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# Dynamics of spreading of a liquid drop across a surface chemical discontinuity 

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#### Abstract

Résumé. - Nous présentons une étude expérimentale de la dynamique d'étalement d'un ruban liquide déposé à cheval sur la discontinuité chimique qui sépare deux surfaces solides différentes. Les mesures de déplacements et d'angles de contact sur les deux bords du ruban permettent de décrire en détail les différentes phases du mouvement et en particulier un régime stationnaire correspondant à une translation uniforme. Ces résultats sont en accord qualitatif avec un modèle théorique, bien qu'ils mettent en évidence sune déformation du ruban par rapport au profil circulaire constituant l'hypothèse couramment admise.


#### Abstract

We report an experimental study of the dynamics of a liquid ridge straddling a chemical discontinuity which separates two different solid surfaces. Measuring the displacements and contact angles on both sides, we describe in detail the different regimes of motion and in particular a stationary regime which corresponds to uniform translation. These results are in qualitative agreement with a theoretical model, although we see a deformation of the drop shape when compared to a circular profile, which is the currently admitted hypothesis.


## 1. Introduction.

In previous articles [1, 2], we have described the preparation and interfacial properties of mixed surfaces i.e. solid surfaces which are partly hydrophilic, partly hydrophobic. These surfaces were prepared with the aim of obtaining amphiphilic solid particles, which present some analogy with the conventional amphiphilic molecules, when located at a liquid interface. Within the framework of these studies, we have observed the behaviour of a liquid drop when deposited on the boundary, between hydrophilic and hydrophobic parts of a plate. The most striking feature is that the drop translates as a whole toward one or the other part, until it covers homogeneous area of the solid. Raphaël has proposed a theoretical analysis of this effect [3], in the convenient geometry of a liquid ridge, and has predicted different regimes for the motion. We present here, in the same cylindrical geometry, an experimental study of this dynamics of spreading.

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## 2. Motion of a liquid ridge across a surface discontinuity.

2.1 DESCRIPTION OF THE EFFECT. - Let us consider a plate consisting of two parts with different surface properties. The preparation of such plates is described in detail in the experimental section. If a liquid drop is deposited on the boundary line, one observes that it moves spontaneously in one direction. This global motion ends when the receding contact line reaches the boundary between the two parts, where it remains anchored. The drop, which is then entirely on a homogeneous surface, spreads on it until it reaches its equilibrium position.

This behaviour has been observed with different liquids, in particular water and different oils. The direction of the displacement is not a priori obvious : if water systematically shifts toward the polar surface, generally lipidic liquids, although apolar, also move toward the hydrophilic part.

The characteristic time of this motion strongly depends on the viscosity of the liquids. In particular, in the case of water the process is achieved in less than one second while it lasts a few minutes for viscous oils. The kinetics is also dependent on the surfaces preparation but in a less marked way.
2.2 QUALITATIVE INTERPRETATION. - This phenomenon may be understood by considering the energies of the interfaces involved in the problem, taking into account not only solidliquid but also solid-air energies. This can be expressed in terms of equilibrium contact angles of the liquid on the two surfaces considered separately.

Let us consider the system represented in figure 1 . We refer to the hydrophilic part of the solid by $P$ (as Polar) and to the hydrophobic one by $A$ (as Apolar); $\theta_{A e}$ and $\theta_{\mathrm{Pe}}$ denote the equilibrium contact angles of the liquid on A and P surfaces respectively. We assume $\theta_{\mathrm{Pe}}<\theta_{\mathrm{Ae}}$ which is the situation generally encountered experimentally. This inequality implies that the liquid has a greater affinity for the $\mathbf{P}$ solid and is expected to move toward this part of the surface.


Fig. 1. - Schematic diagram of the system. $\theta_{\mathrm{Ac}}$ and $\theta_{\mathrm{Pe}}$ represent the equilibrium contact angles on A and $P$ surfaces respectively. $\mathcal{L}$ denotes the boundary line between $A$ and $P$ parts; $\mathscr{L}_{A}$ and $\mathfrak{L}_{P}$ the two contact lines of the ridge.

