

Slippy and sticky microtextured solids

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Abstract

The aim of this paper is to describe the possibility of achieving super-hydrophobic materials by tailoring their surface topography. Water droplets easily slip or roll down on such surfaces. However, it is found that microtextures on a solid can generate sticky surfaces as well, and the conditions for avoiding such an effect are discussed.

1. Adhesive properties of drops

When a drop is deposited onto a solid surface, it develops a contact with the solid. The expansion of this contact can be deduced from the volume of the droplet and the so-called contact angle: the drop meets the surface with an angle fixed by the nature of the three phases coexisting at that place. Since a surface tension can be associated with each interface (we denote the surface tension between phases I and J by γ_{IJ}), the balance of these forces can be written as (as proposed by Young in 1805)

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

where the letters S, L, V designate the solid, liquid and vapour. Since a small drop is a spherical cap of radius R , the solid/liquid interface is just a disc of radius $R \sin \theta$. For common values of θ , a drop thus develops with its substrate a contact of about its own size.

The concept of equilibrium contact angle does not allow us to understand the ability of drops to stick to their substrates (a very common behaviour). On vertical window panes, for example, we can all see millimetric rain droplets stuck in spite of gravity. This phenomenon arises from fluctuations of the static contact angle: the observed value of the contact angle is not unique as expected from equation (1) but spans a range of a typical amplitude of 10° – 50° . The maximum and minimum static values of the angle are respectively called the advancing and receding contact angles, and the difference $\theta_a - \theta_r$ between them the contact angle hysteresis (CAH). For a drop at rest on a tilted plane, the contact angle is larger at the front and than at the rear; this generates a force opposing the weight of the drop (and able, if the drop is small enough, to balance it): the liquid is pinned [1].

CAH is due to heterogeneities (in topography and chemical composition) which are always present at a solid

surface, and induce fluctuations of the quantities γ_{SV} and γ_{SL} [2]. In this short review, we first discuss how the CAH generates an adhesion force; then we describe how the contact angle and the CAH can be controlled by tailoring the surface topography of the solid substrate.

The derivation of the adhesion force acting on a drop is quite subtle, and must generally be done numerically, as shown in a very comprehensive way by Dussan and Chow [1]. However, there is one special case where the adhesion force can be calculated exactly, which is the case for a drop inside a capillary tube. Then the (maximum) angle at the front is θ_a , while the (minimum) angle at the rear is θ_r , which generates a maximum sticking force of $2\pi b\gamma_{LV}(\cos \theta_r - \cos \theta_a)$ (where b is the tube radius). We easily deduce that the maximum length L for a stuck drop is $2(\cos \theta_r - \cos \theta_a)\kappa^{-2}/b$, introducing the capillary length κ^{-1} ($\kappa^{-1} = (\gamma_{LV}/\rho g)^{1/2}$, with ρ the liquid density). L can be larger than 10 cm for a tube radius of the order of 100 μm .

For a drop on a (tilted) plate, calculation of the maximum drop size is complicated by the variation of the angle all along the contact line. A convenient approximation consists of dividing the drop into two halves, and assuming that each half joins the solid with an angle of (at least) $\theta_r = \bar{\theta} - \Delta\theta/2$ at the rear, and (at most) $\theta_a = \bar{\theta} + \Delta\theta/2$ at the front (where $\bar{\theta}$ is the mean contact angle) [3]. To a first approximation, the sticking capillary force can be written as $\pi b\gamma_{LV}(\cos \theta_r - \cos \theta_a)$, where b is the mean radius of the solid/liquid contact (quasi-circular for $\Delta\theta \ll \bar{\theta}$). This force is bounded, which means that for a given tilt angle there is a threshold in size above which a drop starts moving. Quite commonly, this size is of the order of κ^{-1} , i.e. a few millimetres for water. Yet this threshold can be considerably lowered by decreasing either the CAH (responsible for the sticking) or the solid/liquid contact b —which of course implies an increase of the contact angle. We discuss here how a microtexture at a surface reinforces the

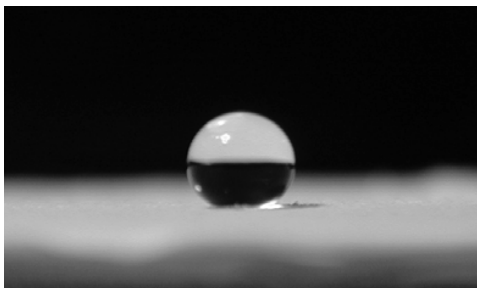


Figure 1. On a surface which is both rough and hydrophobic, the contact angle of water is observed to be very high (typically between 160° and 170°). This situation is often referred to as super-hydrophobic.

natural hydrophobicity of this surface, leading to anti-adhesive properties.

