23rd International Congress of Theoretical and Applied Mechanics

Size effects of surface roughness to superhydrophobicity

Quanshui Zheng*, Cunjing Lü

Department of Engineering Mechanics and Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China

Abstract

Water droplets placed on a superhydrophobic surface act like soft balls that can easily deform, roll and bounce, leading to various novel behaviors such as self-cleaning and anti-icing. Thousands of plant and animal species have been observed to have superhydrophobic surfaces and all these surfaces seem to have roughness sizes in the micro-submicron range. The classical models don not predict this kind of specified size phenomenon. Here we review some recent findings, which show that scaling down the surface roughness into the micro-submicron range is a unique and elegant strategy to not only achieve superhydrophobicity, but also increase its stability against environmental disturbances. We further demonstrate that these findings can guide fabrication of stable and extreme liquid-repellant surfaces.

© 2013 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of Marc Geers and Lallit Anand

Keywords: wetting, superhydrophobicity, size effect, stability

1. Introduction

A droplet resting on a solid surface forms a characteristic contact angle, $\theta$ or $\theta'$, as indicated in Fig. 1, that quantifies the wettability of the solid surface. The surface is named as hydrophobic or hydrophilic if the contact angle is larger or smaller than 90°. There is a simple relationship, the Young equation [1]

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}},$$

that correlated the intrinsic contact angle $\theta$ (the contact angle of a smooth surface) with the solid-vapor, solid-liquid and liquid-vapor interface tensions $\gamma_{SV}$, $\gamma_{SL}$ and $\gamma_{LV}$. For tiny droplets, the three-phase (solid-liquid-vapor) intersection line tension may become crucial, and the Young equation (1) should be modified as [2, 3],

* Corresponding author. E-mail address: zhengqs@tsinghua.edu.cn.
where $\lambda$ and $R_{SL}$ denote the three-phase line tension and the radius of the three-phase contacting circle, respectively.

Superhydrophobic surfaces are highly hydrophobic, i.e., extremely difficult to wet. They are usually referred to have contact angles exceeding 150° and the roll-off angles less than 5° [4]. Since chemically modifying the surface alone can typically lead to contact angles of up to 120°, but not more [5], superhydrophobicity is known to be an enhanced effect of surface roughness - the Lotus’ effect [4]. The basic wetting state of droplets on a rough substrate is either in Wenzel’s [6] or Cassie–Baxter’s [7]. In the former, the liquid follows the surface corrugations, as illustrated in Fig. 1b; in the latter the water drop is attached to the surface but in a position on top of the corrugations, which allows air pockets to be trapped under it, as shown in Fig. 1c. Usually, only one of these states is stable while the other is metastable [8, 9], depending on both the surface chemistry and roughness.

The apparent contact angle, $\theta^*$, in either the Wenzel or Cassie–Baxter state has the following relation with the intrinsic contact angle $\theta$ and the topography of the roughness structure [6, 7]

$$\cos \theta^* = r \cos \theta,$$

$$\cos \theta^* = -1 - (1 + \cos \theta) f,$$

respectively, where the parameter $r$ is the ratio of the wet surface area to its projection on the apparent solid plane, and $f$ is the area fraction of the wet part of the solid. The Wenzel and Cassie–Baxter relations (3) and (4) have classically been used to characterize the apparent contact angles with remarkable success [10]. The latter reveals that $\theta^*$ comes near 180° as the area fraction $f$ approaches to zero. Wetting in the Cassie–Baxter’s state, rather than in the Wenzel state, is generally a requirement for achieving superhydrophobicity [8].

Recently, however, a number of exceptions have been observed that seem to be at odds with the understanding based on Eqs. (3) and (4) [11–17]. For instance, roughness sizes were shown to have a remarkable influence on the apparent contact angles [11–17]; while neither Eqs. (3) nor (4) includes a size term because both the roughness $r$ and area fraction $f$ are dimensionless. Besides, thousands of plant and animal species have been observed to have superhydrophobic surfaces [18, 19], which have roughness sizes in micrometers or smaller. Figure 2 shows one example - the hierarchical structure of a water spider’s leg. The leg is covered by innumerable setae that have diameters in a few to tens of micrometers, see Figs. 2a and 2b, and the seta surface has a groove structure with depth and width in about 100 nanometers, see Fig. 2c. There are more than 1 200 species of water spiders and insects, surprisingly, all of them seem to have similar nanoscale groove structures [19]. Since both $r$ and $f$ are dimensionless, the
above mentioned size effects and naturally chosen micro- to nanoscale roughness cannot be explained by the known models until two recent works [16, 20].