It is impossible for the ridge to be at rest across the boundary with contact angles satisfying the equilibrium conditions on both surfaces simultaneously. This would imply strong deformations of the drop and therefore important pressure gradients within the liquid. Thus, in a first approximation, we suppose that the ridge keeps its circular profile and we refer to the contact angle of the ridge (which is the same on both surfaces) by $\theta$.

In these conditions, the two edges of the ridge are not at equilibrium and are submitted to non compensated Young forces. The horizontal component of these forces is equal to $\gamma\left(\cos \theta_{\mathrm{Pe}}-\cos \theta\right)$ on the P part and to $\gamma\left(\cos \theta-\cos \theta_{\mathrm{Ae}}\right)$ on the A part (where $\gamma$ is the liquid surface tension). The drop is thus expected to move.

In the situation represented in figure 1 , that is to say when $\theta$ lies between $\theta_{\mathrm{Pe}}$ and $\theta_{\text {Ae }}$, the two forces are in the same direction, which explains the global motion observed
experimentally. This situation is the most usual in practice because if the two equilibrium contact angles are different enough, the initial contact angle always lies between these two values.

The behaviour explained above no longer applies when the receding contact line reaches the boundary line. We then have a contact line between four phases so that the Young equation is not valid anymore. The contact angle may take any value between $\theta_{\mathrm{Pe}}$ and $\boldsymbol{\theta}_{\mathrm{Ae}}$. This angular interval, called the canthotaxis sector, applies each time the surface presents a chemical or geometrical discontinuity. In our case, this can be understood by considering that the discontinuity is in fact, at a microscopic scale, a transition zone with surface properties varying continuously between the A and P-like surfaces. The contact line can thus accommodate in this microscopic region in order to verify the Young equation locally while it seems fixed at a macroscopic scale. This explains the anchoring of the contact line on the boundary line.

Once the receding line is fixed on the boundary, the whole drop is on the $P$ surface. The «free» edge of the strip may then spread until the drop reaches its equilibrium contact angle $\theta_{\mathrm{Pe}}$.
2.3 Theoretical predictions. - On the basis of this general ideas, a detailed model has been developed by Raphaël [3]. The fundamental hypothesis is that, in the thick part of the liquid, pressures reach equilibrium in times much shorter than the times involved in the motion of the drop [4]. The profile of the ridge is then always an arc of circle, the curvature of which is given by Laplace condition. The contact angles of the ridge on both sides of the surface are thus supposed to be identical.

Moreover, hysteresis effects are neglected in this theoretical development i.e. the equilibrium contact angles have unique values $\theta_{\mathrm{Ae}}$ and $\theta_{\mathrm{Pe}}$ respectively. This implies very homogeneous surfaces with no significant defects.

Within the framework of these hypotheses it is possible to get the equations of motion $x_{\mathrm{A}}(t)$ and $x_{\mathrm{P}}(t)$ of the two contact lines [5]. They are obtained by balancing the work of the forces applying on the lines, the expression of which are given above, and the viscous dissipation in the liquid edges. For $\theta \ll 1$, one gets :

$$
\begin{align*}
& \frac{\mathrm{d} x_{\mathrm{A}}}{\mathrm{~d} t}=V_{\mathrm{A}}=V^{*} \theta\left(\theta_{\mathrm{Ae}}^{2}-\theta^{2}\right)  \tag{1}\\
& \frac{\mathrm{d} x_{\mathrm{P}}}{\mathrm{~d} t}=V_{\mathrm{P}}=V^{*} \theta\left(\theta^{2}-\theta_{\mathrm{Pe}}^{2}\right) . \tag{2}
\end{align*}
$$

In these formulae $V^{*}=\frac{\gamma}{6 \ell_{\eta}}$ where $\gamma$ is the surface tension of the liquid, $\eta$ the viscosity and $\ell$ a logarithmic factor depending on the maximal and minimal scales of the dissipative zone. $\ell$ is usually taken to be of the order of 12 , $[6,7]$.
The volume conservation permits to couple the two equations (1) and (2) so that we get a differential equation for the angle $\theta$ :

$$
\begin{equation*}
\frac{\mathrm{d} \theta}{\mathrm{~d} t}=-\frac{4 V^{*}}{L_{0} \theta_{0}^{1 / 2}} \theta^{5 / 2}\left(\theta^{2}-\tilde{\theta}^{2}\right) \tag{3}
\end{equation*}
$$

where $L_{0}$ is the initial width of the ridge, $\theta_{0}$ the initial contact angle and

$$
\begin{equation*}
\tilde{\theta}=\left(\frac{\theta_{\mathrm{Ae}}^{2}+\theta_{\mathrm{Pe}}^{2}}{2}\right)^{1 / 2} \tag{4}
\end{equation*}
$$

