On the Landau–Levich Transition

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We discuss here the nature of the Landau–Levich transition, that is, the dynamical transition that occurs when drawing a solid out of a bath of a liquid that partially wets this solid. Above a threshold velocity, a film is entrained by the solid. We measure the macroscopic contact angle between the liquid and the solid by different methods, and conclude that this angle might be discontinuous at the transition. We also present a model to understand this fact and the shape of the meniscus as drawing the solid.

I. Introduction

We all know that a duck is able to come out of a pond dry, owing to its hydrophobic feathers and to the small viscosity of water. More generally, a solid extracted from a bath that partially wets it can remain dry, provided that the extraction velocity is small enough. Above a threshold in velocity, the solid gets coated and entrains a film whose thickness should obey the Landau–Levich law: the quicker the coating velocity, the thicker the film.1,2

Here we focus on this dynamical wetting transition.3 We analyze the characteristics of the meniscus as a function of the solid velocity V and measure the contact angle at its top. This meniscus is distorted if compared with a static meniscus: viscous forces, which tend to induce liquid entrainment, tend to lower the angle, while surface tension opposes the deformation of the free surface. Hence, we expect the dynamic angle to be a function of the so-called capillary number Ca = ñV/γ, which compares both of these forces (ñ and γ are the liquid viscosity and surface tension, respectively).

There are many debates in the literature about the possible variations of the receding contact angle with the capillary number.1–3 Here we show that the results may significantly vary with the way measurements are done. The accuracy or reliability of the data in the transition region is also found to depend on the method. This discussion leads us to the conclusion that the macroscopic dynamic angle might jump to zero at the threshold velocity of entrainment. We compare our results with models recently proposed in this lively topic. These problems are indeed generic, and similar transitions were observed in different contexts, as for selective withdrawal (sucking more and more above an interface),6 or air entrainment (impacting more and more violently a jet on a surface).10 In each case, the structure of the “meniscus” is singular below the threshold, and the concentration of stress inside this singular region provokes the transition.

II. Experiments

A. First Measurements. I. Setup. Our surface is a glass cylinder whose diameter (≈2.5 cm) is much higher than the capillary length (≈1.5 mm), thus it can be regarded as a plate. The cylinder is coated with a fluorinated surfactant FC725 (sold by 3M Company) to make it partially wetted by oils.

We use as liquids, silicone oils with different viscosities (10, 20, 50, 100, 350, 1000 mPa s) which partially wet the coated glass cylinder. Since the silicone oils have almost the same surface tension (≈20 mN/m), all of them have comparable static (receding) contact angles, between 40° and 50°. A system with such a large angle was selected in order to be able to discriminate between a continuous variation of the contact angle and a jump, at the threshold of film deposition. The contact angle hysteresis (the difference between the advancing and the receding static angles) was about 5°, which makes it quite an ideal surface (i.e., smooth and chemically homogeneous).

The oil fills a bath that is displaced by a stepper motor with an accuracy of 1 μm/s. By moving the bath upward, the cylinder goes inside the oil, and, by moving it downward, the cylinder is withdrawn with a receding contact angle at the top of the dynamic meniscus. Above a certain velocity, the meniscus is unstable and oil is entrained on the surface.

The curvature of the cylinder allows us to see the meniscus from any direction and avoid edge effects. We took movies from the meniscus with a charge-coupled device (CCD) camera, which was moving at the same velocity as the bath. Thus the meniscus is observed in the reference frame of the solid, so that we could check the stationarity of the experiment. By analyzing the pictures, we measured the receding contact angle for different velocities, up to the entrainment threshold. A typical picture of the meniscus is shown in Figure 1.

2. First Method: Tangent Line. The simplest way to find the macroscopic apparent contact angle consists of drawing a line tangent...
to the meniscus curve at the top and measuring the angle of this line. We did this for all our data, and the resultant curves (angle as a function of capillary number) are displayed in Figure 2. The error for this method is almost constant and not more than 5° (Figure 3).

The angle is found to decrease with the velocity (or the capillary number), and a jump is observed at the threshold, above which the contact angle is zero and a film of liquid is entrained on the cylinder. The series of curves do not superimpose in a single curve, which might be due to a small difference in the static contact angle for the different oils: the heavier (and more viscous) the oil, the larger the contact angle. In particular, the position of the threshold is observed to increase with the weight of the oil, which might be interpreted as resulting from a strong variation in the threshold velocity with the static contact angle, as discussed later (eq 16).

