FORMATION CONDITIONS AND MECHANISM OF WETTING STATE ON MICRO-/NANOSTRUCTURED SUPERHYDROPHOBIC SURFACE

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Due to its unique wetting properties, the superhydrophobic surface caused by the micro-/nanostructure has shown good application prospects in many fields. Therefore, the relationship between the wetting state and the surface structure should have a deeper understanding. The thermodynamic method, based on the principle of minimum energy, is used to analyze all the nine wetting states of droplet on a micro-/nanostructured superhydrophobic surface, and the existence conditions and corresponding contact angle expressions of each wetting state are derived. On this basis, taking lotus-simulating surfaces as an example, the validity and sufficiency of the two-level micro-/nanostructure on superhydrophobicity is quantitatively clarified. The correlation between the wetting states as well as the transformation process of its structure is further analyzed. The results in this paper provide a reference for designing stable micro-/nanostructured superhydrophobic surface.

KEY WORDS: superhydrophobic surface, micro-/nanostructure, wetting state, thermodynamics

1. INTRODUCTION

Wettability is one of the important properties of solid surfaces, and its regulation is vital for its performance and practical application (Rashidian and Sellier, 2017). The special wettability of a superhydrophobic surface usually has high contact angles (CA > 150 deg) and low contact angle hysteresis (CAH < 5 deg), exhibiting nonadhesive behavior. Thus, it has been exploited for many potential applications, such as anti-corrosion, anti-fog, anti-icing, liquid transportation, oil–water separation, self-cleaning, and water harvesting (Barthlott and Neinhuis, 1997; Wang et al., 2015; Zheng et al., 2017; Zhang et al., 2018). There is a large number of superhydrophobic surfaces in nature.

However, various types of natural superhydrophobic surface could exhibit different wetting states and show different wetting properties (Fernández et al., 2017; Ma et al., 2019), such as low adhesive lotus leaf, the anisotropic superhydrophobic rice leaf, high adhesive rose petal, directional adhesive butterfly wing, and reversible adhesive gecko foot, etc. It is well known that wettability is mainly determined by micro-/nanostructure and surface composition (Bhushan and Nosonovskv, 2010; Suzuki and Ueno, 2017). Therefore, exploration of the different wetting states is essential for understanding the mechanism of wetting properties and designing a biomimetic superhydrophobic surface.

Researchers have proposed a variety of theoretical models to describe the wetting states of superhydrophobic surfaces, including the Young equation with an ideal smooth surface (Young, 1805), Wenzel (W) (Wenzel, 1936), and Cassie-Baxter (C) (Cassie and Baxter, 1944) on a rough surface, and Penetrate (herein referred to as CW) (Patankar, 2004) transition state model. Jiang (Wang and Jiang, 2007) further divided the wetting states into five kinds: Wenzel
NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1, b_1, h_1$</td>
<td>pillar width, pillar spacing, and pillar height of microstructure</td>
</tr>
<tr>
<td>$a_2, b_2, h_2$</td>
<td>pillar width, pillar spacing, and pillar height of nanostructure</td>
</tr>
<tr>
<td>$A_{\text{base}}$</td>
<td>geometric droplet base surface</td>
</tr>
<tr>
<td>$A_{\text{ext}}$</td>
<td>external droplet surface</td>
</tr>
<tr>
<td>$C$</td>
<td>Cassie-Baxter</td>
</tr>
<tr>
<td>CW</td>
<td>penetrate transition</td>
</tr>
<tr>
<td>$E_{\text{total}}$</td>
<td>total free energy</td>
</tr>
<tr>
<td>$E_C^*$</td>
<td>Cassie’s nondimensional energy barrier</td>
</tr>
<tr>
<td>$E_W^*$</td>
<td>Wenzel’s nondimensional energy barrier</td>
</tr>
<tr>
<td>$f$</td>
<td>solid area fraction</td>
</tr>
<tr>
<td>$h_x, h_y$</td>
<td>penetration depth of a droplet in the microstructure and nanostructure</td>
</tr>
<tr>
<td>$r$</td>
<td>roughness factor</td>
</tr>
<tr>
<td>$W$</td>
<td>Wenzel</td>
</tr>
</tbody>
</table>