Fig. 2. Hierarchic structure of a water spider’s leg: (a) A water strider that can walk and jump on water surface; (b) There are innumerable microscale setae covered on each leg, and (c) each seta is covered by nanoscale grooves. (after [21]; see also [22])

An outline of this paper is described below. We present in Sect. 2 a new model, the Line Tension Cassie–Baxter (LTCB) relation, that was independently found recently in two groups lead by Zheng [16] and Ho [20]. Then we review in Sect. 3 the first and a systematical experimental result that quantitatively verifies this model [16]. Size effects to bouncing, rolling, and moving behaviors were examined in Sect. 4. In Sect. 5 we analyze that scaling down the surface roughness into the micro-submicron range is a unique and elegant strategy to not only achieve superhydrophobicity, but also increase its stability against environmental disturbances. We extend the LTCB relations for some most interested roughness types in Sect. 6 and discuss how to more precisely measure the three-phase line tension based on the LTCB relations in Sect. 7. Finally, we conclude this paper with some remarks and perspectives in Sect. 8.

2. Line tension Cassie–Baxter relation for pillar structured surfaces

The modified Young relation (2) considered the influence of droplet size, through the radius $R_{SL}$ of the circumference of the contact circular area of the droplet resting on a smooth solid surface. This influence is, however, negligible for most visible droplets, because the line tensions, $\lambda$, for most solid surfaces are very small, in a range of $10^{-12} – 10^{-8}$ J/m [3]. The corresponding contribution to $\cos \theta$ in Eq. (2) from the line tension of a droplet with $R_{SL} = 100$ $\mu$m, for instance, falls in a very small value range $(1.37 \times 10^{-7} – 1.37 \times 10^{-3})$ and is thus negligible.

When a droplet wets on a rough surface in the Cassie–Baxter state, there can clearly be numerous three-phase intersection lines that are boundaries of wetted caps on the top of the roughness in the wetting area and coexist with the trapped air pockets, as schematically illustrated by the red lines in Fig. 3. It was somewhat surprising that all known contact angle relations before the works [16, 20] overlooked the key fact that the total length, $L_{TP}$, of the three phase intersection lines per unit apparent contact surface area can become very long as the roughness scale shrinks into the micron-submicron range, and correspondingly, the accumulated total line energy can become significantly large. For instance, for a square pillar structure with pillar cross-section side length 1 $\mu$m and the pillar to pillar spacing 1 $\mu$m, the total three phase line length $L_{TP}$ per unit square meter of the apparent area is amazingly equal to 1 000 km!

To formulate a precise and simple relation without losing the physical basis of the formulation, Zheng et al. [16] considered a periodic pillar-structured surface as schematically illustrated in Fig. 3. As schematically illustrated in the insert of Fig. 3b, the cross-section of a representative pillar is arbitrarily shaped and the pillar top surface is flat, with $A$ and $L$ denoting its area and perimeter, respectively. Therefore, the total excess energy per unit apparent contact area of the droplet on the pillar-structured surface is equal to
Fig. 3. A droplet wetting on a pillar-structured surface: (a) The size view in the Cassie-Baxter state; (b) The top view of the Cassie-Baxter state with numerous three-phase lines (red) distributed over the apparent solid-water contact area. The insert in (b) indicates the cross-section shape, area $A$ and perimeter $L$ of a representative pillar, within the apparent area $A_0$.

$$u = A_0 \left( \gamma_{SL} - \gamma_{SV} \right) + \left( 1 - \frac{A}{A_0} \right) \gamma_{LV} \lambda = \gamma_{LV} \left[ 1 - (1 + \cos \theta) \left( 1 - \frac{l_s}{S} \right) f \right],$$  \hspace{1cm} (5)

where $A_0$ denotes the apparent area shared by one pillar, $f = A/A_0$ is the area fraction, $S = A/L$ is a shape-dependent size characteristics of the pillars, and $\lambda$ is a material-chemical parameter has the length dimension. To get the second relation in Eq. (5), the Young relation (1) was used. Using the virtual work principle for the balance state, Zheng et al. [16] equated the above excess energy to $(-\gamma_{LV} \cos \theta^*)$ and obtained

$$\cos \theta^* = 1 + (1 + \cos \theta) \left( 1 - \frac{l_s}{S} \right) f.$$  \hspace{1cm} (7)

Compared with the Cassie–Baxter relation (4), the above new one Eq. (7) weights the term that modifies the intrinsic contact angle by a new factor $(1-l_s/S)$, which plays a similar role to the area fraction $f$ in determining the apparent contact angle. It is apparent that this factor becomes increasingly important as we scale down the surface roughness. This result and its underlying mechanism provide significant new insights into how to achieve superhydrophobicity by shrinking the roughness scale ($S$).

