Non-adhesive lotus and other hydrophobic materials

BY DAVID QUÉRÉ* AND MATHILDE REYSSAT

Laboratoire de Physique et Mécanique des Milieux Hétérogènes, ESPCI, 75005 Paris, France

Superhydrophobic materials recently attracted a lot of attention, owing to the potential practical applications of such surfaces—they literally repel water, which hardly sticks to them, bounces off after an impact and slips on them. In this short review, we describe how water repellency arises from the presence of hydrophobic microstructures at the solid surface. A drop deposited on such a substrate can float above the textures, mimicking at room temperature what happens on very hot plates; then, a vapour layer comes between the solid and the volatile liquid, as described long ago by Leidenfrost. We present several examples of superhydrophobic materials (either natural or synthetic), and stress more particularly the stability of the air cushion—the liquid could also penetrate the textures, inducing a very different wetting state, much more sticky, due to the possibility of pinning on the numerous defects. This description allows us to discuss (in quite a preliminary way) the optimal design to be given to a solid surface to make it robustly water repellent.

Keywords: wetting; roughness; superhydrophobicity

1. Drop on flat solids

When depositing a small drop on a solid, we commonly observe that the liquid makes contact with its substrate, whose size is most often of the order of the drop diameter (figure 1). Owing to the existence of surface tension (denoted as \( \gamma \)), the liquid–vapour interface is spherical (this minimizes the corresponding surface area), so that the contact size is geometrically set by the contact angle \( \theta \) with which the liquid meets the solid

\[
\ell = R \sin \theta,
\]

where \( R \) is the radius of curvature of the spherical cap.

The contact angle itself is obtained by balancing the three surface tensions acting on the contact line. Each interface draws on the line for reducing the surface area of the corresponding interface, and the balance can be written on the horizontal axis

\[
\gamma \cos \theta + \gamma_{SL} = \gamma_{SV},
\]

* Author for correspondence (david.quare@espci.fr).

One contribution of 7 to a Theme Issue ‘Nanotribology, nanomechanics and applications to nanotechnology II’.

doi:10.1098/rsta.2007.2171
Published online 11 January 2008
where $\gamma_{SV}$ and $\gamma_{SL}$ are the solid–vapour and solid–liquid surface tensions, respectively. Equation (1.2), the so-called Young’s relation, thus stipulates that the contact angle is uniquely defined by the nature of the solid and liquid (Young 1805). If this property were practically obeyed, a drop would necessarily slide when tilting the substrate: displacing the liquid along the plane does not modify any surface energy (proportional to the corresponding surface area), yet lowers gravitational energy. However, drops generally remain stuck on inclines (figure 2)—multiple angles are observed for a liquid sitting on a solid. As a result, the apparent angle at the ‘front’ is larger than the angle at the ‘rear’ (this can also be observed when trying to displace a liquid on a solid, using an airflow, for example), which generates a capillary force opposing the motion (Furmidge 1962). This phenomenon is due to the presence of defects on the solid, on which the contact line can pin, hence the existence of larger (or smaller) apparent angles, although some Young condition can be satisfied locally, at the scale of the (microscopic) defects.

The magnitude of the sticking force can easily be estimated. We first assume that the angles at the rear and at the front are, respectively, the receding and advancing angles $\theta_r$ and $\theta_a$ (minimum and maximum possible apparent contact angles). This condition, even if not necessarily verified experimentally, yields a maximum value for the sticking force (Krasovitski & Marmur 2005). Then, the force per unit length acting at the rear of the drop is $\gamma_{SV} - \gamma_{SL} - \gamma \cos \theta_r$ (which tends to retain it), while the force acting at the front is $\gamma_{SV} + \gamma \cos \theta_a - \gamma_{SL}$ (which also tends to retain it). Hence, the maximum sticking force can be written (in absolute value) $\gamma(\cos \theta_r - \cos \theta_a)$. If we naively integrate this force along the contact line, we find a sticking force $F = \pi \gamma R \sin \theta(\cos \theta_r - \cos \theta_a)$, which scales linearly with the drop size and denoting $\theta$ as an average contact angle (Dussan & Chow 1983; Quéré et al. 1998).
Since the sticking force is of the order of $\gamma R$ and the weight of the order of $\rho g R^3$ (here we assume a tilting angle of 90° and denote $\rho$ as the liquid density), only drops larger than the capillary length $k^{-1}=(\gamma/\rho g)^{1/2}$ will slide. This indeed corresponds to the very common observation we can make, looking at window panes on a rainy day—drops larger than a few millimetres slowly creep down, while smaller ones remain immobile. If we wish to make water drops mobile on a solid (to avoid optical distortions or corrosion), the strategy seems simple—we must either minimize the contact angle hysteresis $\Delta \theta \ (\Delta \theta = \theta_s - \theta_a)$ and/or maximize the (average) contact angle $\theta$. Here we show how both these objectives can be achieved using textured hydrophobic materials, restricting our discussion to the (important practically) case of water, as a liquid.