Greek Symbols

- $\xi$ | relative pillar height |
- $\xi_1, \xi_2$ | relative pillar height of microstructure and nanostructure |
- $\eta$ | relative pillar spacing |
- $\eta_1, \eta_2$ | relative pillar spacing of microstructure and nanostructure |
- $\theta$ | apparent contact angle, deg |
- $\theta_C$ | Cassie’s contact angle, deg |
- $\theta_W$ | Wenzel’s contact angle, deg |
- $\theta_Y$ | intrinsic contact angle, deg |
- $\sigma_{\text{LG}}$ | liquid–gas interfacial tension |
- $\sigma_{\text{SG}}$ | solid–gas interfacial tension |
- $\sigma_{\text{SL}}$ | solid–liquid interfacial tension |

state, Cassie-Baxter state, lotus state, CB transition (CW) state, and gecko state. Wenzel state, Cassie state, and CW state represent the wetting state on the single structure surfaces; whereas, most of the superhydrophobic surfaces are the dual micro-/nanostructured surface. Nosonovsky (Bhushan and Nosonovsky, 2010; Hejazi and Nosonovsky, 2013) pointed out that there are nine wetting states: lotus state, rose state, Cassie state, Wenzel state, rose filled microstructure, Wenzel filled microstructure, Cassie filled nanostructure, Wenzel filled nanostructure, and Wenzel filled micro-/nanostructure.

Rahmawan et al. (2009) proposed four possible wetting states on the dual-scale micro-/nanostructure surface: $C_m$-$C_n$, $C_m$-$W_n$, $W_m$-$C_n$, and $W_m$-$W_n$, where $m$ and $n$ denote microstructure and nanostructure. Wu et al. (2016) further analyzed the wetting states of droplet on the micro-/nanostructure surface by means of thermodynamic method: four stable states and five metastable states. Sajadinia et al. (2010) used a thermodynamic method to predict the equilibrium contact angle and found wettability of a dual scale structure may depend on the presence and geometrical parameters of other components. Zhang et al. (2012) proposed an intuitive free energy thermodynamic approach to analyze the contact angle hysteresis and free energy barrier on lotus-simulating surfaces. Liang et al. (2017) employed a 3D model to calculate the equilibrium contact angle, receding and advancing contact angle, as well as contact angle hysteresis, and pointed that nano pillar plays an important role in the wetting state transitions. As stated above, there is little research on the formation conditions and mechanism of wetting states on a dual structured surface. It usually focuses on a single static wetting state under a specific condition, lacks detailed analysis of practical problems, and does not have extensive universality.

In this paper, the micro-/nanostructured superhydrophobic surface of a droplet is taken as the research object, the thermodynamics and kinetic methods are used to study the wetting state under static and dynamic conditions, respectively. Firstly, according to the principle of minimum free energy, all possible wetting state expressions and their existence conditions of a droplet on the surface of a micro-/nanostructure are deduced. The validity and sufficiency of a two-level micro-/nanostructure are clarified. On the basis of the kinetics analysis of a droplet impinging surface, the mechanical equilibrium conditions of a wetting state under dynamic impinging conditions are studied and the relationship between the anti-wetting pressure and the microstructure of micro-/nanostructures that influenced the
transition of the wetting state is discussed. The synergistic and dissimilarity of the anti-wetting energy barrier of the micro-/nanostructure and the influence of the structural parameters on the wetting state under dynamic conditions are analyzed. The results will help us deepen the understanding of the influential role of surface structure on the wettablility, lay a foundation for further theoretical improvement, and expand a superhydrophobic surface’s application.

2. THEORETICAL MODEL

There are lots of biological surfaces with superhydrophobic properties, including plant leaf, insects, spiders, lizards, and water striders. The scanning electron microscopy (SEM) results show that these surfaces are generally composed of intrinsic hydrophobic material (intrinsic contact angle > 90 deg, often ~ 120 deg) with a two-level hierarchical structure. The most well-known is the “lotus effect,” which is induced by its micrometer-scale papillae and nanometer-scale wax tubes (Bartolo et al., 2006).

