On the possibility of superhydrophobic behavior for hydrophilic materials

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Abstract

It has been recognized well that it is necessary to achieve superhydrophobic surfaces on intrinsically hydrophilic materials. However, recently experiments have demonstrated that it is possible to fabricate superhydrophobic surfaces on intrinsically hydrophilic materials by creating adequate roughness. In this study, such a possibility for superhydrophobicity on a hydrophilic surface with an intrinsic contact angle (CA) of 80°, with a comparison to a hydrophobic surface with an intrinsic CA of 120°, is thermodynamically analyzed using a pillared microtexture. Based on the calculations of free energy (FE) and free energy barrier (FEB), it is found that for such hydrophilic materials, generally, the FE for noncomposite or Wenzel’s state is lower than that composite or Cassie’s state for various geometrical wetting systems. Furthermore, even if pillar height or roughness is adequately large, it is hard to realize superhydrophobic behavior because of the surface wicking resulted from its special FE state. In addition, due to the negative FEB of the noncomposite state, there is no transition between noncomposite and composite states no matter how surface geometry varies. The above results also indicate that once noncomposite state is formed, it can hardly be become composite state, or in other words, even if superhydrophobic behavior is possible, it could be temporary and unstable. The present theoretical investigation therefore keeps a reservation on the practicability of superhydrophobic surfaces built on hydrophilic materials.

1. Introduction

It is well known that the wettability of solid surfaces is not only dependent upon their chemical compositions but also closely related to the micro/nano-structures on their surfaces [1–3]. Recently, superhydrophobic surfaces with large water contact angle (CA) and small contact angle hysteresis (CAH) have attracted strong interest in this field due to their ideal liquid-shedding or droplet-sliding properties over the past two decades [4–8]. Such unique wettability for these surfaces has shown wide potential applications, such as self-clearing glasses, biological scaffolds, microfluidics, lab-on-a-chip devices, coatings for automotive and aerospace vehicles, and textiles [9,10].

Although hydrophobicity can be enhanced by a chemical modification that lowers the surface energy, contact angles larger than 120° have never been achieved for water on ideal flat surfaces [11]. Therefore it is generally thought that all superhydrophobic surfaces result from originally hydrophobic substrates with surface microstructures. This has been demonstrated well, e.g., for a CA of the order of 100–120° on such flat surfaces, a microtextured or rough surface shows an amplified CA as high as 150–175° [12–14]. With the successes on the experimental aspect, the relevant theoretical models have been established and such superhydrophobic behavior based on different hydrophobic substrates has been predicted very well [15–18].

However, some recent reports demonstrated that roughness can also lead to a superhydrophobic CA on a hydrophilic substrate. For example, Feng et al. [19] created a superhydrophobic surface with a large CA of 171° from a substrate coated with PVA nanofibers with an intrinsic CA of 72°. Hosono et al. [20] obtained a superhydrophobic surface with a water CA of 178° with the original CA of around 70° by using a bottom-up process based on metal hydroxides. Zhu et al. [21] produced a rough PHBV surface with a CA of 151°, although the intrinsic CA of smooth PHBV is only 75.9°. Cao et al. [22] designed and fabricated different microtextures for inducing a superhydrophobic behavior on hydrogen-terminated Si surfaces with an intrinsic CA of 74°. Very recently, Wang et al. [23] fabricated a T-shape micropillar surface coated with diamond-like carbon on a flat diamond-like carbon with intrinsic CA of 72°; the maximum CA can reach values as high as 158.7–167° through surface microstructure modification. In addition, Karlsson et al. [24] fabricated micrometer-sized nail-head-shaped pillars on an unstructured diamond surface with an advancing CA of below 70°; however, after the surfaces were modified with oxygen, hydrogen, and fluorine, the advancing CA can reach about 160°.