We could reach the same conclusion from a slightly different point of view. In many cases, it is desired to detach from their substrate drops such as the one sketched in figure 1 (think about detergency, for example). It is instructive to calculate the difference of surface energies for the drop in both situations (contacting its substrate or detached from it). If we denote $R_0$ as the drop size once detached, this energy difference is simply found to be $\Delta E = 4\pi \gamma R_0(1 - R_0/R)$, where $R$ is the radius of the spherical cap formed by the drop when it meets the solid with the angle $\theta$ (the smaller $\theta$, the larger $R$). This difference is positive—the surface energy of a drop is lowered as it contacts a solid and reaches its equilibrium position sketched in figure 1. It is commonly of the order of 1 $\mu$J, a very large quantity compared with energies ‘available’ for the system (such as thermal energy). As we can see, $\Delta E$ can be made much smaller by decreasing dramatically the surface tension (which can be done using special surfactants if the interface is a water–oil one) or by approaching (here again) the limit of zero-wetting ($R \rightarrow R_0$), the most efficient way for getting rid of adhesive drops.

### 2. The Leidenfrost effect

As we have understood from the first paragraph, the mobility (and detachment) of a drop should be maximized when making the wetting as low as possible. Mercury is called quicksilver, because it realizes this condition on most solids, which indeed makes it non-sticking. As for water, there is a situation where it is just as quick as mercury—the so-called Leidenfrost effect. This happens, as discovered in 1756 by the German physician Leidenfrost (1996), when depositing water on very hot solids (typically at a temperature higher than 200°C, i.e. much higher than the boiling point of water). Then, the water drops are observed to run everywhere, as we also see when pouring liquid nitrogen on the floor. Leidenfrost correctly interpreted the effect—the drop never contacts the solid, because a film of vapour comes in between the substrate and the liquid, which levitates on this vapour cushion (figure 3).

Young’s relation can be used to calculate the contact angle. We replace in equation (1.2) the solid by the vapour, which yields $\gamma \cos \theta + \gamma = 0$—a Leidenfrost drop makes a ‘contact’ angle of 180° on its substrate, which corresponds to a situation of complete drying, for which the solid–liquid contact vanishes (as observed in figure 3). Hence, the liquid cannot pin anymore on the solid defects, which also yields a zero contact angle hysteresis. The Leidenfrost
situation thus achieves the ultimate non-wetting state (θ = 180°, and Δθ = 0°) and provides the highest conceivable mobility for a drop—photos such as figure 3 are extremely difficult to take (tiny slopes make the liquid immediately run away), and Leidenfrost himself had to trap his drops in hot spoons in order to observe them conveniently.

In spite of a zero wetting, the drop in figure 3 is observed to be non-spherical—the bottom is flattened, so that, if we cannot see the film, we may wrongly measure a large (yet not maximum) contact angle. This flattening plays a key role in the life of a Leidenfrost drop—in this region, the distance between the plate and the liquid is minimal, so that evaporation is enhanced. The existence and size of this zone affect the thickness of the vapour film, which results from a compromise between evaporation (which tends to feed the film) and gravity (the drop presses on the film; Biance et al. 2003). The weight is precisely the reason for this pseudo-contact, as shown by Mahadevan & Pomeau (1999)—it tends to lower the centre of the mass of the liquid, which surface tension opposes. The pressure in the film can be seen as resulting from the action of the weight (then, it is $4/3\pi \rho g R^3 / \pi \ell^2$), or as the Laplace pressure inside the drop $2\gamma / R$ (crossing the liquid–vapour interface below the drop does not induce a pressure jump, since the interface there is flat). Hence the law for the ‘contact’

$$\ell \sim R^2 \kappa,$$  

which is valid as long as the drop is smaller than the capillary length $\kappa^{-1}$, so that it is quasi-spherical ($\ell < R$). The law for this contact is very different from the one found in wetting (equation (1.1))—the contact angle naturally does not matter anymore, and the variation with the drop size is much quicker ($R^2$ instead of $R$). This remark is important in the limit (studied hereafter) of nearly zero wetting. Since adhesion (and friction, if the drop moves) are imposed by the size of the contact, this quickly vanishing law (as a function of the drop size) makes us expect a remarkable mobility for small drops, in this limit (provided that sticking forces arising from the contact hysteresis do not overcome driving forces; Mahadevan & Pomeau 1999).
3. The lotus effect

Several natural materials approach the Leidenfrost limit, at room temperature. Duck feathers or the legs of water striders repel water, and contact angles measured on such substrates are indeed remarkably high, in the range of 150–170° (Gao & Jiang 2004; Feng et al. 2007; Bush et al. in press). In addition, the contact angle hysteresis on these substrates is also very low (smaller than 20°), which also contributes to make water mobile. More than 200 plants are similarly superhydrophobic (Neinhuis & Barthlott 1997; Bhushan & Jung 2006), the most famous one being the lotus, whose leaf does not retain raindrops—the typical contact angle on such a leaf is 160°, with a hysteresis of approximately 10°. Since these mobile drops take dust with them, as they roll, it is often said that such materials are self-cleaning, which is referred to as the lotus effect. Here we extend the definition of this ‘effect’ to the more basic property of material having both a high contact angle and a low hysteresis.