The wetting state of the droplet on the surface is closely related to the interface energy of the system composed of the droplet and superhydrophobic surface. The contact angle of the droplet on the surface is the result of the equilibrium of the surface tension between the solid–liquid–gas interfaces. The surface tension drives the system to be in a state of minimum energy. When the shape of the droplet reaches equilibrium on the surface, the corresponding contact angle is the equilibrium contact angle. Therefore, analyzing the wetting state through the surface energy of the droplet–surface system is equal to the angular analysis of force equilibrium. Analyzing a problem from the perspective of surface energy provides another way to solve the problem. It can fully consider the influence of surface structure on surface wettability. In the following, the correlation function between structure and contact angle is obtained by deriving the interface energy function so as to investigate all possible wetting states on micro-/nanostructured superhydrophobic surface.

According to the applicable conditions of traditional Young, Wenzel, and Cassie equations, the following assumptions are valid: (i) The droplet can be regarded as a spherical shape (Taylor and Michael, 1973; Liu, 2009); (ii) the scale of the surface structure is negligible relative to the volume of the droplet; and (iii) the influence of gravity is ignored. The roughness factor $r$ and the solid area fraction $f$ can be obtained as shown in Table 1.

Taking the system composed of a droplet-superhydrophobic surface as the research objective (Fig. 1), the interface energy of the whole system includes the liquid–gas, solid–liquid, and solid–gas interfaces, which is expressed as follows:

$$E_{\text{total}} = \sigma_{\text{LG}} A_{\text{LG}} + \sigma_{\text{SL}} A_{\text{SL}} + \sigma_{\text{SV}} A_{\text{SV}}$$

3. RESULTS AND DISCUSSION

3.1 Wetting State based on Thermodynamics

As shown in Fig. 1(d), the droplet shows different wetting state when penetration depth $h_x$ and $h_y$ were given different values. If the droplet is in the intermediate transition state, the total interface energy can be further deduced (see Appendix A):

<table>
<thead>
<tr>
<th>Surface Structure</th>
<th>$f$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microstructure square pillar</td>
<td>$f_1 = \frac{a_1^2}{(a_1 + b_1)^2} = \frac{1}{(1 + \eta_1)^2}$</td>
<td>$r_1 = 1 + 4f_1 \frac{h_1}{a_1} = 1 + \frac{4\xi_1}{(1 + \eta_1)^2}$</td>
</tr>
<tr>
<td>Nanostructure square pillar</td>
<td>$f_2 = \frac{a_2^2}{(a_2 + b_2)^2} = \frac{1}{(1 + \eta_2)^2}$</td>
<td>$r_2 = 1 + 4f_2 \frac{h_2}{a_2} = 1 + \frac{4\xi_2}{(1 + \eta_2)^2}$</td>
</tr>
</tbody>
</table>

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\[
E_{\text{total}} = A_{\text{ext}} \sigma_{LG} + A_{\text{base}} (1 - f_1) \sigma_{LG} + A_{\text{base}} f_1 (1 - f_2) \left( 1 + \frac{4h_x}{a_1} \right) \sigma_{LG} \\
+ A_{\text{base}} f_1 f_2 \left( 1 + \frac{4h_x}{a_1} \right) \left( 1 + \frac{4h_y}{a_2} \right) \sigma_{SL} + A_{\text{base}} r_2 \left[ 1 - f_1 + \frac{4f_1(h_1 - h_y)}{a_1} \right] \sigma_{SG} \\
+ A_{\text{base}} f_1 \left( 1 + \frac{4h_1}{a_1} \right) \left[ 1 - f_2 + \frac{4f_2(h_2 - h_y)}{a_2} \right] \sigma_{SG} + (A_{\text{total}} - A_{\text{base}}) r_1 r_2 \sigma_{SG}
\]

After taking the derivative of the above-mentioned energy equation with respect to \( \cos \theta \), and putting \( \partial E / [\partial (\cos \theta)] = 0 \), the following equation can be obtained:

\[
\cos \theta = f_1 f_2 \left( 1 + \frac{4h_x}{a_1} \right) \left( 1 + \frac{4h_y}{a_2} \right) \cos \theta_Y + f_1 (f_2 - 1) \left( 1 + \frac{h_x}{a_1} \right) + f_1 - 1
\]

