Is superhydrophobicity robust with respect to disorder?

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Abstract. We consider theoretically the Cassie-Baxter and Wenzel states describing the wetting contact angles for rough substrates. More precisely, we consider different types of periodic geometries such as square protrusions and disks in 2D, grooves and nanoparticles in 3D and derive explicitly the contact angle formulas. We also show how to introduce the concept of surface disorder within the problem and, inspired by biomimetism, study its effect on superhydrophobicity. Our results, quite generally, prove that introducing disorder, at fixed given roughness, will lower the contact angle: a disordered substrate will have a lower contact angle than a corresponding periodic substrate. We also show that there are some choices of disorder for which the loss of superhydrophobicity can be made small, making superhydrophobicity robust.

1 Introduction

Superhydrophobic surfaces have attracted tremendous interest in the last few years, not only for academic reasons [1–10]. Nowadays, everybody agrees about the phenomenological definition of such surfaces. When a water droplet is deposited, high values of both advancing and receding static contact angles are observed. Superhydrophobicity also induces special characteristics such as the rolling of a deposited water drop at a very low tilt angle (equivalently, a very small hysteresis) or the rebound of a drop on impact with the surface. These properties are often described as self-cleaning or the Lotus effect. In any case the presence of a certain kind of roughness, which is still to be defined precisely, is necessary. On top of such surfaces, it is expected that the drop can be in at least two different states: in contact everywhere with the solid surface, i.e. the so-called wet or Wenzel state, or in contact with only the top elements of the surface, the so-called dry or Cassie-Baxter state. Superhydrophobicity refers naturally to this Cassie-Baxter state. A schematic representation of both states is given in fig. 1. If we compare the free energies of both situations for a periodic substrate, we arrive at the classical conclusion that if the equilibrium contact angle \( \theta_0 \) corresponding to the flat surface satisfies some inequality, the drop will be in the Cassie-Baxter state leading to superhydrophobicity. This inequality is well known and can be written as

\[
\cos \theta_0 < -(1 - \phi)/(1 - \phi),
\]

where \( r \) is the Wenzel roughness of the surface, defined as the total length (area, in 3D) of the surface divided by its projection, and \( \phi \) is the covered fraction, defined as the total length, or area in 3D, at contact divided by the total projected length. As can be easily seen, the larger \( r \), the more the surface is likely to be in the Cassie-Baxter state. This is the reason why it is believed that a very rough hydrophobic surface can be superhydrophobic.

The classical argument sketched above neglects metastability, as will be the case throughout the present paper. Having in mind low-viscosity liquids such as water, we focus on the minimum free-energy configuration without taking into account hysteresis effects where dynamics has to be considered. This approach also excludes large defects, wells or spikes or chemical impurities of size say 100 \( \mu m \) or bigger, which may be present by fabrication, by nature, or by large deviations of disorder. We assume a typical defect size say 10 \( \mu m \) or smaller and drop size or contact line length much bigger than the typical distance between defects. A self-averaging hypothesis can then be used in the thermodynamic limit. For a discussion of metastability associated with a large single defect, in models such as discussed in the present paper, see [11]. For a discussion of metastability associated with large deviations of disorder, see [12,13].

From an experimental point of view, it has been noticed that composite superhydrophobic states can be observed on surfaces with Wenzel roughness \( r \) as low as 1.25 [14]. It is also clear that reducing the details of the topography of the surface \( z(x, y) \) to a unique parameter such as the Wenzel roughness \( r \), as in (1), is a very crude approximation. Recently, an index has been introduced to characterize for a given surface, which part of the surface is superhydrophobic and which part is not. This so-called index of superhydrophobicity [14] allows to see which part
of the surface is in a Cassie-Baxter state and which part is in a Wenzel state. Unfortunately, it does not explain how the details of the roughness can affect the robustness of superhydrophobicity. Will a small change in roughness induce a big change in superhydrophobicity?