Using an electron microscope, one can see on these different materials the presence of microtextures, at the scale of approximately 10 μm (figure 4). Different designs are observed: bumps (for lotus, and for many other plants, see figure 4a), spikes for water striders (figure 4b) or microfibres (for other plants, such as Drosera, the little carnivorous plant). In addition, it is most often reported that a second scale of texture is present (it is generally sub-micrometric), but the question remains open (Neinhuis & Barthlott 1997; Bhushan & Jung 2006; Gao & McCarthy 2006a; Feng et al. 2007). It is also worth mentioning that sandy soils may become superhydrophobic, in particular if organic compounds coat them (Doerr et al. 2000)—the texture is given by the sand grains themselves, and the organic coating provides hydrophobicity. This coating can result from a forest fire or from microorganisms. Such soils are

Figure 4. Different superhydrophobic surfaces, as revealed by electron microscope photographs. In each case, micro- or nanotextures are present, such as (a) bumps (on a magnolia leaf), (b) hairs (on a water strider leg), (c) regular microposts (synthetic surface obtained after etching) and (d) fibrous or spongy design (another synthetic material). (Courtesy of (a) C. Neinhuis, (b) L. Jiang and (d) L. Gao.)

Phil. Trans. R. Soc. A (2008)
particularly fragile—rains cannot be absorbed, so they flow, taking with them the first few centimetres of soil, where most nutrients are present. Superhydrophobic soils are thus often precursors of desertification.

All these natural materials are coated with waxy substances, which follow the microtextures. This provides a chemical hydrophobicity that is enhanced by the presence of microstructures. On a flat hydrophobic substrate, the contact angle of water is typically 100–110°, and the use of fluorinated substances increases this angle up to approximately 120°. Microtextures do not only increase significantly (by approx. 50°) the chemical hydrophobicity, but they also generate a degree of water repellency that the surface chemistry alone would not permit (Shafrin & Zisman 1964). Owing to the large variety of designs at the solid surface (as seen in figure 4, for example), it is often asked which is the most efficient one. This question is not really solved today, maybe because it generally does not make sense—the answer depends on the required function, and we do not expect similar microstructures for anti-rain purposes, for anti-dew properties, for gliding (and potentially stopping) on water surface, etc.

There is, however, a particular design that recently attracted a lot of attention, not only because it might be the simplest one but also because it allows one to establish quantitatively the laws of water repellency. This design consists of regularly spaced microposts, of section either square or circular (Bico et al. 1999; Öner & McCarthy 2000). In principle, three parameters are necessary to define such a topography, namely the post radius $b$, the post height $h$ and the pitch $p$ of the array (supposed to be square; in addition we shall here only consider the limit $b \ll p$). Such structures can be made by etching, or by casting, allowing us to set independently these three parameters, typically in the range of 1–100 μm. We show in figure 4c an example of such a surface, obtained after etching a silicon wafer decorated by a square array of circular spots of chromium—after lifting off these masks, and coating the whole material with a fluorinated substance, a regular array of hydrophobic posts is obtained, on which water drops are observed to make a contact angle of the order of 160–170°, depending on the characteristics of the posts.

4. The Wenzel and Cassie states of wetting

The first natural and simple effect arising from the presence of microstructures is an increase of the surface area of the material. We define the roughness $r$ of a material as the ratio of its actual surface area to its projected (or apparent) one. For regular arrays of long and dilute, cylindrical posts ($b \ll h$ and $b \ll p$), the roughness simply is

$$r = 1 + 2\pi bh/p^2.$$  \hspace{1cm} (4.1)

On these substrates, we can define two levels; namely, the top of the posts and the ground on which they sit. Hence, a second natural parameter is the ratio $\phi_S$ between the top and bottom surface areas, which is also the post density. It can be written as

$$\phi_S = \pi b^2/p^2.$$  \hspace{1cm} (4.2)
For the example displayed in figure 4c, we have $b \approx 1 \mu m$, $h \approx 10 \mu m$ and $p \approx 10 \mu m$, which yields $r \approx 1.6$ (moderate roughness) and $\phi_S \approx 0.03$ (low density). Note that such structures conveniently allow us to vary independently both parameters $r$ and $\phi_S$—for example, increasing the height of the pillars without modifying their radii and distance increases $r$ keeping $\phi_S$ constant. When depositing a water drop on such a solid, it can adopt (at least) two types of configuration—conforming to the solid surface (figure 5a) or sitting on the top of the posts (figure 5b).