In Eq. (3),

i. When \( f_1 = f_2 = 1 \), it is a single contact, indicating that the droplet is in complete contact with the solid surface. There are two wetting states: if \( h_x = h_1 = 0 \) and \( h_y = h_2 = 0 \), it corresponds to the wetting state Young, and if \( h_x = h_1 > 0 \) and \( h_y = h_2 > 0 \), the droplet completely wets the micro-/nanostructure and the corresponding wetting state is Wenzel-Wenzel (W-W).

ii. When \( 0 < f_1, f_2 < 1 \), it is a composite wetting state, indicating that the droplet is not completely in contact with the solid surface: if \( h_x = h_1 = 0 \) and \( h_y = h_2 = 0 \), the droplet is suspended on the surface of the micro-/nanostructure, corresponding to Cassie-Cassie (C-C) wetting state; if \( h_x = 0 \) and \( 0 < h_y < h_2 \), the droplet only partially wets the nanostructure, corresponding to the C-CW intermediate state; if \( 0 < h_x < h_1 \) and \( h_y = 0 \), the droplet only partially wets the microstructure, corresponding to the CW-C state; and if \( 0 < h_x < h_1 \) and \( 0 < h_y < h_2 \), the droplet partially wets the micro- and nanostructures, corresponding to the CW-CW transition state.

iii. When \( 0 < f_1 < 1, f_2 = 1 \): if \( h_x = 0 \) and \( h_y = h_2 \), the droplet only completely wets the nanostructure, corresponding to the CW wetting state; if \( 0 < h_x < h_1 \) and \( h_y = h_2 \), the droplet partially wets the microstructure and fully wets the nanostructure, corresponding to the CW-W wetting state.

iv. When \( f_1 = 1 \) and \( 0 < f_2 < 1 \): if \( h_x = h_1 \) and \( h_y = 0 \), the droplet only completely wets the microstructure, corresponding to the W-C wetting state; if \( h_x = h_1 \) and \( 0 < h_y < h_2 \), the droplet partially wets the nanostructure and fully wets the microstructure, corresponding to the W-CW wetting state. The contact angle expressions and wetting states of these ten corresponding wetting states are shown in Table 2 and Fig. 2.
TABLE 2: Contact angle equation for each wetting state

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Wetting State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1 = f_2 = 1, h_x = h_y = 0$</td>
<td>Young</td>
</tr>
<tr>
<td>$0 &lt; f_1, f_2 &lt; 1, h_x = h_y = 0$</td>
<td>C-C</td>
</tr>
<tr>
<td>$0 &lt; f_1, f_2 &lt; 1, h_x = 0, 0 &lt; h_y &lt; h_2$</td>
<td>C-W</td>
</tr>
<tr>
<td>$0 &lt; f_1, f_2 &lt; 1, 0 &lt; h_x &lt; h_1, h_y = 0$</td>
<td>CW-C</td>
</tr>
<tr>
<td>$0 &lt; f_1, f_2 &lt; 1, 0 &lt; h_x &lt; h_1, 0 &lt; h_y &lt; h_2$</td>
<td>CW-CW</td>
</tr>
<tr>
<td>$f_1 = 1, 0 &lt; f_2 &lt; 1, h_x = h_1, h_y = 0$</td>
<td>W-C</td>
</tr>
<tr>
<td>$f_1 = 1, 0 &lt; f_2 &lt; 1, h_x = h_1, 0 &lt; h_y &lt; h_2$</td>
<td>W-CW</td>
</tr>
<tr>
<td>$f_1 = f_2 = 1, h_x = h_1, h_y = h_2$</td>
<td>W-W</td>
</tr>
</tbody>
</table>

FIG. 2: Schematic diagram of droplet wetting state on micro/nanostructure surface

The thermodynamic analysis of the above wetting states shows that there are nine kinds of wetting states on the surface of the micro-/nanostructure: four kinds of steady states and five kinds of transition states. This is also consistent with the statistical point of view: there are three wetting states on the surface of the first rough structure: Cassie, Wenzel, and Cassie-Wenzel intermediate state. From the point of view of mathematical statistics, introducing the surface of the two-level micro-/nanostructure, we may use $X-Y$ to represent the contact state of the two-level...
micro-/nanostructure, where $X$, $Y$ represents the state of the microstructure and nanostructure. There are three states of Cassie, Wenzel, and Cassie-Wenzel intermediate state in each structure, totaling nine ($C_1^1 C_1^3 = 9$) wetting states. The above analysis of the wetting state has also been confirmed in the literature (Wu et al., 2016).