The analytical solution of equation (3) is quite complex. The important point is that the contact angle $\theta$ tends exponentially towards $\tilde{\theta}$. In this asymptotic limit the two velocities $V_{\mathrm{A}}(\tilde{\theta})$ and $V_{\mathrm{P}}(\tilde{\theta})$ are equal so that the drop moves without deformation at a constant speed* $\tilde{V}$ given by:

$$
\begin{equation*}
\tilde{V}=V^{*} \tilde{\theta}\left(\frac{\theta_{\mathrm{Ae}}^{2}-\theta_{\mathrm{Pe}}^{2}}{2}\right) \tag{5}
\end{equation*}
$$

Thus, this model predicts that the drop reaches, in a time estimated to be $t=\frac{L}{4 V^{*} \tilde{\theta}^{3}}$, a stationary state where it moves at a constant velocity. The value of this velocity is a function of the liquid and surfaces characteristics.

Note that this description is valid as long as the initial contact angle $\theta_{0}$ lies between $\theta_{\mathrm{Pe}}$ and $\theta_{\mathrm{Ae}}$. Other less usual cases are described in Raphaël's original paper.

## 3. Experimental section.

3.1 Preparation of the surface. - As a first step, we render glass slides hydrophobic by chemical grafting of octadecyltrichlorosilane (silanisation). Half of the slide is then protected by an adhesive tape and the whole is exposed to UV rays in an oxygen atmosphere [8]. This treatment, called ozonisation, progressively removes the hydrocarbon chains from the free surface. We obtain, on this part of the slide, a homogeneous surface the property of which can be adjusted between strongly hydrophobic and strongly hydrophilic by changing the exposure time to UV. By removing the adhesive tape, one obtains a surface with two different parts, the discontinuity between the two being a straight line. According to the notation introduced in part II, we refer to the hydrophilic part of the slide, i.e. that which has undergone the UV treatment, by P and to the other one by $\mathbf{A}$. The surface energies of A and P parts are fixed by the conditions used for the silanization and for the ozonisation respectively. These surfaces may be characterized by contact angle measurements. Using the same liquids as those in the experiments described below, we find that the hysteresis is approximately $8^{\circ}$ on P surfaces and about $5^{\circ}$ on A surfaces. Thus, we determine for each surface the static advancing and receding contact angles of the considered liquid, noted $\theta_{\text {adv }}$ and $\theta_{\text {rec }}$ respectively.
3.2 Liquid ridge. - The liquids used are immersion oil and castor oil. The viscosity and surface tension of these liquids are measured by conventional methods i.e. Poiseuille flow and ring tensiometer respectively. We find that these liquids have about the same surface tensions (see Tab. I). They present a situation of partial wetting on all the A-type or P-type surfaces studied. On the contrary, their viscosities differ by one order of magnitude.

The ridges are obtained by depositing on the boundary line $\mathcal{L}$ a glass cylinder coated by the liquid. The liquid flows from the cylinder to the surface by capillary effects and reaches an equilibrium position when it is uniformly distributed along the boundary. When removing the glass cylinder, slowly enough to avoid important hydrodynamic perturbations, we get on the plate a strip with straight edges (cf. Fig. 2). This method permits us to obtain ridges of different widths $L$ controlled by the size of the glass cylinder used. In our experiments, $L$ varies from one to three millimeters a value which is of the order of the capillary length $\kappa^{-1}\left(\kappa^{-1}=2 \mathrm{~mm}\right)$. Note that these ridge sizes are small enough that one can ignore, in a reasonable approximation, the gravity effects compared with capillary ones.
3.3 DIRECT OBSERVATION OF THE MOTION. - We observe the ridge through a microscope. The image is videotaped, thus permitting to obtain a quantitative determination of the motion