Although the above results have experimentally demonstrated that superhydrophobic surfaces can be created from hydrophilic
substrates with surface microstructures. However, the theoretical explanation has not been completely understood. For example, Liu et al. [25] studied closed/airproof microstructures and some special topologies of the pillars or hairs on solid hydrophobic substrates, considering the effect of Laplace pressure and a certain geometric condition on the formation of Cassie’s state. Marmur [26] theoretically analyzed the possibility of high CA from low CA materials for concave and convex roughness topographies and found that concave parts of roughness topographies may not enable a Cassie’s state, while convex roughness features may enable the formation of hydrophobic surfaces from hydrophilic materials. On the contrary, Patankar [27] considered the energy of drops on surfaces with cavities, and theoretically explained the possibility of hydroophobic surfaces with cavities from hydrophilic materials. In addition, Mchale [28] compared the surface free energy (FE) changes based on Young’s law, and explained hydrophobic tendencies induced the roughness hydrophobic solid surfaces. Here it is noted that the above studies are in agreement with specific experimental observations, and can advance our understanding of superhydrophobic behavior on hydrophilic materials, however, they have hardly measured contact angle hysteresis (CAH), which is more important than CA in some cases for superhydrophobicity (e.g., for sliding behavior). In particular, these studies have never addressed the stability for such superhydrophobic behavior.

Recently, we proposed a simple and robust thermodynamic approach for successful analysis of free energy (FE) and free energy barrier (FEB) and hence can simplify calculations of CA and CAH of superhydrophobic surfaces [15,29–31]. In the present study, we extend our analysis to the possibility of superhydrophobic behavior on hydrophilic materials. By the analysis of metastable energy states, we explore the energy landscape including FE and FEB, and systematically investigate the effects of intrinsic hydrophilic materials on CA and CAH as well as composite or Cassie’s state. It is expected that such an analysis could be used to reveal the thermodynamic mechanism of superhydrophobic behavior on hydrophilic materials.

2. Thermodynamic model

2.1. Wetting theories on roughness surface

The CA of a droplet on an ideal smooth solid surface can be given by classical Young’s equation

\[ \gamma_{lv} \cos \theta_v = \gamma_{sa} - \gamma_{sh} \]  

(1)

where \( \theta_v \) is Young’s CA, i.e., intrinsic CA, \( \gamma_{lv}, \gamma_{sa} \) and \( \gamma_{sh} \) are the surface tension at liquid–air, solid–air and liquid–solid interfaces, respectively. For a rough surface, it is well known that two wetting states may occur if a water droplet is deposited on the surface: the noncomposite (i.e., complete liquid penetration into the troughs of a roughness surface) and composite (i.e., the entrapment of air in the troughs of a roughness surface) states. Fig. 1 shows a pillar microtextured surface and the two states. Note that the surface microtextured is uniformly constructed from the constant geometrical parameters of pillar width (a), spacing (b) and height (h). The apparent CA of the noncomposite is given by Wenzel’s equation [32]

\[ \cos \theta_w = r \cos \theta_v \]  

(2)

where \( r \) is the roughness factor as the ratio between the actual area and geometric projected area for a wetting surface; for the 2-D model and can be written as:

\[ r = 1 + 2h/(a + b) \]  

(3)

However, the apparent CA for the composite can be calculated using Cassie’s equation [33]

\[ \cos \theta_c = f_s \cos \theta_v + f_b - 1 \]  

(4)

where \( f_s \) is the solid–liquid contact area fraction of the substrate for the 2-D model and can be written as:

\[ f_s = a/(a + b) = 1/(1 + b/a) \]  

(5)

2.2. Thermodynamic analysis for microtexture-patterned model surface

Based on our previous work [15,29–31], we have used a 2-D model analyze the microtextured-patterned surface with a set of geometrical parameters (see Fig. 1). Therefore the thermodynamic analysis of the wetting states related to the surface texture geometry and numerical calculations of FE and FEB corresponding to CA and CAH respectively can be conducted by the FE and geometrical equations. To this end, some assumptions for the thermodynamic analysis should be followed as:

1. It is generally accepted that the gravity, chemical heterogeneity and interactions between water and solid and between fluidic molecules within droplet and molecules within solid can be ignored.

2. The droplet is millimeter scale and is large enough comparing with the dimension of surface asperities. As a result, the line tension, i.e., the excess free energy of a solid–liquid–air system per unit length of the three-phase contact line [34,35], becomes extremely small and makes little contribution to the wettability for such a macroscopic droplet.