The values this method gives for the contact angle depend on the scale at which we see the meniscus. Because the meniscus is highly curved, the nearer we can get to the top, the more exact our tangent line and, consequently, the measured angle. Thus, the resolution of the images limits the accuracy of our measurements. In our experiments, the resolution was about 20 μm.

**B. Meniscus Analysis.** A more thorough way might be to not only look at the top of the meniscus, but to analyze the whole profile. Considering a one-to-one correspondence between the shape of the meniscus and the dynamic contact angle, this analysis can give us the contact angle. As we do not know the shape of a dynamic meniscus exactly, we assume that the meniscus is quasi-static, with characteristics (height, shape) fixed by the actual dynamic angle with which it meets the solid. We shall discuss further this important hypothesis.

With a program that we wrote in Matlab (version 7.0, The Mathworks, Inc.), we were able to find the position of the points on the dynamic meniscus for each picture with an accuracy of one pixel for both coordinates (x, z). Each pixel on the picture was about 20 μm. The next step was to deduce the angle from the obtained data points.

1. **Second Method: Fitting the Height.** For a static meniscus, a well-known relation exists between the static contact angle $\theta_e$ and the height of the meniscus rise $H$:$$H = \kappa^{-1} \sqrt{2(1 - \sin \theta_e)}$$

where $\kappa^{-1}$ is the capillary length.
We assume that this relation still holds considering a dynamic angle at the top, and then deduce \( \theta_d \) from a height measurement. The results are shown in Figure 4. The precision of about 20 \( \mu \)m for the height measurement gives the error bars that are shown in Figure 5. There again, \( \theta_d \) decreases with \( \text{Ca} \), and a small jump is observed at the threshold of entrainment, as also reported by Delon et al.\(^{11}\)

2. Third Method: Fitting the Whole Profile. In the latter method, we only measure \( H \), which implies that we fit the dynamic curve to the static known curve with just one point, namely, the top of the meniscus. If we fit the whole profile of the dynamic meniscus to the static curve, we can treat the dynamic angle as a fit parameter, which may be a more exact way to define the angle. The static profile \( z(x) \) is given below:\(^6\)

\[
z(x) = \kappa^{-1} \cosh^{-1}\left(\frac{2}{xH}\right) - 2x^{-1}\left(1 - \frac{1}{4}x^2\right)^{1/2} - \kappa^{-1} \cosh^{-1}\left(\frac{2}{xH}\right) + 2x^{-1}\left(1 - \frac{1}{4}x^2H^2\right)^{1/2}
\]

where \( H \) is given by eq 1, with \( \theta_k \) as the angle of contact. The dynamic angle deduced from the fit is displayed in Figures 6 and 7, as a function of the capillary number. Error bars are modest for small \( \text{Ca} \), but unfortunately become larger close to the threshold.

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where the viscous pressure is given by

$$\Delta p_{\text{viscous}} = -\frac{2\eta v}{z} \frac{\sin^2 \alpha}{\alpha - \sin \alpha \cos \alpha}$$  \hspace{1cm} (4)$$

In the above expression, $\alpha(x)$ denotes the local slope of the meniscus at point $x$ and height $z(x)$, as defined in Figure 9, which means that we have an additional geometrical equation Using

$$\tan \alpha = -\frac{\partial z}{\partial x}$$  \hspace{1cm} (5)$$

the definitions of the capillary length as $\kappa^{-1} = \sqrt{\gamma/\rho g}$, and introducing the capillary number $Ca$, we can simplify the force balance equation as

$$_0 \frac{\partial z}{\sqrt{1 + (\partial z)^2}} = -\frac{\partial \cos \alpha}{\partial z} = -\frac{3Ca \sin \alpha}{z} \alpha^2 + \kappa^2 x$$  \hspace{1cm} (6)$$

owing to the fact that the meniscus deviates from the static shape, so that there is no fit for which the static curve is everywhere close to the experimental meniscus. This makes the fit lose its "sensitivity" to the fit parameter, which eventually does not allow us to make any conclusions about whether a jump in $\theta_d$ occurs at the threshold.

3. Quasi-static Hypothesis. A key assumption for our second and third methods is the quasi-static shape of the meniscus. Here we discuss this hypothesis. We display in Figure 8 comparisons between experimental profiles and eq 2.

At low velocities (compared to the threshold velocity, which is 1.63 mm/s), the shape of the meniscus is very similar to the expected static shape (Figure 8a,b). Conversely, the fits are observed to deviate from the static curve close to the top of the meniscus, as we approach entrainment (Figure 8c,d).