Fig. 2. - Photograph of a ricin oil ridge 1 mm wide.
of the two contact lines limiting the ridge. Generally we observe that the two strip boundaries move while keeping straight and parallel. We then determine and plot the two displacements $x_{\mathrm{A}}$ and $x_{\mathrm{P}}$ for the A and P parts, as a function of time. In rare cases, for very small displacement speeds, undulations appear leading to transversal instability. This will be discussed later.
3.4 Measurement of the contact angles. - The contact angles are measured by using the method presented in reference [9]. It consists in illuminating the sample by a large, collimated laser beam and detecting on a screen the light refracted by the lens constituted by the liquid on the solid substrate (Fig. 3). The figure obtained is a rectangle, the width of which is given by the beam size and the length related to the contact angle. From the experimental determination of the refraction angle $\theta^{\prime \prime}\left(\operatorname{tg} \theta^{\prime \prime}=d / h\right)$, one can determine the contact angle $\theta$ via the formula :

$$
\operatorname{tg} \theta=\frac{-\sin \theta^{\prime \prime}}{1-\left(n^{2}-\sin ^{2} \theta^{\prime \prime}\right)^{1 / 2}}
$$

where $n$ is the refraction index of the liquid.
This method is suitable to the present situation : the contact angles $\theta_{\mathrm{A}}$ and $\theta_{\mathrm{P}}$ of the two edges on $A$ and $P$ surfaces, may be determined separately on the same image by using the shadow of the ridge as a reference to measure the length $d$ (Fig. 3). Besides, filming and registering the refracted spot on the screen allows us to determine the variations of $\theta_{\mathrm{A}}$ and $\theta_{\mathrm{P}}$ with time.

It is important to note that, using this method, the contact angles are not measured locally but along a length of ridge of about one centimeter (size of the incident beam). This permits us to verify that the bahaviour is homogeneous at this scale which is large compared with the strip width. When this condition is verified the uncertainty on the contact angle value is less than $2^{\circ}$.


Fig. 3. - Measurement method of the contact angles: the part of the incident beam refracted by the liquid gives an image whose dimension $d$ is a function of the contact angle $\theta$.

## 4. Results and discussion.

4.1 Experimental data. - We have measured the displacements $x_{\mathrm{A}}$ and $x_{\mathrm{P}}$ of the two edges of the ridge, and the values of the corresponding contact angles $\theta_{\mathrm{A}}$ and $\theta_{\mathrm{P}}$, for different liquids and different surface treatments of the $A$ and $P$ parts of the plate. Note that for technical reasons, we cannot measure $x$ and $\theta$ simultaneously. These determinations are achieved successively on each sample under the same conditions.
4.1.1 Contact line displacements. - Typical data for the evolution of $x_{\mathrm{A}}$ and $x_{\mathrm{p}}$ with time are given in figure 4. We observe that after a transitory regime, the system reaches a stationary state where the two contact lines move with the same velocity. Assuming that this corresponds to the stationary regime predicted by the model, we may determine the limit velocity $\tilde{V}=V_{\mathrm{A}}=V_{\mathrm{p}}$. This regime is extended enough to permit the measurement of $\tilde{V}$ with a good accuracy. The values of $\tilde{V}$ are independent of the width of the ridge with a reproducibility of about $10 \%$. On the contrary, they strongly depend on the liquid and surface characteristics. The corresponding results are reported in table I and will be discussed later.

In the early transitory stage, we note that the contact line on the $\mathbf{P}$ surface does not move. This is due to hysteresis effects as evidenced by contact angle measurements (see below).

Finally, we observe a third regime where one of the edges is fixed ( $x_{\mathrm{A}}$ constant) while the other one continues to move. This corresponds to the spreading of the ridge on the $P$ surface when one edge is anchored, by the canthotaxis effect, on the boundary line.
4.1.2 Contact angle measurements. - An example of the evolution of $\theta_{\mathrm{A}}$ and $\theta_{\mathrm{P}}$ as a function of time is plotted on figure 5 . We note that, after a transitory regime, the contact angles regularly increase and reach constant stationary values $\tilde{\theta}_{\mathrm{A}}$ and $\tilde{\theta}_{\mathrm{P}}$. We have to emphasize that these limit values are not identical ; they differ by about two degrees. This difference is