There are in fact two ways to design superhydrophobic surfaces: with a periodic topography using some synthetic procedure for very small areas by lithography or deep reaction ion etching techniques or with some disorder using a natural self-organising process for large areas. Of course, the fabrication of these highly precise microstructures is very complex. The only hope to have a scalable procedure in practice is thus dependent on self-organisation. Moreover, the first types of surfaces are typically based on single-scale topography and the second sets, usually, present several scales as for example do leaves [15]. This has already been observed experimentally. For instance, when several layers of nanoparticles are deposited on a glass substrate by Langmuir-Blodgett techniques, it is easily seen that the distribution of particles in the first layer is different from the one in the second layer. Therefore, we should observe different behavior depending on the number of layers. In fact, the disorder will increase with the number of layers. For such kinds of rough substrate, it has been shown experimentally [16] that disorder leads to a reduction of superhydrophobicity. How much hydrophobicity is lost is not yet clear so far. In Nature, there are many examples of plants or animals that have this remarkable property of superhydrophobicity without exactly periodic surface topography. Topographical defects observed in the living world do not seem to affect the robustness of the superhydrophobicity. It is precisely the aim of the present paper to introduce disorder within superhydrophobicity and to analyze how it will affect the Lotus effect.

2 Square protrusions

Let us start with a simple example. In two dimensions, or in three dimensions with grooves, we can build a regular surface such as the one illustrated in fig. 2. Denoting in three dimensions with grooves, we can build a regular.

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Using Young’s equation for the flat substrate, where the contact angle is $\theta_0$, we obtain that the lower energy state is Cassie-Baxter (state 1) if $c < c_{12}(\theta_0)$, where

$$c_{12}(\theta_0) = -2b\cos\theta_0/(1 + \cos\theta_0)$$

and Wenzel (state 2) if $c > c_{12}(\theta_0)$, with coexistence at $c = c_{12}(\theta_0)$. The Wenzel roughness of the motif is $r(c) = 1 + 2b/(a + c)$ and the covered fraction is $\phi(c) = a/(a + c)$. Then $c < c_{12}(\theta_0)$ is equivalent to inequality (1). In the periodic case, the lengths $a$, $b$ and $c$ are the same everywhere, so that either Cassie-Baxter or Wenzel will be the winner everywhere. The resulting contact angle on the periodic substrate is $\theta = \theta_{CB}$ obtained with $\gamma_{SL}^{CB}$ when $c < c_{12}(\theta_0)$ and $\theta = \theta_{W}$ obtained with $\gamma_{SL}^{W}$ when $c > c_{12}(\theta_0)$, as shown in fig. 3, with

$$\cos\theta_{CB} = \phi \cos\theta_0 + \phi - 1,$$

$$\cos\theta_{W} = r \cos\theta_0.$$  

If $\theta_0 > 3\pi/4$, not a realistic case, a state with water reaching the bottom but keeping air in the corners may be the winner. We ignore it here for simplicity, but air trapped at the bottom corners will be included below when considering 2D-disks or 3D-nanoparticles.

Now, let us assume that the square protrusions are distributed with some disorder, in the sense that $c_1, c_2, c_3, \ldots$ distributed according to some stationary probability law. What will be the effect on superhydrophobicity? Is a natural surface less or more superhydrophobic than a synthetic one? Clearly, we will have a non-trivial combination of Wenzel and Cassie-Baxter states depending on the probability distribution of $c$. For a given sequence $c_1, c_2, \ldots, c_n$, we get a free energy, defining a composite solid-liquid surface tension $\gamma_{SL}^{rr}$, with a superscript $rr$ for the random roughness,

$$\left( na + \sum_i c_i \right) \gamma_{SL}^{rr} = \left( na + 2b(n - n_1) + \sum_i c_i \right) \gamma_{SL}$$

$$+ 2bn_1\gamma_{SV} + \sum_{i:CB} c_i(\gamma_{LV} + \gamma_{SV}),$$

where $\sum_{i:CB}$ refers to the Cassie-Baxter states over the length $n$, the number of which equals $n_1$, and $\sum_{i:W}$ refers to the Wenzel states over the length $n$, the number of which equals $n_2 = n - n_1$. We then get in the thermodynamic limit $n \to \infty$, assuming that the contact line samples a large number $n$ of protrusions,

$$(a + c)\gamma_{SL}^{rr} = a\gamma_{SL} + 2b\gamma_{SV} + c(\gamma_{LV} + \gamma_{SV}),$$

$$(a + c)\gamma_{SL}^{rr} = a\gamma_{SL} + 2b\gamma_{SV} + c(\gamma_{LV} + \gamma_{SV})$$

+ $$(2bp_1 + p_1c_1(\gamma_{LV} + \gamma_{SV}))$$

+ $$(2bp_2 + p_2c_2)\gamma_{SL}.$$  

Fig. 2. The periodic surface characterized by three parameters: $a$, $b$ and $c$.  