3. Based on the above assumptions, the droplet is spherical in the absence of gravity [18,36,37] and liquid volume conservation can be kept. Therefore on a horizontal solid surface, this assumption is reasonable as the gravity centre of the droplet will not change significantly as a result of the liquid front movement. Thus, in the present 2-D model, the droplet area should be constant.

For the noncomposite state (see Fig. 2), if an infinite small change, the drop advances from reference point A (associated with CA of \( \theta_A \) and droplet size \( L_A \)) to the neighboring point B (associated with CA of \( \theta_B \) and droplet size \( L_B \)) (see Fig. 2). Due to the constant droplet area in \( x-z \) plane for the 2-D model, i.e., the constant droplet volume for a 3-D model, the geometrical equation can be expressed as:

\[ \theta_A \frac{L_A^2}{\sin^2 \theta_A} - L_A^2 \cot \theta_A = \theta_B \frac{L_B^2}{\sin^2 \theta_B} - L_B^2 \cot \theta_B \]  

(6)
The FE for the two states can be written as, respectively.

\[
F_A = \frac{\gamma_A}{\sin \theta_A} L_A + \theta_A + C
\]

\[
F_B = \frac{\gamma_B}{\sin \theta_B} L_B + \theta_B + C
\]

where C is the FE of the unchanged portion for the system (e.g., the FE is associated with solid–liquid interface beneath the droplet from A to B). Young’s equation is locally valid, meanwhile, based on Eqs. (7) and (8), the change of FE (i.e., FEB) from A to B can be written as:

\[
\Delta F_{A-B} = \left( \frac{\gamma_A}{\sin \theta_A} - \frac{\gamma_B}{\sin \theta_B} \right) L_B + \left( \frac{\gamma_B}{\sin \theta_B} - \frac{\gamma_A}{\sin \theta_A} \right) L_A + \frac{1}{2} \frac{L_B}{\sin \theta_B} - \frac{L_A}{\sin \theta_A} + 2bh
\]

When the droplet recedes from A to the neighboring point C (associated with CA of \( \theta_c \) and droplet size \( L_c \)) (see Fig. 2), the equivalent equations can be expressed as:

\[
\Delta F_{A-C} = \left( \frac{\gamma_A}{\sin \theta_A} - \frac{\gamma_c}{\sin \theta_c} \right) L_c + \left( \frac{\gamma_c}{\sin \theta_c} - \frac{\gamma_A}{\sin \theta_A} \right) L_A + \frac{1}{2} \frac{L_c}{\sin \theta_c} - \frac{L_A}{\sin \theta_A} + \frac{2bh}{2}
\]

Therefore similarly, for the composite state, the droplet advances from reference point A to the neighboring point B and recedes from A to the neighboring point C (see Fig. 2), the geometrical equation can be expressed as:

\[
\Delta F_{A-B} = \left( \frac{\gamma_A}{\sin \theta_A} - \frac{\gamma_B}{\sin \theta_B} \right) L_B + \left( \frac{\gamma_B}{\sin \theta_B} - \frac{\gamma_A}{\sin \theta_A} \right) L_A + \frac{1}{2} \frac{L_B}{\sin \theta_B} - \frac{L_A}{\sin \theta_A} + 2bh
\]

\[
\Delta F_{A-C} = \left( \frac{\gamma_A}{\sin \theta_A} - \frac{\gamma_c}{\sin \theta_c} \right) L_c + \left( \frac{\gamma_c}{\sin \theta_c} - \frac{\gamma_A}{\sin \theta_A} \right) L_A + \frac{1}{2} \frac{L_c}{\sin \theta_c} - \frac{L_A}{\sin \theta_A} + b
\]

It should be pointed out that a reference FE state is assigned as a value of zero by a random choice (e.g., the instantaneous position A) with the initial drop size \( L_A \) and \( \theta_A \), respectively. Hence, the reference state will not impact the results of FEB, which is a relative value with respect to its neighbors (e.g., B and C). Hence, the FEB such as \( \Delta F_{A B} \) and \( \Delta F_{A C} \) can be determined by successive applications and numerical computations. Similarly, geometrical constraint and FEB equations for other arbitrary instantaneous position can be derived. Note that FE (J/m) as described, i.e., F per unit length of contact line, is normalized with respect to \( \gamma \) (J/m²), and the unit of FE will then be meter.

