interface slope from which we reconstruct the film profile, by integration. The constant of integration is fixed in the flat region of the film, using the value of \( h_f \) measured by spectrometry. There are two sources of error in the final reconstruction: an absolute
FIG. 5. Measurement of the film thickness by spectroscopy. The free charge carriers produced by photon absorption are accumulated during 0.4 s, counted, and displayed as a function of the inverse wavelength $\lambda^{-1}$. This spectrum is averaged over 100 realizations and corrected from the effect of CCD heterogeneities, calibrated previously. It is then split into the sum of a smooth spectrum, characteristic of the light source, and an oscillating spectrum, shown above (symbols). It is finally fitted by a sine modulated in amplitude by a Gaussian envelope (solid line). (a) LLD film at $\mathrm{Ca} = 9.75 \times 10^{-2}$. The best fit gives $h_f = 61.24$ nm with (formally) a statistical accuracy of 0.005 nm. However, the reproducibility of two complete experimental runs is only to within 0.1 nm. (b) Thick film at $\mathrm{Ca} = 8.53 \times 10^{-2}$. The best fit gives $h_f = 214.68$ nm with (formally) a statistical accuracy of 0.05 nm and a reproducibility to within 1 nm. Thick films are at the limit of resolution; hence, the interference pattern is visible only in the near-infrared range of wavelengths.

uncertainty of 3% in the slope and the error from the spatial integration of the random noise present for each point.

Finally, we return to the question of how a particular type of film solution is realized experimentally. As shown in Ref. [8], the front of a liquid film of partially wetting fluid possesses a characteristic speed of recession $\mathrm{Ca}_f$ relative to the substrate, which is essentially set by the contact angle. Since the flux $q$ through the contact line is zero, according to (2) this translates into a characteristic film thickness $h_f = (3\mathrm{Ca}_f)_{1/2}$. Thus if the plate speed $\mathrm{Ca}$ is marginally above $\mathrm{Ca}_f$, the contact line moves up the plate very slowly, and the flux through the liquid film is close to zero: One has prepared the state $(h_f, h_f^2/3)$ at the upper end of the thick film solutions.

If the plate speed is now slowly increased, as we did in an experimental run shown in Fig. 2 by the arrows, one moves horizontally into the gray region, since $h_f$ is fixed by the motion of the contact line. As the end of the gray region is reached, the solution falls off the region of allowed solutions, and a LLD solution is realized instead (cf. Fig. 2). During this transition, the dimple detaches from the bath and moves up the plate, leaving behind the LLD film. In effect, this is the situation described in our earlier Letter [8]. Note that we were not able to take a measurement right above the transition, since the LLD film takes too long to develop. Of course, the above does not imply that thick films can be produced only in partial wetting situations but rather that the thickness is selected by upstream conditions. This selection mechanism deserves further investigation as it would offer considerably more flexibility in preparing thick films.

In conclusion, we have calculated a phase diagram for film coating from a bath. At a given speed, two different types of film solutions are possible. The novel, thick films described here are easily realized experimentally, and experiment agrees extremely well with theoretical prediction.

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[9] At small $\mathrm{Ca}$, viscous effects become negligible whenever $h_f \geq 1$, so that the equation remains valid in the bath.