Influence of structured sidewalls on the wetting states and superhydrophobic stability of surfaces with dual-scale roughness

Huaping Wu,^{1,2,*} Kai Zhu¹, Bingbing Wu¹, Jia Lou³, Zheng Zhang¹, Guozhong Chai^{1*}

¹Key Laboratory of E&M (Zhejiang University of Technology), Ministry of Education & Zhejiang Province, Hangzhou 310014, China

²State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, China

³Piezoelectric Device Laboratory, Department of Mechanics and Engineering Science, Ningbo University, Ningbo, Zhejiang 315211, China

*Corresponding author. Email: wuhuaping@gmail.com; chaigz@zjut.edu.cn.

ABSTRACT

The superhydrophobicity of biological surfaces with dual-scale roughness has recently received considerable attention because of the unique wettability of such surfaces. Based on this, artificial micro/nano hierarchical structures with structured sidewalls and smooth sidewalls were designed and the influences of sidewall configurations (i.e., structured and smooth) on the wetting state of micro/nano hierarchical structures were systematically investigated based on thermodynamics and the principle of minimum free energy. Wetting transition and superhydrophobic stability were then analyzed for a droplet on dual-scale rough surfaces with structured and smooth sidewalls. Theoretical analysis results show that dual-scale rough surfaces with structured sidewalls have a larger “stable superhydrophobic region” than those with smooth sidewalls. The dual-scale rough surfaces with smooth sidewalls can enlarge the apparent contact angle (ACA) without improvement in the superhydrophobic stability. By contrast, dual-scale rough surfaces with structured sidewalls present an advantage over those with smooth sidewalls in terms of enlarging ACA and enhancing superhydrophobic stability. The proposed thermodynamic model is valid when compared with previous experimental data and numerical analysis results, which is helpful for designing and understanding the wetting states and superhydrophobic stability of surfaces with dual-scale roughness.

Keywords: Dual-scale surface roughness, Structured sidewalls, Superhydrophobic stability, Energy barrier

1. Introduction

The superhydrophobicity of biological surfaces with dual-scale roughness has recently received considerable attention because of the unique functionalities such as self-cleaning and drag reduction. For example, the dual-scale structure of lotus leaf surface, which shows high apparent contact angles (ACAs), low contact angle hysteresis and good mechanical stability [1], favors its excellent self-cleaning capability and numerous promising applications, such as self-cleaning window glasses, paints, textiles, solar panels and antifouling. Meanwhile, the dual-scale surfaces of rose petals with called “rose petal effect” [2] exhibit large ACAs and high contact angle hysteresis, making it absorb water and remain fresh. Considering that the self-similar micro/nano hierarchical structures found in nature (Fig. 1a) have fascinating singularity and promising applications, numerous attempts have been carried out to investigate the natural surfaces with dual-scale roughness to understand the mechanisms of their unique properties and to design artificial surfaces with dual-scale roughness. Broadly speaking, two types of artificial micro/nano hierarchical structure models, namely those with structured sidewalls (Fig. 1b, Model I) and with smooth sidewalls (Fig. 1c, Model II), have been reported in previous studies [3–26] (see Table S1 in Supporting Information). It is clear that these micro/nano hierarchical structures present many similar properties, including enhanced hydrophobicity, self-cleaning capability and low adhesion. However, the wetting states might be diversified according to the difference of wetting regime in the local nanostructure or microstructure surfaces (Table S1). Most of previous studies only focus on specific wetting states based on either Model I or Model II, while the relevance of sidewall morphology with wetting states might be neglected. Comprehensive analyses and understanding on how the configuration of sidewalls

influences wetting states are lacking.

Additionally, the wetting states and superhydrophobic stability of micro/nano hierarchical structures could be labile with the changing of external conditions. Experimentally, Lee et al. [27] developed a hierarchical structure with smooth top and bottom surfaces as well as nanostructured sidewalls, and investigated the influence of the hierarchical structures of superhydrophobic surfaces on liquid slip, obtaining enhanced stability of submersed superhydrophobic surfaces. Hensel et al. [28] and Butt et al. [29] verified through experiments that the overhangs on the sidewalls of pillars or cavities could restrict liquid expansion and enable the formation of a liquid–air interface even on intrinsically wet surfaces. Theoretically, Extrand et al. [30] and Xue et al. [31] suggested from the perspective of mechanics that a larger advancing contact angle could be provided by structured sidewalls than smooth sidewalls, and triple-phase contact line (TCL) pinning could then be strengthened by a larger capillary force. Nosonovsky et al. [32] and Whyman et al. [33] also proposed that structured sidewalls could improve the energy barrier of transition to avoid the collapse of liquid–air interface. However, their model only considered the effect of structured sidewalls on wetting stability, the hierarchical structure from the top and bottom surfaces were ignored when compared to the self-similar structure of lotus leaf.

