Applied Surface Science 382 (2016) 111–120

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

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

Huaping Wu[a,b,*], Kai Zhu[a], Bingbing Wu[a], Jia Lou[c], Zheng Zhang[a], Guozhong Chai[a,*]

[a] Key Laboratory of E&M (Zhejiang University of Technology), Ministry of Education & Zhejiang Province, Hangzhou 310014, China
[b] State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, China
[c] Piezoelectric Device Laboratory, Department of Mechanics and Engineering Science, Ningbo University, Ningbo, Zhejiang 315211, China

ARTICLE INFO

Article history:
Received 28 February 2016
Accepted 15 April 2016
Available online 19 April 2016

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

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.

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 it 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

* Corresponding authors at: Key Laboratory of E&M (Zhejiang University of Technology), Ministry of Education & Zhejiang Province, Hangzhou 310014, China.
E-mail addresses: wuhuaping@gmail.com (H. Wu), chaigz@zjut.edu.cn (G. Chai).

http://dx.doi.org/10.1016/j.apsusc.2016.04.101
0169-4332/

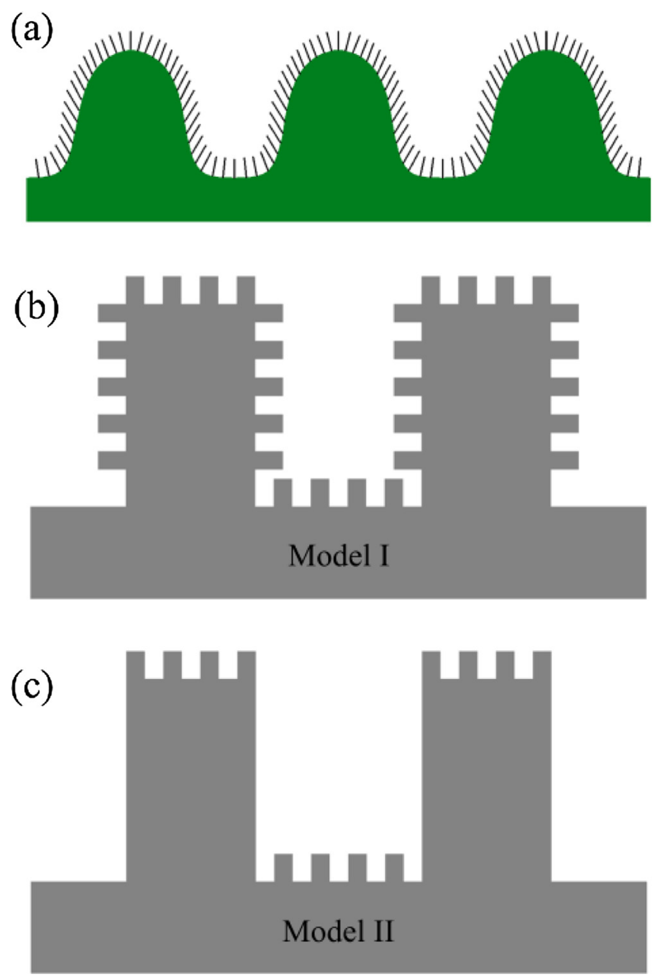

Fig. 1. (a) Schematic diagram of the dual-scale roughness of lotus leaf. Schematic diagrams of dual-scale rough surfaces with (b) structured sidewalls and (c) smooth sidewalls.

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 superhydrohphobic 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.

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 $\eta_1 = h_1L_1/A_1 (\eta_2 = h_2L_2/A_2)$. The W rough factor r can be expressed as $r_1 = 1 + h_1L_1/A_1 = 1 + \eta_1 f_1$ in microstructure and $r_2 = 1 + h_2L_2/A_2 = 1 + \eta_2 f_2$ 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 $r_1 = 1 + 4a_1h_1/(a_1 + b_1)^2$ $\left(r_2 = 1 + 4a_2h_2/(a_2 + b_2)^2\right)$. 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_{real}/S_{flat}), as shown in Fig. 2b.

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 (Fig. 3i–iv), and five transition states, namely CB–CB → CB–W, CB–CB → W–CB, CB–W → W–W, W–CB → W–W and CB–CB → W–W states (Fig. 3v–ix), are illustrated, thereinto 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