Microstructured superhydrorepellent surfaces: effect of drop pressure on fakir-state stability and apparent contact angles

L Afferrante and G Carbone

DIMeG Politecnico di Bari, viale Japigia 182, I-70126 Bari, Italy
and
CEMeC, Politecnico di Bari, via Re David 200, I-70125 Bari, Italy

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Abstract

In this paper we present a generalized Cassie–Baxter equation to take into account the effect of drop pressure on the apparent contact angle $\theta_{\text{app}}$. Also we determine the limiting pressure $p_W$ which causes the impalement transition to the Wenzel state and the pull-off pressure $p_{\text{out}}$ at which the drop detaches from the substrate. The calculations have been carried out for axial-symmetric pillars of three different shapes: conical, hemispherical-topped and flat-topped cylindrical pillars. Calculations show that, assuming the same pillar spacing, conical pillars may be more inclined to undergo an impalement transition to the Wenzel state, but, on the other hand, they are characterized by a vanishing pull-off pressure which causes the drop not to adhere to the substrate and therefore to detach very easily. We infer that this property should strongly reduce the contact angle hysteresis as experimentally observed in Martines et al (2005 Nano Lett. 5 2097–103). It is possible to combine large resistance to impalement transition (i.e. large value of $p_W$) and small (or even vanishing) detaching pressure $p_{\text{out}}$ by employing cylindrical pillars with conical tips. We also show that, depending on the particular pillar geometry, the effect of drop pressure on the apparent contact angle $\theta_{\text{app}}$ may be more or less significant. In particular we show that in the case of conical pillars increasing the drop pressure causes a significant decrease of $\theta_{\text{app}}$ in agreement with some experimental investigations (Lafuma and Quéré 2003 Nat. Mater. 2 457), whereas $\theta_{\text{app}}$ slightly increases for hemispherical or flat-topped cylindrical pillars.

Nomenclature

- $A$: area covered by the elementary cell
- $D$: domain of integration
- $F$: force applied to the pillars by the substrate
- $G$: Gibbs energy
- $H$: Helmholtz free energy
- $R$: pillar radius
- $R$: dimensionless pillar radius
- $S_S$: total surface of the substrate
- $S_{LA}$: liquid–air interface
- $S_{LS}$: liquid–solid interface
- $S_{SA}$: solid–air interface
- $h_0$: function describing the shape of the pillars
- $\hat{h}$: dimensionless pillar height
- $p$: liquid drop pressure defined as the difference between the absolute drop pressure and the environmental pressure
- $\hat{p}$: dimensionless liquid drop pressure
- $p_W$: transition pressure between Cassie–Baxter and Wenzel state
- $\hat{p}_W$: dimensionless transition pressure between Cassie–Baxter and Wenzel state
- $p_{\text{out}}$: pull-off pressure for which the liquid drop is detached from the substrate
- $\hat{p}_{\text{out}}$: dimensionless pull-off pressure
- $p_L$: pressure at which the free liquid–air interface touches the substrate for conical pillars
- $\hat{p}_L$: dimensionless pressure at which the free liquid–air interface touches the substrate for conical pillars
1. Introduction

Roughness-induced hydrophobicity is a well-known effect observed in many plant leaves, e.g. sacred lotus leaves (Nelumbo nucifera) [2], and in other biological systems such as water striders [11] (Gerris remigis) or mosquito (Culex pipiens) eyes [12]. In all such cases the surface asperities make the liquid able to be suspended on the asperity tips, resulting in a very large contact angle (CA). The superlative water repellency of such natural surfaces would be highly appreciated in many micro- and macro-engineering applications, as liquid drops on super-hydrophobic surfaces may be very easily moved from one position to another by simply applying an external force, resulting in the possibility to create a chemical microreactor and microfluidic microchips [13, 41]. Besides these high-tech applications, there is a strong interest of engineers in developing new commercial products such as self-cleaning paints and glass windows [4], or super-hydrophobic optically transparent self-cleaning surfaces [9, 33, 34], which may be used as coatings in the automotive field, e.g. car windshields and biker helmets where impacting raindrops must be easily repelled. Some studies have shown, indeed, that falling drops may fully rebound on such water-repellent surfaces with very high restitution coefficients ~0.9 [36, 39]. As a consequence of the high technological and commercial impact of super-hydrophobic surfaces, in the last decade a great deal of research has been spent trying to mimic the superhydrorepellent surfaces of living organisms. Thus, many artificial surfaces have been prepared attempting to achieve this objective. Figure 1 shows some examples of super-hydrorepellent man-made surfaces. At first sight, different surfaces may appear equally good candidates to mimic the super-hydrophobic properties of natural surfaces. Indeed, being inspired by the solutions offered by Nature, several geometries have been explored, e.g. uniform arrays of flat-topped cylindrical pillars [5] (figure 1(a)) or tapered asperities [20] (see figure 1(b)) or even nanotube forests with rounded tips [19] as shown in figure 1(c). Besides these few examples, also super-hydrophobic fractal surfaces have been produced [10, 35, 40], which show apparent contact angles (CAs) up to 174°. However, the different shapes of such microstructured surfaces, which reflect the variety of natural solutions, should also have some practical implications which makes them not really completely equivalent. Liquid drops on super-hydrophobic microstructured surfaces may be observed mainly in two different states (although intermediate states may also exist [21, 1]): the Cassie–Baxter [7] and the Wenzel [42] states. A drop in a Cassie–Baxter state is just suspended on the asperities of the underlying surface, which therefore behaves as a fakir carpet. The Wenzel state is, instead, characterized by complete contact between the drop and the substrate. The Wenzel state is usually unwanted as it results in a strong adherence between the drop and the substrate and in a very pronounced CA hysteresis [15, 38]. Thus, in order to prevent strong adhesion between the drop and substrate one has to design the super-hydrophobic microstructured surface in such a way to prevent the Wenzel state to be formed and make stable the fakir-droplet state. In such a sense a first attempt was made in [22] where a model employing the capillary rise of a liquid in contact with a stripwise heterogeneous surface was developed to study the effect on contact angles. More recently, in [3] two criteria were proposed to compare the super-hydrorepellent properties of different microstructures from a wetting point of view. However, the proposed criteria do not take into account the effect of the internal pressure of the droplet, which is strictly related to surface tension and curvature of the air–liquid interface and therefore to its volume. An interesting new approach with molecular dynamics was proposed in [43] to study the behavior of liquid nanodroplets on rough surfaces. However, as shown by different authors [8, 15, 25, 38], the drop pressure may have a critical role in determining if a composite interface may be formed at the interface between the drop and the microstructured substrate. Large drop pressures may be generated during the impact of drops on the substrate, and in this case, as shown in [39, 24, 25] high impact velocities (i.e. large impact pressures) may destabilize the fakir state, cause the transition to the Wenzel state and make the droplet not able to bounce. Figure 2 shows indeed two water drops of the same volume on a microstructured super-hydrorepellent surface. The drop on the left has been gently deposited on the substrate, thus allowing the formation of a fakir-droplet state, while the drop on the right has instead undergone a transition to the Wenzel state as a consequence of an increase of the drop pressure above a critical threshold.