3. Results and discussion

3.1. Typical FE and FEB curves

To better understand the computational results, we give a typical example to show how to get various CAs and CAH from the analysis and calculations of FE and FEB. Fig. 3 illustrates two FE curves for composite and noncomposite states \( (a = b = 2 \mu m, h = 2 \mu m) \). One can see that there is only one global FE minimum for each curve, which is associated with the equilibrium CA (ECA/ \( \theta_0 \) and exactly corresponds to generalized Cassie’s CA (e.g., \( \theta_c = 114.4^\circ \)) and Wenzel’s CA (e.g., \( \theta_w = 69.68^\circ \)), respectively. However, it should be noted that if drop advances from a position A to B or recedes from A to C, the CA changes and the local curve can show a fluctuation in FE, as illustrated in the inset of Fig. 3. These fluctuations demonstrate that the FE curve contains multi-valued local minimum FE and maximum FE, indicating that such extremes represent metastable and unstable equilibrium states, which are related to various apparent CAs. Therefore, the FEB refers to the difference between local minimum and maximum in the direction of three-phase line motion, i.e., advancing and receding. Furthermore, there are always two FEBs, i.e., advancing FEB and receding FEB, connected to each CA value (e.g., the advancing \( \Delta AB \) and receding \( \Delta AC \) along the three-phase line as illustrated in the inset of Fig. 2) [38–40].

Fig. 4 shows the advancing and receding FEB for both composite and noncomposite states based on the same geometrical parameters as illustrated in Fig. 2. Hence, the advancing CA \( \theta_A \) and receding CA \( \theta_B \) as well as CAH defined as \( \theta_A - \theta_B \) can be determined by the intersecting values of advancing and receding curves with x-axis, respectively. Furthermore, the ECA can also be determined by FEB curves, i.e., the intersecting point between advancing and receding curves in Fig. 4. One can see that the value of ECA is con-

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**Fig. 2.** Illustration of variation of wetting states for a droplet from state A to B (or to C) along the contact line.

**Fig. 3.** Variation of normalized FE with CA for noncomposite (non) and composite (com) states \( (L = 10^{-2} m, a = b = h = 2 \mu m; intrinsic CA, \theta = 80^\circ; \theta_0 = 69.68^\circ, \theta_c = 114.4^\circ) \). The inset shows an enlarge view of a segment of FE curve illustrating the FEB; positions A–C correspond to those in Fig. 2. \( \Delta AB \) and \( \Delta AC \) represent the FEB for retreating and advancing contact line, respectively.
sistent with the calculated value in Fig. 3. Here it should be pointed out that the external energy, which was first termed by Johnson and Dettre [41], is assumed to have a value of zero. As a result, for the composite state, the advancing \( (\theta_a = 180^\circ) \) and receding \( (\theta_r = 180^\circ) \) CAs as well as the maximum theoretical CAH defined as \( \text{CAH} = \theta_a - \theta_r = 100^\circ \) can be determined, which is described in detail in our previous work [15,29] and consistent with the results of Kusumaatmaja and Yeomans [42]. In addition, there is a positive FE, note that if a wetting system absorbed energy with nonzero from external sources [41], which will help the system to overcome FEB, leading to a small or even a zero of CAH, e.g., the modulated CAH in Fig. 4. However, for the noncomposite state, it is important to note that according to the definition of CAH the advancing CA \( (\theta_a) \) should be \( 80^\circ \), while the receding CA should be \( 59^\circ \), i.e., the advancing CA and receding CA curves should be reversed in Fig. 4, therefore the CAH is \( \theta_a - \theta_r = 21^\circ \). In addition, the FEB value, i.e., the intersecting point between advancing CA and receding CA curves, is negative, implying that there is no “barrier” to move along contact line, this indicates that the noncomposite state will show hydrophilicity.