In this paper, a thermodynamic approach is used to compare the wetting states of two models mentioned above. Particular attention is given to wetting transition on surfaces with dual-scale roughness to study superhydrophobic stability. The influences of micro/nano hierarchical structures with smooth or structured sidewalls on superhydrophobic stability are analyzed in detail.

Fig. 1. (a) Schematic diagram of the dual-scale roughness of lotus leaf. Schematic diagrams of dual-scale rough surfaces with (b) structured sidewalls and (c) smooth sidewalls.

2. Thermodynamic model

For a droplet on a single-scale rough surface at either Wenzel (W) state [34] or Cassie–Baxter (CB) state [35], the following assumptions are usually suggested: (i) a water droplet is hemispherical, and its contact line is circular; (ii) the size of a water droplet is considerably larger than that of roughness asperity; (iii) the contributions of gravity and line tension are neglected; (iv) the volume of liquid in the asperities is negligible with respect to the total liquid volume. For a droplet on the surfaces with hierarchical roughness or dual-scale roughness, the corresponding thermodynamic model should be deduced based on aforementioned assumptions. Considering a unit cell of periodic pillar-like pattern whose surfaces have dual-scale roughness, we denote the cell apparent area by A_{c1} (A_{c2}) in microstructure (nanostructure), the cross-sectional area and perimeter of the pillar by A_1 (A_2) and L_1 (L_2), and pillar height by h_1 (h_2), respectively. Hence, the following pillar

characteristic parameters are introduced: $\lambda_1 = A_1 / L_1$ ($\lambda_2 = A_2 / L_2$) and $\eta_1 = h_1 L_1 / A_1$ ($\eta_2 = h_2 L_2 / A_2$).

The W rough factor r can be expressed as $r_1 = 1 + h_1 L_1 / A_1 = 1 + \eta_1 f_1$ in microstructure and $r_2 = 1 + h_2 L_2 / A_2 = 1 + \eta_2 f_2$ in nanostructure. The Cassie rough factor f can be expressed as $f_1 = A_1 / A_{c1}$ in microstructure and $f_2 = A_2 / A_{c2}$ in nanostructure. In particular, consider a surface with square pillars of the same configuration as shown in Fig. 2a. The system consists of a water droplet (volume V) and a dual-scale rough substrate (total solid surface S_{total}). The characteristic geometric parameters of this surface are as follows. The r of microstructure (nanostructure) with side length a_1 (a_2) and spacing b_1 (b_2) is $r_1 = 1 + 4a_1 h_1 / (a_1 + b_1)^2$ ($r_2 = 1 + 4a_2 h_2 / (a_2 + b_2)^2$). The f can be expressed as $f_1 = a_1^2 / (a_1 + b_1)^2$ in microstructure and $f_2 = a_2^2 / (a_2 + b_2)^2$ in nanostructure. The S_{ext} (external drop surface), S_{base} (geometric drop base surface) and $R(\theta)$ (radius of water droplet) are introduced (Fig. 2b). The θ is the ACA. The x_1 and x_2 are the penetration depth of water in the microstructure and nanostructure, respectively; y_1 and y_2 are the ratio of the true interface vapor–liquid meniscus in the microstructure and nanostructure, respectively, to the horizontal section ($S_{\text{real}} / S_{\text{flat}}$), as shown in Fig. 2b.

Fig. 2. (a) 3D schematic diagram of a dual-scale rough pillared surface with structured sidewalls. (b) Schematic diagram of a general water droplet on a dual-scale rough pillared surface with structured sidewalls.

The free energy of this system should include an interfacial energy term, a potential energy term and a line tension term, as proposed in the literature [36]. The effects of gravity and line tension are generally negligible [31,37]. Therefore, free energy may be restricted to the sum of interfacial energies, which is expressed as [36]

$$G = \gamma_{LV}S_{LV} + \gamma_{SL}S_{SL} + \gamma_{SV}S_{SV}, \quad (1)$$

where subscripts L, V and S denote the liquid, air and solid phases, respectively; subscripts LV, SV and SL denote the liquid–air, solid–air and solid–liquid interfaces, respectively.

3. Results and discussion

3.1. Wetting states of a droplet on the surfaces with dual-scale roughness

In our previous study [38], a thermodynamic approach was used to analyze all wetting states of

a water droplet on dual-scale rough surfaces with structured sidewalls. The wetting states, which include four stable wetting states, namely CB–CB, CB–W, W–CB and W–W states (Figs. 3 i–iv), and five transition states, namely CB–CB $\rightarrow$ CB–W, CB–CB $\rightarrow$ W–CB, CB–W $\rightarrow$ W–W, W–CB $\rightarrow$ W–W and CB–CB $\rightarrow$ W–W states (Figs. 3 v–ix), are illustrated, therein the front and back parts of the labels of the wetting states represent the wetting states of the nanostructures and microstructures, respectively. The corresponding ACA equations are derived based on the principle of minimum free energy. In this paper, the thermodynamic process based on a water droplet on dual-scale rough surfaces with smooth sidewalls is also analyzed to investigate the effect of sidewall microstructure on the wetting states. The detailed derivation is described in Part S1 in Supporting Information (pillared surface with dual-scale roughness as an example). Furthermore, this method can be generalized to other shapes and the ACA equations of these two models for any shape are shown in Table 1. Our results indicate that the sidewall microstructure, whether smooth or not, will not affect the CB–CB, W–CB and CB–CB $\rightarrow$ W–CB states, whereas the other states will be affected.