The transition between the composite (Cassie) and wetted (Wenzel) states has been investigated theoretically in many papers [26–31], but the effect of liquid drop pressure is not
A few examples of artificial super-hydrorepellent surfaces. (a) A uniform array of very slender cylindrical pillars with a flat tip (adapted from [5]), (b) a uniform array of cylinders with tapered shaped tips (adapted from [20]) and (c) an example of a super-hydrorepellent carbon-nanotube forest (adapted from [19]).

Two millimetric water drops of the same volume on a microstructured super-hydrorepellent surface (adapted from [6]). A fakir state (i.e. Cassie–Baxter state) is obtained by gently placing the drop on the substrate (on the left). A full contact condition (Wenzel state) is obtained by increasing the drop pressure (on the right).

Recently an interesting study [32] has been presented where the super-hydrorepellent properties of a surface with cavities has been investigated and the effective energy of such systems has been studied by also including the influence of drop pressure. In the present paper we study the system by means of an energy approach in which the most general formulation has been given by Lipowsky [16], who by means of a minimization technique proposed a generalization of the Cassie–Baxter and Wenzel laws for a liquid drop sitting on chemically heterogeneous but flat substrates, where the area fraction of each phase was given a priori. Also, there are others paper treating the problem of hydraulic pressure in determining the stability of a Cassie–Baxter state. References [18] and [44], for example, treated this problem in the case of pillars with flat tips with sharp edges so that the fraction of the projected area that is wet is assigned a priori. In particular, reference [44] gave an expression of the critical hydraulic pressure for which the transition process between the Cassie–Baxter wetting mode and the Wenzel one occurs. Reference [18] studied the effect of the contact line length by varying the shape of the pillars while maintaining the area constant. However, there are many cases where the wetted area is not fixed a priori and should be determined as part of the problem, e.g. through a energy minimization technique. In [17] the authors studied the case of a surface with an array of small spheres on it and determined the pressure required to force the meniscus to bend sufficiently and touch the underlying surface. However, if the pillars are sufficiently tall the transition to a Wenzel state may be achieved before the meniscus touches the underlying surface because of thermodynamic instability, as we show in the following.

In a preceding paper [8] it has been shown that to prevent the impalement transition it is necessary to increase the critical pressure $p_W$ at which this transition occurs (we refer to $p_W$ as the Wenzel pressure). Here the drop pressure was defined as the difference between the absolute pressure of the drop and the external pressure. High values of $p_W$ are indeed a strict
requirement in those engineering applications where falling raindrops have to be supported by the substrate. However, in many cases we also want the liquid drops to be very easily detached from the substrate, i.e. the pull-off pressure \( p_{\text{out}} \) to be reduced almost to zero. This property is, for example, found in many insects that usually walk or skate on the free liquid–air surface. Such insects not only need not to sink into the water, but also need to detach easily from the free liquid–air surface and move and run easily on it.

In the same paper [8] one of the authors has analyzed the wetting/non-wetting properties of a liquid drop in contact with an extremely idealized 1D rough profile, i.e. a simple sinusoidal profile. The analysis clarified some theoretical points (mainly from a qualitative point of view) of the wetting/non-wetting behavior of super-hydrorepellent surfaces. In the present paper the study is extended to 2D microstructured surfaces with a periodic distribution of axial-symmetric micropillars, which on the other hand are very commonly utilized in such applications. Some hints on designing such super-hydrophobic surfaces to achieve both the aim of large \( p_W \) values and low pull-off pressures \( p_{\text{out}} \) are also provided.