The angle deduced from the fit is always smaller than the actual angle (at the scale of the measurement), which explains why the data obtained from the tangent line method are systematically above the data obtained with the second and third methods. Comparing the two latter methods, we find that (as observed in Figures 5 and 7) the angles deduced from a fit of the meniscus profile are smaller than those obtained from measuring the meniscus height. Since these deviations increase as the transition is approached, the error bars increase in this region (Figure 7), which makes the data less reliable in this case.

III. Theory

In this section, we briefly present a theoretical formulation that could be used to determine the shape of the dynamic meniscus. We will use this formulation to describe some of the features of the experiment.

A. Force Balance. The shape of the meniscus, which is parametrized by the profile $z(x)$, as shown schematically in Figure 9, is determined by a balance between the viscous force, the gravitational force (proportional to the liquid density $\rho$ and the gravity acceleration $g$), and the surface tension $\gamma$. The corresponding local force balance equation can be written as

$$\gamma \frac{\partial z}{\sqrt{1 + (\partial z)^2}} = \Delta p_{\text{viscous}} + \rho gx$$  \hspace{1cm} (3)$$

where the exponential—integral function is defined as $E_n(z) = \int_0^z (dt/\Gamma(t)) e^{-t}$.

The viscous profile given in eq 10 is plotted in Figure 9 (inset) for various values of the capillary number. It can be seen that this profile is very similar to a straight line (except for a singularity close to the origin), with the asymptotic curve for small capillary numbers being \( z = \theta_c (H - x) \). Moreover, the viscous profile is always curved downward, with a curvature increasing with the capillary number, as it can be directly seen from eq 7.

2. Gravitational Region. When the wetting layer becomes thicker, viscous force becomes negligible compared to the gravitational force, and the force balance equation (eq 6) can be simplified as

\[
\frac{\partial^2 z}{\partial x^2} = \kappa^2 x
\]  

This static equation has a first integral

\[
\sin \alpha = -\frac{\partial z}{\sqrt{1 + (\partial z)^2}} = 1 - \frac{\kappa^2 x^2}{2}
\]  

This expression can be readily integrated to give the profile of the meniscus in the gravitational regime as in eq 2. Note that in the gravitational region, the profile is always curved upward (see Figure 9).

3. Matching Region. The shape of the dynamic meniscus as found from full solution of eq 6 should contain asymptotic behaviors consistent with the above two regions and an intermediate region to match them. Since the curvature should change its sign in this matching region, one can generally imagine that the curvature term can be considered negligible there. The balance of forces in eq 6 will be realized by a direct competition between viscous and gravitational forces. The fact that the curvature is small in this region can be used as a way of defining a dynamic contact angle that would correspond to the tangent line method discussed above: in the matching region, the angle between the meniscus profile and the vertical should remain nearly constant.

One can construct an approximate solution that is made up of the viscous and gravitational profiles that match each other at a point. The position of the point can be found by imposing the additional constraint of a vanishing curvature. Let us denote the coordinates of the matching point as \( x_d \) and \( z_d \) and the corresponding slope as \( \theta_d \), as shown in Figure 9. Making the curvature vanish requires (see eq 3)

\[
\frac{3Ca \sin \theta_d}{z_d} = \frac{\theta_d^3}{\theta_d^3} = \kappa^2 x_d
\]  

At the matching point, the profile should be continuous, which yields

\[
\theta_d^3 = \theta_c^3 - 9Ca \ln \left(\frac{z_d}{z_m}\right)
\]  

and

\[
\sin \theta_d = 1 - \frac{\kappa^2 x_d^2}{2}
\]  

The above three equations (eqs 13, 14, and 15) can be solved to give the following equation for the dynamic contact angle \( \theta_d \) in the usual limit of small \( \theta_d \). This result can be considered an empirical formula for the dynamic contact angle. In Figure 10, eq 16 is solved numerically as a function of the capillary number for \( \theta_c = 49^\circ \) and various values of \( \kappa z_m \). The transition in the dynamic contact angle is predicted to be abrupt, due to the presence of dynamical variables in the logarithm term. In most previous studies, this logarithm was treated as a number (as, for example, in the Cox–Voinov model; see also eq 17), so that the dynamical angle varies continuously and vanishes (critically) as \( Ca \) reaches \( Ca_c \) divided by this number. Contrasting with this behavior, it is clear that \( \theta_d = 0 \) is not a solution of eq 16. Instead, this equation suggests that \( \theta_d(Ca) \) has a vertical tangent for a nonzero value of the dynamic angle, on the order of \( Ca^{1/3} \). At this point, \( \theta_d \) is found to be a fraction of \( \theta_c \), from which we deduce that the critical capillary number of entrainment \( Ca_c \) nearly increases as \( \theta_c \)^2 (owing to the large value of the parameter \( \kappa z_m \)). This agrees with our observations, where we reported the high sensitivity of \( Ca_c \) toward \( \theta_c \), as seen, for example, in Figure 4: comparing the angles for silicone oils 10 mPa s and 1000 mPa s, we have \( \Delta \theta_d^3 / \theta_d^3 \approx 0.2 \) and \( \Delta Ca / Ca_c \approx 0.55 \), compatible with a \( \theta_c^3 \) dependence for \( Ca \). Remarkably, a dynamic angle on the order of \( Ca^{1/3} \) at the transition fits with the Landau–Levich scaling: \( \kappa \) then, the dynamic meniscus has a thickness and length scaling of \( Ca^{2/3} \) and \( Ca^{1/3} \), respectively, and thus a slope scaling of \( Ca^{1/3} \).