It should be noted that the derived results of this paper for the superhydrophobic interface of the square pillar structure is in the form of general parameters, such as the advancing contact angle, the solid phase area fraction, the area fraction of solid-liquid portion on the interface, and other characteristic structural parameters. Therefore, the analytical methods and results are equally applicable to the superhydrophobic surface formed by other convex array structures.

### 3.2 Validity and Sufficiency of the Two-Level Micro-/Nanostructure

The “lotus effect” has attracted a large number of researchers to carry out related research for mimicking its surface. Many structural surfaces in nature have self-similar fractal features, and their partial elements have similar characteristics to the overall structure, namely, $\eta_1 = \eta_2 = \eta$, $\xi_1 = \xi_2 = \xi$. Referring to the structural scale of Lotus superhydrophobic surfaces under SEM (Zhang et al., 2012), we simulated the relevant parameters of the surface of the lotus in the specific example analysis. Specifically, as for the single micrometer-scale square pillar, its average width is $a_1 = 10 \mu m$, the average spacing is $b_1 = 12 \mu m$, and the average height is $h_1 = 15 \mu m$; We presume that the pillar width corresponding to the micro/nano square pillar has the same proportional coefficient; the side length of the nano square pillar is $a_2 = 200 \text{ nm}$, pillar spacing $b_2 = 240 \text{ nm}$, and height $h_2 = 300 \text{ nm}$.

On the basis of the assumptions of the above structural parameters and the setting of the geometric model, the effects of structure and material on the wetting state are analyzed from the perspective of solid area fraction, roughness factor, contact angle, and nondimensional energy barrier. First, the influence of the microstructure level and structure scale on the solid area fraction under Cassie contact state is analyzed. The solid area fraction gradually decreases as the relative pillar spacing $\eta$ increases, and does not change with the relative pillar height $\xi$. When $\eta = 1.2$, the corresponding solid area fractions of the single-, two-, and three-level structures are 0.2066, 0.2066$^2$, and 0.2066$^3$, respectively, and the solid area fraction of the single structure is 0.2066, which is close to the result 0.2056 caused by the mastoid process on the surface of the lotus scanned by SEM (Feng et al., 2002). It can be seen from Fig. 3(a) that the solid area fraction of the two- and three-level structures is reduced by 79.33 and 95.74%, respectively, with the increase of $\eta$. The variation range of the three-level structure is rather small compared to two-level structure growth.

Figure 3(b) shows the effect of structure and material (characterized by intrinsic contact angle, taking it as 80, 100, and 120 deg, respectively) on the apparent contact angle in the Cassie contact state. It can be seen that the superhydrophobic surface with different grades of microstructures increases in apparent contact angle as the relative pillar width $\eta$ increases. Even for hydrophilic materials (intrinsic contact angle is 80 deg), if the surface of the single-, two-, and three-level microstructures $\eta$ is greater than 1.96, 0.72, and 0.44, respectively, the corresponding equilibrium apparent contact angle (CA) is still $> 150$ deg. It shows that the surface of a hydrophilic material having a multi-level structure possesses the possibility of obtaining hydrophobicity by rationally designing the surface structure. For hydrophobic material, if the intrinsic contact angle is 120 deg, the single-, two-, and three-level microstructure surfaces can achieve the same hydrophobic effect with a small relative pillar width $\eta$ (0.93, 0.39, 0.25) (CA $> 150$ deg). This means that it is possible to improve the mechanical properties of the same grade of the material made of a more hydrophobic material due to the large square pillar width ($a$ value). When $\eta = 1.2$ and the intrinsic contact angle is 105 deg, the apparent contact angle of the two-level structure is 165.5 deg, which is similar to the experimentally observed result of 164 deg (Nosonovsky and Bhushan, 2005). It also illustrates the validity of the two-level structure.

