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Optimal design of superhydrophobic surfaces using a paraboloid microtexture

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ABSTRACT

Due to the crucial role of surface roughness, it has been recently proposed to design optimal and extract geometrical microstructures for practical fabrications of superhydrophobic surfaces. In this work, a paraboloid microtexture is employed as a typical example to theoretically establish a relationship between surface geometry and superhydrophobic behavior for a final optimal design. In particular, based on a thermodynamic approach, the effects of all the geometrical parameters for such a paraboloid microtexture on free energy (FE) and free energy barrier (FEB) as well as equilibrium contact angle (ECA) and contact angle hysteresis (CAH) of a superhydrophobic surface have been systematically investigated in detail. It is interestingly noted that the droplet position for metastable state is closely related to the intrinsic CA of the surface. Furthermore, the paraboloid base steepness plays a significant important role in ECA and CAH, and a critical steepness is necessary for the transition from noncomposite to composite states, which can be judged using a proposed criterion. Moreover, the superhydrophobicity depends strongly the surface geometrical dimension for noncomposite state, while it is not sensitive for composite state. Additionally, both vibrational energy and geometrical dimension affect the transition from noncomposite to composite wetting states, and a comprehensive criterion for such transition can be obtained. Finally, using such criterion, it is revealed that the paraboloidal protrusion is the most optimal geometry among the three typical microtextures for ideal superhydrophobicity.

1. Introduction

Due to their water-repellent and self-cleaning properties, superhydrophobic surfaces with a contact angle (CA) larger than 150° and a contact angle hysteresis (the difference between advancing angle and receding contact angles) smaller than 10° have recently attracted great interest in both academic research and practical applications such as micro-channels [1], antifouling [2], solar panels [3], self-cleaning window glasses [4], and drug delivery [5]. Such surfaces require both appropriate surface roughness and generally low surface energy. There are two dominant approaches to fabricate a superhydrophobic surface, i.e., using low free energy materials and enhancing surface roughness [6]. While the former is limited to the maximum CA of about 120° [7], the latter may lead to almost the maximum CA, i.e., 180° even for a hydrophilic material [8]. As a result, numerous methods to prepare superhydrophobic surfaces have been reported [9–13]. With rapid improvements of micro or nano fabrication techniques, it is now becoming possible to control and tailor micro or nano-scale chemical structures on solid surfaces to achieve the ideal superhydrophobic surfaces with regular or ordered patterns [13,14].

However, in spite of significant advances in fabrication techniques for such surfaces, to date the effects of surface patterns or geometries on superhydrophobicity have not been completely understood, especially, in the theoretical aspect, such as CAH, and wetting state transition (e.g., between noncomposite and composite state). It has therefore been a challenge to design optimal geometry for ideal superhydrophobic behavior. To this end, considerable theoretical efforts have been made during the recent years. For example, Extrand [15,16] proposed a criterion contact line density criterion and asperity height criterion for the suspension and collapse of a droplet on the surface. Quere et al. [17] proposed a criterion of asperity ratio for the formation of a stable Cassie state. Patankar [18] analyzed the wetting state transition for a periodical

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pillar microtextured surface and emphasized the effect of the ratio between pillar height and width on transition. In addition, Nosonovsky and Bhushan [19] stressed the role of aspect ratio and meniscus force for different rough surfaces and further designed the optimal microtextured surfaces with hemispherical topped cylindrical and pyramidal asperities. The above studies have succeeded in the establishments of a quantitative correlation between different microtextured geometries and superhydrophobicity and are in agreement with specific experimental observations. However, two main issues have still remained. One is what pattern or microtexture is optimal and the other is how all geometrical parameters for a specific pattern or microtexture affect superhydrophobic behavior.

Recently, a simple thermodynamic approach for analysis of free energy (FE) and free energy barrier (FEB) of a metastable energy state have been proposed by Li and Amirfazli [20,21]. The approach is based on a two-dimensional model, but it can offer a concise physical picture of energy status and hence can simplify calculations of CA and CAH associated with FE and FEB. Unfortunately, the model is used mainly to analyze the pillar microtexture, which is ideal and different from the practical surfaces.

In the present work, based on the thermodynamic approach, we extend the analysis to a more general surface structure, paraboloid protrusions microtexture, as illustrated in Fig. 1. Here it should be indicated that compared to the pillar microtexture, the paraboloid microtexture hardly involves shape edges and corners, and hence can be fabricated using the practical micro- or nano-techniques. Meanwhile, such a paraboloid microtexture is similar to the natural microstructure (e.g., lotus), and can resist effectively erosion and breakage, indicating excellent mechanical properties. Therefore, the present study could be helpful for the optimal design of economical practical superhydrophobic surfaces.