We call Eq. (7) the line tension Cassie–Baxter relation, or in brief, LTCB relation.

Compared with the size dependent term in the modified Young relation (2) that could only become significant for very small droplets and does not take account effect of roughness size, the size dependent term in the line tension Cassie–Baxter relation (7) should be taken into account for any sized drops and reflects the influence of roughness scale, whenever the roughness scale falls in a micrometer or smaller scale as detailed in the next section.

Similar relation to Eq. (7) was independently derived by Wong and Ho [20]. The major difference between the work of Zheng et al. [16] and that of Wong and Ho [20] is that the relation was for the first time experimentally confirmed in the former.

Historically, even some of the previous proposed models that included the effect of line tension on contact angles for rough substrates, they only considered line tension at the boundary of the contact area [23–25], and these models confused single droplet in small size and droplet with small contact area. Since these models
omit the much larger contribution of line energy arose from the contact area, their results could not capture the major physics of the size effect on the wetting properties.

3. Extreme superhydrophobicity

An important physics revealed by the LTCB relation (7) is that the material-chemical parameter $l_{cr}$ plays as a critical length for wetting. As $S$ approaches $l_{cr}$, the term $(1-l_{cr}/S)$ approaches zero, and consequently the apparent contact angle $\theta^*$ would always come near $180^\circ$, in regardless what area fraction $f$ and what pillar cross-section shape would be. This suggests a means to achieve superhydrophobicity in its extreme case ($\theta^* = 180^\circ$).

The cross-section area-to-perimeter ratio of the pillars, $S$, is a shape-dependent size characteristics. For the familiar shapes: circular, square, triangle, crossed, and fractal-like shapes (four-layer), as illustrated in Fig. 4, the corresponding values of $S$ are

$$\frac{\pi}{4}, \frac{a}{4}, 0.577 \times \frac{a}{4}, 0.234 \times \frac{a}{4}, 0.072 \times \frac{a}{4},$$

respectively. In generally, more complex of the boundary shape is, smaller value of $S$ becomes. This guides fabrication of pillar structures with smaller $S$.

![Fig. 4. Cross-sections of pillar-like structures: circular, square, triangle, crossed, and fractal-like.](image)

It was shown [16, 20] that most of previous observations of the roughness size dependence of contact angles can be qualitatively explained by using the new relation (7). However, because of the lack of detailed sizes and/or shapes, these observations do not constitute quantitative vilification of the LTCB relation (7).

To experimentally and quantitatively validate the LTCB relation (7), Zheng et al. [16] first fabricated three sets of pillar-structured surface samples of size 1 cm x 1 cm on a silicon wafer using photolithography (see Fig. 5). Samples in Sects. I and II are square-shaped with two different but fixed area fractions $f \approx 0.15$ and 0.24, respectively, and those in Sect. III are cross-shaped with the same fixed $f \approx 0.24$ as in Sect. II. In contrast to $f$ being constant, the pillar sizes $S$ were designed to be variable. All had their surfaces become hydrophobic by grafting a self-assembled monolayer of octadecyltrichlorosilane (OTS, C$_{18}$H$_{37}$Cl$_3$Si, 95%) onto the samples [16, 26]. They used de-ionized water as the liquid, formed into droplets of 10 $\mu$L (spherical diameter 2.67 mm). The contact angles were measured using a commercial goniometer (OCAH200, Dataphysics). The intrinsic contact angle was measured on a flat OTS coated surface to be $\theta = 105^\circ \pm 1^\circ$. The measured contact angles for these structured surfaces are plotted as solid symbols in the graph shown in Fig. 6; they progressively diverge from the values predicted by the Cassie–Baxter relation (the horizontal dashed lines) as the pillar sizes shrink. The red and blue solid lines are the least-square fits of the measured values to the LTCB relation (7) with the single unknown parameter $l_{cr}$. The relationship’s excellent fit to the data with the single fit parameter $l_{cr} = 0.29 \mu$m across all the scales confirms that, compared to the Cassie-Baxter relationship, the new model (7) captures important physical effects of great consequence at small scales.
Fig. 5. Selected top (and side, insert) viewed SEM images from 17 pillar-structured surface samples with different $S$ that are larger than the critical value $l_{cr}$ and (a) fixed square shape and $f \approx 0.15$, (b) fixed square shape and $f \approx 0.24$, and (c) fixed cross shape and $f \approx 0.24$. Selected top (and side) viewed SEM images from 8 pillar-structured surfaces with different $S$ that are near or smaller than the critical value $l_{cr}$: (d) irregular shaped with $S = 0.281 \, \mu m$ and $f = 0.079$, (e) square shaped with $S = 0.063 \, \mu m$ and $f = 0.51$, (f) cross-shaped with $S = 0.2 \, \mu m$ and $f = 0.16$. The scale-bar is 20 $\mu m$ for (a)–(c) and 2 $\mu m$ for (d)–(f). (Cite from Ref. [16])