Fig. 1. Wenzel state (left), Cassie-Baxter state (right).
Baxter configurations or only Wenzel configurations were
present. Both (8) and (9) and positive. This shows that
any disorder will lower the contact angle \( \theta \). Naturally,
there will always be some specific distribution that mini-
mizes this difference, which could be significant for prac-
tical applications.

These expressions can be evaluated for any probability
distribution for the \( c \)'s. The resulting plots of \( \cos \theta \) versus
\( \cos \theta_0 \) are shown in fig. 3 for two examples discussed below,
together with the periodic case.

As a first example, the squares may be distributed ran-
domly uniformly on the surface, with the \( c \)'s exponentially
distributed, leading to

\[
\cos \theta = \phi \cos \theta_0 + (1 - \phi) \left( \frac{(1 + \cos \theta_0) e^{-\frac{\gamma_{SV}}{\cos \theta_0}}}{\cos \theta_0} - 1 \right),
\]

which shows interestingly that the Wenzel roughness \( r \)
is not enough to describe the properties of the surface. Such
disorder should be expected in the case of adsorption from
a gas phase or a solvent.

A second example is a Bernoulli variable taking value
\( c_1 \) with probability \( p_1 \) and value \( c_2 \) with probability \( p_2 \),
with parameters such that \( c_1 < c_1 < c_2 \). Then (6) holds
with \( p_1, p_2, c_1, c_2 \) now independent of \( \theta_0 \) and here \( \cos \theta \)
is linear in \( \cos \theta_0 \) in the corresponding range. The asso-
ciated result corresponds to the central part of the red
line in fig. 3 supplemented by a piece of the Cassie-Baxter
straight line on the left and a piece of the Wenzel straight
line on the right.

3 Disks

Let us now consider the case of disks with diameter \( D \)
distributed along a line with distance \( c \) between successive
disks. The disks are made of the same material as the plane
substrate. The dry and wet cases are presented in fig. 4. The
Wenzel state only exists when \( c > c_{\text{min}} \), where

\[
c_{\text{min}} = -D + 2 \cot \theta_0.
\]

When \( c < c_{\text{min}} \), the two traps of air shown in fig. 4 in
the Wenzel case would be overlapping. The condition \( c > c_{\text{min}} \)
is a restriction only when \( c_{\text{min}} > 0 \) or \( \theta_0 > \arctan (-2) \approx 116.6^\circ \). However, it can be checked that, for all \( \theta_0 \)
in \( (\pi/2, \pi) \), \( c_{12} > c_{\text{min}} \). Thus, consistently, Wenzel states
characterized by \( c > c_{12} \) always obey \( c > c_{\text{min}} \). The same
reasoning as for the squares leads in the periodic case to

\[
(a + c) \gamma_{SL}^C = A_1 \gamma_{SL} + (B_1 + c) \gamma_{SV} + (C_1 + c) \gamma_{LV},
\]

(12)

with

\[
A_1 = D(\pi - \theta_0), \quad B_1 = D(1 + \theta_0), \quad C_1 = D(1 - \sin \theta_0)
\]

and

\[
A_2 = D(1 - 2 \theta_0 + 2 \cot \theta_0 + 2 \pi), \quad B_2 = D(2 \theta_0 - 2 \cot \theta_0 - \pi), \quad C_2 = D \frac{1 + \cos(2\theta_0)}{\sin \theta_0}.
\]
The resulting Cassie-Baxter and Wenzel contact angles on a periodic arrangement of disks in 2D or tubes in 3D are

\[
\cos \theta^CB = \frac{D(\pi - \theta_0) \cos \theta_0 - D(1 - \sin \theta_0) - c}{D + c},
\]
\[
\cos \theta^W = \frac{(D(2\pi + 1 - 2\theta_0) + c) \cos \theta_0}{D + c}.
\]

From (12) we have \(\gamma^CB_{SL} < \gamma^W_{SL}\) when \(c < c_{12}(\theta_0)\), and conversely, with

\[
c_{12}(\theta_0) = \frac{\cos \theta_0(\theta_0 - \pi - 1) - 1 + \sin \theta_0}{1 + \cos \theta_0}.
\]

Therefore, the true contact angle on such a periodic substrate is \(\theta = \theta^CB\) when \(c < c_{12}(\theta_0)\) and \(\theta = \theta^W\) when \(c > c_{12}(\theta_0)\). A corresponding plot of \(\cos \theta\) versus \(\cos \theta_0\) is shown in fig. 5.

