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Wetting and Dewetting Transition: An Efficient Toolbox for Characterizing Low-Energy Surfaces

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The capillary bridge formed between a solid spherical surface and an infinite liquid bath is an efficient technique for characterizing the adhesion property of a solid surface. When the solid surface is pulled out of the liquid at a sufficiently high velocity, a thin liquid film is deposited on the solid and drains more slowly than the central capillary bridge. The retraction kinetics of this "pancake" and the critical velocity above which it appears are studied as a function of the viscosity of the liquid or the wettability of the solids. The dynamics of the liquid film follows the classical law of dynamic dewetting. This makes the capillary bridge test, used in the dynamical regime, a very efficient tool for discriminating between antiadhesive coatings.

1. Introduction

A number of practical situations such as antidirt or antifouling coatings[1] deal with extremely weakly adhesive surfaces. Although the exact level of adhesion is often crucial for applications, such very weak levels of adhesion are difficult to characterize in an objective manner. It then becomes quite difficult to correlate the molecular characteristics of the weakly adhesive surfaces to the macroscopic adhesion energy, whereas it is well admitted that these molecular characteristics should deeply affect the intermolecular interactions with materials placed into contact with the surface. Various techniques and methods have been developed to characterize these kinds of surfaces in a qualitative manner. The most common test is based on wetting[2−6] and indirectly characterizes the critical surface tension of the surfaces through contact angle measurements with various liquids.[7] With this technique, the important parameter is the equilibrium contact angle θ_e of a given liquid on a solid surface, and a series of test liquids with decreasing surface tension but similar intermolecular interactions are usually used to estimate the critical surface energy of the substrate (i. e., the surface tension of the liquid that would just reach the total wetting of the surface). However, this technique is not always sensitive enough and remains a local characterization because small liquid drops are usually used and thus provide information only on the actual surface where they are deposited. Moreover, an equilibrium contact angle is always very difficult to measure because of the always present heterogeneities (chemical and geometrical roughness), which leads a real surface to exhibit contact angle hysteresis, with differences between advancing and receding contact angles that may be larger than the differences in the contact angle resulting from small changes in the molecular characteristics of the surface. Despite these deficiencies, the wetting method is widely applied in surface characterization.[3−6,8]

Another test now widely used is the Johnson, Kendall, and Roberts (JKR) test,[9,10] which opposes elastic deformation forces to adhesion forces. JKR instruments usually utilize an optical microscope to measure the contact area between a spherical elastic cap (lens) and a flat substrate. The lens is pressed against the substrate, and it is subsequently retracted until separation occurs. Under the imposed displacement (d), the contact area (A) and the external load (P) are recorded. Using the measured values of the radius of the contact area, a, and P, the work of adhesion between the contacting surfaces can be quantitatively determined by the JKR contact mechanics theory.[9]

With very weakly adhesive surfaces, however, even very soft elastomers have an elastic modulus that is too high to provide a balance between elastic and adhesive energies for detectable strains: even very small pull-off displacements lead to a loss of contact. The work of adhesion can be extracted from P and a measured for the loading part of the experiment, but nothing can be deduced from the unloading part.

To overcome this difficulty and gain better insight into the molecular mechanisms leading to extremely weak adhesion, we have recently proposed a quantitative JKR-like test that is based on the formation and breakage of a capillary bridge between the investigated surface and a liquid bath. In this new test, capillary forces are opposed to adhesion forces and noticeable deformations can be achieved before the rupture of contact between the liquid and the surface.[11] By changing the distance between the