To test the extreme case $S = l_{cr}$, additional four samples were fabricated using photolithography. The obtained pillar structures have $S$ values ranging from 0.23 to 0.40 but have irregular-shaped cross-sections (Fig. 5d) due to the fabricated sizes being close to the photolithography limit. The solid triangle symbols in Fig. 6 show the measured contact angles, which are all larger than 170°. The different roughness shapes and area fractions used in these experiments and the measured very high apparent contact angles further confirm the validity of Eq. (7) and its ability to predict contact angles when the surface features are in the micron-submicron range.

To exclude the possibility that the increased contact angles arose as a result of finer surface roughness on the pillar tops, perhaps as a result of the photolithography, Zheng et al. [16] examined these using an atomic force microscope. They were observed to be as smooth (with fluctuations on the scale of several Angstroms) as the un-etched silicon wafers, thus confirming that this was not the cause of the large contact angles at small scales seen in the experiments.

The experimental observations presented by dots in Fig. 6 show the tendency of $\theta^*$ to approach 180° as $S$ trends downwards toward $l_{cr}$. Also apparent from the figure is how well the new relation Eq. (7) predicts the contact angle. As $S$ further decreases across the critical value, $l_{cr}$, the value in the right-hand side of Eq. (7) passes through a transition from larger to smaller than $-1$. While the right-hand side of Eq. (7) becomes smaller than $-1$, this means that attaching water drops onto such rough substrates would be energetically unfavorable compared to their free state in air. As a consequence, the contact angles with $S \leq l_{cr}$ would always take the extreme value of 180°, regardless of the area fraction. To test this, Zheng et al. [16] fabricated four square- or cross-shaped pillar-structured samples as exampled in Figs. 5e and 5f with $S$ ranging from 0.06 to 0.24 $\mu m$ using an E-beam technique and made it hydrophobic again by grafting an OTS. The measured values of $\theta^*$ were plotted as solid symbols in the insert of Fig. 6. To be disappointed, the contact angles for samples with relatively high area fractions are significantly lower than 180°.
Fig. 6. The roughness size dependence of measured contact angles (solid dots) and the least-square fitted curves (solid lines) based on the new relation (7). The data are classified into three sets according to the approximately same area fractions and shapes: red circle and blue diamond solid dots for $f \approx 0.15$ and $f \approx 0.24$ with square-shaped cross-section, and blue crosses for $f \approx 0.24$ with X-shaped. The horizontal dashed lines in red and blue give the respective Cassie–Baxter predictions. The fitted value of $l_c$ for all studied 17 samples in the above three sets is equal to 0.29 $\mu$m. The triangle symbols are for 4 samples with $S$ near $l_c$. The insert shows the measured contact angles, with their respective area fractions, for 8 pillar-structured samples with $S$ near or smaller than $l_c$.

Some possible explanations for this novel observation are given below. The first was attributed by Zheng et al. [16] to the existence of long-range hydrophobic interactions that can pull a hung water drop at a distance from tens to hundreds of nanometers to suddenly adhere to the substrate [27]. These long-range interaction forces come into effect for pillar structures with pillar separations within the submicron range, and make ideal contact angles of 180° impossible. As the second explanation, we note that droplet vibration due to environments (mechanical, thermal, noise, et al.) may also result in a “long-range” interaction between the water surface and the pillar tops, and thus larger attachment area than that in the exactly static contact. Such vibration-induced larger contact area can be stable due to the contact angle hysteresis or pillar edge pinned effect.