The first and simplest picture is the so-called Wenzel state (figure 5a)—the drop just follows the structures on the material (Wenzel 1936). This will affect both the wetting (the value of the equilibrium angle, that is the one which minimizes the surface energy of the drop) and the adhesion (characterized here by the value of the contact angle hysteresis). As for the wetting, it is as if the solid surface energies in equation (1.2) are multiplied by the same factor $r$, which immediately yields an equilibrium contact angle $\theta_W$

\[
\cos \theta_W = r \cos \theta.
\tag{4.3}
\]

A Wenzel state will thus enhance the chemical affinity of a drop towards a solid—a hydrophilic situation ($\theta < \pi/2$) becomes more hydrophilic ($\theta^" < \theta$), while a hydrophobic one ($\theta > \pi/2$) tends to be superhydrophobic ($\theta^" > \theta$). This effect (in principle) can be amplified by increasing the roughness (that is, in our case, by making the posts either higher or denser).

As for the hysteresis, it will generally be large in this situation (Johnson & Dettre 1964; Lafuma & Quéré 2003). If we try to remove a drop, it pins very strongly on the sides and at the edges of the microstructures, allowing the

Figure 5. Two possible states for a drop on a microtextured surface: (a) the drop either follows the structures on the solid (Wenzel situation) or (b) sits at the top on the posts (Cassie or fakir state). The observed behaviour depends on the chemical properties of the solid (expressed by its Young contact angle) and on the characteristics of the design. However, different states can coexist, as described further in the text.
receding angle to reach values as small as 0 (even on hydrophobic solids). Therefore the Wenzel regime will be used to make a liquid stick on its substrate, in contrast to what we expect from a lotus-type material.

We guess that the Wenzel configuration should not be obeyed if the solid roughness is (too) large. Then, it is energetically unfavourable for the liquid to follow the solid asperities, owing to the large solid–liquid energy stored in such a configuration (Bico et al. 2002; Patankar 2003; Marmur 2004). Rather, the liquid should sit on the top of the posts (Cassie & Baxter 1944), contacting the solid surface on a surface area reduced by a factor \( \frac{r}{f_S} \), compared with the Wenzel state (this factor can typically be 10–100 on surfaces decorated with pillars). Conversely, this Cassie state (sometimes referred to as the fakir state, for an obvious reason—see figure 5b) implies the creation of a liquid–vapour interface below the drop, on a fraction of surface of the order of \( 1 - \phi_S \), considering these interfaces as flat (the drop is large compared with the pillars, implying a negligible curvature of the liquid–vapour interface at the scale of pillars). The cosine of the apparent contact angle is then an average between the cosine of the Young angle and the cosine of 180°, the angle of a water drop on air, where the weights for the average are, respectively, \( \phi_S \) and \( 1 - \phi_S \). Hence an angle \( \theta_C \)

\[
\cos \theta_C = -1 + \phi_S (1 + \cos \theta).
\] (4.4)

It is worth noticing that the Leidenfrost limit can be approached if the post density \( \phi_S \) vanishes. But it cannot be reached: the pillars must sustain the liquid, which implies \( \phi_S \) greater than 0. For a density of posts of the order of 5–10% and a Young contact angle of 110–120°, the Cassie angle \( \theta_C \) is expected from equation (4.4) to be of the order of 160°, in agreement with many observations on such surfaces. More complex designs such as fractal ones (for which the effective \( \phi_S \) is not obvious to predict) were observed to lead to still higher values of contact angles, up to 175° (Onda et al. 1996). For the loose network of thin fibres seen in figure 4d (where the elasticity of the network might play a role in the value taken by the parameter \( \phi_S \)), Gao & McCarthy could not even distinguish the value of the contact angle from 180° (note, however, that, for such high values, the experimental determination of the angles is difficult; Gao & McCarthy 2006b, 2007).