Fig. 3. Wetting states of a water droplet on a dual-scale rough pillared surface with structured sidewalls: (i) CB–CB state, (ii) CB–W state, (iii) W–CB state, (iv) W–W state, (v) CB–CB $\rightarrow$ CB–W

state, (vi) CB–CB $\rightarrow$ W–CB state, (vii) CB–W $\rightarrow$ W–W state, (viii) W–CB $\rightarrow$ W–W state, and (ix) CB–CB $\rightarrow$ W–W state.

Table 1

ACA equations of all wetting states for the two models.

Wetting state	Structured sidewalls	Smooth sidewalls
CB–CB	$\cos \theta_{\text{CB-CB}} = f_1 f_2 \cos \theta_0 + f_1 f_2 - 1$	$\cos \theta_{\text{CB-CB}} = f_1 f_2 \cos \theta_0 + f_1 f_2 - 1$
CB–W	$\cos \theta_{\text{CB-W}} = r_1 [f_2 \cos \theta_0 + (f_2 - 1)]$	$\cos \theta_{\text{CB-W}} = (r_1 + f_2 - 1) \cos \theta_0 + f_2 - 1$
W–CB	$\cos \theta_{\text{W-CB}} = f_1 r_2 \cos \theta_0 + f_1 - 1$	$\cos \theta_{\text{W-CB}} = f_1 r_2 \cos \theta_0 + f_1 - 1$
W–W	$\cos \theta_{\text{W-W}} = r_1 r_2 \cos \theta_0$	$\cos \theta_{\text{W-W}} = (r_1 + r_2 - 1) \cos \theta_0$
CB–CB $\rightarrow$ CB–W	$\cos \theta_{\text{CB-CB} \rightarrow \text{CB-W}} = f_1 f_2 (1 + \frac{x_1}{\lambda_1}) \cos \theta_0 + f_1 (f_2 - 1) (1 + \frac{x_1}{\lambda_1}) + (f_1 - 1) y_1$	$\cos \theta_{\text{CB-CB} \rightarrow \text{CB-W}} = f_1 (f_2 + \frac{x_1}{\lambda_1}) \cos \theta_0 + f_1 (f_2 - 1) + (f_1 - 1) y_1$
CB–CB $\rightarrow$ W–CB	$\cos \theta_{\text{CB-CB} \rightarrow \text{W-CB}} = f_1 f_2 (1 + \frac{x_2}{\lambda_2}) \cos \theta_0 + f_1 (f_2 - 1) y_2 + (f_1 - 1)$	$\cos \theta_{\text{CB-CB} \rightarrow \text{W-CB}} = f_1 f_2 (1 + \frac{x_2}{\lambda_2}) \cos \theta_0 + f_1 (f_2 - 1) y_2 + (f_1 - 1)$
CB–W $\rightarrow$ W–W	$\cos \theta_{\text{CB-W} \rightarrow \text{W-W}} = r_1 f_2 (1 + \frac{x_2}{\lambda_2}) \cos \theta_0 + r_1 (f_2 - 1) y_2$	$\cos \theta_{\text{CB-W} \rightarrow \text{W-W}} = (f_2 (1 + \frac{x_2}{\lambda_2}) + r_1 - 1) \cos \theta_0 + (f_2 - 1) y_2$
W–CB $\rightarrow$ W–W	$\cos \theta_{\text{W-CB} \rightarrow \text{W-W}} = r_2 f_1 (1 + \frac{x_1}{\lambda_1}) \cos \theta_0 + (f_1 - 1) y_1$	$\cos \theta_{\text{W-CB} \rightarrow \text{W-W}} = f_1 (r_2 + \frac{x_1}{\lambda_1}) \cos \theta_0 + (f_1 - 1) y_1$
CB–CB $\rightarrow$ W–W	$\cos \theta_{\text{CB-CB} \rightarrow \text{W-W}} = f_1 f_2 (1 + \frac{x_1}{\lambda_1}) (1 + \frac{x_2}{\lambda_2}) \cos \theta_0 + f_1 (f_2 - 1) (1 + \frac{x_1}{\lambda_1}) y_2 + (f_1 - 1) y_1$	$\cos \theta_{\text{CB-CB} \rightarrow \text{W-W}} = \left[f_1 f_2 (1 + \frac{x_2}{\lambda_2}) + f_1 \frac{x_1}{\lambda_1} \right] \cos \theta_0 + f_1 (f_2 - 1) y_2 + (f_1 - 1) y_1$