2. Super-hydrophobic states

A highly hydrophobic state should naturally lead to a reduction of drop pinning. Then, the contact angle tends towards π (and we shall note $\theta = \pi - \varepsilon$ in this limit), and the expansion $R \sin \theta$ of the solid/liquid contact scales as $R\varepsilon$, and thus efficiently vanishes as we get close to zero wetting. This effect is exploited in detergency, where one tries to remove an oil stain from a piece of cloth. When the polluted solid is immersed in soapy water, the surfactant molecules adsorb at interfaces (in particular at the solid/water and water/oil interfaces), and they lower the corresponding surface tensions. In equation (1) (where we now consider oil as a liquid, and water as the surrounding phase), if γ_{OW} almost vanishes while γ_{SW} is made smaller than γ_{SO} , a contact angle of order π is ideally produced, which leads to easy detachment of the oil.

The situation is, however, quite different when a liquid droplet surrounded by air is deposited on a solid. In this case there is generally no chemical to generate such high values of contact angle. With water, for example, the most hydrophobic material is Teflon[®], which exhibits contact angles between 110° and 120° [4] (the expansion of the contact zone is therefore comparable with the radius of the drop). Because of the obvious practical interest in getting higher contact angles, surface chemists and physicists have tried to imagine methods other than chemical ones—and it was indeed found that the hydrophobicity of a solid can be dramatically increased by texturing the solid. This effect was first reported by Wenzel [5], Cassie and Baxter [6] and Johnson and Dettre [7]. They found that the typical water contact angles on rough surfaces jump to values of the order of 160° , and researchers from the Kao Corporation recently observed water contact angles as high as 174° on a very disordered surface [8]. As an example, we show in figure 1 a water drop on a rough hydrophobic surface (obtained by gluing a hydrophobic powder on glass), for which the contact angle is about 165° .

Two possible scenarios can explain the so-called super-hydrophobic effect. The first idea, due to Wenzel, is that increasing the surface area of a hydrophobic solid necessarily increases its hydrophobicity [5, 9, 10]. More precisely, if we denote as r the ratio between the actual surface area of a rough solid and its projected (or apparent) surface area, the actual

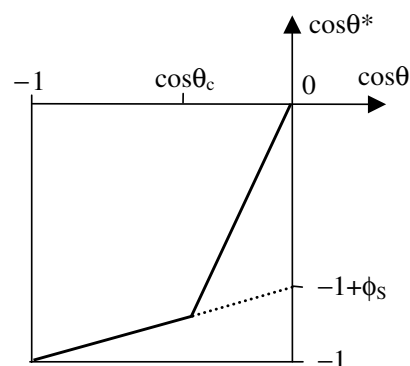


Figure 2. The different models of super-hydrophobicity. At moderate hydrophobicity ($90^\circ < \theta < \theta_c$), the Wenzel state (equation (2)) should be selected; for very hydrophobic materials ($\theta > \theta_c$), air should be trapped below the drop, and the Cassie model (equation (3)) followed. The respective slopes of the lines are r and ϕ_s . We also indicate that the Cassie model can persist in the Wenzel region. This metastable situation is indicated by the dotted line.

surface energies of the solid are multiplied by this quantity r , so that the apparent contact angle θ^* on a rough surface can be deduced very simply from equation (1):

$$\cos \theta^* = r \cos \theta \quad (2)$$

where θ is the Young contact angle.

The second idea, first expressed by Cassie and Baxter [6], is quite different. A rough hydrophobic surface can be considered as a kind of porous medium where the penetration of the liquid is not favourable. Thus, air pockets remain trapped below the liquid, which sits above a patchwork of solid and air. A contact angle can also be deduced in such a case: a drop on a flat solid makes an angle θ , while it does not spread at all on a pure film of air (contact angle of π), and the average value it takes on the patchwork is an average on the cosines (since equation (1) shows that the surface energies lead to such a function), weighted by the respective proportions of solid and air below the drop. Hence we get [11]:

$$\cos \theta^* = -1 + \phi_s (\cos \theta + 1) \quad (3)$$

where ϕ_s defines the fraction of solid remaining in contact with the drop. This factor is not necessarily easy to define in the case of a rough surface, but can be determined very precisely for textured surfaces, such as those consisting of posts, or parallel channels. Then ϕ_s is just the ratio between the surface area of the peaks of the texture and the total surface area: the drop behaves like a fakir sitting on a bed of nails. For ϕ_s between 5 and 10% and θ of about 120° , we get apparent contact angles around 170° , very close to the observed values [11]. Note finally that a condition for observing such a state is the possibility for the numerous contact lines associated with the air pockets to meet the solid with the Young contact angle θ . This implies either high slopes on the solid (and the line fixes at the place where it satisfies Young's condition, which implies that ϕ_s should itself depend on θ in such a case), or edges where the contact line can pin [7, 11]. The two laws of super-hydrophobicity predict quite different behaviours, as shown in figure 2.

