

Superhydrophobic states

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It is well known that the roughness of a hydrophobic solid enhances its hydrophobicity^{1–10}. The contact angle of water on such flat solids is typically of the order of 100 to 120°, but reaches values as high as 160 to 175° if they are rough^{3–5} or microtextured^{6–7,9–10}. This result is remarkable because such behaviour cannot be generated by surface chemistry alone. Two distinct hypotheses are classically proposed to explain this effect. On one hand, roughness increases the surface area of the solid, which geometrically enhances hydrophobicity (Wenzel model)¹. On the other hand, air can remain trapped below the drop, which also leads to a superhydrophobic behaviour, because the drop sits partially on air (Cassie model)². However, it is shown here that both situations are very different from their adhesive properties, because Wenzel drops are found to be highly pinned. In addition, irreversible transitions can be induced between Cassie and Wenzel states, with a loss of the anti-adhesive properties generally associated with superhydrophobicity.

For both the Cassie and Wenzel superhydrophobic states, minimizing the surface energy of a drop yields its apparent contact angle θ^* on a rough (hydrophobic) substrate, as a function of the Young's contact angle θ (determined on a flat surface of the same nature). In the Wenzel model, the surface roughness r is defined as the ratio of the actual over the apparent surface area of the substrate (r is a number larger than unity), and we have:

$$\cos\theta^* = r \cos\theta. \quad (1)$$

For a Cassie drop, the contact angle is an average between the value on air (that is, 180°) and on the solid (that is, θ), which can be calculated for a simple geometric texture such as posts, or parallel channels⁷. Denoting ϕ_s as the fraction of solid in contact with the liquid (there again ϕ_s is dimensionless, but smaller than unity), we find:

$$\cos\theta^* = -1 + \phi_s(1 + \cos\theta). \quad (2)$$

Equation 2 should hold for substrates either very hydrophobic (large θ) or very rough (large r)^{11,12}. In both these limits, the Wenzel formula predicts a total drying of the surface ($\theta^* = 180^\circ$), which is not physical because of the contact that must exist between a drop and its substrate. Similarly, we expect the Wenzel equation to hold for solids that are slightly hydrophobic (θ just above 90°): then, air pockets, which imply that many liquid/vapour interfaces of high surface energy exist, should not be favoured.

Equations 1 and 2 should therefore be successively obeyed as the contact angle increases, and the threshold value θ_c between the two

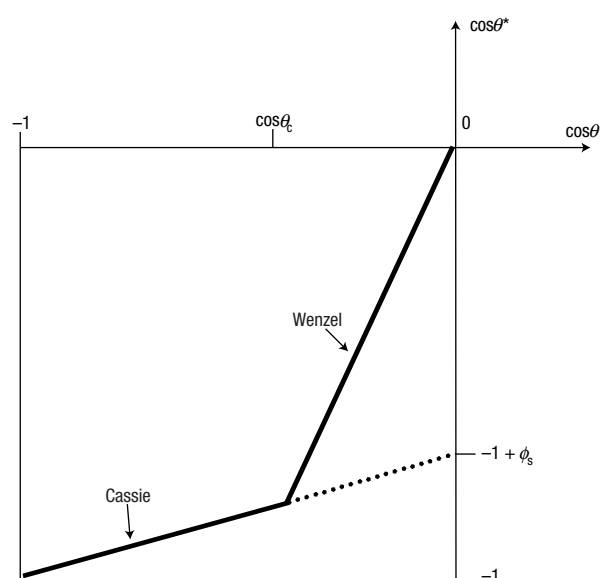


Figure 1 The two models of superhydrophobicity. For a moderate hydrophobicity ($90^\circ < \theta < \theta_c$, where θ is the contact angle on a flat surface, and θ_c is fixed by the texture design, as defined in the text), the apparent contact angle θ^* should be given by the Wenzel model (equation 1). If θ is larger than θ_c , air remains trapped below the drop, which sits on a composite surface made of solid and air; ϕ_s is the fraction of solid in contact with the liquid (Cassie regime, equation 2). However it has often been reported that the Cassie regime can also be observed for $\theta < \theta_c$, in spite of a higher energy. This metastable situation is represented by a dotted line.

regimes given by equating the two¹¹. This yields: $\cos\theta_c = (\phi_s - 1)/(r - \phi_s)$, a quantity that is indeed between -1 and 0 . A comparison between the interfacial energies associated with the Wenzel and the Cassie situations confirms that air pockets should be favoured only if θ is larger than θ_c . Figure 1 summarizes this discussion: the apparent contact angle θ^* is plotted as a function of the Young angle θ , and the expected behaviours are shown by a solid line. We also represented the Cassie regime at a moderate hydrophobicity ($90^\circ < \theta < \theta_c$; dotted line) to stress its metastability in this region.

