Hydrophobic mechanism and criterion of lotus-leaf-like micro-convex-concave surface

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According to the principle that the contact angle of liquid droplet always increases on a limited liquid-solid interface, it is suggested that the integration of many small-size limited liquid-solid interfaces results in the increase of the hydrophobicity of lotus-leaf-like micro-convex-concave surfaces. Mathematical equations of the stability of liquid-droplets on the surface of lotus-leaf-like structure were established. The relationship between the theoretical critical-radius of the void of micro-convex-concave surface and the nature of the solid and the liquid was drawn. The three conditions of realizing hydrophobicity were described. The result of computation has shown that when the radius of the void of micro-concave-convex surface is less than the theoretical critical-radius $r_c$, the droplets may always be in a stable state on the solid surface with the contact angle greater than 90°. The minimum area of the liquid-solid interface and low surface energy of solids are important factors in realizing hydrophobicity. The effective work of adhesion $W_a$ was proposed as a criterion for measuring the hydrophobic ability of the solid surface.

limited liquid-solid interfaces, hydrophobicity, contact angle, critical radius, work of adhesion

Water droplets fall on lotus leaf surface to form free rolling water globules. The exploration on hydrophobic mechanism of the lotus leaf surface has become a hot spot in the field of artificially preparing bionic hydrophobic and self-cleaning materials. In recent years, the research on new hydrophobic materials has continually achieved remarkable achievements in the fields of chemical engineering, daily use sanitary wares, clothing, fluid drag reduction, mechanical anti-corrosion and so on. After long-term observations, the researchers have found [1–3] that there are very complex multiple micron and nano-scale structures on the lotus leaf surface. It can be clearly seen under the scanning electron microscope that the lotus leaf surface has many small papillae, on the surface of each of which there are a lot of “hill” shaped convex top with the diameter of about 200 nm. The sunken parts between the papillae and the “hills” are filled with air. When rainwater lands on the leaf surface, it only constitutes partial point contact with the “hill” shaped convex top on the leaf surface. Researches have shown that, the micro-nano-structured morphology exists not only in the lotus leaf surface but also in the surface of other plants and skin of some animals [4]. However, the current research only clarifies the special constructs of the surface of hydrophobic materials, that is, the hydrophobic material should have a rough surface and low surface energy [5,6]. However, researches on the reason why the contact angle of rough surface is greater than that of smooth surface and the quantitative researches on the microstructure size are not sufficient. Wenzel [7] proposed that water droplets were completely wetted on the rough surface, whose apparent contact angle could be expressed as: $\cos\theta_r = r \cos\theta$, where $r$ was the surface roughness. He considered that, for the hydrophobic surface, due to $\theta \geq 90^\circ$, increasing the surface roughness $r$ would cause the increase of the apparent contact angle $\theta_r$ of
liquid droplets, while for the hydrophilic surface, due to $\theta \leq 90^\circ$, increasing the surface roughness $r$ would cause the decrease of contact angle $\theta_i$ of liquid droplets. Cassie [8] believed that there existed two interfaces when water droplets were on the rough surface, namely, the contact interface between the water droplets and the solid and the interface between the water droplets and the air formed because the water droplets were not able to enter microscopic holes due to the capillary phenomenon. The contact angle of water droplets on the rough surface was expressed as: $\cos \theta_r = -1 + \Phi_s (\cos \theta + 1)$, where $\Phi_s$ was the proportion of the solid-liquid interface. Cassie’s model showed that, the smaller the $\Phi_s$ value was, the larger the apparent contact angle $\theta_r$ was. However, it is not clear what conditions have led to hydrophilic or hydrophobic state and the transformation thereof. And there is no specific quantitative concept about the value of the definite solid surface roughness.

Aiming at resolving the problems existed in the current research, the study explored the hydrophobic mechanism of lotus-leaf-like surface on the basis of the researches on the wetting system [9,10] of limited liquid-solid interface.

1 The principle that the apparent contact angle of liquid always increases on a limited liquid-solid interface

The study established the wettability characterization system of a limited liquid-solid interface in the literature [9,10], as shown in Figure 1. The liquid is located on a finite cylindrical solid surface, and the angle between Surface A and Surface B of the cylindrical solid is $90^\circ$. It is concluded from the calculations and experiments that under the equilibrium state ($\theta_2 \rightarrow \theta_{\text{max}}$, the maximum contact angle of the liquid on a limited liquid-solid interface without loss), the numerical range of the contact angle of any liquid phase on the limited solid phase surface is $90^\circ \leq \theta_2 \leq 180^\circ$. Compared with the wetting system of the infinite solid surface (Young’s wetting system) shown in Figure 2, the apparent contact angle $\theta$ significantly increases, and the mathematical relationship [9] between $\theta_2$ and $\theta_1$ is

$$\cos \theta_1 = \sin \theta_2 + \cos \theta_2. \quad (1)$$

Figure 1 The wetting state of liquid on the limited liquid-solid interface.