Therefore, further careful experiments with roughness scales smaller than the critical one are required in order to check a novel prediction from Eq. (7) – creating ideal superhydrophobic surfaces that water could not wet.

In a recent work, Raspal [17] developed the line tension model on nanotextured alumina surface, Raspal’s experiments enriched the size independent observation by Zheng [16].

4. Bouncing, sliding, and moving

Nevertheless, the above experiments showed that pillar-structured surfaces with $S = l_c$ is at the extreme case that the surfaces have the highest hydrophobicity. As an interesting consequence, these extreme superhydrophobic surfaces would have better bouncing capability. This prediction is supported by the experimental observations reported in Eq. (16), as shown in Fig. 7. It is seen that both the first bouncing heights and the total number of bounces increase while reducing the roughness scale for the square pillar-structured surfaces with the same area fraction $f \approx 0.15$.

It was known that droplets placed on a surface with gradient of contact angles will tend to move spontaneously toward the lower contact angle region [28]. Combined with Eq. (7), droplets placed on a pillar-structured surface with same area fraction $f$ but varying $S$, should appear such motion. Experiments performed in [16] confirmed this prediction. Figure 7c shows the representative SEM images of pillars from a pillar-structured surface we made with the constant area fraction $f = 0.16$, same square shape, but
gradient pillar sizes $S$. As we vibrate this gradient surface, which is placed horizontally, droplets on the surface move toward the area with larger scales, see Fig. 7d.

![Fig. 7. The roughness size effects to bouncing and moving behavior on pillar-structured surfaces with fixed area fraction $f = 0.15$.](image)

(a) Images selected from a movie showing water drops bouncing with time on pillar-structured surfaces with different size $S$; (b) The bouncing heights versus scale $S$, the red triangle, blue square and green circle symbols correspond to the first, second and third bounces, respectively; (c) SEM images of the typical pillars on the pillar-structured surface with gradient pillar sizes; (d) Selected frames at different times of a video recording of directional horizontal rolling on the horizontally placed gradient surface that vibrates (Cite from [16]).

Hereinafter we report a new experimental result that scaling down roughness size helps to achieve smaller sliding angle [26]. Rolling or sliding property of droplets on solid surfaces is the second (after contact angle) most important characteristics of wettability and depends mainly upon the contact angle hysteresis [10, 29]. It is known that the contact angle hysteresis is caused by the existence of various factors that make the surface is not ideally smooth, such as surface containments, defects, roughness, and so on [10, 29]. There have been very rare quantitative correlations between the sliding angle and any of the above factors. One such a correction, in an explicit analytic form, was recently established by Lü et al. [26] as the factor is the roughness of a square-shaped pillar-structured surface, see Fig. 5. The result is as follow [26]

$$\rho g V \sin \alpha = 2 R_{SL} \gamma_{LV} (1 + \cos \theta) \sqrt{f} ,$$

where $\alpha$ denotes the sliding angle, $\rho$ is the liquid mass density, $g$ is the gravity constant $V$ is the droplet’s volume, and $R_{SL}$ is the radius of the wetted area. Substituting $R_{SL}$ as a function of $V$ and the apparent contact angle $\overline{\theta}$ into Eq. (9), one can easily obtain an explicit expression of $\sin \alpha$. Finally, for small $f$ we can further obtain the following approximation by ignoring higher order terms of $f$

$$\sin \alpha \approx \frac{1}{2} \left(1 + \cos \theta \right)^{3} \left(1 - \frac{L_c}{S} \right) \frac{3 \lambda_c^2}{\pi R^2} f ,$$

where $R$ is the droplet radius when it is sphere, and $\lambda_c = (\gamma_{LV}/\rho g)^{1/2}$ is the capillary length ($\approx 2.7$mm for water-air interface). Figure 8 is a comparison between the experimentally measured sliding angles and the prediction of Eq. (10), that shows clearly the size effect to sliding behavior.
5. Superhydrophobicity stability

Wetting in the Cassie–Baxter state, rather than Wenzel’s is generally considered to be a requirement for achieving superhydrophobicity [8]. Therefore, how to make a Cassie–Baxter wetting state more stable against environmental disturbances is a key issue. In this section we shall consider three types of instabilities that may destroy the superhydrophobicity.