2. Thermodynamic analysis

2.1. General theoretical considerations on a paraboloid microtexture surface

It is well known that, the CA of a water droplet on an ideal smooth solid surface can be given by the classical Young's Equation

$$\gamma^{la}\cos\theta_Y = \gamma^{sa} - \gamma^{ls} \tag{1}$$

where θ_Y is intrinsic CA. γ^{la}, γ^{sa}, and γ^{ls} are the surface tension at liquid–air, solid–air, and liquid–solid interfaces, respectively. For a rough surface, there are two wetting states: the non-composite state (i. e., complete liquid penetration into the troughs of a roughness surface) and composite state (i. e., the entrapment of air in the troughs of a roughness surface).

In the experiment, the contact angle and hysteresis angle usually can be measured by a two-dimensional surface along specific planes. In previous article [20,21], in order to develop a simple analysis of a system and its boundary conditions to find metastable states of the system; a 3-dimensional pillar structure illustrated can be simplified into a 2-dimensional system by analyzing the system along specific planes. Similarly, in principle, based on minimizing free energy (FE) of a system, a 3-dimensional paraboloid microtexture surface as shown in Fig. 1(c) can be also simplified into a 2-dimensional system as illustrated in Fig. 1(a) and (b) by analyzing the system along specific planes such as $y = 0$. Based on such simplification, the analysis of thermodynamic status related to surface geometrical configurations of the system and subsequent numerical calculation of FE barrier can be readily conducted. The free energy barrier refers to the FE difference between a local minimum and an adjacent maximum in the direction of three-phase line motion (i.e., advancing or receding). A point to note is that the methodology suggested here will not be applicable for nonsymmetric drops (such systems are not very common in practical cases). The assumptions in this study are that the drop profile is spherical (i.e., millimeter sized drop or the absence of gravity), and that drop size is much larger than surface microtexture feature size. In a two-dimensional surface, the FE of the system is given by

$$F = \gamma^{la} l^{la} + \gamma^{sl} l^{sl} + \gamma^{sa} l^{sa} \tag{2}$$

where γ is liquid surface tension, l is the interfacial line length, and the subscripts s, l, and a stand for the solid, liquid, and air, respectively. The interfacial line length and drop radius are calculated as follows. The liquid–gas interfacial line length consists of two parts, the outside interface of the spherical cap and the liquid–air interface within the grooves, i.e., $l^{la} = 2\,R'\theta + 2(1-f)\,R'\sin\theta$, where R' is the radius of the droplet, and θ is the apparent contact angle at a given state of the drop (see Fig. 2), not necessarily at equilibrium. The solid–liquid line length is given by $l^{sl} = 2\,R' r_f f \sin\theta$. The solid–air interfacial line length also consists of two parts, the interface outside the drop and the solid–air interfacial line length within the grooves, i.e., $l^{sa} = (l_{tot} - 2R' r \sin\theta) + 2R' r_{1-f}(1-f)\sin\theta$, where l_{tot} is the total line length of the solid surface, and r_{1-f} is the roughness ratio of the dry part. The roughness ratios of the wet and dry areas are related by $r_f f + r_{1-f}(1-f) = r$ and the drop radius is related to its volume by $R' = S(\theta - \sin\theta\cos\theta)^{-1/2}$, where S is area of the droplet. Substituting the above Eqs. into Eq. (2), one gets the expression for the FE, which can be written in the following dimensionless form

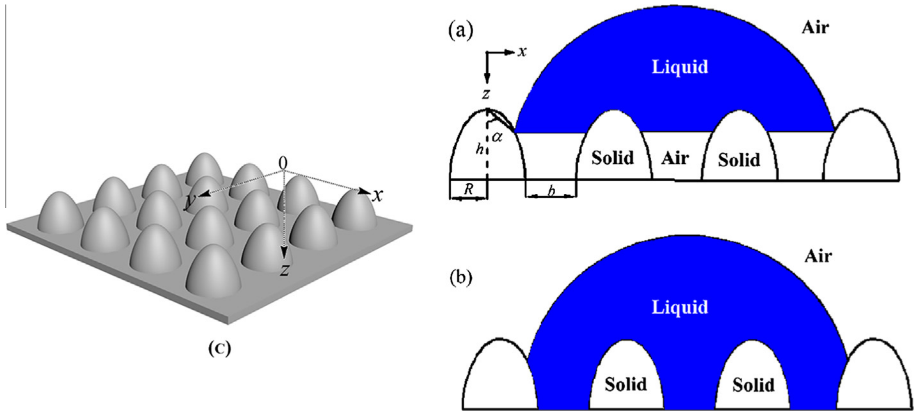

Fig. 1. (a) A typical 2-D paraboloid microtexture with composite wetting state; (b) a typical 2-D paraboloid microtexture with noncomposite state; (c) an enlarged view of a typical 3-D paraboloid microtexture.