Figure 3 shows the functional relationship curve between $\theta_2$ and $\theta_1$. Eq. (1) shows that in the limited liquid-solid interface, when $\theta_2 \rightarrow \theta_{\text{max}}$, the apparent contact angle of any liquid will be greater than $90^\circ$. This characterization and calculation method is verified in the wettability tests of four high surface energy solids [11] and six high polymers [12] to obtain highly consistent calculation results.

Neinhuis and Feng et al. [1–3] made a research on the microcosmic morphology of the lotus leaf surface by the scanning electron microscope, and found that a large number of papillae with average diameter of 5–9 μm were orderly distributed on the lotus leaf surface. The sunken void was arranged between the papillae, the surface of each of which was distributed with villi with a diameter of hundreds of nm, between which there were even smaller voids. The authors of this study believe that such a micro-concave-convex surface is actually a surface integrated by a large number of limited liquid-solid interfaces. According to eq. (1), the contact angle of liquid droplets on the surface of this structure would increase, which is the reason why the apparent contact angle of liquid droplets on the micro-concave-convex solid surface increases and also the first condition achieving the hydrophobicity. These papillary, fiber strip shaped [4,13] and network-like [14,15] limited liquid-solid interface structures have been verified in a large number of hydrophobic materials. Recently, the measurement results of the contact angle of the hydrophobic surface of chemically etched H62 brass showed [16] that the maximum contact angle obtained on the ladder-like rough surface was 131.8°, which was very close to the theoretical calculation value of 129.8° obtained by eq. (1), which indicated that, the theory of limited liquid-solid interface could well explain

Figure 2 The wetting state of liquid on the infinite solid interface.

Figure 3 The functional relationship between $\theta_1$ and $\theta_2$. 

$\cos \theta_1 = \sin \theta_2 + \cos \theta_2$
2 The theoretical critical-radius of the void

According to the micro-morphology of the lotus leaf surface, Patankar [17] further characterized the hydrophobic surface into micro-nanometer secondary columnar structure model, whose characteristics were shown in Figure 4. This kind of surface was actually a surface integrated by more micro-sized limited liquid-solid interfaces. However, one of the conditions for the hydrophobic state of liquid droplets on the solid surface is that they cannot infiltrate into a large number of capillary microscopic holes because of wetting. If they do, the apparent contact angle thereof will become smaller and the rolling resistance thereof will increase. Whether infiltration can be avoided or not is closely related with the radius of the microscopic hole.

Figure 5 is a schematic diagram of the hydrophobic state of liquid droplets made in this study on the surface of the lotus-leaf-like structure. In order to facilitate the analysis, one unit of such a structure was here extracted for calculation, as shown in Figure 6.

It is assumed that at the first level of this secondary structure, there is a wafer-shaped limited liquid-solid interface with the thickness of δ, on the center of which a hole with the radius of r is arranged, and a liquid droplet with the radius of R in the tension equilibrium state covers the surface of the solid. The upper surface of the wafer is the primary surface of the microstructure, while the side surface (first layer) of the central hole is the secondary surface. According to the balance of three-phase tension, the liquid would not stagnate in any part of the inner hole to achieve stability under the condition that the hole is a through-hole, that is, the liquid would pass through the inner hole to protrude downward which is supported by the upward tension component on the surface of the segment (anti-gravity direction). For the definite solid and liquid, under the influence of the 3-phase (γsg, γlg and γsl) surface (interface) tension, θ2 and θ3 in equilibrium are both constant and comply with the following relationships [9,10]:

\[
\gamma_{sl} = -\gamma_{lg} \cos \theta_2, \quad 90^\circ \leq \theta_2 < 180^\circ, \quad (2)
\]

\[
\gamma_{se} = \gamma_{lg} \sin \theta_2, \quad 90^\circ < \theta_2 < 180^\circ. \quad (3)
\]

It is concluded from eqs. (2) and (3) that when θ2 and θ3 are in equilibrium, that is, when they are the maximum values, θ2=θ3=θmax, the contact angle in the following study is expressed as θ if without any special descriptions.

It is assumed that due to gravity, once the actual contact angle θ is greater than θmax, the state is unstable and the liquids will flow out of the hole and then infiltrate into more capillary microscopic holes at the sub-layer.

It is concluded from Figure 6 that the total tension on the surface of the segment preventing the liquids from flowing out of the hole with the radius of r is \(2\pi \cos \theta \gamma_{lg}\).

