The Trail of the Drops.

D. QUÉRÉ and E. ARCHER

Laboratoire de Physique de la Matière Condensée (URA 792 du CNRS)
Collège de France - 75231 Paris Cedex 05, France

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Abstract. - What remains on a solid withdrawn out of bath of liquid (or the converse issue raised by the trail of a moving drop) is a question of considerable practical importance, and which has been discussed at length in the case of wetting liquids. Here we are interested in what happens when the liquid only partially wets the solid. We observe a sharp cry-wet transition as a function of the velocity. The position of the threshold is shown to depend strongly on the wetting conditions. We then study the dry regime more carefully. It is shown in particular that even at low velocities microscopic traces of liquid are deposited on the solid.

Introduction. - A drop which slides along an inclined plate, a pane of glass for example, sometimes leaves the pane dry. Other times a trail of liquid signs the passage of the drop. We try here to characterize what determines the appearance of these trails for liquid slugs moved inside capillary tubes.

The amount of liquid left behind a drop which completely wets the inside of the tube has been extensively studied since the work of Bretherton [1]. Otherwise, the existence of a critical velocity for the deposit of a film has been established and studied in partial-wetting situations, in particular by Blake [2] or by Petrov and Sedev [3]. We propose here to study in a more systematic way the transition itself: how varies the amount of liquid left behind a drop in a tube that it partially wets?

Partial wetting. - An obvious necessary condition for observing no trail at the rear of the drop is to be in a situation of partial wetting. The stationary drop must only partially wet the solid upon which it is deposited: it joins it with Young's angle \( \theta_s \), if the solid is ideal. In most practical situations, the solid has defects (it is rough, or patched with chemical heterogeneities), and the contact angle can vary between two equilibrium values, the receding and the advancing static angles (respectively, \( \theta_r \) and \( \theta_a \)). Thus, a condition for observing no trail behind a moving drop is that the static receding angle is non-zero.

So, we have chosen to work with drops of alcanes (from octane to hexadecane) inside commercial teflon tubes. The values of \( \theta_r \) and \( \theta_a \) for this series of alcanes were measured inside the tube. First the capillary forces acting on the tube slowly moved up and down in a bath of alcane were measured. Then a stopper was put at the bottom of the tube, and the
advancing and receding forces at the outside of the tube were recorded. They give access to the cosines of the contact angles, and thus angles close to zero are difficult to measure accurately by this method. The values of the contact angles inside the tube deduced from these measurements are displayed in fig. 1.

*Experiment.* A teflon capillary tube (inside diameter of 0.91 mm and length about 60 cm) is put horizontally and forms a loop. On one side it is open and on the other one connected with a syringe, the piston of which being moved at constant velocity by a motor. So a drop of alcane first placed at the beginning of the tube is pushed by slightly compressed air. The tube is transparent. Hence it is possible to take photographs of the drop. A first one is taken at the beginning of the loop, and a second one after the drop went round, corresponding to a run of known length. The pictures are compared and the change in length of the slug

Fig. 1. – Advancing and receding contact angles between alcanes and teflon inside the tube, as a function of the surface tension of the alcanes (octane, mixture of octane and nonane, nonane, decane, dodecane, tetradecane and hexadecane). The surface tensions are measured by the ring method.

Fig. 2. – Average thickness of the trail left behind a drop of alcane as a function of the capillary number $Ca$ to the power 2/3, for various alcanes: octane (empty square), mixture of octane and nonane (triangle), nonane (plus), decane (full square), dodecane (full circle), tetradecane (asterisk) and hexadecane (square with a cross).
gives the amount of liquid left behind. The sensitivity of this method (expressed for the average thickness of the film) is less than 0.1 μm.

The results of this experiment are gathered in fig. 2, for different alcanes and various slug velocities V. V varies from 0.4 mm/s for the first point with octane to 24 mm/s for the last one with hexadecane. The mean thickness of the film e is plotted as a function of the capillary number Ca to the power 2/3. If τ and γ are the viscosity and surface tension of the liquid, the capillary number is defined by: Ca = τV/γ.