Figure 3(c) shows the normalized energy barrier at $\eta = 1.2$, $\xi = 1.5$. The global minimum energy point corresponding to the normalized energy barrier curve in the nine states is the contact angle corresponding to the Cassie state as shown in Table 3, which corresponds to the contact angle indicated in Fig. 3(b). Moreover, at the same morphology parameters of the single-, two-, and three-level structures, the global minimum energy increase with intrinsic contact angle ($\theta_y$), which implied that more hydrophobicity of material surface are more proper for preparation of the superhydrophobic surface. This also verifies the correctness of the analysis method in the Section 3.1.
Formation Conditions and Mechanism of Wetting State

FIG. 3: Property of the composite wetting state (Cassie State): (a) Solid area fraction $f$, (b) apparent angles, and (c) nondimensional energy barrier

TABLE 3: Value of $\theta_C$ under different wetting state

<table>
<thead>
<tr>
<th>$\theta_Y$ (deg)</th>
<th>Single Structure</th>
<th>Two-Level Structure</th>
<th>Three-Level Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>139.2</td>
<td>161.8</td>
<td>171.7</td>
</tr>
<tr>
<td>100</td>
<td>146.0</td>
<td>164.7</td>
<td>173.1</td>
</tr>
<tr>
<td>120</td>
<td>153.7</td>
<td>168.1</td>
<td>174.6</td>
</tr>
</tbody>
</table>

Figure 4 shows the roughness factor, contact angle, and normalized energy barrier in a noncomposite wetting state. Figure 4(a) shows roughness factor at $\eta = 1.2$, which shows that $r$ increases as the relative pillar width $\xi$ increases. It is clear that the roughness factor can be effectively increased by increasing the height of the micro/nano square pillar. When $\eta = 1.2$, $\xi = 1.5$, the surface roughness factor $r$ of the single-, two-, and three-level structure is about 2.24, 5.02, and 11.23, respectively. The roughness factor of the two-level structure, 5.02, is already large enough, which determines the lotus-droplet system being in a composite wetting state (Cassie state), and it is also consistent with experimental observations and related theoretical analysis. It also illustrates the sufficiency of the two-level structure.

Figure 4(b) shows that, in the noncomposite wetting (Wenzel) state, the roughness factor has the effect of amplifying the wetting, making the hydrophilic material more hydrophilic ($\theta_Y = 80$ deg), the hydrophobic material more...
hydrophobic ($\theta_Y = 100, 120 \text{ deg}$). For this reason, in order to gain composited wetting state, hydrophobic material should be selected. Because the droplets under the same condition in the noncomposite state usually have a large hysteresis, some researchers try to make the droplet-surface system avoid the noncomposite wetting contact when design the artificial superhydrophobic surface. If the surface droplet system is in a noncomposite rewetting state, then for a superhydrophobic surface of the same dimension made of a more hydrophobic material, a smaller micro-roughness can be obtained from a material having a lower hydrophobicity. The higher roughness achieves the same hydrophobic effect on the superhydrophobic surface, and the three-level structure has no more space for improving the hydrophobicity on the basis of the two-level structure. Figure 4(c) shows the normalized energy barrier at $\eta = 1.2, \eta = 1.5$. As shown in Fig. 4(c), the normalized energy barrier of hydrophilic material ($\theta_Y = 80 \text{ deg}$) increased all along. Only the hydrophobic material ($\theta_Y = 100, 120 \text{ deg}$) has a global energy minimum. For this reason, in the noncomposite wetting state (Wenzel state) we should select hydrophobic materials to obtain superhydrophobic surface.

3.3 Wetting Transformation Process

On the basis of the common choice, the intrinsic contact angle $\theta_Y$ is set to 120 deg. The four types of stable wetting states, C-C state, W-W state, C-W state, and W-C, of the two-level micro-/nanostructure corresponding to the general
Formation Conditions and Mechanism of Wetting State

FIG. 5: Wetting curve of the two-level micro-/nanostructure in four stable wetting states: (a) Cloud maps of wetting state, (b) Apparent contact angle as the function of $\eta$, (c) apparent contact angle as the function of $\xi$, and (d) nondimensional energy barrier formula of the contact angle of each wetting state is solved in Section 3.1. According to these results, Fig. 5(a) shows a distribution cloud map, where the contact angles of these four states change with relative pillar width $\eta$ and pillar height $\xi$. When the composite is wetted in the C-C state, the distribution of the contact angle is effective in all regions.