And the liquid gravity exerted on the surface of the segment can be separated into 3 parts for calculation: the weight of the liquids of the segment part \(m_1\), the weight of the liquids in the inner hole \(m_2\), and the effective weight of liquid droplets on the columnar liquid-solid interface \(m_3\), where

\[
m_1 = \pi \frac{1}{3} \rho r^3 \left(1 + \sin \theta\right) \left(2 - \sin \theta\right) \frac{1}{\cos^2 \theta}, \quad m_2 = -\pi \rho \delta \theta, \quad m_3 = -\pi r^2 \rho R (1 - \cos \theta),
\]

where \(\gamma_{lg}\) is the liquid surface tension, \(\rho\) is the density of the liquid, and \(\theta\) values are \(90^\circ \leq \theta < 180^\circ\). Because \(m_1\) is a constant negative value, \(m_2\) and \(m_3\) should be set as negative values so as to maintain the gravity of each part of the liquid in the same direction. When the liquid droplets are in a stable state, that is, when the liquid
droplets are just not able to flow out of the hole:
\[
\frac{\pi}{3} \cdot \rho \cdot r_c^3 \cdot (1 + \sin \theta)^2 \cdot (2 - \sin \theta) \cos \theta
\]
\[
-\pi r_c^3 \cdot \rho [\delta + R(1 - \cos \theta)] = 2 \pi r_c \cdot \cos \theta \cdot \gamma_{ls}.
\] (4)

From resolving eq. (4), the following equation is obtained:
\[
r_c = 3 \cos \theta \cdot \left\{ \rho \cdot [\delta + R(1 - \cos \theta)] \right\}^\frac{1}{3} + \frac{8}{3} \cdot \rho \cdot \gamma_{ls} \cdot (1 + \sin \theta)^2 \cdot (2 - \sin \theta) \cos \theta \]
\[
\times \left[ 2 \cdot \rho \cdot (1 + \sin \theta)^2 \cdot (2 - \sin \theta) \right]^{-1},
\] (5)

The result of computation shows that with the contact angle \( \theta \) of the water droplet on the solid surface becoming smaller, the critical pore diameter \( r_c \) when the water droplet is in a stable state becomes smaller; on the contrary, the more non-wetting the water droplet and solid have, the more bigger the critical pore diameter when the water droplet in a stable state. Due to the big contact angle \( \theta \), the solid of low surface energy is favorable to realizing the hydrophobicity; secondly, the critical pore diameter \( r_c \) becomes smaller with the increase of the radius \( R \) of the water droplet. Figure 7 shows that, in theory, the liquid droplet on any solid will stay in a stable state as long as the actual pore diameter of the solid is less than the theoretical one \( r_c \). This is a prerequisite for the free rolling of the liquid droplet.

The concave-convex surface of the actual hydrophobic materials is usually irregularly papillary. The included angle of the surface of each cylinder is not necessarily 90° (right angle) as shown in the theoretical model of this study. When there is a cambered surface, due to the constant contact angle \( \theta \), the apparent contact angle \( \theta_a \) should be greater than the actual angle \( \theta \), where newly increased \( \Delta \theta \) is the angle between the cambered surface and the horizontal plane. Therefore, the data of \( \theta_a \) is obtained from the literature [12], where the data of \( \theta \) come from the literature [12], the numerical values of \( \theta_a \) and \( r_c \) are respectively obtained by eqs. (1) and (5).

The result of computation shows that for the water droplet with the radius of 5 mm, each solid has its own theoretical critical pore diameter. The critical radius \( r_c \) becomes larger with the increase of the contact angle \( \theta \), so the low-energy
modification of the solid surface is extremely important. If the average contact angle \(\theta_1\) of the water droplet on the surface of solid paraffin is 100.2°, in the limited liquid-solid interface system, the contact angle \(\theta_2\) obtained by calculating eq. (1) increases to 142.2°. Therefore, when the radius of the water droplet is 0.005 m, the corresponding critical pore diameter \(r_c\) is 0.00095 m (0.95 mm), indicating that as long as the radius of the microscopic hole is less than 0.95 mm, the liquid droplet can maintain a stable state on the wax-filmed surface with the secondary composite structure as shown in Figure 7. However, the calculated value of the above theoretical pore diameter is much greater than the known one of the actual hydrophobic materials, because the calculation model is built at the theoretical critical state free of interferences of other physical factors except the gravity (static state). Moreover, the surface of the pore canal was designed to be ideally smooth and the included angle of the surface of each cylinder was 90°, while the surface of the actual hydrophobic materials is moderately curved rather than the sharp pore canal boundary, and the environment is very complex and harsh.