**The dry-wet transition.**

1) For each alcane, two regimes can be observed. i) At low velocity, there is no film (at least in view of the sensitivity of the measurement). This defines the dry regime. The rear of the moving drop joins the tube with a non-zero dynamical receding angle. ii) Above a threshold velocity, a macroscopic film is left, the thickness of which increases with V.

2) The threshold velocity V* above which a trail is left depends on the liquid. For example, in the case of hexadecane, for which the transition is particularly sharp, V* is equal to (7.0 ± 0.2) mm/s. In fig. 3, the threshold capillary number Ca* (measured in fig. 2 at the beginning of the rising of e) is plotted as a function of the equilibrium receding angle θr. The choice of this abscissa is logical, since we should have Ca* = 0 for θr = 0. Ca* is highly dependent on θr and can be shown to be close to θr³.

Several theoretical attempts have been done to describe this transition, among which the molecular-kinetic theory of Blake [4] and the hydrodynamic models of Voinov, Cox and de Gennes [5]. Blake's model is based on adsorption-desorption processes at the rear of the drop, and is hard to compare with our results because of the unknown values of some adjustable parameters. In hydrodynamic theories, capillary and viscous forces in the rear corner of the drop are balanced, which gives the maximum velocity V* for which the liquid corner can hold the viscous dissipation. On an ideal surface, V* is shown to vary asymptotically as θr³. The change to a θr³ law can be done in a phenomenological way [6], but is not obvious to justify (especially for large receding angles).

3) Figure 2 also shows that the transition is all the softer since the alcane is light (and thus wetting and volatile at the same time). At the transition, the film is always visible to the naked eye except in the case of octane. In the latter case, just above V*, a mist appears after

![Graph](image-url)
a moment behind the drop and evokes a breath figure. So an evaporation/recondensation process can occur (at least in this particular case) at the transition.

4) We have also managed to construct a mixture of octane (38%) and hexadecane (62%) of nearly the same viscosity and tension as pure dodecane (respectively, 1.43 cP and 24.7 dyn/cm instead of 1.40 cP and 25.4 dyn/cm). Although the threshold is not located exactly at the same place, probably because of a small difference in the static receding angle, the two obtained curves $e(Ca-Ca^*)$ are completely superimposable. This indicates that the shape of the transition essentially depends on the macroscopic properties of the liquid (i.e. $\gamma$ and $\gamma'$) but not on its detailed composition.

The forced spreading regime. – Above $V^*$, the liquid is forced to wet the tube. Figure 2 shows that the film thickness increases linearly with $Ca^{2/3}$, as predicted by Bretherton for completely wetting liquids [1]. More precisely, Bretherton’s law indicates that $e$ should vary as $abCa^{2/3}$ with $a = 1.34$ ($b$ is the radius of the capillary tube). This is in agreement with the value deduced from fig. 2: we find $a = 1.36 \pm 0.10$.

The deposited film is essentially unstable. First it dewets, at a velocity which can be seen comparable with $V^*$, but of course slightly smaller. Moreover, the film has a cylindrical symmetry. So the tension of the liquid makes it unstable: it tends to break into an array of droplets (Rayleigh instability). Note that the trail of a small drop sliding on a plate is a hemicylindrical rivulet, also subjected to this instability.

The dry regime. – In the case where there is apparently no trail ($V < V^*$), we have wondered to what extent the tube was dry after the passage of the drop. By measuring the shortening of the slug, we can only reveal a film of thickness larger than 500 Å. So we moved, after the drop of alcane, a «brush-drop» to collect the traces of alcane possibly left by the first one.