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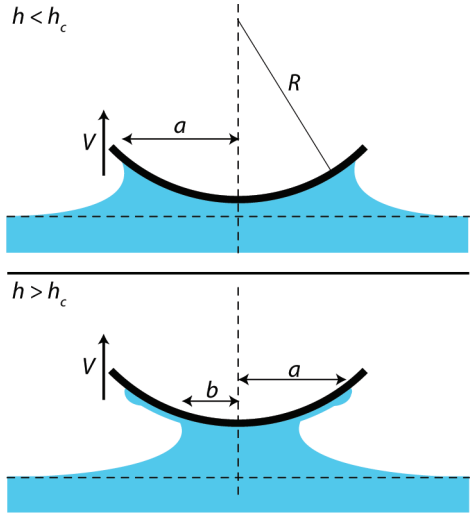

Figure 1. Capillary bridge between a spherical surface of radius R and the liquid.

liquid bath and the surface, one can tune and monitor the deformation of the capillary bridge, providing an efficient way of differentiating otherwise quite apparently similar surfaces.[12] The exact shape of the capillary bridge thus results from a balance between wetting forces at the liquid−surface interface and capillary forces on the bridge, which can be smoothly changed by changing the distance between the liquid bath and the surface. In a recent paper,[12] we described in detail this new test and qualitatively identified two velocity regimes. For low pull-off velocities, a quasi-static regime (regime A) is observed that is well described by capillary equations and is sensitive to the hysteresis of the contact angle of the fluid on the coating. Above a critical pull-off velocity that depends on the fluid viscosity, a dynamic regime (regime B) is observed that is characterized by the formation of a flat "pancake" of fluid on the tested surface, which recedes more slowly than the capillary bridge itself. This film entrainment is due to the wetting transition phenomenon that is close to the liquid entrainment occurring in the Landau−Levich transition.[13−17] After the breakage of the capillary bridge, a small drop can remain attached to the surface. The volume of this drop depends on the dynamic regime and is strongly affected by very small differences between coatings.

In this article, we present new results concerning the dynamics of the capillary bridge in the high-velocity regime (regime B) and quantitatively analyze them in terms of dynamic dewetting. We show that this dynamic regime is even more sensitive to tiny details of the molecular characteristics of the surface than is the quasi-static one. Thus, the capillary bridge test, in the dynamic regime, appears to be a particularly sensitive tool for characterizing weakly adhesive surfaces.

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Table 1. Contact Angle of Water Measured Using the Capillary Bridge Technique on the Three Studied Coatings

system	θ_r	θ_a	$\Delta\theta$
coating A − water	92.5	111.7	19.2
coating B − water	105.2	111.2	6.0
coating C − water	101.7	113.4	11.3

Table 2. Physical Properties of Silicon Oils

liquid	viscosity (mPa·s)	density ($g\cdot cm^{-3}$)	surface tension ($mJ\cdot cm^{-2}$)
47 V100	100	0.965	20.9
47 V300	300	0.97	21.1
47 V500	500	0.97	21.1
47 V5000	5000	0.97	21.1

2. Experimental Section

The capillary bridge apparatus has been described in detail in a previous paper.[11] It consists of bringing a spherical watch glass (coated with the material to be tested) into contact with a bath of silicone oil. The capillary bridge that forms spontaneously when the surface touches the liquid bath is observed from the top and from the side. The glass surface is pulled out of the bath at a chosen velocity . The evolution of the shape of the capillary bridge as a function of h, the distance between the surface and level of the liquid bath, is monitored through two synchronized video cameras providing the contact area of the liquid on the solid and the profile of the capilary bridge (Figure 1).

The surfaces used in the present investigation were spherical watch glasses with a radius of curvature of $R = 10$ cm and were covered by three types of slightly different perfluorinated coatings. All coatings, obtained by grafting functionalized perfluoroalkane chains by vapor deposition, have a thickness in the range of 3 to 7 nm (qualitatively controlled with a quartz microbalance during the deposition process) and a small roughness of 1.5 nm rms as measured through AFM in contact mode. These coatings differ essentially in the exact chemistry of the grafted polymer molecules and cannot be detailed more accurately for confidentiality reasons. Contact angles of water measured using the capillary bridge techniques on these coatings are reported in Table 1.