Owing to the absence of a solution between \( \theta_d(Ca_c) \) and 0, we get the discontinuous behavior reported in Figure 10, in agreement with our experimental results. We show in the same figure how the value of \( Ca_c \) depends on the choice of cutoff \( \kappa z_m \). We also calculated the position of the crossover height \( z_d \) as a function of the capillary number; the result is shown in Figure 10 (inset). While the value of \( z_d \) is linearly proportional to \( Ca \) for most \( Ca \) values, it increases rapidly near the critical point up to a maximum value. The typical values found show that our experimental resolution is generally too low for observing the viscous region, except throughout the transition domain.

IV. Discussion

If we want to compare both the three experimental determinations of the dynamic angle (summarized in Figure 11) and the results with the model, we should first look at Figure 10. At very low capillary numbers, we have \( \kappa z_d \ll 1 \), which implies that \( z_d \) is less than the resolution of the pictures. Thus, if we draw a tangent line on the pictures, it will not be at the position of \( z_d \) in the pictures, but rather on the gravitational meniscus. Owing to the upward curvature of the gravitational meniscus, this line gives a value larger than \( \theta_d \) defined in our model. We conclude that, for low capillary numbers, the second and third methods should give results that are closer to the theoretical estimate.

If we move to larger capillary numbers near the threshold \( Ca_c \), \( \kappa z_d \) increases and reaches a maximum at the threshold. In this region, the quasi-static assumption is not valid anymore, in good agreement with the observed profiles (Figure 8c,d). It is found that the meniscus meets the solid with an angle larger than expected from a quasi-static assumption, which can be interpreted as resulting from a visible change of curvature close to the contact line. Since the slope is expected to be nearly constant in this region of change in curvature (as indeed observed in Figure 8c,d), we assume that a direct measurement of the angle by the tangent method gives more reliable results for such capillary numbers.
We can conclude that, for Ca, Ca_c, the quasi-static methods (second and third) give results closer to theory; on the other hand, the first method should be more reliable when approaching the threshold velocity of film deposition. Figure 12 shows a comparison between the theoretical curve and experimental data for three different silicone oils. The theoretical curve is plotted for \( \theta_d = 49^\circ \) and \( \kappa_d = 10^{-6} \) and fits well the experimental points. In particular, it captures the existence of a jump in the contact angle at the threshold. However, it fails to accurately describe the position of the threshold in the capillary number. Why is the experimental threshold less than the predicted value? To answer this, we first review some theoretical and experimental works done so far on this question.

Cox and Voinov proposed a hydrodynamic model to solve the problem, which was used later to derive a formula for the dynamic contact angle as a function of the capillary number:

\[
\frac{\theta_d}{\theta_c} = 9 \text{Ca} \ln \left( \frac{\kappa^{-1}}{\zeta_m} \right) \tag{17}
\]

As emphasized above, this formula gives a contact angle decreasing continuously to zero without a jump. Later, Eggers worked on this problem (within the framework of the lubrication theory) in more detail and numerics, and his results showed the same continuous behavior. In his definition for the dynamic angle, he used the angle equivalent to the one of our second and third methods.

The threshold found in these hydrodynamic treatments is extremely sensitive to the value of the contact angle at molecular length scales. While this value is often assumed to be equal to the equilibrium contact angle (as in our simple treatment above), it has been argued in the literature that local molecular dissipation mechanisms could modify this molecular-scale contact angle as well when the contact line is in motion, supported by evidence from molecular dynamics simulation. Hydrodynamic theories that take this effect into account in a self-consistent way have also been developed. The molecular dissipation channel becomes more important for fluids with relatively smaller

viscosities, and can shift the threshold toward smaller capillary numbers which might explain the above-mentioned disparity, especially for the less viscous fluids.