2. Formulation

Let us consider a periodic distribution of chemically hydrophobic (e.g. fluorinated) pillars (thermodynamic contact angle \( \theta_r > \pi/2 \)). We assume that the elementary cell of the periodic structure is a square, although we can deal with any type of periodic distribution of micropillars. We develop the analysis for three types of micropillars: conical pillars, hemispherical-topped cylindrical pillars and flat-topped cylindrical pillars. We assume that the micropillars are stiff enough to consider as negligible their deformation under the action of the drop pressure. This, indeed, is a very good approximation in many practical cases, and is always employed in theoretical investigations dealing with super-hydrorepellence. We also assume that the liquid is incompressible (i.e. we neglect the contribution of the liquid elastic energy) and the drop is very slowly evaporating (i.e. the timescale to reach local equilibrium is much shorter than the timescale of evaporation). We observe that, the diameter of the liquid drop being in the range of millimeters whereas the linear spacing \( 2\lambda \) between the pillars being in the range of micro- or even nanometers, the drop can be considered as a semi-infinite liquid space when we analyze the problem at the microscale. Thus, when we look the drop–substrate interface at very large magnifications the state of the system is completely determined by the following state parameters: the drop pressure \( p \) at the liquid–substrate interface, the real solid–liquid contact area, the liquid–air free surface at the interface and the penetration \( \Delta \) (see below) of the liquid drop inside the pillar forest. Notice that in the present paper the drop pressure \( p \) is defined as the difference between the drop pressure and the external (environmental) pressure.

Figure 3 shows the geometry of the pillars and the parameters we use to describe the position of the triple line. The reference plane \((x, y, 0)\) is placed at the base of the pillars and the \( z \) coordinate is directed toward the top of the pillars. The \( z \) coordinate of the free liquid surface will be referred to as \( u(x, y) \). Because of the substrate corrugation, the liquid can either wet the whole substrate surface or be in stable or metastable partial contact with it. In the case of partial contact the liquid/air interface must satisfy the Laplace formula. Assuming that the slope of the liquid–air interface is sufficiently small, which simply requires that \( p\lambda/(2\gamma_{LA}) \ll 1 \), the Laplace formula is

\[
\nabla^2 u(x, y) = u_{xx}(x, y) + u_{yy}(x, y) = \frac{p}{\gamma_{LA}} \tag{1}
\]

where \( u_{xx} = \frac{\partial^2 u}{\partial x^2} \), \( u_{yy} = \frac{\partial^2 u}{\partial y^2} \) and \( \gamma_{LA} \) is the liquid–air surface tension. The condition \( p\lambda/(2\gamma_{LA}) \ll 1 \) is satisfied in most cases, e.g. in the case of water \( \gamma_{LA} = 72 \text{ mJ m}^{-2} \) and assuming \( \lambda \approx 1 \mu\text{m} \) one obtains \( p < 1.4 \text{ bar} \), which is in most cases true.

Equation (1), because of periodicity, can be solved over a quarter of the elementary square cell. However, we need also
to specify boundary conditions. A first boundary condition has to be written at the triple line, which represents the contour delimiting the liquid–solid interface. Let us denote the projection of this contour on the \((x, y, 0)\) reference plane by the symbol \(L\). We observe that, in general, the curve \(L\) (for which the mathematical expression in implicit form can be given as \(f_L(x, y) = 0\)) is not known \textit{a priori} and has to be determined by requiring that the total energy of the system is stationary at equilibrium (see below). Therefore at the triple line the following equation must hold true:

\[
u(x, y) = h_0(x, y); \quad (x, y) \in L \tag{2}
\]

where \(L = \{(x, y) \in \mathbb{R}^2 \mid f_L(x, y) = 0\}\) and \(h_0(x, y)\) is the function describing the shape of the pillars. Equation (2) simply states that the liquid–air interface and the solid–liquid interface must intersect at the triple line. Also the following Neumann boundary conditions must be satisfied to account for periodic conditions:

\[
\begin{align*}
\nu_x(0, y > y_0) &= 0; & \nu_x(\lambda, y) &= 0 \\
\nu_y(x > x_0, 0) &= 0; & \nu_y(x, \lambda) &= 0
\end{align*} \tag{3}
\]

where \(\nu_x = \partial \nu / \partial x, \nu_y = \partial \nu / \partial y, x_0\) satisfies the condition \(f_L(x_0, 0) = 0\) and, similarly, \(y_0\) satisfies the condition \(f_L(0, y_0) = 0\).

Observe that for flat-topped cylindrical pillars the function \(f_L(x, y)\) is known \textit{a priori}, being simply \(f_L(x, y) = x^2 + y^2 - R^2\), where \(R\) is the radius of the pillar. In the other two cases \(f_L(x, y)\) is not known \textit{a priori} and must be determined as a part of the solution of the problem. Indeed, the physical problem we are dealing with belongs to the class of free boundary problems and requires an additional condition to achieve the complete solution. This additional condition is simply the requirement that, at equilibrium, for any given drop pressure \(p\), the total energy of the system (in our case the Gibbs energy \(G\)) is stationary. Of course, in the general case, the Gibbs energy is a functional defined on the vector space of functions \(f_L(x, y)\) and one should require that \(G\) is stationary at equilibrium to find the Euler–Lagrange equations and determine the quantity \(f_L(x, y)\) (indeed the problem belongs to the class of variational problems). Therefore, the complete solution seems to be very complicated and expensive from a numerical point of view. However, we can strongly reduce the complexity of the problem if we recall that \(p \lambda^2/(2 \gamma_{LA}) \ll 1\), in such a case the slope of the free liquid–air surface is small. This implies that the slope of the contour representing the triple line is also small and we conclude that, under this assumption, the triple line will only negligibly deviate from a circumference in the case of axial-symmetric pillars. (Reference [18] showed that the variation of the angle that the free surface forms with the pillars, due to the tortuosity of the triple line, is limited to about \(3\%\).) Thus, the unknown function \(f_L(x, y)\) takes a much simpler form \(f_L(x, y) \approx x^2 + y^2 - r_0^2\), where \(r_0\) is the unknown radial position of the triple line and the total energy of the system simply becomes a function of the free parameter \(r_0\). Thus, \(r_0\) can be determined by enforcing the equilibrium condition, i.e. by requiring that \(\partial G / \partial r_0 = 0\). However, despite the apparent simplicity of equation (1), the particular shape of the domain of integration (see figure 4) does not make it possible to obtain a solution in closed form. We therefore have employed a finite difference approach to solve equation (1) with the mixed boundary equations (2) and (3). For isothermal conditions and constant pressure the Gibbs energy is