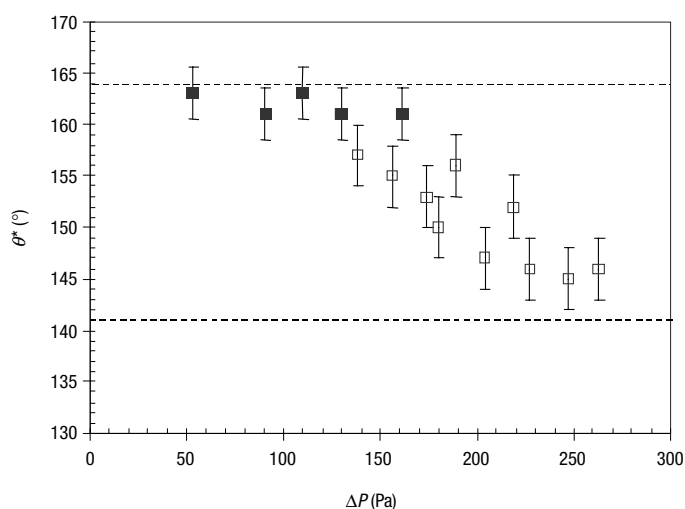
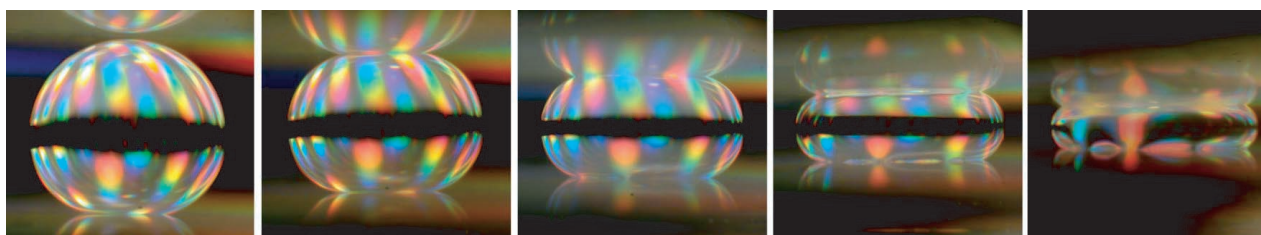


Figure 2 Compression of a millimetric water drop between two identical microtextured hydrophobic surfaces. The apparent contact angle θ^* is measured as a function of the imposed pressure ΔP (open points). The filled points are obtained by varying the size of drops deposited on a single microtextured surface, which modifies the pressure ΔP applied by the drop on the surface. The upper and lower dotted lines are, respectively, the values measured for a large drop initially formed either by deposition or condensation.

In many cases, it turns out that drops on textured materials are observed to be in the Cassie regime, even for a moderate hydrophobicity or, equivalently, for a moderate roughness^{5,7,9,10}. This is revealed in particular by a discontinuity of the contact angle when entering the hydrophobic region (equation 2 predicts that the angle should then be given by $\cos\theta^* = \phi_s - 1$), as reported previously⁵. This suggests that two superhydrophobic states might coexist, which raises the question of the transitions between these states. It has been reported that pressing on a drop may change the contact angle⁷, and that the drop size can also influence θ^* (ref. 10, also Pantankar, private communication). Here we discuss the existence of such transitions and the differences between both states. We stress in particular that even if the contact angles are comparable, their fluctuations (that is, the so-called hysteresis of the contact angle) are dramatically affected, which leads to a huge difference in adhesion properties, and can deeply affect the self-cleaning properties generally associated with superhydrophobic states. These experiments thus reveal a natural limit of microtextured surfaces, and also suggest a condition on the design of the surface for achieving a robust anti-adhesive state.