Fig. 4. - Plots of the contact lines $\left(\mathcal{L}_{\mathrm{A}}\right.$ and $\left.\mathcal{L}_{\mathrm{P}}\right)$, displacements $x_{\mathrm{A}}(\Delta)$ and $x_{\mathrm{p}}(\bullet)$, as a function of time in the case of immersion oil ridge ( $L=1.5 \mathrm{~mm}$ ) on two different surfaces characterized by: a) $\theta_{\text {Arec }}=35.2^{\circ} ; \theta_{\text {Padv }}=26.7^{\circ}$; b) $\theta_{\text {Arec }}=38^{\circ} ; \theta_{\text {Padv }}=19.2^{\circ}$. Note that we have brought the two curves nearer by a vertical shift in order to put into evidence the parallelism of the two curves in the stationnary regime.

Table I. - Experimental features of the liquids $(\gamma, \eta)$ and of the solid surfaces ( $\theta_{\text {Arec }}, \theta_{\text {Padv }}$ ), measured values of the limit velocities $\tilde{V}$ and corresponding values of $\ell$ (see text).

|  | $\theta_{\text {Pad }}\left({ }^{\circ}\right)$ | $\theta_{\text {Arec }}\left({ }^{\circ}\right)$ | $\tilde{V}(\mathrm{~mm} / \mathrm{min})$ | $\ell$ |
| :---: | :---: | :---: | :---: | :---: |
| Immersion oil <br> $\gamma=37.11 \mathrm{mN} / \mathrm{m}$ | 19.2 | 38 | 20 | 13.5 |
| $\eta=98 \mathrm{cP}$ | 23 | 35.4 | 13.6 | 12.8 |
| Castor oil |  |  |  |  |
| $\gamma=35.17 \mathrm{mN} / \mathrm{m}$ |  |  |  |  |
| $\gamma$ <br> $\eta=950 \mathrm{cP}$ | 24.8 | 37.9 | 1.6 | 12.7 |
|  | 21.4 | 29.3 | 0.6 | 12.4 |

systematically observed in all our experiments. In order to verify that this is not an artifact due to the experimental method, we have realized the same contact angle measurements in the case of ridges deposited on homogeneous $\mathbf{A}$ or $\mathbf{P}$ surfaces : in these cases, the contact angles are found to be identical. Thus, we conclude that, in the experiments reported above, the ridge does not keep a circular profile but is deformed during its translation. However, we


Fig. 5. - Plot of contact angles, $\theta_{A}(\triangle)$ and $\theta_{P}(\bullet)$, as a function of time in the case of a ricin oil ridge ( $L=2.5 \mathrm{~mm}$ ) on a surface characterized by : $\theta_{\text {Arec }}=32.5^{\circ} ; \theta_{\text {Padv }}=19.5^{\circ}$.
stress that this deformation remains small and is not expected to modify the predictions in a significant way.
At longer times, the contact angles $\theta_{\mathrm{A}}$ and $\theta_{\mathrm{P}}$ decrease and tend asymptotically toward a constant common value $\theta$ which corresponds to the advancing angle on the $P$ surface $\theta_{\text {Padv }}$ (measured independently). This value has also some importance in the early stage of the phenomenon: when the contact angle $\theta_{\mathrm{P}}$ reaches the value of $\theta_{\text {Padv }}$, we observe a discontinuity of the slope in the $\theta_{\mathrm{P}}$ curve, while the contact angle $\theta_{\mathrm{A}}$ begins to increase from the value it has taken quasi instantaneously at the start of the motion.
4.1.3 Ridge instabilities. - As already mentioned, the use of liquid ridges can lead to the appearance of instabilities [10], as currently observed in cylindral geometries : in order to lower their surface energy, they break into droplets with a diameter of about $L$, in a typical time $t_{0}$ of the order of $L V^{*-1} \theta_{\mathrm{e}}^{-3}$. In principle, we expect that this time is of the same order of magnitude as the duration of the motion of the ridge on a mixed surface i.e.

$$
\tau=L / \tilde{\boldsymbol{V}}=L\left[V^{*} \tilde{\theta}\left(\frac{\theta_{\mathrm{Ae}}^{2}-\theta_{\mathrm{Pe}}^{2}}{2}\right)\right]^{-1}
$$

However, in our experiments, we have nearly always observed that $\tau>\tau_{0}$ which means that the motion is undisturbed by the growth of instabilities. This may be verified by incorporating small solid particles with the liquid in order to put into evidence the flow lines : when instabilities begin to appear these lines are no longer perpendicular to the ridge axis but become longitudinal. This happens only when the two surfaces have very close surface properties which corresponds to a small velocity $\tilde{V}$. The results obtained under these conditions cannot be taken into account.