The CB–CB state in our study is similar to the superhydrophobic lotus leaf model which is beneficial for various industrial production processes, such as self-cleaning [3], enhancing condensation heat transfer [39] and anti-icing [40]. Hence, the reasonable design of pillar structure size is highly significant in enhancing superhydrophobic stability to ensure a water droplet in the CB–CB state, called “stable superhydrophobic region” (SSR). The corresponding size ranges of microstructure and nanostructure for surfaces with square pillars are listed in Table 2. The relative height (h_1/a_1 , h_2/a_2) and the intrinsic contact angle (θ_0) are the main parameters of the “SSR”. Specific to, we assign $h_1/a_1 = h_2/a_2 = 0.25$ and $\theta_0 = 120^\circ$. Fig. 4a shows the wetting phase diagram of dual-scale rough surfaces with smooth and structured sidewalls. The “SSR” is located at the lower left corner of the diagram. The dual-scale rough surfaces with structured sidewalls have a larger “SSR” than those with smooth sidewalls. The wetting map in Figs. 4b and 4c shows the ACAs of water droplets on the dual-scale rough surfaces with smooth sidewalls (Fig. 4b) and structured sidewalls (Fig. 4c) for all possible stable wetting states in terms of the relative spacing of microstructures and nanostructures. A synergetic effect of microscale and nanoscale roughnesses on wettability can be observed, which results in different wetting states. Additionally, the influences of relative height (h_1/a_1 , h_2/a_2) and intrinsic contact angle (θ_0) on the “SSR” are also analyzed, as shown in Figs. S2-1 and S2-2. Large h_1/a_1 , h_2/a_2 and θ_0 values can enlarge the “SSR.” On the basis of the aforementioned analysis, the dual-scale rough surfaces with structured sidewalls exhibit an advantage over those with smooth sidewalls in terms of enhancing superhydrophobicity.

Fig. 4. (a) Wetting phase diagram of four stable wetting states. The apparent contact angle (ACA) of a water droplet on a surface with dual-scale roughness in four stable wetting states as a function of the relative spacing of microstructures and nanostructures: (b) smooth sidewalls, (c) structured sidewalls.

Table 2

Size ranges of sidewall microstructure in the “SSR” for the two models.

Sidewall microstructure	Size range
Structured sidewalls	$\left\{ \begin{array}{l} 0 < b_1 / a_1 < \sqrt{\frac{1 + 2k + k^2 - 4(h_1 / a_1)(k + k^2)}{1 + \alpha}} - 1 \\ 0 < b_2 / a_2 < \sqrt{1 - \frac{4(h_2 / a_2) \cos \theta_0}{(1 + \cos \theta_0)}} - 1 \end{array} \right.$ $(k = f_2 \cos \theta_0 + f_2 - 1)$
Smooth sidewalls	$\left\{ \begin{array}{l} 0 < b_1 / a_1 < \sqrt{\frac{f_2 \cos \theta_0 + f_2 - 4(h_1 / a_1) \cos \theta_0}{(f_2 - 1) \cos \theta_0 + f_2 - 1}} - 1 \\ 0 < b_2 / a_2 < \sqrt{1 - \frac{4(h_2 / a_2) \cos \theta_0}{(1 + \cos \theta_0)}} - 1 \end{array} \right.$

To check the validity of our ACA equations in Table 1, a comparison between our equations with the experimental results and ACA equations reported by Bhushan et al. [3] is performed. Bhushan et al. investigated the influence of microstructure spacing on wettability under a given nanostructure for Model I with circular pillars (i.e., spacing P_1 , diameter D_1) and found increased spacing during the transition from the CB–CB state to the CB–W state, giving the ACA equation as [3]

$$\cos \theta = R_f \cos \theta_0 - f_{LA} (R_f \cos \theta_0 + 1), \quad (2)$$

where R_f is a roughness factor defined as a ratio of the solid–liquid area to its projection on a flat plane, the R_f is the sum of $R_{f(\text{micro})}$ and $R_{f(\text{nano})}$, and f_{LA} is the fractional flat geometric area of the liquid–air interface under the droplet. Eq. (2) is available only for the CB–CB state and out of operation after transition. According to our ACA equations of CB–CB and CB–W states (Table 1),