Several commercial trimethyl-terminated silicon oils (Rhodia silicone, 47 VX where X is the kinematic viscosity in $mm^2\cdot s^{-1}$) were used as a liquid bath, allowing a change in the the liquid viscosity over a wide range, keeping the surface tension constant. The relevant characteristics of these oils are reported in Table 2. The contact angle was measured for the three silicon oils and the surfaces using the classical sessile drop method and found to be $\theta = 55 \pm 3°$, independently of coating or oil. It was not possible to determine a contact angle hysteresis on these surfaces with the silicon oils.

3. Results

When the surface is pulled off at high velocity, the capillary bridge first behaves qualitatively similarly to a quasistatic bridge, but after a given pull-off distance h_c ($h_c = 2519$ μm for the particular conditions of the experiment shown in Figure 2), a thin film develops, which is retained by the surface, while the central part of the capillary bridge continues to decrease in size almost as if no thin film was present. We have called this thin film the pancake. Its thickness is not constant when going from the central capillary bridge to the edge, where a ridge progressively appears close to the triple line. The ridge and the pancake are well visible in Figure 2c−e. The appearance of this pancake is similar to the phenomenon of thin film liquid entrainment that has been extensively studied in vertical plate geometry with respect to the

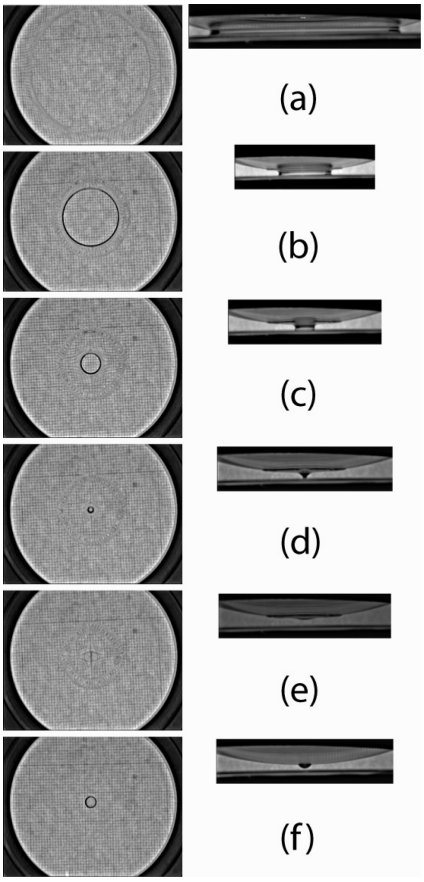

Figure 2. Aspect of the capillary bridge for different distances h between the bath and the solid. (Coating C, 120 μm/s, silicon oil 47 V500). (a) $h = 0$. The capillary bridge has a static shape. (b) $h = 2519$ μm. Transition between a quasi-static meniscus and a film plus a bridge. (c, d) $h = 3041$ μm and $h = 3170$ μm. A capillary bridge and a developed liquid film coexist. (e) $h = 3434$ μm. Liquid film when the capillary bridge is broken. (f) $h = 5130$ μm. Final spherical drop.

Landau−Levich transition.[13−17] The detailed analysis of the evolution of the geometrical characteristics of the pancake (thickness and radius) as a function of the parameters of the experiment (surface, pull-off velocity, and liquid) has been conducted in a systematic manner. We focus here on the evolution of the radius of the pancake as a function of both the pull-off velocity and the nature of the surface because this radius is far easier to measure accurately than the full thickness profile.

One can monitor the evolution of the horizontal projection of the contact area, $A(h)$, with h, the distance between the surface and the liquid bath. Indeed, two contact areas can be defined: that of the central capillary bridge and that of the pancake when it develops ahead of the central capillary bridge. The evolutions with time of these two contact areas are reported in Figure 3 for one particular coating in contact with the 47 V500 silicon oil. Filled symbols correspond to the contact area of the central bridge, and open symbols correspond to that of the capillary bridge.