\[
G(r_0, p) = H(r_0, p) - p \lambda^2 \Delta(r_0, p) \tag{4}
\]

where \(\Delta(r_0, p)\) is the penetrational of the rigid substrate into the semi-infinite liquid and \(H\) is the Helmholtz free energy. The penetrational \(\Delta\) is given by

\[
\Delta(r_0, p) = h - s(r_0, p) \tag{5}
\]

where \(s\) is the average profile of the liquid:

\[
s(r_0, p) = \frac{1}{\lambda^2} \left\{ \int \nu(x, y) \, dx \, dy + \frac{1}{4} \int_{r < r_0} h_0(x, y) \, dx \, dy \right\} \tag{6}
\]

where \(D\) is the domain of integration defined in figure 4 and \(\mathbf{i} = x \mathbf{i} + y \mathbf{j}\), \(\mathbf{i}\) and \(\mathbf{j}\) being the unit vectors of the \(x\) and \(y\) axes, respectively.

Equation (5) represents the equation of state of the system since it allows us to determine one of the three quantities, \(\Delta\), \(r_0\) and \(p\) once the other two are known. To define the Gibbs energy we first need to express the Helmholtz free energy \(H\) which, in our case, is just the total surface energy of the system \(H(r_0, p) = \gamma_{LA} S_{LA} + \gamma_{LS} S_{LS} + \gamma_{SA} S_{SA}\), where \(\gamma_{LA}, \gamma_{LS}\) and \(\gamma_{SA}\) are the surface energies at the liquid/solid, liquid/air and solid/air interfaces, respectively. Utilizing the Young’s equation \(\gamma_{LA} \cos \theta_e + \gamma_{LS} - \gamma_{SA} = 0\), with \(\theta_e\) being the Young’s CA at equilibrium, the Helmholtz free energy is

\[
H(r_0, p) = \gamma_{LA} (S_{LA} - S_{LS} \cos \theta_e) + \gamma_{SA} S_{SA} \tag{7}
\]

and the Gibbs energy becomes

\[
G(r_0, p) = \gamma_{LA} (S_{LA} - S_{LS} \cos \theta_e) - p \lambda^2 \Delta + \gamma_{SA} S_{SA} \tag{8}
\]
In equations (7) and (8) $S_L$ represents the total surface of the substrate over the domain $D$. We now require that at fixed load (i.e. at fixed drop pressure $p$) the Gibbs energy is stationary to enforce equilibrium conditions and close the system of equations with the following condition:

$$\frac{\partial G}{\partial r_0} = 0. \quad (9)$$

Stability or instability of equilibrium can be easily determined by looking at the sign of $\partial^2 G/\partial r_0^2$: local stability is guaranteed when the energy has a local minimum, i.e. when $\partial^2 G/\partial r_0^2 > 0$, whereas instability is detected when $\partial^2 G/\partial r_0^2 \leq 0$.

2.1. The apparent contact angle

Now let us observe the drop at the macroscopic scale. At this length scale one notices that the total volume of the drop is constant and therefore that the total energy of the system is just the Helmholtz free energy $H$ instead of the Gibbs free energy $G$. Moreover, since the microstructure of the substrate completely disappears at the macroscale the observer will, then, measure an apparent liquid–solid surface energy $\gamma_{LS}$ given by

$$(\gamma_{LS})_{\text{eff}} = H/\lambda^2. \quad (10)$$

Using equation (7) $(\gamma_{LS})_{\text{eff}}$ becomes

$$(\gamma_{LS})_{\text{eff}} = \frac{\gamma_{LA}(S_{LA} - S_L \cos \theta_e)}{\lambda^2} + (\gamma_{SA})_{\text{eff}} \quad (11)$$

where we have defined $(\gamma_{SA})_{\text{eff}} = (\gamma_{SA})/\lambda^2$ as the effective solid–air interfacial energy. At equilibrium the above definition equation (11) allows us to write a modified Young’s equation and evaluate the apparent contact angle $\theta_{app}$ as

$$\cos \theta_{app} = \frac{(\gamma_{LS})_{\text{eff}} - (\gamma_{SA})_{\text{eff}}}{\gamma_{LA}} = \frac{S_{LA} - S_L \cos \theta_e}{\lambda^2}. \quad (12)$$

The above equation (12) represents a generalization of the Cassie–Baxter equation [7], which takes into account the influence of the interfacial drop pressure and, of course, holds true only at equilibrium.

The above simple considerations make it clear that a design criteria based on the maximization of the apparent contact angle is effective only if we include the effect of drop pressure. Therefore, an optimization of the surface topography only based on the apparent contact angle evaluated by the Cassie–Baxter equation can lead to misleading conclusions.