We guess that the contact angle hysteresis will be generally very small in the Cassie state, since the liquid mainly sits on air, on which it cannot stick (Lafuma & Quéré 2003). It contacts only the solid at the top of the posts (or more generally of the structures present on the solid), on which it can pin—the smaller \( \phi_S \), the less efficient the pinning, and thus the smaller the hysteresis: in the limit of dilute defects, each one contributes to the pinning of the line, so that we (roughly) expect a hysteresis proportional to the defect concentration \( \phi_S \) (Joanny & de Gennes 1984). Measurements indeed confirm a very low hysteresis in the Cassie state, as has been emphasized by Johnson & Dettre (1964), of typically 5–20° instead of more than 100° in a Wenzel situation. Öner & McCarthy (2000) interestingly reported that the strength of each defect is related to the form of the pillar (pillars with a star cross-section will pin more efficiently to the contact lines than to those with a circular cross-section). When approaching the ultimate value of 180°, as observed with the texture displayed in figure 4c, the value of the hysteresis is so low that it becomes basically non-measurable (Gao & McCarthy 2006b, 2007): as it reaches the maximum possible angle, a drop logically loses its adhesive properties, as if it

*Phil. Trans. R. Soc. A* (2008)
were of a Leidenfrost type. These examples stress that the Cassie situation, which is characterized by both a large contact angle and a low hysteresis, is the one which must be practically achieved for generating non-stick behaviours for drops. We now discuss the condition to be given to the solid design for favouring a Cassie state rather than a Wenzel one.

5. Stable and metastable states

In order to predict the most favoured state for a drop, we can recall that the energy gained by a spherical drop when it is placed on a substrate is $\Delta E = 4\pi R_0^2 \gamma (R_0/R - 1)$. This energy gain will be (generally) different in a Wenzel or in a Cassie state—the angles given by equations (4.3) and (4.4) being (generally) not the same, we can define for each state a Cassie radius or a Wenzel radius. From the relationship for $\Delta E$, we learn that the state of lower energy is the one of larger radius, that is, of smaller contact angle.

A comparison between the cosines given by equations (4.3) and (4.4) thus immediately tells us the state of lower energy. For example, a Cassie state will be favoured provided that $\cos \theta_C > \cos \theta_W$, that is

$$\cos \theta < (\phi_S - 1)/(r - \phi_S). \tag{5.1}$$

In the limit $\phi_S \ll r$, this condition can be rewritten as $r > 1/|\cos \theta|$, which implies roughness factors larger than 2–3 (the Young contact angle is commonly in the range of 110–120°, for hydrophobic compounds). Using equation (4.1), we thus find that the pillar height must exceed the ratio $p^2/2\pi b$, which implies a large aspect ratio $h/b$ (larger than $1/2\phi_S$). This might make the structures very fragile, explaining why in many cases fractal-like surfaces will be preferred (they are very rough, yet more compact). However, long hairs such as those observed on the legs of water striders fulfil this criterion, and their flexibility makes them able to resist shocks and deformation. In figure 6, you can check that the leg of Microvelia, a small bug walking on water, does not contact its reflection in the water mirror, but is instead separated from the surface by thin hairs, clearly indicating a Cassie state (Bush et al. in press).

Figure 6. Microvelia walking on water (the bar indicates 1 cm). A close-up on the leg shows that this bug is in a Cassie state—the leg does not contact the water, owing to thin (hydrophobic) hairs, which allows Microvelia to be repelled by water and to skate on it. (Courtesy of D. Hu and J. W. M. Bush.)
However, it is often observed that a drop can sit at the top of dilute posts, in a Cassie state instead of a Wenzel one of smaller surface energy (Yoshimitsu et al. 2002; Lafuma & Quéré 2003; Barbieri et al. 2004; Patankar 2004). Figure 7 shows such a drop, deposited on a solid with $f_S = 0.01$. For this particular surface, we have $b = 1.5\,\mu m$, $p = 25\,\mu m$ and $h = 12\,\mu m$, from which we deduce $r = 1.2$. Since we also have on this surface a Young angle $\theta = 100^\circ$, the criterion $r > 1/|\cos \theta| \sim 6$ is far from being satisfied. However, we clearly see in figure 7 light passing below the drop (behind which a lamp is placed), which implies a Cassie state. This can be proved even more firmly by measuring the distance between the drop and its reflection, which is found to be $24\,\mu m$, twice the pillar height.

How can we understand the existence of these metastable states? It is quite obvious that a drop gently brought into contact with a microstructured solid will be (at least transiently) in a Cassie state—the contact first occurs at the top of the defects. Assuming a zero velocity at the contact (the meaning of the word ‘gently’ in the previous sentence), we can evaluate the energy gain passing from this Cassie state to the Wenzel one. Looking at figure 5, we understand that this transition implies the creation of a solid–liquid interface on a surface proportional to $r - \phi_S$, the suppression of a solid–air interface on the same surface area, together with the suppression of a liquid–vapour interface on an area proportional to $1 - \phi_S$. The change of surface energy per unit area is thus $\Delta E = (\gamma_{SL} - \gamma_{SV}) (r - \phi_S) - \gamma (1 - \phi_S) = -\gamma [(r - \phi_S) \cos \theta + (1 - \phi_S)]$, a quantity that is indeed negative in the case we are considering here (condition (5.1)).