In the random case, with \(p_1, p_2, c_1, c_2\) defined as after (5), using \(c_{12}(\theta_0)\) in (14), one may compute

\[
\gamma_{SV}^{rr} = \gamma_{SV}^{\pi D + D + \langle c \rangle \over D + \langle c \rangle}.
\]

and

\[
(D + \langle c \rangle)\gamma_{SL}^S = p_1(A_1 \gamma_{SL} + B_1 \gamma_{SV} + C_1 \gamma_{LV})
\]
\[
+ p_2(A_2 \gamma_{SL} + B_2 \gamma_{SV} + C_2 \gamma_{LV})
\]
\[
+ p_1c_1(\gamma_{LV} + \gamma_{SV}) + p_2c_2\gamma_{SL},
\]

leading to

\[
\cos \theta - \cos \theta^CB = p_2(1 + \cos \theta_0)\frac{c_2 - c_{12}}{D + \langle c \rangle},
\]
\[
\cos \theta - \cos \theta^W = p_1(1 + \cos \theta_0)\frac{c_{12} - c_1}{D + \langle c \rangle},
\]

where \(\cos \theta^CB\) and \(\cos \theta^W\) are given by (13) with \(c\) replaced by \(\langle c \rangle\), which is very similar to (8), (9). Again (15) and (16) are positive.

The distribution of disks might be considered to be like a quenched hard sphere fluid. In one dimension the distance \(c \geq 0\) between neighboring disks would then follow an exponential distribution, with

\[
p_1 = 1 - e^{-c_{12}/\langle c \rangle}, \quad p_1c_1 = \langle c \rangle - (\langle c \rangle + c_{12})e^{-c_{12}/\langle c \rangle}.
\]

But disks may have a small attractive interaction, electrostatic or due to the solvent, before drying. Then the distribution of inter-particle distances will be more weighted at small distances, at the expense of distances around the range of the interaction. This may be modeled for instance by a Gamma distribution, where the probability density of \(c\) is

\[
f(c) = \frac{\beta^\alpha}{\Gamma(\alpha)} e^{\alpha - 1} e^{-\beta c},
\]

with \(\beta = \alpha/\langle c \rangle\), from which (15), (16) can be computed with

\[
p_1 = 1 - \int_0^{c_{12}} f(c) dc, \quad p_1c_1 = \int_0^{c_{12}} cf(c) dc.
\]

In fig. 5 we choose \(\alpha = 0.2\), corresponding to more \(c\)'s both at 0 and at infinity compared to the exponential distribution with the same \(\langle c \rangle\). The Gamma model is the highest curve in fig. 5, and next is the curve for the exponential model. Globally, superhydrophobicity is reduced. In the limit \(\alpha, \beta \downarrow 0\) keeping \(\alpha/\beta = \langle c \rangle\) fixed, producing large clusters of disks, superhydrophobicity is completely lost: \(\cos \theta = \cos \theta_0\). This is the worst case given the convexity property.

In the opposite direction, disks could be deposited on a structured substrate, where \(c\) would take values on a discrete set corresponding to the minima of the structured substrate. For example, on top of a compact arrangement of disks of diameter \(d\), neighboring disks of diameter \(D\) bigger than \(d\) but smaller than \(2d\) would be at distances \(c + D\) in the range \{2d, 3d, . . . \}. Experimentally, this could be achieved for instance by Langmuir-Blodgett depositions or successive spin coatings. On this set we choose a geometric distribution, with the same \(\langle c \rangle\) as the other models

\[
\mathbb{P}(c = nd) = \frac{1 - e^{-\lambda d}}{e^{-2\lambda d} - e^{-\lambda d}}, \quad n \geq 2,
\]

with

\[
\lambda = \frac{1}{d} \log \frac{D + \langle c \rangle - d}{D + \langle c \rangle - 2d},
\]
from which (15), (16) can be computed with

\[
p_2 = \exp\left(-\lambda d \left[\frac{c_{12} + D}{d}\right]\right),
\]

\[
p_{2c2} = \frac{p_2 d}{1 - e^{-\lambda d}} \left(\frac{c_{12} + D}{d}\right) (1 - e^{-\lambda d}) + e^{-\lambda d} - Dp_2,
\]