The first important result is the remarkable reproducibility of the experiments, as demonstrated by the almost perfect superposition of the different symbols in Figure 3 where each category of symbol corresponds to an independent experiment. Two characteristic heights, h_c and h_r, can easily be defined with such data. h_c corresponds to the distance at which the pancake appears, and h_r corresponds to the distance at which the capillay bridge

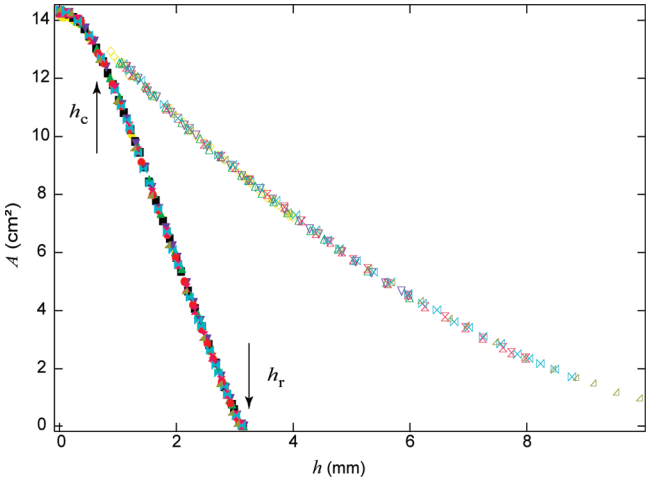

Figure 3. Evolution of the contact area with the distance between the surface and the liquid bath. Coating C in contact with the 47 V500 silicon oil. Filled symbols correspond to the contact area of the central bridge, and open symbols correspond to that of the pancake. Different symbols correspond to independent experiments and show the high reproducibility of the experiment.

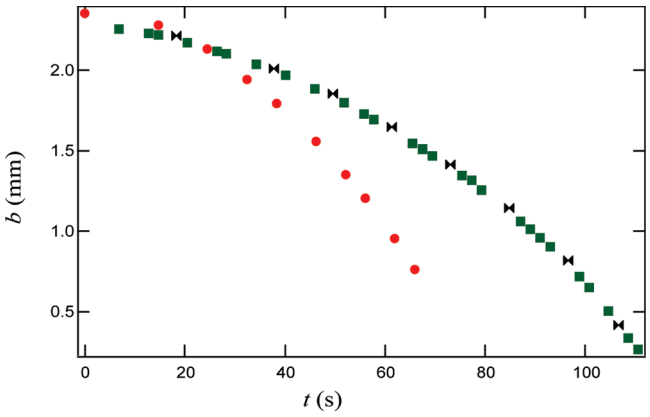

Figure 4. Influence of the coating on the dynamics of the central part of the capillary bridge: (■) coating A, (●) coating B, (⋈) coating C.

breaks. One can then think to examine in a systematic way how the nature of the surface and the pull-off velocity will affect both h_c and h_r.

A second observation is that no accident is observed on the pancake evolution when the capillary bridge breaks at a distance h_r. This seems to indicate that the mechanism responsible for the decrease in the size of the pancake is not suction by the capillary bridge even if the Laplace pressure inside the central meniscus is negative.

Because the two curves (central capillary bridge and pancake) in Figure 3 have a different slope, it is clear that the receding velocity of the bridge is different and faster than the velocity of the pancake.