However, there is an energy barrier to overcome, in order to find this groundstate (Barbieri et al. 2004; Ishino et al. 2004; Patankar 2004). The height of this barrier defines the robustness of a metastable Cassie state, and it can be evaluated by considering the motion of the liquid–vapour interface along the walls of the posts keeping this interface flat. While this interface sinks along the post, its surface area remains unchanged, and so does the solid–liquid interface at the top of each post—the only changed surface energy corresponds

Figure 7. Millimetric drop (of radius $R = 400\,\mu m$) gently deposited on a solid decorated with dilute microposts ($\phi_S = 0.01$), and of moderate hydrophobicity ($\theta = 100^\circ$). However, the drop is clearly observed to be in a Cassie state—the interval between the bottom of the drop and its reflection is $24\,\mu m$, i.e. twice the post height $h = 12\,\mu m$, indicating that the drop sits on the top of the bed of micronails (fakir effect).
to the (unfavourable) wetting of the posts walls, implying a (positive) energy per unit area \( \Delta E = (\gamma_{SL} - \gamma_{SV})(r - 1) = -\gamma (r - 1) \cos \theta \). Using equation (4.1), we thus find for the energy barrier between the Cassie and the Wenzel states \( \Delta E = 2\pi bh/p^2\gamma|\cos \theta| \). The barrier is proportional to the height of the pillar, which appears as a natural parameter (yet not the only one) for tuning this quantity.

As emphasized earlier, this energy barrier is generally too large to be supplied by thermal energy, or even by small vibrations of the substrate. However, it can be brought about by an external source of energy—pressing on the drop (Lafuma & Quéré 2003), an impact (Bartolo et al. 2006; Reyssat et al. 2006) or vibrating the substrate (Bormashenko et al. 2007) can all provoke a transition to the Wenzel state. As expected from our expression for the energy barrier, it is indeed found that the higher the post, the better the drop resists impalement in the structure (Reyssat et al. 2008). When the liquid penetrates the texture to the bottom, it remains strongly pinned inside it, the ‘printed’ drop even being able to conform its shape to the network of microposts (Reyssat et al. 2006). But the scenario for the nucleation of the solid–liquid contact can be different from the one suggested here, as proved by looking at the evaporation of a drop in a metastable Cassie state. It is observed that the drop impales when its size is smaller than a critical size, which is significantly larger than the inter-pillar distance \( p \) (McHale et al. 2005; Reyssat et al. 2008), as seen in figure 8.

The same result is also observed by gently depositing small and large drops on a given substrate—if condition (5.1) is not satisfied, the little drops are of a Wenzel type, while the large ones are in a Cassie state (Lafuma & Quéré 2003). In this quasi-static limit, we can think of two conditions for establishing a solid–liquid contact—or expressed conversely, for conserving a drop in the non-stick Cassie state, in spite of a higher surface energy (Ishino et al. 2004; Patankar 2004; Bartolo et al. 2006; Reyssat et al. 2006, 2008). The sketch in figure 9, which shows the liquid–vapour interfaces below a Cassie drop state, helps us to precisely know these conditions.
Firstly, all the different contact lines must be at equilibrium below the drop. Here the presence of ‘favourable’ designs, for the structures, helps—if the solid is decorated with microspheres, for example, there is always a position above the equator of the sphere (supposed to be hydrophobic) where the Young condition can be satisfied. For pillars, the equilibrium arises from the presence of sharp edges at their tops—as first noted by Gibbs, there is a place on the edge (at a nanoscopic scale) where the Young condition is also fulfilled. This possibility of having an equilibrium of the contact line on the solid suggests that it should be possible to make a superhydrophobic solid with a hydrophilic surface, thus generating (metastable) super-oleophobicity (Morra et al. 1989; Herminghaus 2000; Woodward et al. 2003; Cao et al. 2007; Tuteja et al. 2007). For example, having overhangs on the posts (Herminghaus 2000) and/or multiscale roughness (Nosonovský & Bhushan 2007a, b), or using microspheres or microfibres, should generally allow such states (the problem being the robustness of these metastable states, compared with the more stable impregnated ones).