The first is about the structural instability. It is well known that if the hydrophobic surface is sufficiently rough, then wetting in the Cassie–Baxter state, rather than Wenzel state, is energetically favorable. For pillar-structured surfaces, the measure of roughness is \( r = 1 + \frac{Hf}{S} \), where \( H \) denotes the pillar height. Therefore, for given \( f \) and \( S \) that define the apparent contact angle, a larger roughness means a larger pillar height (or slenderness). However, from the theory of elasticity it is known that a larger slenderness brings a higher risk of structural instability and a weaker rigidity against deformation. A solution to the above problem in nature is to use a double-scale structure such as in lotus’ surface [4, 30], or even multiscale or hierarchical structure such as the surface of a water strider’s leg [21, 22].

The second is about that only one of the Cassie–Baxter and Wenzel states would be stable while the other is metastable. For a pillar-structured surface, the total access energy per unit apparent contact area of a droplet wetting in Cassie–Baxter state was given in Eq. (5), and that in Wenzel’s can be expressed as [9]:

\[
\sigma _W = - (1 + HS^{-1}f) \gamma _{LV} \cos \theta .
\]

Substituting this relation and Eq. (5) into the condition \( u \leq \sigma _W \) yields \( H \geq H_{cr} \), with [16]

\[
H_{cr} = \left( l_c + \frac{1-f}{f} S \right) \frac{1 + \cos \theta}{-\cos \theta}.
\]  

(11)

In other words, \( H_{cr} \) is a critical height such that Cassie–Baxter’s wetting state is more stable than Wenzel’s whenever the pillar height is larger than \( H_{cr} \). A degenerated result of Eq. (11) without accounting \( l_c \) was given in [9].

The third is about the stability of superhydrophobicity against pressure. This important issue was first addressed in [9], as commented by Lobaton [31]. The suspended liquid-vapor interface, \( A_{sus} \), among pillars is always under a certain pressure, at least the pressure \( p_c = 2 \gamma _{LV}/R \) induced by the liquid-vapor interfacial tension \( \gamma _{LV} \), where \( R \) denotes the droplet’s curvature radius. This pressure itself can become very high when \( R \) is very small. Besides, the impacting pressure of a raining water droplet can be as high as \( 10^5 \) Pa [32]. As increasing the pressure, the interface \( A_{sus} \) will be forced to sink more and more. The
maximum pressure, $p_{\text{max}}$, sustainable by a pillar structured surface to prevent the transition from the
Cassie–Baxter to the Wenzel state due to the pillars piercing into the water was established in the
following form [9]

$$p_{\text{max}} = -\frac{f}{1-f} \frac{1}{S} \gamma_{LV} \cos \theta. \quad (12)$$

This result is exact for any cross-section shaped pillar structure.

The result (12) clearly shows the trade off between the impacts of the scale of the roughness ($S$) versus
the effect of the wet area faction ($f$). These act in opposition to each other in determining the maximum
pressure that can be withstood to maintain the Cassie–Baxter state, which is generally required for
water-repellency. On the one hand, reducing $f$ results in superhydrophobic surfaces, but this is
accompanied by a reduced capacity to withstand the pressure of the liquid; on the other hand, reducing
the scale of the roughness yields not only a larger contact angle but also better superhydrophobicity.

Similarly, the result (11) is not only simple, but also precise for any cross-section shaped pillar
structure. It shows that the scale of the roughness and wet area faction act also in opposition to each other
in determining the minimum pillar height for a stable Cassie–Baxter state. On the one hand, reducing $f$
results in superhydrophobic surfaces, but this is accompanied by increased $H_c$ and thus reduced capacities
against elastic instability as well as deformation that may both result in the fail of superhydrophobicity;
on the other hand, reducing the scale of the roughness yields not only a larger contact angle but also better
superhydrophobicity.

The above analyses provide the basis to understand the finest micron or submicron scale of naturally
occurring superhydrophobic surfaces. It also reveals how such surfaces remain superhydrophobic even in
potentially destructive environments. The results equations (11) and (12) also guide the design for better
superhydrophobicity.

6. LTCB relations for some other roughness types

For most of naturally occurring superhydrophobic surfaces, the roughness geometries do not consist of
flat top surfaces plus vertical side surfaces. In this section we generalize the result (7) in order to take
account of the influence of different roughness geometries.

First of all, we point out that all the relations (7), (11), and (12) are also valid for roughness made by
drilling vertical holes from a flat surface, as illustrated in Fig. 9a. In this case, the parameters $f$ and $S$
hold the same meanings as in the pillar-structured case, namely, $f$ is the ratio of top area $A$ to the apparent area
$A_0$, and $S$ is the ration of the perimeter $L$ of the hole to $A$.