On the contrary, we have observed that if the surfaces have different enough properties, a ridge anchored on the boundary remains stable while it would be instable on the homogeneous P or A surfaces. From this experimental observation, we conclude, without any
definitive theoretical explanation, that instabilities are less perturbating in a heterogeneous geometry than expected.
4.2. Description of the motion. - On the basis of the results presented above we are able to describe the whole dynamics of the drop. This is conveniently done by schematically representing on a same graph, the plots of both $x_{\mathrm{A}, \mathrm{P}}$ and $\theta_{\mathrm{A}, \mathrm{P}}$ evolutions in a common time scale (see Fig. 6).

t
Fig. 6. - Schematic plot of both $x_{\mathrm{A}, \mathrm{P}}$ (full line) and $\theta_{\mathrm{A}, \mathrm{P}}$ (dotted line) as a function of time.

In a first stage (phase I), the contact line $\mathcal{L}_{\mathrm{P}}$ is fixed by hysteresis while the other line $£_{\mathrm{A}}$ moves with a constant angle. When the angle $\theta_{\mathrm{P}}$ reaches the advancing angle $\theta_{\text {Padv }} \mathfrak{L}_{\mathrm{P}}$ begins to move. After a transitory regime (phase II) where the width of the strip diminishes, the system reaches a stationary state (phase III) : the ridge moves at a constant velocity, with a small deformation when compared to a circular profile. The angle of the advancing edge is found to be smaller than the receding one. After the anchoring of $\mathscr{L}_{\mathrm{A}}$ on the boundary by canthotaxis effect, the ridge spreads on the P surface (phase IV). At the end of the motion, the strip is at equilibrium on the P surface with both contact angles equal to the advancing angle on $P$ surface $\theta_{\text {Padv }}$.
4.3 DISCUSSION. - The results presented above permit a detailed description of the motion of a liquid ridge deposited on the boundary line between two different solid surfaces. The whole behaviour is reasonably understood; in particular, we observe a stationary regime corresponding to a uniform translation, as predicted by the theoretical model in its asymptotic limit. However, a more careful analysis indicates some disagreements with the model : the two contact angles are not exactly equal during the stationary regime so that the drop is deformed when compared to circular profile. This proves that the pressure is not uniform within the liquid, in opposition to one of the hypotheses of the model which assumes an infinitely rapid pressure equilibrium. In order to check this interpretation, it is important to
determine the order of magnitude of the characteristic time involved in the pressure equilibrium. With that aim, we have prepared a sample with an appropriate geometry: the ridge is deposited so that its contact line $\mathscr{L}_{A}$ is very close to the boundary $\mathcal{L}$. Thus, the line $\mathcal{L}_{\mathrm{A}}$ anchors on $\mathbb{L}$ before the contact angle $\theta_{\mathrm{P}}$ reaches the advancing angle $\theta_{\text {Padv. }}$. We thus obtain a deformed ridge, the two edges $\mathcal{L}_{A}$ and $\mathcal{L}_{\mathrm{P}}$ of which are fixed by canthotaxis and hysteresis respectively. The time needed to obtain identical contact angles on both sides is then only due to the pressure balancing within the drop. We find that, in the case of ricin oil, few seconds are necessary to reach pressure equilibrium i.e. identical contact angles $\theta_{\mathrm{A}}$ and $\theta_{\mathrm{P}}$. This time is of the order of those involved in the motion of the ridge, this explains the deformation of the ridge during the motion.