From the Wenzel model (equation (2)), we expect a continuous variation of the contact angle as a function of the hydrophobicity of the material, and the possibility of inducing a drying transition ($\theta^* = 180^\circ$) provided that the substrate is rough enough ($r > r^* = 1/|\cos \theta|$). The latter fact contradicts all the available data. On the other hand, equation (3) predicts a discontinuous variation of the contact angle θ^* when the material becomes hydrophobic ($\theta > 90^\circ$), since the contact angle is found to jump to a value given by the equation: $\cos \theta^* = -1 + \phi_s$. Moreover, total drying cannot be observed (except in the obvious case $\theta = 180^\circ$), since solid/liquid contact remains on a fraction of ϕ_s .

Comparing the surface energies of both states allows us to understand which one should be selected by the system [12, 13]. The result can be understood qualitatively: if the hydrophobicity of the material is very high, it is not favourable for the liquid to follow the accidents of the solid surface, and air pockets should be favoured. On the other hand, such pockets imply a liquid/vapour energy, and they are not likely to develop if the hydrophobicity is not high enough (i.e. if the energetic price of replacing a dry surface by a wet one is not too high). More precisely, the behaviours expected from equations (2) and (3) should be successively followed, increasing the hydrophobicity of the solid (i.e. increasing θ), as indicated in figure 2 with full lines.

The threshold between both states occurs for $\cos \theta_c = (\phi_s - 1)/(r - \phi_s)$, which corresponds to the matching point of both regimes. This formula fits with the qualitative expectations: for a very rough surface ($r \rightarrow \infty$), we find $\theta_c = 90^\circ$, which means that as soon as the substrate is hydrophobic ($\theta > \theta_c = 90^\circ$), air pockets should form. Conversely, many artificial microtextured surfaces consist of collections of spikes or posts, which are often rather dilute (to get ϕ_s as small as possible): this leads to quite small values of the roughness factor r , which means that the Wenzel state should be generally achieved for such surfaces. As we shall see later, both states may coexist and can easily be distinguished by their sticking properties.

3. High-contact-angle hysteresis

We have seen that a very efficient way to get very high values for the contact angle consists of achieving microtextured hydrophobic surfaces, which lead to very small solid/liquid contacts for the drops. Moreover, it is most often reported that for such super-hydrophobic surfaces, the CAH is dramatically reduced as well (with typical values of the order of 5° – 10°) [7, 11, 14]. This implies that both causes of adhesion are reduced at the same time, which makes these surfaces extremely non-adhesive. Millimetric (or even smaller) drops generally roll (or slide) off these surfaces. The maximum volume of liquid that gets stuck on the surface is reduced by a factor of order 100 (or even more), compared with usual surfaces. This property is obviously one major cause of the interest raised by these materials, and justifies why they are often referred to as water-repellent.

Since CAH originates in the defects of the solid substrate, we could expect a large hysteresis on rough or microtextured super-hydrophobic materials. As indicated above, this is not the case for most observations. This effect can be understood qualitatively if we assume that we are in a Cassie state

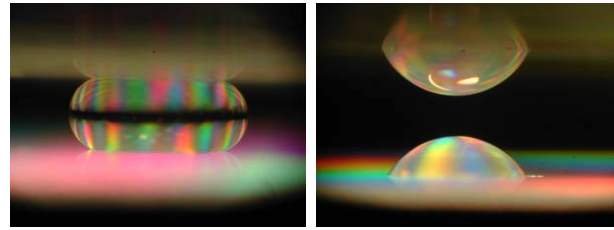


Figure 3. Compression of a millimetric water drop between two super-hydrophobic plates (left). Above a threshold in pressure, such a compression induces a transition to a Wenzel state, as shown when separating the plates (right): then, the receding contact angle is observed to be very low, because of a pinning in the microtexture.

(equation (3)). The ‘substrate’ is then mainly composed of air, which eventually leads to a strong reduction of the CAH. The opposite effect is observed in the Wenzel regime, where the number of pinning defects is amplified. Even if both situations lead to an increase of the contact angle, their main difference relies on the magnitude of the CAH.