As illustrated in Fig. 9b, if the wet part is not flat but curved, then the representation (5) for the total
excess energy per unit apparent contact area of the droplet should be modified as

$$u = \frac{rA}{A_0} (\gamma_{SV} - \gamma_{LV}) + \left[ 1 - \frac{A}{A_0} \right] \gamma_{LV} + \frac{L}{A_0} \frac{A}{A}. \quad (13)$$

where $r$ is the roughness of the wet part that is defined as the ratio of the real wet area to its projection
area $A$, $L$ is the perimeter of the wet part, and $f = A/A_0$ is the projection area fraction. Thus, the following
generalized result to Eq. (7) can be obtained

$$\cos \theta^* = -1 + \left[ (1 + r \cos \theta) - (1 + \cos \theta) \frac{L}{S} f \right]. \quad (14)$$
Some particularly interested roughness types are discussed below. First, the roughness is made of pillars with semi-spherical caps with radius \( R \), as illustrated in Fig. 9c. With the parameters indicated in Fig. 9c, the wet area, its projection area, and three phase contact line length per pillar are equal to \( \hat{A} = 2\pi R^2(1+\cos \theta) \), \( A = \pi(R \sin \theta)^2 \), and \( L = 2\pi R \sin \theta \). Therefore, we can write the following result

\[
\cos \theta' = -1 + \left[ 1 + r \cos \theta - (1 + \cos \theta) \frac{l_w}{S} \right] f
\]

\[
= -1 + \left[ 1 + \frac{2}{1 - \cos \theta} \cos \theta - (1 + \cos \theta) \frac{l_w}{(R \sin \theta)/2} \right] \frac{\pi (R \sin \theta)^2}{A_0}.
\]

(15)

Introducing the pillar projection area fraction \( f_0 = \frac{2 R}{(2 R + s)} \) is the area fraction as the wall would have a flat top, \( s \) is the spacing of the two neighbor pillars. The degenerated form of (17) as \( l_w/R \rightarrow 0 \) was given by Feng et al. [22].

\[
\cos \theta' = -1 + \left( 1 + \cos \theta \right)^2 \left[ 1 - \left( \frac{\tan \frac{\theta}{2}}{R} \right) \frac{2 l_w}{R} \right] f_0.
\]

(16)

The third type is a roughness structure consisting of cones as illustrated in Fig. 9d. If denoting by \( \beta \) the half-apex angle, \( R = z \tan \beta \) the radius of the conical cross-section at distance \( z \) to the cone tip, then the wet area, roughness, and perimeter length are equal to \( \hat{A} = \pi R^2/\sin \beta \), \( 1/\sin \beta \), and \( 2\pi R \), respectively. We obtain the free energy expression as follows

\[
\frac{u}{\gamma_{LV}} = 1 - \left[ 1 + \frac{\frac{1}{\sin \beta} \cos \theta - (1 + \cos \theta) \frac{2 l_w}{z \tan \beta}}{\frac{2 \pi (z \tan \beta)^2}{A_0}} \right].
\]

(18)

As an ideal model, Eq. (18) does not consider the influence of the pressure induced by the water-vapor interfacial tension.
The classical counterpart of Eq. (18) does not contain the term with \( l_{cr} \). However, since \( z \) can approach to zero, this term can not be ignored for small \( z \); otherwise, the linear dependence upon \( z \) in Eq. (18) without \( l_{cr} \)-term will give the prediction that the wetting would be either in an impractical Cassie–Baxter state—wet only at the corn tips, or in the Wenzel state—wet the whole corn surfaces. After considering \( l_{cr} \)-term, the free energy \( u \) expressed in Eq. (18) has an extremum at \( z = z_{ex} \), with

\[
    z_{ex} = \frac{(1 + \cos \theta) \cos \beta}{\sin \beta + \cos \theta} l_{cr}.
\]  

(19)

Whenever \( \beta > \theta - \pi/2 \), \( z_{ex} \) is negative and the free energy is maximum at \( z_{ex} \). Therefore the water will tend to wet the whole conical surfaces; whenever \( \beta < \theta - \pi/2 \), the free energy is minimum at \( z_{ex} \). With the above discussion we can finally obtain the following wetting relation

\[
    \cos \theta' = -1 - \frac{(1 + \cos \theta)^2 \pi l_{T}^2}{1 + \cos \theta / \sin \beta \ A_{o}}.
\]  

(20)

7. Three phase line tensions

The line tension plays a key role in small size and even indispensable in various processes, such as dislocation in crystal [34], micro-nano-fluidics in chips [35], soft lithography techniques [36], surface nucleation of nanoparticles [37], cell adhesion to biological membrane [38], and so on. For example, line tension inhaled particles may land on the surface of the lung’s airspaces and contact with the airway wall, which will cause lung disease. Schürch’s result showed that line tension is a possible explanation for the dependence of particle displacement on particle size [39].