the ACA curves as a function of the relative spacing of the microstructure are illustrated in Fig. 5a. Our ACA equation of CB–CB state agrees more with the experimental results of Bhushan et al. Moreover, the ACA equation of CB–W state can also predict the experimental results after transition, although a deviation is observed because of the effect of contact hysteresis or the different measurement methods of ACA. Additionally, Sajadinia et al. [25] had numerically predicted ACA for Model II in a dual-scale rough surface with smooth sidewalls, in which a normalized term ξ ($\xi = \begin{cases} x_2 / h_2, 0 \leq x_2 \leq h_2 \\ 1 + x_1 / h_1, h_2 \leq x_1 \leq h_1 \end{cases}$ for CB–CB $\rightarrow$ CB–W state, $\xi = 2 + x_2 / h_2, 0 \leq x_2 \leq h_2$ for CB–W $\rightarrow$ W–W state) is used to represent the relative height of the roughness components. For the CB–CB $\rightarrow$ CB–W and CB–W $\rightarrow$ W–W states, the changing trend of ACA in our results agrees with the numerical result of Sajadinia et al. [25] (Fig. 5b). However, a deviation is evident between the ACA of W–W state and the numerical result of Sajadinia et al. [25] when the microstructure and nanostructure are under a complete wetting state, i.e. the W–W state ($\xi = 3$). This could be attributed to the difference in preliminary assumptions.

Fig. 5. (a) Apparent contact angle (θ) as a function of the relative pitch P_1/D_1 of a cylindrical microscale structure in. (b) Apparent contact angle (θ) of the $\text{CB-CB} \rightarrow \text{CB-W}$ state as a function of relative height ξ .

3.2. Wetting transition and superhydrophobic stability

The transition process from the CB state to the W state on surfaces with single-scale roughness has been studied extensively because of Laplace pressure [37,41]. Transition is achieved in two ways, i.e., a depinning mechanism or a sag mechanism. For depinning transition, the initial sagging causes the depinning of TCL from the edge of the asperity, which subsequently propagates along the sidewalls until the liquid front reaches the bottom of the groove. For sag transition, the liquid-air interface sags into the grooves underneath, and the position of TCL remains unchanged. Wetting transition occurs when the sagging fluid front reaches the bottom of the groove. Fig. 6 shows a

typical transition from the CB–CB state (the “lotus effect”) to the CB–W state (the “rose petal effect”) by the depinning mechanism for dual-scale rough surfaces with structured sidewalls. (A similar process for surfaces with smooth sidewalls is shown in Fig. S3.) Depinning transition can be divided into two processes, namely the TCL pinning of CB–CB state (Figs. 6a–6c) and downward movement of TCL (Figs. 6d–6f). In the first process, the meniscus expands continuously as the sag angle α_1 . TCL depinning occurs when liquid pressures reach the collapse pressure P_{cr} of TCL depinning, that is, sag angle α_1 reaches advancing angle θ_{adv}^{app} on the sidewalls of the microstructure, which is called high-energy CB–CB state. The ACA equations for two different surfaces with dual-scale roughness and single-scale roughness in this process are shown in Table 3. The detailed derivation is described in Part S3 in Supporting Information. In the second process, the sidewalls of the microstructure begin to get wet. The system turns into a transition state, that is, the CB–CB $\rightarrow$ CB–W state. Liquid pressure overcomes capillary force to cause TCL movement. The wetting of the substrate occurs when the meniscus comes in contact with the substrate, which is called quasi CB–W state. This process releases energy because the liquid–air interface and the solid–air interface are replaced with the solid–liquid interface. Previous experimental results [42] have shown that this process will be completed within a few milliseconds; thus, this process is spontaneous. The ACA equations for two different surfaces with dual-scale roughness and single-scale roughness are shown in Table 3. The detailed derivation is described in Part S3 in Supporting Information.

Fig. 6. Schematic illustration of the depinning transition process of a water droplet on dual-scale rough surfaces with structured sidewalls: (a–c) TCL pinning of the CB–CB state from low energy to high energy; (d–f) TCL movement from the transition state to the CB–W state.

Table 3

ACA equations in the first and second processes of depinning transition.

Process	Dual-scale roughness		Single-scale roughness
	Structured sidewalls	Smooth sidewalls	
First	$\cos \theta_{\alpha_1 \rightarrow \theta_{adv}^{app}} = f_1 f_2 \cos \theta_0$ $+ f_1 (f_2 - 1) + (f_1 - 1) y_1$	$\cos \theta_{\alpha_1 \rightarrow \theta_{adv}} = f_1 f_2 \cos \theta_0$ $+ f_1 (f_2 - 1) + (f_1 - 1) y_1'$	$\cos \theta_{\alpha \rightarrow \theta_{adv}} = f \cos \theta_0 + (f - 1) y$
Second	$\cos \theta_{\alpha = \theta_{adv}^{app}, x_1 \rightarrow h_1} = f_1 f_2 \left(1 + \frac{4x_1}{a_1}\right) \cos \theta_0$ $+ f_1 \left(1 + \frac{4x_1}{a_1}\right) (f_2 - 1) + (f_1 - 1) y_{1max}$	$\cos \theta_{\alpha = \theta_{adv}, x_1 \rightarrow h_1} = f_1 \left(f_2 + \frac{4x_1}{a_1}\right) \cos \theta_0$ $+ f_1 (f_2 - 1) + (f_1 - 1) y_{1max}'$	$\cos \theta_{\alpha = \theta_{adv}, x \rightarrow h} = f \left(1 + \frac{4x}{a}\right) \cos \theta_0$ $+ (f - 1) y_{max}$