There are other possible sources for the discrepancy. One of them is the fact that \( z_{\infty} \) is not constant for all the oils, and it has been suggested\(^6\) that it is proportional to the molecular size of the liquid, which, in our case, increases with viscosity; thus the threshold should shift to smaller values for less viscous oils. Another source lies in the different values of \( \theta_s \), which we discussed at the end of section III.

Our results can also be compared to existing data in the literature. Sedev and Petrov\(^{20}\) pulled glass rods out of water–glycerine mixtures, and found zero dynamic angle at the threshold, that is, a continuous transition. On the other hand, in experiments on sliding drops,\(^2^1\) the contact angle was observed to be nonzero at the transition threshold. Delon et al.\(^{11}\) conducted the experiment with silicone oils and a fluorinated silicone wafer. They also found a nonzero angle at the threshold, which was measured by our second method. Hence our data might help to clarify the nature of the transition.

Finally, note that Snoeijer et al.\(^{22}\) reported the existence of a “rim” at the top of the meniscus at the threshold. They assumed that this rim is responsible for making the transition discontinuous and at a capillary number less than the one predicted by Voinov or Eggers. We also observed a rim as seen in Figure 13, but this rim stands (and moves) above the meniscus, and its origin rather seems to be related to the dewetting of the entrained film.\(^{23}\) Once deposited, the film dewets at a constant velocity \( V_d \), which can be easily deduced from the measurement of the velocities of the contact line \( V_{CL} \) and of the withdrawal \( V_{withdraw} \):

\[
V_d = V_{withdraw} - V_{CL}
\]  

We measured \( V_d \) for three experiments, in which we pulled the cylinder with velocities larger than \( V_c \) (the threshold velocity

Figure 13. Appearance of a rim at the threshold. The liquid is silicone oil with a viscosity of 50 mPa-s, and the velocity is 1.63 mm/s. The time difference between panels a and b is 1.13 s.

of film deposition), from a bath of silicone oil of viscosity 20 mPa-s. The results are displayed in Table 1.

The dewetting velocity is indeed found to be a constant (\( V_d = 3.4 \pm 0.1 \) mm/s), which is observed to be very close to (yet slightly smaller than) the threshold velocity of entrainment \( V_c = 3.7 \pm 0.2 \) mm/s. The dewetting velocity cannot, of course, be larger than \( V_c \), but it is still (to the best of our knowledge) an open question to determine whether these velocities are identical. Comparing the results of our model (where \( V_c \) is close to scale as \( \gamma \theta_s^2 / \eta \)) with existing models and experiments on dewetting (where \( V_d \) is found to scale as \( \gamma \theta_s c / \eta \))\(^{23}\) indicates that both quantities should indeed be of the same order, but a precise comparison between them is still missing. Another reason for the discrepancy between the predicted and observed value of the threshold might be the surface roughness. The surface roughness causes the transition to take place at larger angles and smaller capillary numbers,\(^7\) and thus \( z_{\infty} \) gets smaller, which is consistent with the experiments.

| Table 1. Measurements of the Contact Line and Dewetting Velocities |
|----------------------|----------------------|----------------------|
| \( V_{withdraw} \) (mm/s) | \( V_{CL} \) (mm/s) | \( V_d \) (mm/s) |
| 5.0                  | 1.5                  | 3.5                  |
| 6.0                  | 2.5                  | 3.5                  |
| 7.3                  | 4.0                  | 3.3                  |

We report in this paper measurements of the variation of the dynamic receding contact angle (defined macroscopically) as a function of the capillary number, for a plate withdrawn out of a bath in a situation of partial wetting. We compare the results obtained by different methods, and find that significant deviations towards a quasi-static meniscus are observed at the top of the meniscus, as it approaches the critical velocity above which the plate entrains a film. This observation makes it doubtful to deduce a dynamic angle from an assumption of a quasi-static shape for the meniscus. Alternatively, directly measuring the macroscopic angle by drawing a tangent to the profile seems to suggest that the dynamic contact angle discontinuously jumps from a macroscopic value (typically a fraction of the static contact angle) to zero, the value corresponding to film deposition. These findings are supported by an empirical model, where the classical Cox–Voinov approach is corrected by a logarithmic term containing dynamical quantities, leading to a similar discontinuity of the dynamic contact angle. However, a few problems remain (as expected in this historical and problematic field of research on interfaces), such as the position of the threshold of entrainment. It would also be useful to elucidate the exact link between entrainment and dewetting.

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