where \(\lfloor x \rfloor\) is the smallest integer above \(x\). One obtains for \(\cos \theta\) as function of \(\cos \theta_0\) a continuous broken curve with infinitely many discontinuities of the derivatives accumulating at \(\cos \theta_0 = -1\). A discontinuity occurs at every value of \(\cos \theta_0\) such that \(c_{12}(\theta_0) + D\) is a multiple integer of \(d\). As fig. 5 shows, this \(d\)-geometric model really enhances superhydrophobicity as compared to the exponential model. The analysis also allows to compare the effect of square blocks with that of disks on superhydrophobicity. We find that disks are more favorable since they increase a little more the contact angle \(\theta\): compared to fig. 3, the curves in fig. 5, starting with the periodic CB and W, are below.

4 Convex 2D particles

Let us now consider more general 2D nanoparticles such as ellipses, or disks which may have fused partly with the substrate, or any smooth convex solid with a vertical axis of symmetry. Denote \(D\) their diameter (extension) parallel to the substrate plane, and \(c > 0\) the random distance between neighboring nanoparticles. The nanoparticles are identical, and the quenched distances \(c_1, c_2, c_3, \ldots\) make a stationary sequence, in particular all \(c_i\) have the same probability density. Denote \(F_{SL}(c_1, \ldots, c_n)\) the free energy for such a sequence, where on each interval the fluid chooses the configuration of minimum energy, Cassie-Baxter or Wenzel. As for disks or squares, there is a \(c_{12}\) depending upon \(\theta_0\) and upon the shape of the nanoparticles, such that the Cassie-Baxter state is chosen when \(c < c_{12}\) and the Wenzel state is chosen when \(c > c_{12}\). Denote \(F_{SL}^W(c_1, \ldots, c_n)\) the free energy for the sequence \(c_1, \ldots, c_n\), where on each interval the fluid chooses the Cassie-Baxter configuration, and similarly \(F_{SL}^W(c_1, \ldots, c_n)\) for the Wenzel case. Denote \(1_{c_{12}}\), the indicator function, with value 1 when the event is true and 0 otherwise. Then

\[
\frac{1}{n} \left(F_{SL}(c_1, \ldots, c_n) - F_{SL}^W(c_1, \ldots, c_n)\right) = (1_{c_{12}} (F_{SL}^W(c) - F_{SL}^B(c))) = 0,
\]

\[
\frac{1}{n} \left(F_{SL}(c_1, \ldots, c_n) - F_{SL}^W(c_1, \ldots, c_n)\right) = (1_{c_{12}} (F_{SL}^W(c) - F_{SL}^W(c))) < 0.
\]

The solid-liquid free energy is less than the Cassie-Baxter or Wenzel approximations. Therefore the contact angle \(\theta\) will be less than the approximations \(\theta^B\) or \(\theta^W\). This demonstrates clearly and very generally that the disorder always reduces superhydrophobicity.

The solution may be pursued further: \(F_{SL}^W(c)\) is an affine function of \(c\) with slope \(\gamma_{SL}\), and \(F_{SL}^B(c)\) is an affine function of \(c\) with slope \(\gamma_{SL} + \gamma_{LV}\). Using \(F_{SL}^W(c_{12}) = F_{SL}^W(c_{12})\) and Young’s equation we get

\[
F_{SL}^W(c) - F_{SL}^B(c) = -(1 + \cos \theta_0)(c - c_{12}).
\]

Therefore

\[
\langle 1_{c_{12}} (F_{SL}^W(c) - F_{SL}^B(c)) \rangle = -(1 + \cos \theta_0) \langle 1_{c_{12}} (c - c_{12}) \rangle,
\]

which leads to the same formulas (15) as for disks, allowing a computation of the effect of disorder on the contact angle. Now \(D\) has a more general definition, and \(c_{12}\) may have to be computed numerically. Like for disks, there is a \(c_{\text{min}}\) such that the Wenzel state only exists when \(c > c_{\text{min}}\).