For our experiments we used surfaces decorated with a square lattice of triangular spikes (of typical height and spacing 2 μm ; Autotype, Oxford). These textures were created by ultraviolet microreplication against a nickel master structure. The ultraviolet-curable material was a complex mixture of perfluoroacrylates and non-fluorinated acrylates that had been optimized to ensure migration (confirmed by secondary-ion mass spectrometry) of the fluorinated side-chains to the nickel interface before crosslinking (S. Abbott, personal communication).

On such flat solids, the so-called (static) advancing contact angle of water measured using a goniometer was found to be $\theta = 110 \pm 3^\circ$ (confirming the hydrophobic nature of the material), and the (static) receding angle was found to be $80 \pm 3^\circ$. The contact-angle hysteresis $\Delta\theta$ was therefore 30° . A water drop deposited on the microtextured surface (first snapshot in Fig. 2) was indeed found to have a much larger angle, at $\theta^* = 164 \pm 3^\circ$. In addition, the hysteresis was observed to be extremely low: $\Delta\theta^* = 5^\circ$, which is a sign of air trapping³; because the drop sits on a cushion of air, its pinning on the solid (which is responsible for the hysteresis) is highly reduced. However, as is usually the case with solids decorated with a single pattern, the substrate is not very rough, and its hydrophobicity is moderate ($\theta = 110^\circ$). We should thus be in the metastable part of the Cassie regime defined by the dotted line in Fig. 1; we tried to understand if a transition could be induced between this metastable state and the Wenzel regime.

Our first attempt consisted of measuring the contact angle of a drop obtained by condensing water vapour on the same textured solid (a flux of oversaturated vapour was directed towards the substrate until a macroscopic drop was obtained). In this situation, water should explore the cavities of the solid, and the condensation should lead to a Wenzel drop. We indeed found that such a drop has an advancing contact angle significantly smaller than in a deposition experiment. Instead of 164° , we observed $\theta^* = 141 \pm 3^\circ$. Moreover, the contact angle hysteresis $\Delta\theta^*$ is greatly affected: it was found to be $100\text{--}105^\circ$ (instead of 5°). Both these measurements confirm that we induced a Wenzel situation. In particular, the contact-angle hysteresis should indeed increase by a large amount in this state: as it recedes, the drop is in contact with a textured solid surface

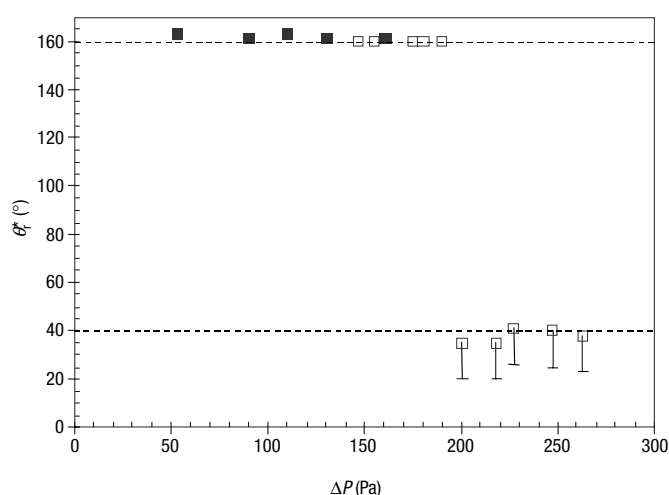
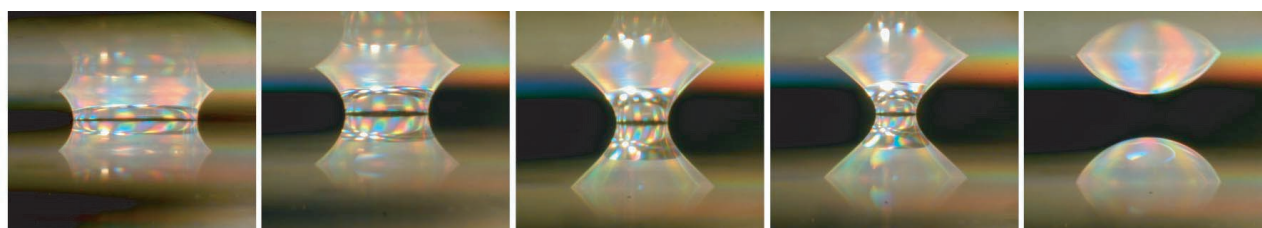