3. Equilibrium condition: a simplified approach

The general approach considered above, leading to an optimization procedure to find Gibbs’ energy stationary points, is very time-consuming. For this reason here we present a much simpler procedure to determine the equilibrium conditions without the need for a complicated and computationally expensive procedure. Indeed, if we were able to enforce the equilibrium condition before solving equation (1), we would be able to ‘bypass’ the minimization of the Gibbs energy and readily calculate the contact radius $r_0$ for any given drop pressure $p$. Enforcing the equilibrium condition is, indeed, equivalent to require that the CA at the triple line is just equal to Young’s contact angle $\theta_e$. Thus, assuming (as discussed before) that the triple line negligibly deviates from a circumference, this allows us to calculate the real liquid–solid contact area for any given drop pressure. Of course, the determination of the complete thermodynamic state of the system still requires the calculation of the free liquid–air interface $\mu(x, y)$ to determine the total interfacial energy and therefore the apparent contact angle $\theta_{app}$ and penetration $\Delta$. However, this calculation can be carried out a posteriori by solving equation (1), with the conditions (2) and (3), without handling the minimization problem of the total energy.

3.1. Conical pillars

Let us observe figure 5(b) where the forces acting on a conical pillar are shown to be the force $F$ that the rigid substrate applies to the pillar, the surface tension $\gamma_{LA}$ at the triple line and the pressure $p$ of the liquid. Thus, the equilibrium is written as

$$2\pi r_0 \gamma_{LA} \cos(\theta_e - \alpha) + F - \pi r_0^2 p = 0 \quad (13)$$

where $\alpha$ is the half-cone angle. Now let $A$ be the measure of the area covered by the elementary cell (not necessarily square) of our periodic distribution of asperities (in the case of a square cell the quantity $\lambda$ is simply $\lambda = A^{1/2}/2$) and enforce the equilibrium of the whole single cell. Because of the Neumann boundary condition equation (3) the liquid–air surface tension at the outer boundaries of the single cell will not give any contribution to the equilibrium along the $z$ direction. Therefore we can write $F = pA$ and the above equation (13) becomes

$$\hat{p} = -\frac{\pi (\hat{r}/2) \cos(\theta_e - \alpha)}{1 - \pi (\hat{r}/2)^2} \quad (14)$$

where $\lambda = r_0/\lambda$ and $\hat{p} = pA/\gamma_{LA}$, $\lambda = A^{1/2}/2$ being a characteristic length. Notice that when $\alpha > \theta_e - \pi/2$ the pressure becomes negative and the drop wets the substrate in a Wenzel state. Hence the angle $\alpha$ has to satisfy the condition $0 < \alpha < \theta_e - \pi/2$ to guarantee a positive value of the drop pressure $\hat{p} > 0$. In such a case the drop pressure $\hat{p}$ continuously increases with the radius $\hat{r}$, i.e. stability of equilibrium is always guaranteed. The pull-off pressure can be easily evaluated as $\hat{p}_{\text{out}} = \hat{p}(\hat{r} = 0)$, which as shown by equation (14) is zero, i.e. drops on conical pillars can be very easily detached from the substrate. We observe that in all practical cases the conical tip will never present a real sharp corner. However, this does not change our conclusion. The conical pillar will always guarantee a negligible pull-off pressure, as the radius of curvature of its rounded tip is always much smaller than the radius of the pillar itself.

3.2. Hemispherical-topped cylindrical pillars

For hemispherical pillars (see figure 5(a)), we can follow the same procedure outlined above to write the equilibrium:

$$2\pi (R \sin \varphi) \gamma_{LA} \sin(\theta_e + \varphi) + F - \pi (R \sin \varphi)^2 p = 0 \quad (15)$$
where $R$ is the radius of the sphere and $\psi$ represents the angular coordinate of the liquid–pillar triple line (see figure 5(a)). Equation (15) can be conveniently rewritten in a dimensionless form as

$$
\hat{p} = -\frac{(\pi/2)\hat{R}\sin\psi\sin(\theta_e + \psi)}{1 - (\pi/4)\hat{R}^2\sin^2\psi}
$$

(16)

where we have still used that $\hat{p} = p\lambda/\gamma_{LA}$ and $\hat{R} = R/\lambda$. At fixed load, stability implies $d\hat{p}/d\psi > 0$, which is equivalent to having $\partial^2 G/\partial r_0^2 > 0$, whereas unstable equilibrium conditions are characterized by the value of $d\hat{p}/d\psi \leq 0$, i.e. $\partial^2 G/\partial r_0^2 \leq 0$. Therefore, the threshold value of pressure at which instability occurs can be determined by enforcing the condition $d\hat{p}/d\psi = 0$, i.e.

$$
-\pi\hat{R}^2\sin\theta_e - 8\cos(2\psi)\sin\theta_e + \pi\hat{R}^2\cos(2\psi)\sin\theta_e - 8\cos\theta_e\sin(2\psi) = 0.
$$

(17)

We observe that two unstable conditions can be found in general: the first one corresponds to the impalement transition to the Wenzel state and is reached when the pressure increases over a value $\hat{p}_W$ (see below); the second one is achieved when the pressure decreases below a value $\hat{p}_{out}$ which we call the pull-off pressure. In particular we stress that the pull-off pressure $\hat{p}_{out}$ represents the lowest value of the pressure at which it is still possible to find a stable minimum of the total energy of the system. If the liquid pressure decreases below this threshold value the liquid drop detaches from the substrate. However, the drop does not detach as a whole, but rather via the edge propagation of the triple line toward the inner region of the liquid pillar. We also observe that, from a conceptual point of view, the pull-off pressure defined in the present paper is analogous to the maximum detachment force defined in [23] for capillary bridges. In fact, in our case the thermodynamic contact angle is $\theta_e > \pi/2$ and in this case the maximum detachment force for capillary bridges occurs exactly at the transition I point defined in [23] (see figure 5 of the cited paper). Beyond this point stable contact conditions cannot be achieved and the drop will necessarily detach from the substrate.