When the noncomposite wetting state is in the W-W state, the contact angle distribution needs to satisfy the condition that

$$\xi < \sqrt{\frac{2(\eta + 1)^2 - 1}{4} - (\eta + 1)^2}$$

(4)

In the same way, the conditions of the C-W state need to satisfy

$$\xi < \frac{\eta^2 + 2\eta}{4}$$

(5)
And the conditions of the W-C state need to satisfy

\[
\xi < \frac{\eta^2 + 2\eta}{8\eta^2 + 16\eta + 4}
\]

Further analysis of the inequalities for the above four stable wetting states shows the effective region distribution map of the four stable wetting states, C-C state, W-W state, C-W state, and W-C state, corresponding to the two-level micro-/nanostructure as shown in Fig. 5(a). The specific distribution is as follows: Region 1 satisfies the equations of the W-C state; Region 2 can satisfy the equations of the W-W state; Region 3 can satisfy the equations of the C-W state; and Region 4 can satisfy the equations of the C-C state, where there is an effective superhydrophobicity region with a larger contact angle. When \( \eta = 1.2, \xi = 1.5 \), the wetting state of the droplet was in the C-C state, which is in good agreement with the literature result (Zhang et al., 2012).

Figure 5(b) shows the effect of relative pillar width \( \eta \) on the wetting state distribution at \( \xi = 1.5 \). As the relative pillar width increases, the wetting state undergoes three processes: when \( 0 < \eta < 1.65 \), the system is in the C-C wetting state and the contact angle is 150 deg corresponding to \( \eta = 0.39 \). Thus, the designed effective superhydrophobic scale range is 0.39 < \( \eta < 1.65 \) [please refer to Fig. 5(b)]; when \( 1.65 < \eta < 2.87 \), the system is in the C-W wetting state; when \( \eta > 2.87 \), the system transfer to the W-W wetting state. Figure 5(c) shows the effect of relative pillar height \( \xi \) on wetting state at \( \eta = 1.2 \). As the relative pillar height increases, the wetting state also undergoes three processes: when \( 0 < \xi < 0.44 \), the system is in the W-W wetting state; when \( 0.44 < \xi < 0.96 \), the system is in the C-W wetting state; and when \( \xi > 0.96 \), the system transfer to the C-C wetting state.

Figure 5(d) shows the normalized energy barrier curves for the four stable wetting states at \( \eta = 1.2, \xi = 1.5 \). The droplet has two minimum states of energy, namely, the W-W and C-C states, and the corresponding apparent contact angles are 128.9 and 168.1 deg, respectively. The relative energy barrier between them is 0.3506. This part takes the pillar structure as an example for the convenience of modeling and analysis. The analysis process and analysis method have universal adaptability and can be extended to the analysis of other microstructure wetting states and structures, which can provide reference for designing a stable superhydrophobic surface.

4. CONCLUSIONS

In this paper, the wetting state of the droplets on the micro-/nanostructured superhydrophobic surfaces was studied by the established thermodynamic model. The main conclusions are as follows:

1. On the basis of the thermodynamic analysis method, the expressions of nine possible wetting states (including four stable wetting states: C-C, C-W, W-C, and W-W and five transition states: CW-C, C–CW, CW-CW, W-CW, and CW-W) were deduced. The formation conditions and mechanisms of each wetting state were given.

2. The validity and sufficiency of the hydrophobicity on the micro-/nanostructure is quantitatively discussed. Taking lotus-simulating surfaces as an example, the relationship between \( f, r, CA, \) and surface structure (single-, two-, and three-level structures) parameters were analyzed. The \( f, r, \) and \( \theta_C \) (C-C wetting state’s apparent contact angle) of the two-level micro-/nanostructure are about 4.27\%, 5.02, and 164.7 deg (intrinsic contact angle \( \theta_Y = 100 \) deg), which is very close to the lotus effect.

3. The wetting transition process from composite (C-C state) to noncomposite wetting (W-W state) is analyzed. Forming the stable composite wetting state requires a large intrinsic contact angle (\( \theta_Y \)) and a large relative pillar height (\( \xi \)). But the relative pillar spacing \( \eta \) should keep in a certain range to guarantee the surface with a larger contact angle and meanwhile the wetting state in the C-C state.