Secondly, the liquid–vapour interface itself is curved, either because of a pressure applied on the drop (a dynamical one, for example, in the case of an impact), or simply owing to the shape of the drop, which is curved at a large scale. The interface curvature, as defined in figure 9, should scale as $\delta/p^2$, while the drop curvature increases as $1/R$. Hence, the depth of penetration $\delta$ of the interface inside the texture should obey the relationship—$\delta \sim p^2/R$: the smaller the drop (as it becomes if it evaporates), the larger $\delta$. If this quantity becomes of the order of the pillar height $h$, a solid–liquid contact should nucleate on the bottom of the substrate and propagate if the Cassie state is of lower energy than the Wenzel one (see the corresponding discussion around equation (5.1)). The critical radius for a Cassie drop is thus of the order of $p^2/h$ (much larger than $p$, if $h<p$). This quantity can be made very small (robust Cassie state) either by making $h$ large or by reducing the different sizes $p$ and $h$—a reduction in size affects the resistance of the Cassie state, which might explain the existence of such very small scales in many natural materials. It would be useful to understand how these simple ideas apply (or not) for multiple-scale textures, for which we could imagine successive similar transitions, and thus mixed Wenzel–Cassie states. The understanding of these kinds of substrates would certainly help to design optimized superhydrophobic materials, able in particular to resist high water pressure (for underwater applications, for example) or other kinds of aggression (Marmur 2006; Shirtcliffe et al. 2006; Nosonovsky & Bhushan 2007c).

Figure 9. Liquid–vapour interfaces below a fakir drop are curved, owing to the curvature of the drop (or to the pressure applied to the drop, if there is any). We characterize the lowering of the interface below the top of the posts by a length $\delta$. 

\[\text{Figure 9. Liquid–vapour interfaces below a fakir drop are curved, owing to the curvature of the drop (or to the pressure applied to the drop, if there is any). We characterize the lowering of the interface below the top of the posts by a length } \delta.\]
Note finally that the other types of ‘transitions’ were observed between the two states. For example, condensing water vapour on a cold superhydrophobic material should favour a Wenzel state, even on lotus leaves (Cheng & Rodak 2005). The observed intermediate states can be Wenzel/Cassie mixtures (Wier & McCarthy 2006), and the figures of condensation are the object of active research (Dorrer & Rühe 2007), which might help to design anti-dew materials. It would also be interesting to see if a material for which condition 8 is satisfied (stable Cassie state), and on which water would be condensed (favouring a Wenzel state), is subjected to a reverse Wenzel–Cassie transition, which should be much more difficult to initiate owing to the large pinning in the Wenzel state. Coming back to the more classical case of a Cassie–Wenzel transition, it was shown that external fields can be used for triggering such a transition (and thus for getting a material of tunable wettability)—let us quote here the possibility of using an electrical field (Krupenkin et al. 2004), light for a photocatalytic texture (Feng et al. 2004; Zhang et al. 2004), or heat for temperature-sensitive coatings (Sun et al. 2004).

6. Slippery behaviour

A remarkable property of the lotus-like surfaces is their ability to (possibly) generate slip at their surface. The classical hydrodynamic boundary condition at a solid–liquid interface is a no-slip condition, which was shown to be verified at a microscopic scale for hydrophilic solids. For hydrophobic materials, however, a nanoscopic slip has often been reported (Cottin-Bizonne et al. 2005). A convenient way to quantify the amplitude of this slip consists of evaluating, for a given flow, the distance inside the solid for which the extrapolated velocity of the flow vanishes. For hydrophobic solids, this length was observed to be of the order of 20 nm, which implies that significant effect on the flow (for example, reduction of the viscous drag associated with it) will be observed if the thickness of the flowing film is of the same order—most of the usual flows (even in micrometric channels) will not be affected by such a modest slip.

However, the slip can be amplified in a superhydrophobic case, as is the hydrophobicity. There again, Wenzel and Cassie situations are very different. Richardson showed that the roughness on a solid surface dramatically damps any (potential) slippage, provided that the liquid follows the solid surface structure (figure 5a; Richardson 1973). Conversely, we can guess that a flow in a Cassie state should enhance the slip—liquid literally glides on air (as we can see with a Leidenfrost drop), owing to the large viscosity ratio between water and air (typically a factor of 100). The associated slip length can be taken as infinite, while part of the drop (on a surface area \(\phi_S\)) flows on the posts, so that the smaller \(\phi_S\), the better the slippage.

This naive argument is correct, and it can be made more quantitative in order to be precise about the amplitude of the slip (Ybert et al. 2007). For a flow of typical velocity \(V\), the spatial zone ‘affected’ by the presence of a post should scale as \(b\), the post radius (taken again as smaller than \(p\), the pitch of the array of posts). The total friction force on such a surface should thus scale as \(N\eta Vb\), denoting \(N\) as the total number of posts. Since the total surface area of the
material can be written as $Np^2$, we get a viscous stress on the surface scaling as $\eta Vb/p^2$. By definition of the slip length, this stress can also be written as $\eta V/\lambda$, from which we deduce an effective slip length $\lambda$:

$$\lambda \sim p^2/b \sim p/\phi_S^{1/2}.$$  

(6.1)