One can check that \(c_{12} > c_{\text{min}}\) by the triangular inequality whatever the shape of the nanoparticles. One can also prove in this generality that \(\cos \theta\) is a convex function of \(\cos \theta_0\). Indeed from Young’s equation it is equivalent to show that

\[
\int_{c_{12}}^{\infty} \mu(c) F_{SL}^W(c) + \int_{c_{12}}^{\infty} \mu(c) F_{SL}^W(c)
\]

is a concave function of \(\cos \theta_0\). This follows from

\[
\frac{1}{2\gamma_{LV}} \frac{d^2 F_{SL}^B(c)}{d(\cos \theta_0)^2} = \frac{R(\theta_0)}{\sin \theta_0},
\]

\[
\frac{1}{2\gamma_{LV}} \frac{d^2 F_{SL}^W(c)}{d(\cos \theta_0)^2} = \frac{4R(2\theta_0 - \pi)}{\sin \theta_0},
\]

\[
- \frac{1}{(\sin \theta_0)^3} \int_0^{2\theta_0 - \pi} R(\theta) \sin \theta\, d\theta,
\]

where \(R(\theta) = d\ell/d\theta\) is the radius of curvature at any point on the curve defining the nanoparticle where the slope of the curve is \(\tan \theta\). Like for the circle in fig. 4, special points on the curve play a role: at a point in contact with the three phases, we have \(\theta = \theta_0\) in the Cassie-Baxter case and \(\theta = 2\theta_0 - \pi\) in the Wenzel case.

5 Towards the 3D nanoparticles case

The exact results presented so far are for 2D models or 3D grooves. A true 3D situation will not be exactly soluble in general because liquid penetration into one region is likely to influence penetration into another region. There are however situations where the 3D nanoparticle case is soluble and where the solution gives an insight into what may be specific to 2D and what may extend to 3D. Consider once more fig. 4, now as a side view of a three-dimensional system. Suppose that \(\theta_0\) and the random distribution of nanoparticles on the plane surface are such that either the Cassie-Baxter (left) configuration wins everywhere or the Wenzel (right) configuration wins everywhere. Then the liquid-vapor interface either will be plane everywhere, with spherical caps emerging, or will be made of catenoid ribbons around each nanoparticle, as shown in fig. 6. Indeed the catenoid is then the minimal surface, given the boundary conditions on the spheres. The resulting free energies and contact angles depend only on the density of
nanoparticles. Of course this is valid only if the variance of the disorder is sufficiently small so that one or the other wins everywhere, a severe restriction to the exact solution compared to the 2D case. The arrangement of nanoparticles makes a random triangulation of the plane, with the centers of the spheres as vertices of the triangulation. The free energy per unit projected area for an extended system is the same as the free energy per unit projected area for an equilateral triangle corresponding to the given density of nanoparticles, or even for any triangle of same area, which is the average area of the triangles in the random triangulation, denoted $A_{\text{tri}}$. The free energies for a triangle in a dry, Cassie-Baxter, or Wenzel configuration are then computed exactly, using fig. 7,

$$F_{SV}^{rr} = (A_{\text{tri}} + 2\pi R^2)\gamma_{SV},$$

$$F_{SL}^{CB} = (A_{\text{tri}} + \pi(1 - \cos \theta_0)R^2)\gamma_{SV} + \pi(1 + \cos \theta_0)R^2\gamma_{SL} + \pi \sin^2 \theta_0 R^2 \gamma_{LV},$$

$$F_{SL}^{W} = \left( A_{\text{tri}} + \frac{1}{2} \pi \rho_0^2 \right) \gamma_{SV} + \left( A_{\text{tri}} + A_{\text{L sph}} - \frac{1}{2} \pi \rho_0^2 \right) \gamma_{SL} + A_{\text{cat}} \gamma_{LV},$$

where $\rho_1$ and $\rho_0$ are the catenoid radii on the sphere and the plane respectively, and $A_{\text{cat}}$ is the area of the catenoid.

Let us now explain the derivation of (20). In the formula for $F_{SV}^{rr}$, the term $2\pi R^2$ corresponds to one half of a sphere in contact with air, as is obvious from fig. 7. The formula for $F_{SL}^{CB}$ comes from

$$F_{SL}^{CB} = (A_{\text{tri}} + A_{\text{L sph}})\gamma_{SV} + A_{\text{L sph}} \gamma_{SL} + A_{LV} \gamma_{LV},$$

where $A_{\text{L sph}} = \pi(1 - \cos \theta_0)R^2$ is the nanoparticle area in contact with the vapor in the Cassie-Baxter configuration, within the triangle; $A_{\text{L sph}} = \pi(1 + \cos \theta_0)R^2$ is the nanoparticle area in contact with the liquid in the Cassie-Baxter configuration, within the triangle; $A_{LV} = A_{\text{tri}} - \pi \sin^2 \theta_0 R^2$ is the area of the liquid-vapor interface within the triangle in the Cassie-Baxter configuration. The formula for $F_{SL}^{W}$ comes from