In the static regime, we had shown[12] that measuring the capillary bridge radius was a simple way to characterize antiadhesive coatings. In Figure 4, the evolution of radius b of the center of the bridge is reported as a function of time for the same silicon oil and three different surface treatments. Clear differences are observed but not for all coatings. The dynamic central capillary bridge is not able to provide a sensitive enough test to discriminate between the three slightly different coatings investigated here. In fact, a naive interpretation would lead us to expect no influence of the coating on the central capillary bridge because this central

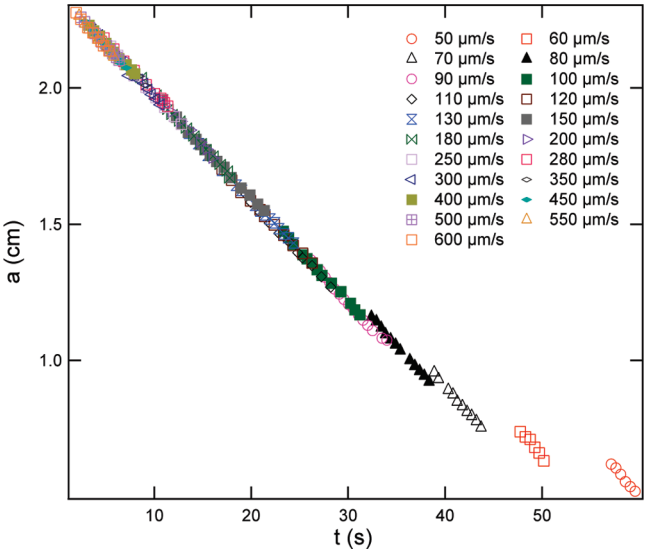

Figure 5. Radius of the pancake a as a function of time t elapsed from the beginning of the withdrawal for several pull-off velocities for coating C out of a bath of oil 47 V500.

bridge is connected to the pancake and not to the solid. In fact, small differences appear but they are difficult to use to easily compare surface treatments.

The situation appears to be quite different for the pancake. To investigate more precisely the velocity of the pancake, the radius a of the pancake as a function of the time rather than the distance h has been reported in Figure 5 for one specific surface and for different pull-off velocities. Almost all of the data points collapse on a single straight line with a slope $V_1 = -da/dt$. This allows one to conclude that the velocity of the triple line V_1 at the extremity of the pancake is essentially constant for a given coating and a given fluid and does not depend on the pull-off velocity. The fact that this velocity is constant, independent of the pull-off velocity, is somehow counterintuitive. Before the formation of the pancake, the receding velocity of the triple line is not a constant even at fixed pull-off velocity, due to the curved geometry of the surface. When the pancake forms, the receding velocity at the triple line becomes constant, independent on the pull-off velocity, while the thickness of liquid entrained by the surface do depends on both the pull-off velocity and the viscosity of the oil.

Small deviations in this constant receding velocity of the pancake are observed at large times. The corresponding points are obtained for low pull-off velocities, when the pancake appears at the end of the procedure for large h_c. Then there is no time to obtain a well-developed pancake, and it becomes difficult to clearly separate the pancake from the central part of the capillary bridge. The accuracy of this final part of the curve is thus not as good as that for the data obtained at large pull-off velocities.

The receding velocity of the pancake V_1 has been investigated for a given liquid on the three slightly different coatings (A, B, and C). The corresponding data are shown in Figure 6. This Figure again allows us to see that the receding velocity of the pancake is independent of the pull-off velocity. A remarkable result is the clear differences in the receding velocities V_1 of the pancake observed for the three different coatings: V_1 for this specific silicon oil varies from 22 to 55 μm/s on going from coating A to C, and neat differences are visible for coatings that were not discernible by the characterization of the evolution of the central capillary bridge nor by classical contact angle and contact angle