For that, a drop of carbon tetrachloride was used. Slowly moved, in such a way that it has no trail itself, this drop is picked up at the exit of the tube and then titrated by gas chromatography. With this method, the sensitivity of the film thickness measurement increases of a factor of 1000. If a second «brush-drop» is moved after the first one, it only brings back less than 1% of the quantity of alcane brought by the first one. Note that for this experiment another teflon tube was used, which was shown to be slightly less wetting than the one used for obtaining fig. 1, 2 and 3, and thus exhibiting a larger threshold value $Ca^*$. First we verified that the results obtained in the forced spreading regime ($V > V^*$) were the same using this method and the previous one. Then the «dry» regime was studied for a drop of dodecane. The results are displayed in fig. 4a), b) and c), corresponding to an increasing scale for the thickness axis. It can be seen that a microscopic film always remains behind the drop. Its thickness seems independent of the slug velocity and is $(20 \pm 10)$ Å. Hence the dry regime is actually pseudodry. Now we comment on the results.

Comments.

1) Electron microscope photographs have revealed that the inside surface of the teflon tubes is very rough. In particular, axial grooves can be seen, with a depth of about one micrometer. In complete-wetting situations, such grooves have been shown to be responsible for trapping films of thickness of the order of the grooves depth and independent of $V$[7].

But here the thickness of the film is much smaller than the scale of roughness. To understand further the influence of trapping by the roughness, we moved a drop composed of a mixture of decane and hexadecane through the tube. Titration of the brush-drop indicated that the microscopic film did not have the same composition as the original drop. The composition was 70%-30% in favour of decane, instead of the original 50%-50%. This fact
suggests that recondensation of a volatilized phase could participate in the appearance of the microscopic film.

2) The alcane drop, as it is slowly moved, is in equilibrium with its vapour. If we consider that the brush-drop totally collects the vapour (for example because this vapour condensed on the teflon surface), we obtain from the theoretical values of the vapour pressures equivalent thicknesses of 35 Å for the decane, 7 Å for the dodecane and less than 1 Å for the hexadecane. So, a drop of hexadecane was moved at a velocity between 0.3 and 3 mm/s. Titration of the brush-drop indicated that some hexadecane had been left behind, corresponding to a thickness $e = (30 \pm 10)$ Å which cannot be explained by such vapour pressure considerations.

3) Our method of measurement only gives an average film thickness over 50 cm. Local investigations would be very useful to establish that the microscopic film continuously coats the tube. Otherwise fig. 4b) and c) seem to indicate that between 5 mm/s and 7 mm/s there is a kind of pretransition. In this small regime (if it exists), the thickness is velocity dependent: this region could correspond to fluctuations of the local contact angle (due to surface heterogeneities) and thus of $V^*$, implying that small discontinuous pieces of film are left below the macroscopic transition.
Conclusion. – A drop sliding on a window always has a trail as soon as the liquid makes a zero static receding angle with the solid, as does water on a well-cleaned glass. The amount of liquid left behind increases with the drop velocity (Bretherton’s law). On the contrary, if the equilibrium receding angle of the drop is non-zero, as is usually the case for water on glass, the drop does not leave behind a trail provided that the sliding velocity is low enough. The velocity at which a trail appears depends on the liquid viscosity (and surface tension), but is mainly determined by the degree of wettability, in particular by the static receding angle.

In partial-wetting situations, the existence of such a transition could be due to long-range forces as van der Waals ones. If the film is thinner than the range of these interactions (often about 1000 Å), then the van der Waals forces tend generally to thin the films in partial-wetting situations. But here, at the transition, the film is still macroscopic (1 to 5 μm). That is why other mechanisms, such as viscous dissipation, have to be put forward to explain the transition.

The existence of a dry regime refutes the hydrodynamic principle of non-slippage at a solid wall. This paradox has remained unsolved for a long time, and the study of this transition is one of the several ways of investigation. Among the other ones, let us mention experimental studies of the dynamic contact angles: direct optical observations by Dussan et al. [8] or Petrov et al. [3], tensiometric measurements by Hayes and Ralston [9] (besides, [9] contains a summary of dynamic-contact-angle investigations since 1923), and computer simulations by Thomson and Robbins [10]. In our case, evidence of a microscopic film may help explain what happens in the immediate vicinity of the contact line.

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REFERENCES