Consider a surface with dual-scale roughness, e.g., $\theta_0 = 95^\circ$, $\theta_{\text{adv}} = 103.5^\circ$ (polyethylene surface [43]), the geometric size of the microstructure $a_1 = b_1 = 2h_1$ is selected with given nanostructure $f_2 = 0.5$. The free energy of transition process is normalized in the following discussion for brevity. The normalized free energy $(G^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}$ in the first process ($\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}$) of transition can be expressed as

$$(G^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}} = \frac{2(1 - \cos \theta) + \cos \theta_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}} \sin^2 \theta}{(2 - 3 \cos \theta + \cos^3 \theta)^{2/3}}. \quad (3)$$

For the second process ($\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1$) of transition, the normalized free energy $(G^*)_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1}$ can be expressed as

$$(G^*)_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1} = \frac{2(1 - \cos \theta) + \cos \theta_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1} \sin^2 \theta}{(2 - 3 \cos \theta + \cos^3 \theta)^{2/3}}. \quad (4)$$

Here $\cos \theta_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}$ and $\cos \theta_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1}$ can be obtained from Tables 3. The normalized free energy $(G^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}}$ ($(G^*)_{\alpha \rightarrow \theta_{\text{adv}}}$) and $(G^*)_{\alpha_1 = \theta_{\text{adv}}, x_1 \rightarrow h_1}$ ($(G^*)_{\alpha = \theta_{\text{adv}}, x \rightarrow h}$) for a surface with dual-scale roughness and smooth sidewalls (or single-scale roughness) can be obtained. The detailed derivation of the expression is shown in Part S3 in Supporting Information. All the values of the normalized free energy of the two different surfaces with dual-scale roughness (Figs. 7ai and 7bi for structured sidewalls, Figs. 7aai and 7bai for smooth sidewalls) and single-scale roughness (Figs. 7aiii and 7biiv) for depinning transition are presented, providing a general idea on how the system will behave. A droplet on a surface system will move from its initial state toward states with lower free energy until it stops in a free energy minimum, which may either be local or global. The normalized free energy exhibits a local minimum for $\alpha_1 = 90^\circ$ in the first process and for $x_1 = 0$ in the second process, followed by an increase in $(G^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}$ ($(G^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}}$, $(G^*)_{\alpha \rightarrow \theta_{\text{adv}}}$) with higher α_1 and

$(G^*)_{\alpha_1=\theta_{adv}^{app}, x_1 \rightarrow h_1}$ ($(G^*)_{\alpha_1=\theta_{adv}, x_1 \rightarrow h_1}$, $(G^*)_{\alpha=\theta_{adv}, x \rightarrow h}$) and higher x_1 . That is, free energy increases continuously in the entire process of depinning transition. Compared with surfaces with single-scale roughness, higher free energy and higher ACA for given α_1 and x_1 are obtained in surfaces with dual-scale roughness, particularly those with structured sidewalls. External pressures, such as the vibrations and evaporation of a droplet [44,45], are required for a system at rest to start moving toward higher free energy states.

Fig. 7. Normalized free energy as functions of (a) apparent contact angle (θ) and sag angle (α_1 or α) and (b) apparent contact angle (θ) and protrusion depth (x_1/h_1 or x/h). (i) Dual-scale rough surface with structured sidewalls, (ii) dual-scale rough surface with smooth sidewalls, and (iii) surface with single-scale roughness.

The normalized minimum free energy $(G_{min}^*)_{CB-CB \rightarrow CB-W}$ for the transition from the CB–CB state to the CB–W state consists of two parts. The first part is $(G_{min}^*)_{\alpha_1 \rightarrow \theta_{adv}^{app}}$ in the first process, and the second part is $(G_{min}^*)_{\alpha_1=\theta_{adv}^{app}, x_1 \rightarrow h_1}$ in the second process. The $(G_{min}^*)_{CB-CB \rightarrow CB-W}$ and the

corresponding ACA should be provided for each relative protrusion depth $\Delta h_1 / h_1$ to describe where the minimums are located accurately. Δh_1 is the sum of the height h_{meniscus} of the meniscus ($h_{\text{meniscus}} / h_1 = (\sin \alpha_1 - 1) / \cos \alpha_1$) and protrusion depth x_1 . For the first process ($\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}$) of transition, the normalized minimum free energy $(G_{\text{min}}^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}$ can be expressed as

$$(G_{\text{min}}^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}} = \frac{2(1 - \cos \theta_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}) - \cos \theta_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}} \sin^2 \theta_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}}{(2 - 3 \cos \theta_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}} + \cos^3 \theta_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}})^{2/3}} \quad (5)$$