Since in the case of hemispherical-topped pillars $0 < \psi < \pi/2$, the equation $d\hat{p}/d\psi = 0$ gives just one solution $\psi = \psi_{out}$, which corresponds to the pull-off condition $\hat{p}_{out} = \hat{p}(\psi_{out})$. The impalement transition to the Wenzel state is instead obtained at $\psi = \psi_W = \pi/2$:

$$
\hat{p}_W = \hat{p}(\psi_W) = -\cos\theta_e\frac{\pi\hat{R}/2}{1 - \pi\hat{R}^2/4}.
$$

(18)

### 3.3. Flat-topped cylindrical pillars

In the case of flat-topped cylindrical pillars the liquid–solid contact area on each pillar is fixed and equal to $\pi R^2$. In such a case, depending on the drop pressure values, the slope of the liquid profile at the triple line can vary between two different limiting values as clearly shown in figure 6. We can, therefore, easily determine the critical pressure $\hat{p}_{out}$ at pull-off (see figure 6(a)) as

$$
\hat{p}_{out} = -\sin\theta_e\frac{\pi\hat{R}/2}{1 - \pi\hat{R}^2/4}
$$

(19)

and the critical dimensionless pressure $\hat{p}_W$ (see figure 6(b)) as (see also [21])

$$
\hat{p}_W = -\cos\theta_e\frac{\pi\hat{R}/2}{1 - \pi\hat{R}^2/4}
$$

(20)

which, as expected, is exactly equal to the value found for hemispherical pillars (see equation (18)). It is noteworthy that, in the case of flat-topped cylindrical pillars, the ratio $\hat{p}_{out}/\hat{p}_W = \tan\theta_e$ does not depend on the cylinder radius.
4. Results

In what follows we assume that the Young’s contact angle is \( \theta_e = 109^\circ \), i.e. we assume that the underlying microstructured surface is chemically hydrophobic.

4.1. Conical pillars

Conical pillars have been analyzed assuming that \( \hat{R} = R/\lambda = 0.5 \), where \( R \) is the radius of the base circle. Figure 7 shows the contact radius \( \hat{r} \) as a function of the dimensionless drop pressure \( \hat{p} \) for different values of the dimensionless pillar height \( \hat{h} \). The black solid curves are obtained by equation (14) whereas the red-dashed ones are obtained by minimizing the total energy of the system as explained in section 2. Notice the very good agreement between the two approaches. Also figure 7 shows that \( \hat{r} \) initially increases proportionally to the drop pressure \( \hat{p} \), as indeed predicted by equation (14). However, as the drop pressure is increased further, the contact radius also increases and the denominator in equation (14) may become not negligibly smaller than one. This, in turn, causes the drop pressure \( \hat{p} \) to increase more than linearly with \( \hat{r} \), thus explaining the deviation from linearity of the curves shown in figure 7. Since for conical pillars the partial fakirdroplet state is always stable (i.e. increasing the pressure does not force the system to undergo a spontaneous transition to the Wenzel state), a different threshold pressure \( \hat{p}_L \) has to be defined. This is simply the drop pressure at which the free liquid–air interface touches for the first time the base of the pillars. This condition, indeed, has been shown experimentally to easily trigger a sharp transition to the Wenzel state [21]. Figure 8 shows the dimensionless limiting pressure \( \hat{p}_L \) as a function of the pillar aspect ratio \( \hat{h} \). Observe that increasing \( \hat{h} \) also increases the limiting pressure \( \hat{p}_L \), since (at fixed \( \lambda \)) the liquid–air interface will be farther from the bottom of the pillar. However, \( \hat{p}_L \) cannot increase above the limiting asymptotic values obtained for \( \hat{h} \rightarrow \infty \), i.e. \( \alpha \rightarrow 0 \). When this happens, the conical pillar becomes an infinitely tall cylinder of dimensionless radius \( \hat{R} \) for which the Cassie–Baxter state becomes unstable when the drop pressure reaches the values \( \hat{p}_W \) given by equation (20) which indeed is just the asymptotic value \( (\hat{p}_L)_\infty \) shown by the dashed line in figure 8.
Figure 8. The threshold pressure $p_L$ as a function of the pillar aspect ratio $h$. Results are presented for $R = R/\lambda = 0.5$ and $\theta_e = 109^\circ$. Observe that as $h$ is increased the limiting pressure approaches an asymptotical value $(p_L)_\infty$ which is just the values given by equation (18).

Figure 9 shows the dimensionless penetration $\hat{\Delta} = \Delta / \lambda$ of the liquid drop into the pillar forest as a function of the dimensionless pressure $\hat{\rho}$. As expected, $\hat{\Delta}$ increases as the pressure $\hat{\rho}$ and aspect ratio $\hat{h}$ are increased. Indeed, increasing $h$, at fixed $R$ and $\lambda$, makes the cone sharper and sharper. This would in turn reduce the liquid–solid contact radius if the penetration were maintained fixed. But, since the dimensionless pressure $\hat{\rho}$ at equilibrium decreases if the contact radius $\hat{r}$ is reduced (see equation (14)), the drop actually needs to increase the penetration to increase $\hat{r}$ and, thus, sustain the applied pressure $\hat{\rho}$.

It is noteworthy to observe that, if the dimensionless height of the conical pillar is strongly reduced, we should expect an increase, instead of a decrease, of the dimensionless penetration $\hat{\Delta}$ as a function of $\hat{h}$. Indeed, in such a case the half-cone angle $\alpha$ would increase towards the limiting value $\theta_e - \pi/2$ at which the drop spontaneously undergoes a transition to the Wenzel state (which is obviously characterized by $\Delta = \hat{h}$). This increase of the penetration, as a consequence of the strong reduction of $\hat{h}$, is, indeed, also observed in figure 9 for $\hat{h} = 2$, where the corresponding $\hat{\Delta}$ values are larger than those obtained for $\hat{h} = 4$ over a large range of $\hat{\rho}$.