This formula would be slightly different for an anisotropic texture such as a groove. Then, denoting $b$ as the width of the wall, and $p$ the distance between grooves ($b \ll p$), we expect the friction on each groove to be given by an Oseen-type formula, a groove being highly analogous to a cylinder—for a groove of length $L$, this friction should scale as $\eta VL/\ln(p/b)$. The logarithmic factor is a characteristic of this friction on a slender body, and the cut-off lengths are taken as the lateral distance on which the friction takes place (i.e. $b$) and the shortest distance where another similar object is found (i.e. $p$). Again, we have a total force scaling as $N\eta VL/\ln(p/b)$, with $N$ the number of the grooves. Since we also have a surface area scaling as $NpL$, the force per unit surface is now $\eta V/p \ln(p/b)$, from which we deduce a slip length $\lambda$

$$\lambda \sim p \ln(p/b) \sim p \ln(1/\phi_S).$$  

(6.2)

Since we know that the friction along a cylinder is twice as small as that perpendicular to it, we immediately deduce that the slip length should be twice as small, if the flow is perpendicular to the grooves rather than parallel. The flow is anisotropic, with an easier motion (larger slip) in the direction parallel to the striations. This property was indeed demonstrated by Lauga & Stone (2003).

In the limit we consider here ($b \ll p$, that is, $\phi_S \ll 1$), these estimations imply very large slip lengths, compared with values on flat solids—$\lambda$ is of the order of $p$, the typical width of the groove, and thus can be approximately 10 $\mu$m, 1000 times larger than on a hydrophobic solid! This effect is even more spectacular with posts, on which the slip length is ‘amplified’, compared with grooves, by a factor $p/b$, which can typically be 10 (corresponding to a factor $\phi_S$ of approx. 1%). Note finally that this anisotropy of slip, for a solid decorated with grooves, also exists as for the wetting properties—a liquid will glide much more easily along the grooves rather than perpendicular to them, owing to a smaller contact angle hysteresis in this direction (Bico et al. 1999; Yoshimitsu et al. 2002; Chen et al. 2005; Zheng et al. 2007).

There is experimental evidence of very large slip in a Cassie state. Ou et al. (2004) were the first ones to deduce micrometric slip lengths from the measurements of the pressure needed to drive a given flux of water inside a channel of typical size (width and depth) $W$. Poiseuille flow makes this flux to be $W^4\nabla p/\eta$, denoting $\nabla p$ as the pressure gradient along the flow. For a flow with a large slip ($\lambda > W$), a similar calculation yields a flux of $\lambda W^3\nabla p/\eta$. The reduction of pressure needed for driving this flux is thus of the order of $\lambda/W$, and Ou et al. (2004) indeed reported significant pressure reduction (by approx. 40%), suggesting slip lengths of the order of 10 $\mu$m (see also Truesdell et al. 2006). More recently, Roach et al. (2007) found unusual responses of superhydrophobic microbalance, which could be interpreted by considering an interfacial slip. Joseph et al. (2006) were able to deduce slip lengths from microparticle imaging velocimetry for water flowing on hydrophobized pyramids of carbon nanotubes. These authors confirmed that the slip length dramatically depends on the state.
of hydrophobicity—in a Wenzel state (induced by the application of pressure on the liquid), there is basically no slip; conversely, in the Cassie state, there is a slip that increases linearly with the post distance \( p \), in agreement with equation (6.1) (these experiments are performed at a constant \( \phi_S \)). Similar experiments are currently done by the same group, with the hope of reaching even larger values of \( \lambda \). Note however a natural difficulty. Decreasing the value of \( \phi_S \) makes the Cassie state fragile (as seen earlier), so that an irreversible transition towards the sticky Wenzel state might be expected—all the more since some pressure is required to drive the liquid in the channels, encouraging this transition.

7. Conclusion

As we saw, hydrophobic microstructures on solids allow one to generate water-repellent materials, on which water does not stick, easily runs off and even slips. The condition for achieving such a situation consists of placing a cushion of air below the drop (Cassie state), which can be made with very rough substrates. Highly robust metastable Cassie states are also possible, on substrates of smaller roughness, and the optimization of the design remains to be fully understood. On the other hand, many questions still remain to be solved, the most important one being the applicability of these materials. For synthetic materials, water repellency is practically a non-permanent property, owing to pollution or fragility of the materials. As a consequence, very few products based on the principles described here exist today on the market. Despite the numerous potential applications, the domain of application of superhydrophobic materials remains to be invented.

It is a pleasure to thank Anne-Laure Biance, José Bico, Aurélie Lafuma and Ko Okumura for stimulating exchanges. In addition, I do thank Hervé Arribart, Catherine Barentin, Bharat Bhushan, Lydéric Bocquet, John Bush, Stefan Doerr, L. Mahadevan, Thomas McCarthy, Glen McHale, Lei Jiang, Christian Marzolin and Christoph Neinhuis for precious discussions and providing pictures for this article.

References