Figure 3 Separation of the two plates after having imposed a pressure ΔP of about 250 Pa. The (receding) angle is much smaller (around 40°), and the drop sticks on both plates, which eventually leads it to split in two similar pieces. The receding angle θ^* , observed after imposing and relaxing a pressure ΔP , is plotted as a function of ΔP (open points). The filled points correspond to drops deposited on a single surface, and ΔP is then the pressure applied by the drop on the surface; its variation is obtained by taking different drop sizes. The upper and lower dotted lines respectively indicate the value of θ^* for a drop deposited on the substrate or obtained by condensing a vapour. In the Cassie regime (upper points) the contact-angle fluctuations were small, and the error bars are therefore of the size of the data points.

filled with liquid, and the contact angle is then given by a Cassie average between θ , the angle on the solid, and θ_0 the angle of the liquid on itself. From a practical viewpoint, the two superhydrophobic states thus appear to be extremely different: although the apparent (advancing) contact angles remain comparable, the adhesion is dramatically increased in the Wenzel state.

In a second series of experiments, we tried to induce direct transitions between both states. We started from a drop deposited on the microtextured surface, and increased the pressure exerted by this drop on its substrate. Two different methods can be used for this purpose. (1) We varied the drop size: the larger the drop, the smaller the pressure. Large drops are flattened by gravity g to a thickness h first described by Taylor¹³: $h = 2a \sin(\theta^*/2)$, where a is the capillary length ($a = (\gamma/\rho g)^{1/2}$, with γ the liquid surface tension and ρ its density; a is 2.7 mm for water). Such a flattened drop exerts a hydrostatic pressure ρgh on its substrate—of the order of 50 Pa in our case. For drops small enough that the effect of gravity is negligible (that is, radius R smaller than a), the internal pressure, ΔP , in the superhydrophobic limit is given by the Laplace law ($\Delta P = 2\gamma/R$), which is also the pressure exerted by the drop on its substrate, hence the smaller the drop, the larger the pressure. We let R vary between 4 and 0.9 mm, which allowed us to increase the pressure up to 150 Pa. (2) To reach higher pressures, we placed the drop between two identical substrates, and compressed it by using a micrometric screw, which also allowed us to measure the gap x between the plates. The pressure was simply deduced using the Laplace equation ($\Delta P = 2\gamma \cos \theta^* / x$, for $x \ll R$). Figure 2 shows a sequence of these

experiments (note that because of the texture, the surface is iridescent and reflects in the drop, giving the colours). For each pressure ΔP , we took numerical micrographs of the edge of the drop, from which we could deduce the contact angle θ^* with a precision of 5° ; its value is plotted as a function of ΔP in the same figure.

It is observed that the contact angle first has a plateau value, which corresponds to the air-pocket regime described above. The contact angle then decreases, which can be interpreted as a progressive sinking of the drop inside the texture (as seen in equation 2, exploring the textures, that is, increasing ϕ_s , leads to a decrease of θ^*). For high pressures, the contact angle tends towards $\theta^* = 145 \pm 3^\circ$, in close agreement with the value obtained by condensing a water drop. We thus interpret this limit as a Wenzel state.

We then monitored what happens when relaxing the pressure. In Fig. 3 is a series of snapshots showing the separation between the plates after imposing a pressure of about 250 Pa. Although the contact angle hysteresis was very small in the Cassie regime, a huge hysteresis is observed here, which reveals the irreversibility of the transition. The receding contact angle θ^* is found to be $35\text{--}40^\circ$, and the hysteresis about 105° , again in good agreement with our data for a condensed drop. This confirms the hypothesis of a Wenzel state in this limit of high pressure. Then, the drop can pin on the surface textures, which makes it split into two identical droplets while the plates are separating.