Since the introduction of three-phase interaction line tension, \( \lambda \), by Gibbs [2], it has been lack of precise measurements or reliable theoretical estimates of \( \lambda \). Reported values of line tensions ranged from \( 10^{-11} \) to \( 10^{-5} \) J/m experimentally, and \( 10^{-12} \) to \( 10^{-10} \) N theoretically [3], even with positive and negative value. Various factors are responsible for the wide discrepancies in the experimental measurement, for example, heterogeneity, poor techniques, noise, roughness, sample preparation and so on. The most challenge factor to measure \( \lambda \) through experimentally observing its influence to the contact angle of droplets on a flat surface is that this influence can only become significant for extremely small droplets. However, how to measure precisely the contact angles of very small droplets has been itself a technical challenge up to now.

The LTCB relations provide a basis for easily and precisely measure the line tensions. As reviewed in Sects. 2 and 3, the critical length \( l_{cr} \), and thus the line tension \( \lambda \) through the relation (6), for wetting of water on pillar-structure surfaces coated with OTS were determined to fit the roughness size dependence (Fig. 3). The same value of \( \lambda \) gives excellent predictions to the apparent contact angles for all 17 samples of different roughness scales and shapes. A key difference using Eq. (7) instead of Eq. (2) for measuring \( \lambda \) is that the line tension effect can become significant for ever large drops through Eq. (7), while in Eq. (2) only very small droplets have the line tension effect.

Originally, a three-phase interaction line is defined as the interaction line of a flat solid surface, liquid, and vapor. However, the three-phase interaction lines in the Cassie–Baxter state on a pillar-structured surface are not really the conventional ones because the places of the contact lines occurs actually along the solid edges, rather a flat plan. Therefore, the line tension \( \lambda \) appeared in Eq. (7) should be understood as three-phase edge line tension, say \( \lambda_{edge} \). In other words, the measured value \( 1.57 \times 10^{8} \) J/m is for \( \lambda_{edge} \), rather than \( \lambda \).

Nevertheless, the relation (19) constitutes a basis for better measuring the real line tension, since the wetted conical surface can be smooth, at least in a theoretical sense.
8. Concluding remarks

Scaling down the roughness into the micro-submicron range is a unique and elegant strategy to achieve not only superhydrophobicity, but also to increase its stability against environmental disturbances. The model (7) recently established by Zheng et al. [16] and Wong and Ho [20], named line tension Cassie–Baxter relation (or in brief, LTCB relation) here, captures important physical effects of great consequence at small scales. Stability of superhydrophobicity is another key issue. Three kinds of factors that influence the superhydrophobicity stability have been considered: (1) the elastic deformation and elastic buckling [30, 40, 41], (2) the minimum pillar height (11) to insure the Cassie–Baxter state is more stable than the Wenzel state, and the maximum sustainable pressure (12). These results help us to understand why naturally occurring superhydrophobic surfaces commonly have micron-submicron roughness [4, 8, 18, 19] and guide the fabrication of stable super water-repellant surfaces [16, 42].

As also revealed, the roughness scale is reduced as the maximal contact angle of the roughness scale approaches a fundamental critical length, \( l_{cr} \). Further reduction of scale sees the contact angle again drop, probably as a result of entering a new dynamic regime in which new forces play a role. This presents an intriguing insight into nature’s selection of optimal resistance to wetting, with further research needed to fully understand the transition across the critical length scale.

Of particular interest is that the LTCB relations (7) and (14), as well as the specific forms (16) and (17) of (14), constitute a rational basis for guiding fabrications of rough surfaces with nearly the extreme superhydrophobicity \( \theta \), that may have important applications in a wide range.

Acknowledgements

Financial support from the NSFC under (10872114, 10672089, and 10832005) is gratefully acknowledged.

References