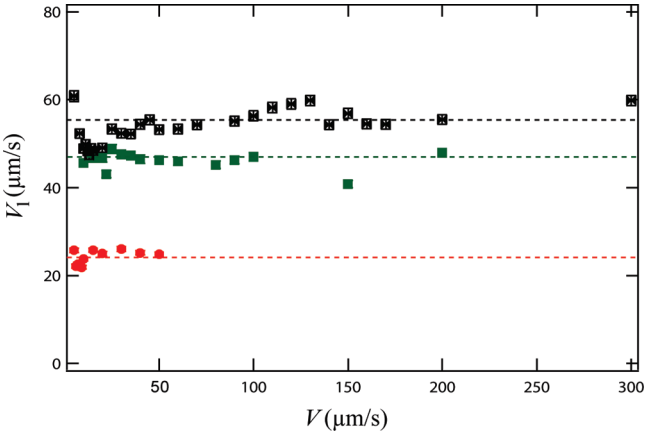

Figure 6. Influence of the coating on the pancake velocity. The three sets of points correspond to two different surfaces with similar coatings. For these points, we used a 47 V5000 silicon oil: (●) coating A, (■) coating C, and (⋈) coating B.

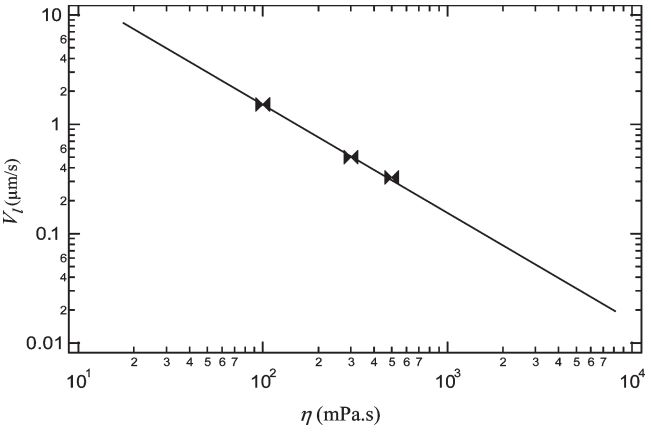

Figure 7. Influence of the silicon oil viscosity on the pancake velocity for a same coating in a log−log plot. The straight line has a slope of −1. Each point correspond to the average of the velocities measured in a Figure, such as Figure 6.

hysteresis measurements with silicon oils using the sessile drop method.

To understand better the physical origin of the pancake, the influence of the viscosity of the liquid on V_1 has been investigated in a systematic manner. In Figure 7, the average receding viscosity V_1 (extracted from data analogous to those shown in Figure 6) has been reported as a function of the silicon oil viscosity. The higher the viscosity, the smaller the receding velocity of the pancake, in agreement with intuition. More quantitatively, the data reported in the log−log plot show that the scaling dependency of V_1 versus the liquid viscosity is

$$V_1 \propto \frac{1}{\eta} \qquad (1)$$

4. Discussion

The important role played by viscosity in eq 1 suggests that the movement of the triple line at the extremity of the pancake is controlled by a competition between capillary forces and viscous flow. Such an effect has already been observed by Redon[18] in analyzing the opening of a dry hole in a metastable film. Indeed,

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there is a great similarity between the two problems: the pancake being similar to a dynamic wetting film, tending to dewet the surface, with the formation of a rim collecting the liquid displaced from the dried surface. Only the geometry differs with more conventional investigations of dewetting films. It is then tempting to analyze the results obtained with the capillary bridge test in the dynamical regime within the framework of theories of drying and dewetting. Close to the triple line, a rim collects the liquid. The profile of this rim is a portion of a circle (with a dynamic contact angle θ_d) because the pressure is expected to equilibrate rapidly inside the rim. For small angles (θ_e, $\theta_d = 1$), one can estimate the velocity of the triple line:

$$\frac{1}{2}\gamma{\theta_d}^2 = 3\eta L{\theta_d}^{-1}V_l \quad (2)$$

The left-hand side of eq 2 represents the unbalanced horizontal Young force on the triple line, and the right-hand side is the viscous force due to the flow in a wedge of angle θ_d. L is a logarithmic factor of order 10 and is due to the divergence of the dissipation in a wedge. Using the same kind of arguments to calculate the velocity inside the rim leads to the classical dewetting velocity:

$$V_l = \frac{\gamma}{\eta}\frac{1}{12L\sqrt{2}}{\theta_e}^3 \quad (3)$$

A simple numerical estimate with $\theta_e = 55°$, $\eta = 5$ P·s, and $\gamma = 20$ mN/m gives $V_l \approx 20$ μm/s, a good order of magnitude compared to the data in Figure 6. The receding velocity of the pancake in the capillary bridge experiments can indeed be understood as a dewetting velocity: when the spherical glass surface is placed into contact with the liquid bath, a capillary bridge forms and part of the surface is wetted by the liquid. When the solid is pulled off the liquid, the triple line has to recede on the surface. Because of the curvature of the surface, a constant pull-off velocity does not imply a constant velocity of the triple line: V_l increases when the bridge's size decreases. When the velocity of the triple line reaches a threshold velocity, a wetting transition occurs and a liquid film (the pancake) remains trapped by the spherical surface. When this pancake is sufficiently developed, its dynamics becomes independent of the central part of the capillary bridge: it dewets. The triple line recedes on the solid with the classical dewetting velocity on this particular solid.

The velocity of the pancake appears to be a useful tool for characterizing antiadhesive surfaces. Antiadhesive surfaces are usually hydrophobic, and the contact angle with water is not sensitive enough to discriminate between nearby surfaces. Indeed, all classical wetting experiments are sensitive to cos θ_e. A major result of the dewetting results, as shown in eq 3, is that the pancake velocities evolve like

$$V_l = \frac{\gamma}{\eta}k{\theta_e}^3 \quad (4)$$

where k is a constant depending on the liquid. The dependence of the pancake on the wettability is emphasized by the dynamic-process dewetting, and this is what makes this technique very sensitive to very small differences in the physical chemistry of the surface treatments. This is indeed the main origin of the high sensitivity of the capillary bridge technique used in the dynamical mode in the low-angle regime.

5. Conclusions

We have presented in the past a new adhesion test, the capillary bridge test, specifically designed to analyze very weakly adhesive surfaces. In this test, the deformations of a liquid surface are used to trace the adhesive properties of the investigated surface. The surface to be investigated has a spherical shape and is placed into contact with a liquid bath so that a capillary bridge forms. Pulling the surface of the bath allows one to deform the capillary bridge progressively. Monitoring the evolution of the capillary bridge with the pull-off distance yields both qualitative and quantitative information on the adhesive properties of the surface. We show here that for large enough pull-off velocities the shape of the capillary bridge deviates from its quasistatic shape. Signatures of the non-quasi-static behavior are the appearance of a thin liquid film, the pancake, remaining on the surface behind the central capillary bridge and the fact that the viscosity of the liquid becomes an important parameter. We have analyzed in detail the receding velocity of this pancake and have shown that it behaves as a dewetting film. We have also shown that this pancake is very sensitive to tiny differences in the properties of the surface. In particular, it reveals otherwise invisible heterogeneities of the surface treatment. An additional important aspect is the fact that when a pancake is formed the volume of liquid remaining trapped on the surface after the breakage of the capillary bridge appears to be larger than in the quasi-static pull-off regime and depends on both the viscosity of the liquid and the wetting properties of the surface. Again, this volume is related to the adhesive power of the surface, with a sensitivity that appears to be enhanced compared to that of the quasi-static case. From a practical point of view, the capillary bridge test thus provides an easy way for objectively comparing otherwise very similar surfaces in terms of the adhesive strength.

Because of its high sensitivity and convenient geometry, the above presented test opens the route to systematic investigations of still open questions concerning the dynamics of wetting and dewetting such as what fixes the receding contact angle on a molecular level, what is the exact role of the friction of the liquid on the surface, and what allows a triple line to remain pinned or to sweep and at what velocity? We believe that the capillary bridge test should help to illuminate these questions that remain pending because of the experimental difficulties first in controlling the surfaces down to the nanometer or molecular scale and second in being able to characterize the response of a triple line to tiny perturbations of these surfaces.

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