3.2. Effect of hydrophilic materials

Fig. 5 shows the variations of FE with respect CA for noncomposite and composite wetting systems with the intrinsic CA of \( 80^\circ \) for different pillar heights. One can see that the FE curves of both noncomposite and composite states intersect at \( 180^\circ \) for the same geometry, indicating the same energy state for the noncomposite and composite states [18]. The FE of composite states for the present system is always higher than that of noncomposite states for different pillar heights; this means that composite states for this system are more unstable than noncomposite states [26]. Note that when pillar height is small (e.g., \( h = 1 \mu m \)), the calculated equilibrium CA (with lowest FE), \( \theta_r \) of noncomposite state exactly corresponds to that predicted by Wenzel’s equation, which is smaller than the intrinsic CA and decreases with an increase in pillar height. However, when pillar height is large enough (e.g., \( h = 9 \mu m \)), there is no minimum FE for a noncomposite state, which means sufficiently high pillar height can lead to the surface wicking (as discussed in detail in the J–D model [41]). For the composite state, the \( \theta_r \) also exactly corresponds to the predicted value by Cassie’s equation, which is larger than the intrinsic CA.

In contrast, Fig. 6 shows the variations of FE with respect CA for noncomposite and composite wetting systems with an intrinsic CA of \( 120^\circ \) for different pillar heights. One can see that the composite state is more stable that the noncomposite state for different pillar heights. In particular, compared Figs. 5 and 6, it is important to note that the FE of hydrophilic materials (i.e., \( \theta_r = 80^\circ \)) is higher than that of hydrophobic materials (i.e., \( \theta_r = 120^\circ \)); the former has a magnitude of \( 10^{-2} \) m, whereas the later has a magnitude of \( 10^{-3} \) m. This indicates that thermodynamic state for hydrophobic materials is more unstable than that for hydrophilic materials. Therefore, even though a composite state for hydrophilic materials can be formed, the corresponding superhydrophobicity may be temporary and tend to transfer to hydrophilicity with time, especially, in case of external stimulus such as vibrational energy [41].

In order to further reveal the intrinsic effect of different materials, Figs. 7 and 8 shows variations of FE for the noncomposite and composite wetting systems with the intrinsic CA of \( 80^\circ \) and \( 120^\circ \),
The above analysis on the effect of hydrophilic materials is based on different pillar heights. In order to gain comprehensive understanding on this effect, the present analysis is also extended to the same geometrical system with different pillar widths or solid fractions. Fig. 9 shows the variations of FE with respect CA for noncomposite and composite wetting systems with the intrinsic CA of $\theta_i = 80^\circ$ for different solid fractions. One can see that the FE of composite states are higher than that of noncomposite states for any pillar widths, indicating that composite states for this system are more unstable than noncomposite states [26]. The ECA of the composite increases dynamically with the decreasing of solid fraction (e.g., the ECA is 114.4°, 139.9° and 153.3° for $f_s = 0.5 \mu m$, 0.2 $\mu m$ and 0.09 $\mu m$ respectively. For example, for hydrophilic materials with an intrinsic CA of 70° [43] or 77° [44], a transition from noncomposite to composite states can occur if the depth of surface topography pores (a similar parameter to the pillar height in the present work) is very large. This happens perhaps because the difference in FE and FEB between noncomposite to composite states is so small due to adequate roughness that the transition between the two states can be easily realized under the experimental conditions where external resources may be available [45].

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4. Summary

The effect of hydrophilic materials with an intrinsic CA of 80° on superhydrophobic behavior has been theoretically investigated using a pillar microtexture, with a comparison to hydrophobic materials with an intrinsic CA of 120°. Based on a proposed thermodynamic approach, FE and FEB as well as CAs and CAH for the hydrophilic materials at different surface geometrical parameters have been analyzed in detail. It is found that that for such hydrophilic materials, generally, the FE for noncomposite or Wenzel's state is lower than that composite or Cassie's state, implying that superhydrophobic behavior is not energetically favorable for this geometrical wetting system. Furthermore, for some special geometrical systems such as large pillar heights, there is no transition between the noncomposite and composite states due to the negative FEB. In particular, compared to the hydrophobic materials, although the superhydrophobic behavior may occur, the thermodynamic state is not stable for the present geometrical conditions, or in other words, such a behavior is temporary and can transfer to hydrophilic behavior. Therefore, the present theoretical investigation keeps a reservation on the practicability of superhydrophobic surfaces built on hydrophilic materials.

Acknowledgements

The authors would like to acknowledge financial support from the National Natural Science Foundation of China (No. 20973146), the Scientific Research Fund of Hunan Provincial Education Department (No. 08A068), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

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