### 3 The effective work of adhesion

The fact that the limited liquid-solid interface causes the apparent contact angle of the liquid droplets to increase is only one of the conditions for realizing hydrophobicity. For small liquid droplets, a big apparent contact angle indicates a small actual liquid-solid contact area, while for the liquid of a large volume, due to the gravity, the actual liquid-solid contact area is very large and the flow resistance of the liquids increases. Therefore, the third condition for realizing hydrophobicity is to lower the surface energy of the solid and reduce the contact area of the liquid-solid interface as much as possible so as to reduce the flow resistance of liquid droplets on the solid surface. At present, this characteristic is often represented by the size of the rolling angle or the retardation angle [18], of which the two calculation methods are related to the values of the advance angle and the receding angle of the liquid droplets [19,20]. The authors of this study believe that this representation method did not reflect the internal causes affecting the hydrophobicity. The hydrophobicity is newly characterized quantitatively as follows: The difficulty in the rolling of liquid droplets on the solid surface depends essentially on the size of the work of adhesion \(W_a\) between liquid-solid interfaces. In the infinite solid-phase plane system, the relationship is expressed by the well-known Young-Dupre Equation [9]:

\[
W_a = \gamma_{sl} (1 + \cos \theta), \quad 0 < W_a < 2 \gamma_{sl}, \quad 0 < \theta_s < 180°. \tag{6}
\]

The work of adhesion \(W_a\) means the energy per unit needed for separating the liquid phase from the surface of the solid phase [9].

\[
W_a = \gamma_{sl} + \gamma_{lg} - \gamma_{sl}\tag{7}
\]

It can be seen that the smaller the work of adhesion is, the easier the liquid droplets can break away from the bondage of the solid surface to roll; the authors deduced in [9] the expression of the work of adhesion of the wetting system on the limited liquid-solid interface:

\[
W_a = \gamma_{sl} (1 + \sin \theta_2 + \cos \theta_1), 90° < \theta_2 < 180°, 0 < W_a < 2 \gamma_{sl}. \tag{8}
\]

The wetting systems characterized by eq. (8) and the Young-Dupre Equation are different, but the results are the same. When the nature of the liquid is determined, the work of adhesion mainly depends on the nature of the solid surface, while the solid with low surface energy can obtain a bigger contact angle.

Secondly, the smaller the actual liquid-solid interface is, the smaller the total work of adhesion is. There are a large number of holes on the hydrophobically good solid surface. Here, \(\omega = A' / A\) is called the effective liquid-solid interface fraction, where \(A'\) is the area of the actual liquid-solid interface excluding the holes, \(A\) is the area of the liquid-solid interface without holes, and \(0 < \omega < 1\). Therefore, the actual work of adhesion of the hydrophobic solid surface is

\[
W_a' = W_a - \omega = \gamma_{lg} - (1 + \sin \theta_2 + \cos \theta_1), 90° < \theta_2 < 180°. \tag{9}
\]

\(W_a'\) defined as the effective work of adhesion in this study, decreases with the decrease of \(\omega\). Therefore, the hydrophobic ability of the solid surface can be measured with the size of the effective work of adhesion \(W_a'\) as a criterion. It reflects the internal reasons of the difficult levels of rolling of the liquid droplets, and the contact angle \(\theta\) and the effective liquid-solid interface fraction \(\omega\) can be obtained through the experimental measurement. Eq. (9) shows that the key technology of preparing lotus-leaf-like surface materials is to build structures of microscopic holes on the surface and minimize the liquid-solid interface area in addition to low-energy modification of the solid surface layer. Refs. [1–3] shows that the area of the void on the primary structure surface of lotus is greater than that of the papilla, the surface of the papilla of its secondary structure still has a large number of more thinner microscopic holes, which form many small air cushions, and there are few liquid-solid interfaces supporting the liquid droplets, so the lotus leaf surface has excellent hydrophobicity.
4 Conclusions

(1) The fact that the liquids cover the solid surface integrated by a large number of limited liquid-solid interfaces is the reason why the apparent contact angle increases, which is the first condition for achieving hydrophobicity.

(2) For the definite wetting system, that the size of the void of the micro-concave-convex surface is smaller than the theoretical critical pore diameter ensures the liquid droplets are in a stable state, thus realizing the second condition for hydrophobicity. The result of computation shows that when the radius of the void of the micro-concave-convex surface is smaller than the critical radius \( r_c \) (the liquid droplets are in a stable state), the hydrophobicity of the surface of any solid can be theoretically improved.

(3) The third condition for realizing hydrophobicity is to minimize the area of the actual liquid-solid interface and lower the surface energy of the solid. The size of the effective work of adhesion \( W'_a \) can act as a criterion for measuring the hydrophobic ability of the solid surface.

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