For the second process ($\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1$) of transition, the normalized minimum free energy $(G_{\text{min}}^*)_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1}$ can be expressed as

$$(G_{\text{min}}^*)_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1} = \frac{2(1 - \cos \theta_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1}) - \cos \theta_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1} \sin^2 \theta_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1}}{(2 - 3 \cos \theta_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1} + \cos^3 \theta_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1})^{2/3}} \quad (6)$$

The normalized minimum free energies $(G_{\text{min}}^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}}$ ($(G_{\text{min}}^*)_{\alpha \rightarrow \theta_{\text{adv}}}$) and $(G_{\text{min}}^*)_{\alpha_1 = \theta_{\text{adv}}, x_1 \rightarrow h_1}$ ($(G_{\text{min}}^*)_{\alpha = \theta_{\text{adv}}, x \rightarrow h}$) can be obtained on dual-scale rough surfaces with smooth sidewalls (surfaces with single-scale roughness). The detailed derivation of the expression of normalized free energy is provided in Part S3 in Supporting Information. For a surface with dual-scale roughness and structured sidewalls (smooth sidewalls, surface with single-scale roughness), the normalized minimum free energy $(G_{\text{min}}^*)_{\text{CB-CB} \rightarrow \text{CB-W}}$ and the corresponding ACA, as functions of the relative protrusion depth $\Delta h_1 / h_1$, are shown in Figs. 8a and 8b. The TCL pinning process occurs from point A (A' , A'') to point B (B' , B''), namely from the low-energy CB–CB state to the high-energy CB–CB state, as shown in Figs. 6a to 6c. The free energy difference between point A (A' , A'') and point B (B' , B'') is a normalized energy barrier $\Delta G_{\text{meniscus}}^*$ ($\Delta G_{\text{meniscus}}^{*'} , \Delta G_{\text{meniscus}}^{*''}$) of the meniscus. $\Delta G_{\text{meniscus}}^*$ can be expressed as

$$\Delta G_{\text{meniscus}}^* = (G_{\text{min}}^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}(\alpha_1 = \theta_{\text{adv}}) - (G_{\text{min}}^*)_{\alpha_1 \rightarrow \theta_{\text{adv}}^{\text{app}}}(\alpha_1 = 90^\circ). \quad (7)$$

Fig. 8a shows that the value of $\Delta G_{\text{meniscus}}^*$ ($\Delta G_{\text{meniscus}}^{*'} , \Delta G_{\text{meniscus}}^{*''}$) is 4.74×10^{-3} (0.87×10^{-3} , 1.71×10^{-3}). Compared with surfaces with single-scale roughness, the energy barrier of the meniscus increases thrice on dual-scale rough surfaces with structured sidewalls but reduces by half on dual-scale rough surfaces with smooth sidewalls. The process of TCL moving downward occurs from point B (B' , B'') to point C (C' , C''). The free energy difference between point B (B' , B'') and point C (C' , C'') is the normalized capillary energy barrier $\Delta G_{\text{capillary}}^*$ ($\Delta G_{\text{capillary}}^{*'} , \Delta G_{\text{capillary}}^{*''}$). $\Delta G_{\text{capillary}}^*$ can be expressed as

$$\Delta G_{\text{capillary}}^* = (G_{\text{min}}^*)_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1} (x_1 = h_1, y_1 = y_{\text{max}}) - (G_{\text{min}}^*)_{\alpha_1 = \theta_{\text{adv}}^{\text{app}}, x_1 \rightarrow h_1} (x_1 = 0, y_1 = y_{\text{max}}). \quad (8)$$

The values of $\Delta G_{\text{capillary}}^{*'}$ and $\Delta G_{\text{capillary}}^{*''}$ in Fig. 8a are 2.46×10^{-3} and 5.54×10^{-3} , respectively. The capillary energy barrier is reduced by more than half, and the transition becomes easier although ACA can be increased on dual-scale rough surfaces with smooth sidewalls. Free energy per unit of area increases until it exceeds γ_{LV} when TCL moves downward (point B to point C) on a dual-scale rough surface with structured sidewalls, at which ACA (θ) reaches 180° , indicating that this transition state is highly unstable, and the continuous wetting of the sidewalls is thermodynamically less favorable. Hereafter, the free energy dramatically decreases when the meniscus comes in contact with the substrate (Point C (C' , C'')) unless external pressure suddenly pushes the droplet down. The process of wetting the substrate occurs from point C (C' , C'') to point D (D' , D''), which is spontaneous. Hence, point C (C') is called the metastable CB–W state. The intensity and velocity of this spontaneous process depend on the free energy difference between point C (C' , C'') and point D (D' , D''). Therefore, the structured sidewalls can hinder the downward movement of TCL and delay the process from the CB–CB $\rightarrow$ CB–W state to the CB–W state.