Other phenomena that interfer in these experiments and are not taken into account in the simple theoretical description, are the hysteresis effects. A first consequence of this effect has already been mentioned : the line $\mathfrak{L}_{P}$ does not move at the beginning of the process because the ángle $\mathcal{L}_{\mathrm{P}}$ has not reached the advancing angle $\theta_{\mathrm{Padv}}$. Hysteresis may also have another less evident consequence if we try to verify quantitatively the validity of the expression of $\tilde{V}$ as a function of liquid and surface characteristics: the contact angles which appear in formula (5) are equilibrium angles while the only ones available experimentally are static advancing or receding angles. In the case of surfaces with hysteresis, there exists no theoretical expression of the dynamic contact angle as a function of the velocity of the contact line. In the following, we use the relationships obtained for a surface without hysteresis given in the theoretical section, but replace the equilibrium contact angles by the static angle corresponding to the direction of motion of the line considered i.e. advancing angle $\mathscr{L}_{\mathrm{P}}$ and receding one for $\mathfrak{L}_{\mathrm{A}}$.

It is possible to modify the theoretical model by introducing the non circular profile of the ridge. Thus, we consider a ridge with two edges of contact angles $\tilde{\theta}_{\mathrm{A}}$ and $\tilde{\theta}_{\mathrm{P}}$. We then balance the work of the forces acting on the two edges and the total viscous dissipation. We get :

$$
\tilde{V}=V^{*} \tilde{\theta}^{\prime}\left(\frac{\theta_{\text {Arec }}^{2}-\theta_{\text {Padv }}^{2}}{2}-2 \tilde{\theta}^{\prime} \Delta \theta\right)
$$

where

$$
\begin{aligned}
\tilde{\theta}^{\prime} & =\frac{\tilde{\theta}_{\mathrm{A}}+\tilde{\theta}_{\mathrm{P}}}{2} \\
\Delta \theta & =\frac{\tilde{\theta}_{\mathrm{A}}-\tilde{\theta}_{\mathrm{P}}}{2}
\end{aligned}
$$

Note that this expression of $\tilde{V}$ takes into account the modifications due to hysteresis effects. We may then compare the experimental values of the velocity measured during the stationary regime and those obtained by this formula. This can be done for different values of the liquid viscosity and surface tension, and for different surfaces characterized by contact angles. The results are reported in table I. We find a reasonable agreement for all our data and a unique value of the only adjustable parameter $\ell$. The value of $\ell$ for which the experimental measures and theoretical calculations coincide is

$$
\ell=13 \pm 0.5 .
$$

An accurate theoretical estimate of this logarithmic factor is delicate; from previous results [11] in a situation of partial wetting comparable to the present one, we have deduced $\ell \approx 12$. Consequently, the order of magnitude of the value of $\ell$ obtained from our data appears to be reasonable.

## 5. Conclusion.

We have reported an experimental study of the behaviour of a liquid droplet when deposited on the boundary line between two different solid surfaces: one observes that, due to unbalanced Young forces on the contact lines, the droplet shifts toward one of the two surfaces. Choosing a convenient cylindrical geometry, we have measured, under the same experimental conditions, the displacements of the two contact lines and the corresponding contact angles. These coupled measurements permit a detailed description of the motion of the liquid ridge which exhibits several regimes. The whole results are qualitatively well understood. In particular, we observe a stationary regime where the ridge moves with a constant velocity, in good agreement with a theoretical prediction [3]. However, one of the main conclusions of this study is that the ridge does not exhibit a circular profile during the motion. From the evidence of this deformation, even during the stationary regime, we may conclude that the pressure within the drop does not reach equilibrium in times infinitely short as usually assumed. Moreover, we have been able to measure the order of magnitude of the characteristic time involved in the pressure balancing. Another surprising result concerns the growth of instabilities of the ridge : we have observed that they develop more slowly than expected from similar experiments on homogeneous surfaces where a ridge tends to split in spherical droplets. In the same way, a ridge may remain stable for a very long time (several weeks) when anchored on the boundary line by canthotaxis effects (if the two parts of the plate have different enough surface properties). This provides additional evidence of the specific properties of a line of chemical discontinuity as already observed in the case of amphiphilic solid particles [1, 2].

For the sake of comparison, it would be interesting to extend this study to situations where the surface properties vary in a continuous way, as for instance in chemical or thermal gradients.

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