$$F_{SL}^{W} = \left( A_{\text{tri}} + \frac{1}{2} \pi \rho_0^2 \right) \gamma_{SV} + \left( A_{\text{tri}} + A_{\text{L sph}} - \frac{1}{2} \pi \rho_0^2 \right) \gamma_{SL} + A_{\text{cat}} \gamma_{LV},$$

where now $A_{\text{L sph}}$ is the nanoparticle area in contact with the vapor in the Wenzel configuration, within the triangle; $A_{\text{L sph}}$ is the nanoparticle area in contact with the liquid in the Wenzel configuration, within the triangle, and $A_{\text{cat}}$ is the catenoid area within the triangle. The equations of the sphere and of the catenoid, in cylindrical coordinates using the vertical axis of symmetry of the sphere, are respectively

$$\rho = R \sqrt{1 - \left( 1 - \frac{z}{R} \right)^2}, \quad \rho = \rho_c \cosh \left( \frac{z - z_c}{\rho_c} \right),$$

where $z_c$, $\rho_c$ are free parameters. We denote $z_1$, $\rho_1$ the solution of this system of equations, with smaller $z$, and we define $\alpha_1$ by $\cos \alpha_1 = 1 - z_1/R$. The catenoid also intersects the substrate plane at $z = 0$, $\rho = \rho_0$. At $z_1$, $\rho_1$ and at $z = 0$, $\rho = \rho_0$, the liquid contact angle must equal $\theta_0$, solution of Young’s equation $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_0$. This fixes the parameters $z_c$, $\rho_c$ and can be used to get numerical values for $z_1$, $\rho_1$, $\alpha_1$, $\rho_0$. Then

$$A_{\text{V sph}} = \pi(1 - \cos \alpha_1)R^2,$$

$$A_{\text{L sph}} = \pi(1 + \cos \alpha_1)R^2,$$

$$A_{\text{cat}} = \frac{1}{2} \pi \rho_0^2 \left( \frac{z_1}{\rho_c} + \frac{\pi}{\rho_c} \sin \frac{z_c}{\rho_c} + \frac{\pi}{\rho_c} \sin \frac{2z_1 - 2z_c}{\rho_c} \right).$$

From (20) and Young’s equation $\gamma_{SV} = \gamma_{LB} + \gamma_{LV} \cos \theta_{LB}$ or $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_{LV}$ the resulting contact angles $\theta_{LB}$ or $\theta_{LV}$ can be computed exactly, and are shown in fig. 8. The true contact angle $\theta$ on the random substrate will be $\min(\theta_{LB}, \theta_{LV})$, or the maximum of their cosines shown on the figure.

We may also ask for conditions on a given triangle for a Cassie-Baxter or Wenzel configuration to be a minimizer. The formulas above show that the area alone can tell which of the two is the minimizer, as function of $\theta_0$. 


be maximized in order to maximize the amount of air trapped. As fig. 9 shows, with a zoom around \( \cos \theta_0 = -0.05 \), a Cassie-Baxter state can be achieved whenever \( \cos \theta_0 < -0.034 \) or \( \theta_0 > 92^\circ \). But \( \theta_0 \) should be a little larger to leave some room for disorder and to achieve a larger final contact angle \( \theta \). In 2D, \( \theta_0 > 90^\circ \) suffices, and the \( d \)-geometric model with \( 2d < c_{12} \) and \( \langle c \rangle \simeq c_{12} \) achieves the desired goal.

### 6 Conclusion

We have thus generalized to different types of geometries the classical formulas describing the Cassie-Baxter and Wenzel states for wetting of rough substrates for 2D systems or 3D grooves geometries or 3D-nanoparticles. Those include explicitly rectangular protrusions and nanoparticles (or nanotubes). We have shown how to introduce the concept of surface disorder within the problem. Our result, quite generally, shows that disorder will lower the contact angle observed on such substrates compared to the periodic case. We have also shown that there are some choices of disorder for which the loss of superhydrophobicity can be made relatively small, making superhydrophobicity relatively robust. As an indirect result, this work may open the way for new numerical simulation studies.

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