Fig. 8. (a) Normalized minimum free energy $(G_{\min}^*)_{\text{CB-CB} \rightarrow \text{CB-W}}$ and (b) corresponding apparent contact angle (θ) as a function of relative protrusion depth $\Delta h_1/h_1$.

The aforementioned theoretical analysis shows that θ and $(G_{\min}^*)_{\text{CB-CB} \rightarrow \text{CB-W}}$ are influenced by the solid fraction f_2 of the nanostructure. The contours of the color fill plots of θ as functions of f_2 and relative protrusion depth $\Delta h_1/h_1$ for the two models are shown in Figs. 9a and 9b. For dual-scale rough surfaces with smooth sidewalls, the critical position of TCL depinning is independent of f_2 , as shown in Fig. 9a. The critical position is enlarged as f_2 decreasing on a dual-scale rough surface with structured sidewalls (Fig. 9b), because a larger advancing contact angle $\theta_{\text{adv}}^{\text{app}}$ can be provided for structured sidewalls than the original θ_{adv} on smooth sidewalls [46]. Hence, $\cos \theta_{\text{adv}}^{\text{app}}$ is expressed by a modified CB equation [31,47–48] as

$$\cos \theta_{\text{adv}}^{\text{app}} = f_2 \cos \theta_{\text{adv}} + f_2 - 1. \quad (9)$$

Consequently, TCL pinning can be strengthened, and transition from the CB–CB state to the CB–W state can be delayed.

Fig. 9. Apparent contact angle (ACA, θ) as a function of relative protrusion depth $\Delta h_1/h_1$ and solid fraction f_2 : (a) dual-scale rough surface with smooth sidewalls and (b) dual-scale rough surface with structured sidewalls.

The normalized minimum free energy of the CB–CB state $(G_{\min}^*)_{\alpha_1=90^\circ}$ and the high-energy CB–CB state $(G_{\min}^*)_{\alpha_1=\theta_{\text{adv}}^{\text{app}}}$ ($(G_{\min}^*)_{\alpha_1=\theta_{\text{adv}}}$), as functions of f_2 for dual-scale rough surfaces with structured sidewalls (smooth sidewalls), are shown in Fig. 10. The free energy difference between the CB–CB state and the high-energy CB–CB state is the normalized energy barrier of the meniscus

$\Delta G_{\text{meniscus}}^*$ ($\Delta G_{\text{meniscus}}^{*'}$) at a certain f_2 . The $\Delta G_{\text{meniscus}}^{*'}$ decreases as f_2 decreases on a dual-scale rough surface with smooth sidewalls, and the maximum $\Delta G_{\text{meniscus}}^{*'}$ is obtained when $f_2 = 1$. In this case, a surface with dual-scale roughness degenerates into a surface with single-scale roughness. The minimum $\Delta G_{\text{meniscus}}^*$ is obtained when $f_2 = 1$ ($0.45 \leq f_2 \leq 1$) on a dual-scale rough surface with structured sidewalls. The high-energy CB–CB state is highly unstable and continues to expand when $f_2 < 0.45$, at which ACA reaches 180° , because the meniscus is thermodynamically less favorable. Therefore, the dual-scale rough surfaces with smooth sidewalls can enlarge the ACA but weaken the stability of CB–CB state. By contrast, the dual-scale rough surfaces with structured sidewalls not only enlarge the ACA but also enhance the stability of the CB–CB state.

Fig. 10. Normalized minimum free energy of the high-energy CB–CB state and the CB–CB state as a function of the solid fraction f_2 of nanostructures.

4. Conclusions

The influence of sidewall configurations (i.e., structured and smooth) on the wetting states and superhydrophobic stability of surfaces with dual-scale roughness was investigated based on a proposed thermodynamic approach and the principle of minimum free energy. The proposed thermodynamic model was proven valid when compared with previous experimental data and numerical studies. Micro/nano hierarchical structures with structured sidewalls had a larger “SSR” than those with smooth sidewalls. Thus, surfaces with dual-scale roughness and structured sidewalls exhibited an advantage over those with smooth sidewalls in terms of enhancing superhydrophobicity. Furthermore, particular attention should be given to the wetting transition of surfaces with dual-scale roughness to study superhydrophobic stability. Surfaces with dual-scale roughness and smooth sidewalls could enlarge apparent contact angle (ACA) but reduce the energy barrier of the transition from the CB–CB state to the CB–W state and weaken superhydrophobic stability. While, surfaces with dual-scale roughness and structured sidewalls could enlarge ACA, increase the energy barrier and enhance superhydrophobic stability. Therefore, designing dual-scale rough surfaces with structured sidewalls and ensuring water droplets in the CB–CB state are highly significant in enhancing superhydrophobicity and superhydrophobic stability. Although our formulation is based on micro/nano hierarchical structures, a similar theoretical framework can be used to analyze self-similar N-level structures. The present theory helps improve understanding on the wetting states and superhydrophobic stability of surfaces with dual-scale roughness.

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Graphical Abstract