It indeed turns out that a Wenzel drop is much more adhesive, even if it exhibits a high contact angle. This can be proved by forcing this state, which can be achieved in different ways: either by condensing a vapour, or by applying an external pressure on a deposited drop. Let us quote a recent experiment we performed on a microtextured surface consisting of triangular spikes (this sample was kindly provided by Holmes and Abbott) [15]. These spikes, which are micrometric in size, are coated with a fluoropolymer, which confers super-hydrophobic properties on the surface. A drop of water deposited on this substrate indeed exhibits a very high contact angle, of about 161° , together with a very small hysteresis (between 5° and 10°), which can be interpreted as resulting from air entrapment below the drop (Cassie state). If we now make the drop by condensing water vapour, we observe a very different behaviour. Firstly, the contact angle is slightly (but significantly) smaller: we measured 143° , instead of 161° . Secondly, the CAH was found to be dramatically increased: its value was found to be about 110° , instead of 10° .

Condensing a vapour should indeed lead much more naturally to a Wenzel state, and we interpret the latter experiment as forcing such a state. For moderate roughness and hydrophobicity we indeed expect Wenzel angles to be smaller than Cassie ones (see figure 2). But the most important fact is the dramatic increase of the CAH. This can be simply understood: as it recedes, the liquid is in contact with water trapped inside the texture, so that the contact angle should be given by an average between θ and 0 , yielding a very low value for the receding angle. Thus, rather than a small difference in contact angles, the main difference between both super-hydrophobic states lies in the adhesion properties: a Wenzel drop will adhere very efficiently to its substrate, in spite of a high contact angle.

On the other hand, we stressed that on many microtextured surfaces Cassie drops are observed naturally. They should be metastable if the Wenzel angle is smaller than the Cassie one, as in the example described above. This can be shown qualitatively by squeezing a water drop in between two identical microstructured hydrophobic surfaces (figure 3). The advancing contact angle can be measured as a function of the

applied pressure. For the particular triangular spike texture we mentioned above, we found that it decreases from the Cassie value to the Wenzel one, as on increasing the pressure [15]. After separating the surfaces, we can find two different final states, depending on the applied pressure. Below a certain threshold (of about 200 Pa in this particular experiment) we recover a Cassie drop, while above it the drop remains deeply stuck to both substrates; on separating them (figure 3) a Wenzel state is induced, in an irreversible way.

Both states should also lead to different friction properties, when a liquid flows on such solids. It is generally assumed that for a solid object moving in a liquid, the boundary condition at the solid/liquid interface is a continuity condition on the velocity (no-slip condition). For a liquid flowing on a solid at rest, the velocity should cancel at the solid/liquid boundary—which generates velocity gradients perpendicular to the flow direction, and thus a viscous resistance. Barrat and Bocquet showed numerically that this condition becomes questionable in a hydrophobic situation ($\theta > 90^\circ$) [16]. They found that slippage of the liquid can then occur on the solid: a depletion of the liquid is expected close to a hydrophobic surface (which prefers to remain dry than wet) [17], which leads to a possible slippage when the liquid flows. Together with Cottin-Bizonne and Charlaix, the same group recently discussed what happens if a textured hydrophobic surface is considered [18]. Their results finally lead to a conclusion very similar to what was discussed above: the effect of a texture is ambiguous, depending on the way the liquid follows (or not) the irregularities of the solid. If it does (Wenzel case), the slippage is greatly lowered and the friction increased (compared to a planar surface); on the other hand, if air remains trapped below the liquid, the slippage is (quite logically) reinforced. Thus our conclusions exceed the only case of wetting: Cassie states quite generally induce anti-adhesive behaviours.

4. Conclusions

Super-hydrophobicity is the reinforcement of (chemical) hydrophobicity by a texture. A drop deposited on such a substrate exhibits very high contact angles, and two different scenarios, respectively due to Wenzel and Cassie, can explain this effect: an increase of the surface area, assuming that the solid/liquid interface follows the solid topography, or air entrapment below the drop. Although both these states lead to a high contact angle, the CAH is found to be very different:

while it is extremely small in the Cassie state, it takes very large values in the Wenzel one, for which drop pinning is favoured. A similar distinction might exist for friction properties.

It is thus practically important to design textures which not only induce air trapping but which also make this state more stable than the Wenzel one. As shown above, this condition should be met if the contact angle verifies the inequality $\cos \theta < (\phi_s - 1)/(r - \phi_s)$; that is, if the roughness factor r is large enough. Practically, it should be made larger than $1/|\cos \theta|$, and thus all the larger since the solid is less hydrophobic. This suggests that all the microtextures are far from being equivalent—the air trapping must not only be favoured on these surfaces, it must also be maintained, which should be realized by increasing the roughness. Natural super-hydrophobic materials often exhibit two scales of roughness, which not only amplifies super-hydrophobic behaviours [19] but which should also keep the low-friction (or Cassie) regime stable.

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