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REFERENCES


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APPENDIX A. SUPPORT INFORMATION AND CALCULATION OF APPARENT CONTACT ANGLE

$$E_{\text{total}} = A_{\text{ext}} \sigma_{\text{LG}} + A_{\text{base}} (1 - f_1) \sigma_{\text{LG}} + A_{\text{base}} f_1 (1 - f_2) \left(1 + \frac{4h_x}{a_1}\right) \sigma_{\text{LG}}$$

$$+ A_{\text{base}} f_1 f_2 \left(1 + \frac{4h_x}{a_1}\right) \left(1 + \frac{4h_y}{a_2}\right) \sigma_{\text{SL}} + A_{\text{base}} r_2 \left[1 - f_1 + \frac{4f_1(h_1 - h_x)}{a_1}\right] \sigma_{\text{SG}}$$

$$+ A_{\text{base}} f_1 \left(1 + \frac{4h_1}{a_1}\right) \left(1 - f_2 + \frac{4f_2(h_2 - h_y)}{a_2}\right) \sigma_{\text{SG}} + (A_{\text{total}} - A_{\text{base}}) r_1 r_2 \sigma_{\text{SG}}$$

where $A_{\text{ext}}$, $V$, $R$ are the external surfaces, volume, and radius of droplet, respectively; $\theta$ is the apparent contact angle; $A_{\text{base}}$ is the geometric drop contact surface; $r_b$ is the radius of contact surface; $h_x$, $h_y$ are the penetration depth of droplet in the microstructure/nanostructure of square pillars, $0 \leq h_x \leq h_1$, $0 \leq h_y \leq h_2$. Combining with Fig. 1, the $A_{\text{ext}}$, $A_{\text{base}}$, $r_b$, $V$, and $\theta_y$ are given by

$$A_{\text{ext}} = 2\pi R^2, \quad A_{\text{base}} = \pi r_b^2, \quad R \sin \theta$$

$$V = \frac{\pi R^3}{3} (1 - \cos \theta)^2 (2 + \cos \theta)$$

$$\cos \theta_v = \frac{\sigma_{\text{SG}} - \sigma_{\text{SL}}}{\sigma_{\text{LG}}}$$

Substituting the above formula into the energy equation, take $\cos \theta$ with respect to $E_{\text{total}}$, and put $\partial E_{\text{total}}/\partial (\cos \theta) = 0$, to get the expression of the apparent contact angle

$$\cos \theta = f_1 f_2 \left(1 + \frac{4h_x}{a_1}\right) \left(1 + \frac{4h_y}{a_2}\right) \cos \theta_v + f_1 (f_2 - 1) \left(1 + \frac{h_x}{a_1}\right) + f_1 - 1$$

APPENDIX B. SUPPORT INFORMATION AND NONDIMENSIONAL ENERGY $E^*$

Through rearranging the energy equation, the basic equation of deformations is derived, as follows:

$$E_{\text{total}} = \frac{3V}{\pi (\cos^3 \theta - 3 \cos \theta + 2)} \left[2 (1 - \cos \theta) \sigma_{\text{SG}} + C(h_x, h_y) \sin^2 \theta \sigma_{\text{SG}} \right] + A_{\text{total}} r_1 r_2 \sigma_{\text{SG}}$$

Simple transformation yield

$$\frac{E_{\text{total}} - A_{\text{total}} r_1 r_2 \sigma_{\text{SG}}}{\sigma_{\text{LG}} \pi^{1/3} (3V)^{2/3}} = \frac{2(1 - \cos \theta) + C(h_x, h_y) \sin^2 \theta \sigma_{\text{SG}}}{(\cos^3 \theta - 3 \cos \theta + 2)}$$

where

$$C(h_x, h_y) = - \left[ f_1 f_2 \left(1 + \frac{4h_x}{a_1}\right) \left(1 + \frac{4h_y}{a_2}\right) \cos \theta_v + f_1 (f_2 - 1) \left(1 + \frac{h_x}{a_1}\right) + f_1 - 1 \right]$$

At last, the nondimensional energy $E^*$ can be given as follows:

$$E^* = \frac{E_{\text{total}} - A_{\text{total}} r_1 r_2 \sigma_{\text{SG}}}{\sigma_{\text{LG}} \pi^{1/3} (3V)^{2/3}} = \frac{2(1 - \cos \theta) + C(h_x, h_y) \sin^2 \theta \sigma_{\text{SG}}}{(\cos^3 \theta - 3 \cos \theta + 2)}$$