Figure 10 shows the calculated apparent contact angle $\theta_{\text{app}}$ (see equation (12)) as a function of the radius of the base circle $\hat{R}$ and different drop pressures $\hat{\rho}$. In the limit case of zero pressure $\theta_{\text{app}} = 180^\circ$ independently of $\hat{R}$, since in this case the stable state is a perfect Cassie–Baxter state with the drop just touching the tip of the conical pillars. Increasing $\hat{\rho}$ the apparent contact angle decreases in qualitative agreement with some experimental observations [15]. Notice that for each given pressure $\hat{\rho} > 0$ a minimum value of the base radius is needed to avoid that the liquid–air interface might bend to touch the substrate and undergo a transition to the Wenzel state. This explains why the curves at different drop pressures in figure 10 are plotted, starting from different values of the base radius $\hat{R}$.

4.2. Hemispherical-topped pillars

To analyze the behavior of hemispherical-topped pillars we use the simplified approach described in section 3 to calculate the area of liquid–solid contact as a function of pressure, then we solve equation (1) to determine the shape of the free liquid–air interface and therefore the penetration of the liquid drop and the apparent contact angle. Figure 11 shows the dimensionless liquid–pillar contact radius $\hat{r}$ at equilibrium (figure 11(a)) and the dimensionless penetration $\hat{\Delta}$ (figure 11(b)) as a function of the dimensionless drop pressure $\hat{\rho}$. Two types of lines are shown. Solid lines are stable equilibrium branches, whereas
Figure 11. The dimensionless radius $\hat{r}$ at equilibrium (a) and the dimensionless penetration $\hat{\Delta}$ at equilibrium (b) as a function of the dimensionless drop pressure $\hat{p}$ for hemispherical pillars. Full lines are stable branches, whereas dashed lines are unstable branches at fixed load (at fixed penetration the stability extends to the point where $\hat{\Delta}$ has a minimum). Results are presented for different values of the dimensionless spherical radius $\hat{R} = 0.2, 0.3, 0.4, 0.5$ and for $\theta_e = 109^\circ$. Each curve ends at a certain value of $\hat{p} = \hat{p}_W$, which only depends on the pillar radius and contact angle $\theta_e$. When this value of drop pressure is reached the penetration sharply jumps to the unit value, i.e. the drop undergoes a sharp transition to the Wenzel state.

dashed lines represent unstable branches at fixed load. As expected, on the stable branches, the contact radius and the penetration increase with the applied drop pressure, but this time the $\hat{r}$ versus $\hat{p}$ law strongly differs from being linear. Finite negative values of $p_{\text{out}}$ are related to the finite size of the liquid–solid contact that still exists when the drop is about to detach from the substrate. This is often strongly unwanted since, beside the large detaching force, it usually leads also to large contact angle hysteresis [14, 37]. Also observe that for hemispherical-topped cylindrical pillars an impalement transition occurs spontaneously when the drop pressure reaches the limiting value $p_w$ (at which the penetration $\Delta$ jumps to $h$), in contrast with what we have found for the conical pillars. Therefore, for hemispherical pillars the height should be chosen by taking care that at $p = p_w$ the free liquid–air interface does not touch the bottom of the pillar forest.

In the case of hemispherical-topped pillars, figure 12 shows that the apparent contact angle slightly increases with pressure $\hat{p}$. Figure 12 also shows the original Cassie–Baxter solution which corresponds to $\hat{p} = 0$.

4.3. Flat-topped cylindrical pillars

In this case, for any value of the drop pressure between the two limits $p_{\text{out}}$ given by equation (19) and $p_w$ given by equation (20), the contact liquid–pillar area will always be equal to $\pi R^2$ with $R$ the radius of the cylinder. This makes the problem (1)–(3) linear and, in turn, leads to a direct proportionality between the drop pressure $p$ and the penetration $\Delta$, as indeed confirmed experimentally in [21].

Figure 12. The apparent contact angle $\theta_{\text{app}}$ as a function of the radius $\hat{R}$ for hemispherical-topped pillars. Results are shown for different dimensionless drop pressures $\hat{p}$.

Notice that, since $|p_{\text{out}}|/p_w = |\tan \theta_e|$ and $\theta_e$ is usually not larger than $120^\circ$, the pull-off pressure is always larger than $p_w$. Therefore we expect that, although a forest of flat-topped cylinders can stabilize the Cassie–Baxter state, a drop suspended on such a microstructured surface is relatively difficult to detach from it and should suffer from strong contact angle hysteresis.