The value of the receding contact angle after such a relaxation is also plotted in Fig. 3, as a function of the pressure imposed on the drop.

The situation there appears to be clear-cut: up to a pressure $\Delta P^* = 200$ Pa, although the advancing angle was found to decrease significantly, after relaxing the pressure the drop recovers its Cassie state, with a very low hysteresis (high value for θ_i^*). But above ΔP^* , that is, for pressures for which the advancing angle was close to the Wenzel value, the receding angle becomes very small (around 40°), confirming the pinning of the drop in the texture. The value of ΔP^* is low (much smaller than the Laplace pressure associated with invasion of a micrometric texture, which would be of the order of 10^5 Pa), which betrays the fragility of a Cassie state when it is metastable. A systematic study of ΔP^* as a function of the characteristics of the texture should help understanding what fixes its value.

This discussion can finally be summarized by comparing the drop adhesion in both states. We measured the maximum volume of water able to stick on the material tilted by 20° , by using a calibrated micropipette to deposit drops of a controlled volume with a precision smaller than $1 \mu\text{l}$. This maximum volume was found to be less than $1 \mu\text{l}$ if depositing the drop (that is, in the Cassie regime), and $205 \pm 25 \mu\text{l}$ if condensing it (that is, in a Wenzel situation): there is a factor larger than 200 between these values, which stresses how different the two states are. On throwing a spray (using a commercial water spray that provides a polydisperse collection of droplets) on the inclined surface, and taking macrophotographs of the resulting droplet distribution, we observed that droplets with a radius smaller than 0.6 mm (thus of internal Laplace pressure above 230 Pa) remained stuck, and exhibited advancing angles significantly smaller than in a Cassie state. There again, we interpret the sticking by a transition to a Wenzel state, due to the internal pressure of the drop. All these different effects, demonstrated here with a given texture, were also found using either the same texture with different characteristics (height or density of the spikes), or a different texture (posts instead of a triangular pattern).

Hence two superhydrophobic states can coexist on a microtextured hydrophobic substrate. In the regime of moderate hydrophobicity (which is always the case with water, where Young angles θ never exceed typically 120°), the Cassie regime of air-trapping often observed is found to be metastable. By applying a pressure on the drop, it is possible to induce an irreversible transition towards another regime that we interpreted as a Wenzel state, for which the solid/liquid interface follows the texture of the solid surface. The contact angles in both states are comparable (the Wenzel angle is slightly smaller than the Cassie one, but both are significantly larger than the Young angle θ), but the hysteresis is dramatically affected by the change of state: it is found to be 10 to 20 times larger in the Wenzel regime. This is of practical importance, because a drop in this regime will adhere much better to its substrate, contrasting with what is expected in a superhydrophobic situation. In particular, the so-called self-cleaning effect is totally suppressed by the drop adhesion. In addition, it was shown recently that the friction properties of these materials should be extremely different according to

the state: a Cassie state should lead to a strong reduction of the friction properties, whereas a Wenzel one was found to have greater friction properties than a flat hydrophobic material¹⁴.

This study thus emphasises a weakness of superhydrophobic materials: if the textures are filled with water, the material loses its water-repellent properties. The invasion can occur through the vapour phase (condensation of a dew, evaporation of a drop), or by an external pressure (which can be dynamic for impacts, due to the drop curvature for tiny drops, or hydrostatic, for example, a boat with a microtextured coating): for the particular texture we studied, invasion occurs quite easily, for a pressure corresponding to that below 20 cm of water. Conversely, this discussion suggests how a superhydrophobic material should be designed to avoid a sticking transition: θ_c must be as small as possible, because the Cassie regime is stabilized for $\theta > \theta_c$. Because of the phenomenological nature of the parameter ϕ_s , this condition is not so easy to create, but is necessarily fulfilled if we have $\cos\theta < -1/r$, which corresponds for a given hydrophobic material to a large value of r , the substrate roughness. It was often noticed that superhydrophobic plants indeed exhibit a large r , due to having two levels of texture⁶. Such a hierarchical structure does not only enhance the hydrophobicity⁸, it also stabilizes the Cassie regime, and thus favours water repellency.

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Competing financial interests

The authors declare that they have no competing financial interests.