Figure 13 shows the variation of the apparent contact angle $\theta_{\text{app}}$ as a function of the cylinder radius $\hat{R}$ for different drop pressures. Similarly to the case of hemispherical pillars the apparent contact angle grows with the pressure, although in this case this increment is less pronounced.
**5. Discussion and design suggestions**

Very robust super-hydrorepellent surfaces should possess the ability to support large drop pressures, and should also allow the drops to easily abandon the substrate, roll on it with almost zero contact angle hysteresis or even easily bounce on it. As already stated, these properties are very desirable in applications such as microfluidic chips and micro-chemical reactors, where drops have to be easily moved and positioned. But, also on the macroscale, they represent a strict requirement for self-cleaning windows, water-hydrorepellent windshields, or even hydrorepellent clothing. In these latter cases, the droplet pressure may reach large values as a consequence of large inertia forces due to the impact of raindrops. As an example, assuming the raindrop falls at a speed of about \( v_0 = 10 \text{ m s}^{-1} \), we can easily estimate the maximum impact pressure \( p_{\text{max}} \approx \rho v_0^2 = 1 \times 10^5 \text{ Pa} \). Therefore, a self-cleaning super-hydrorepellent window should be necessarily characterized by large values of the critical Wenzel pressure such that \( p_W > p_{\text{max}} \). Thus, assuming that the substrate is constituted of hemispherical-topped cylindrical pillars, and recalling equation (20), we found

\[
\lambda < \hat{p}_W \frac{\gamma_{LA}}{p_{\text{max}}} = -\cos \theta_e \frac{\pi \hat{R}/2}{1 - \pi \hat{R}^2/4} \frac{\gamma_{LA}}{p_{\text{max}}} = \lambda_{\text{max}}. \quad (21)
\]

So taking for \( \hat{R} \) the value 0.5, recalling that the liquid-water surface tension is \( \gamma_{LA} \approx 72 \times 10^{-3} \text{ J m}^{-2} \), and assuming a thermodynamic contact angle \( \theta_e = 109^\circ \), one ends up with the value \( \lambda \approx 230 \text{ nm} \), i.e. nanotube forests [19] should be employed in such applications, provided that the pillar height is sufficiently large to avoid direct contact between the free liquid–air interface and the bottom of the solid surface (we also observe incidentally that nanometer spacing between the pillars is also necessary not to alter the transparency of the glass).

In the case of conical pillars the critical pressure \( p_L \) is determined by the condition that the air–liquid interface touches the pillar forest ground. It has been observed that the pressure \( \hat{p}_L \) is always smaller than the critical Wenzel pressure \( \hat{p}_W \) calculated for hemispherical-and flat-topped cylindrical pillars, and approaches this value only for infinitely large values of \( h \). Therefore, one may be tempted to conclude that, if large drop pressures have to be supported, the conical pillar shape is not a viable solution. However, we can easily correct for this by slightly modifying the pillar design to turn it into a cylinder with a conical tip on the top, i.e. in a conical-topped cylindrical pillar. The new conical pillar design guarantees the same critical Wenzel pressure \( p_W \) as given by equations (18) or (20), but has the fundamental benefit of presenting a vanishing or negligible pull-off pressure \( \hat{p}_{\text{out}} \). As a consequence, a drop on a forest of conical-topped cylindrical pillars should not suffer from CA hysteresis, as indeed is experimentally observed in [20], and should be able to easily roll or slide on the substrate or even to bounce on it with very high restitution coefficients. This should also explain why some biological systems, such as water striders, which usually walk on the free surface of the water, possess a conically shaped distribution of asperities on their super-hydrorepellent legs [11]. Also note that it is useless to have pillars taller than the minimum height necessary to prevent the contact of the liquid surface with the bottom of the pillar forest, in contrast to what is often asserted, i.e. that the taller the pillars the greater the super-hydrorepellence of the surface. The argument, which is usually provided, is that, as the pillar height is increased, more energy has to be spent to push the drop into full contact with the substrate. Thus, making pillars taller and taller should lead to a very large resistance against the impalement transition [37]. However, one should observe that this energy can always be provided by the pressure \( p_W \) acting inside the drop independently of the pillar height, and that the real critical condition for the transition to the Wenzel state to occur is \( p = p_W \). Only in the case of very small drops (diameter comparable with the spacing \( \lambda \) between the pillars) the physical scenario may change. In this case, it may be shown that the pillar height can actually play an additional role: because of mass conservation, an additional resistance against impalement transition and drop penetration is generated [21].

**6. Conclusions**

In this paper the behavior of a liquid drop on super-hydrorepellent surfaces constituted of a periodic distribution of pillars has been analyzed. In particular, the critical drop pressure \( p_W \) which destabilizes the fakir-droplet state causing a transition to a Wenzel (full contact) state and the critical pressure \( p_{\text{out}} \) which causes the detachment of the drop from the substrate have been studied for three types of periodic microstructured surfaces: conical, hemispherical-topped and flat-topped cylindrical pillars, regularly disposed on a rigid substrate. Both \( p_W \) and \( p_{\text{out}} \) are equally important to assess the super-hydrorepellent properties of surfaces. In fact, high \( p_W \) values are requested in all those applications in which very high pressures must be supported, e.g. self-cleaning glasses and super-hydrorepellent windshields, whereas small values of \( p_{\text{out}} \) are desirable to guarantee very small contact angle hysteresis, which allows the drop to easily move on the substrate (e.g. microfluidic chemical reactor, microfluidic...
chips) or, in the case of impacting drops, easily rebound from it (e.g. self-cleaning windows, super-water-repellent windshields and biker helmet visors). We have shown that the conical pillars have a pull-off pressure $p_{\text{out}}$ vanishingly small (that is an advantage in those applications in which liquid drops have to be easily removed from the surface), but the Cassie–Baxter state is destabilized for pressures smaller than the critical value $p_W$ found for hemispherical- or flat-topped cylindrical pillars. However, a surface microstructured with cylindrical pillars with conical tips would have both the advantages of large pressure $p_W$ and zero pull-off pressure $p_{\text{out}}$. Finally, the effect of pressure on the apparent contact angle $\theta_{\text{app}}$ has been studied. The analysis has shown that $\theta_{\text{app}}$ reduces significantly with pressure in the case of conical pillars (in agreement with previous experimental observations), whereas it slightly increases for hemispherical-or flat-topped cylindrical pillars.

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