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Wetting transition of water droplets on superhydrophobic patterned surfaces

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The relationship between water droplet size and surface geometric parameters governs the transition from composite solid–air–liquid interface to homogeneous solid–liquid interface on superhydrophobic surfaces. This study presents the effect of varying droplet size on the wetting properties of patterned Si surfaces. We propose a criterion that the transition from the Cassie–Baxter regime to the Wenzel regime occurs when the droplet droop is greater than the depth of the cavity. The trends are explained based on experimental data and in terms of the proposed transition criterion.

Keyword: Interface wetting

Advances in nanotechnology, including micro/nanoelectromechanical systems (MEMS/NEMS), have stimulated the development of new materials which require hydrophobic surfaces and interfaces with low adhesion and friction. Hydrophobicity of a surface (wettability) is characterized by the static contact angle between a water droplet and the surface. The contact angle depends on several factors, including energy, roughness, preparation and cleanliness of the surface [1–5]. Hydrophobic surfaces can be constructed by using low surface energy materials such as polytetrafluoroethylene or wax, or by increasing surface area through the introduction of surface roughness and/or creation of air pockets. Air trapped in the cavities of a rough surface results in a composite solid–air–liquid interface, as opposed to a homogeneous solid–liquid interface [6–10].

Recent studies have investigated wetting behavior during condensation [11] and the stability of the composite interface of artificial superhydrophobic surfaces and the transition from composite to homogeneous interface under pressure [12,13], vertical vibration [14] and the effect of contact angle hysteresis [15]. Nosonovsky and Bhushan [16] suggested that destabilizing factors responsible for such a transition have different characteristic scale lengths, and thus multiscale (hierarchical) roughness plays an important role in stabilizing the composite interface. Various criteria, such as the contact line density [17], the energy barrier [18] and the spacing factor [19], have been formulated to predict the transition from a metastable composite state to a wetted state. In addition, Bhushan and Jung [20] proposed a transition criterion obtained from the curvature of droplet governed by the Laplace equation, which relates pressure inside the droplet to its curvature. However, we believe that more systematic investigations are needed to validate this transition criterion. Recent experiments have not considered how the size of a water droplet distributed on a surface affects the contact angle. Also, the effect of water droplet size and the geometric parameters of the surface on the contact angle and transition needs to be understood. This information is critical in designing a superhydrophobic surface for applications requiring water repellency.

Evaporation studies are useful in characterizing wetting behavior because droplets with various sizes can be created to evaluate the transition criterion on a patterned surface. Many researchers have considered the evaporation of small droplets of liquid on solid surfaces [21–23]. These researchers have developed models to calculate the diffusion of the water droplets into the surrounding atmosphere and compared the experimental data with the models. In addition, it has been shown

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that the wetting state changes from the Cassie–Baxter state to the Wenzel state as the droplet becomes smaller than a critical value on patterned surfaces during evaporation [24]. However, this study used only a few samples and a model to relate the transition criterion with water droplet size and geometric parameters of the surface was not proposed.

In this paper, we present a study of droplet evaporation on silicon surfaces patterned with pillars of two different diameters and heights and with varying pitch values in order to investigate how the droplet size influences the transition. A video camera is used to observe the evaporation process as a droplet with initial radius of about 1 mm decreases to a radius of a few hundred micrometers. A transition criterion is developed to predict the change from the Cassie–Baxter regime to the Wenzel regime on the patterned surfaces. To verify the transition, the presence of dust traces after droplet evaporation is examined. The trends are explained in terms of the experimental data and a numerical model.

A theoretical background for the transition criterion is described as follows. Consider a small water droplet suspended on a superhydrophobic surface consisting of a regular array of circular pillars with diameter D, height H and pitch P, as shown in Figure 1. The local deformation for small droplets is governed by surface effects rather than gravity. The curvature of a droplet is governed by the Laplace equation, which relates pressure inside the droplet to its curvature [1]. The curvature is the same at the top and the bottom of the droplet [25–27]. For the patterned surface considered here, the maximum droop of droplet occurs in the center of a square formed by four pillars as shown in Figure 1a. Therefore, the maximum droop of a droplet (δ) in the recessed region can be found in the middle of two pillars which cross diagonally as shown in Figure 2b, which is $(\sqrt{2}P - D)^2/(8R)$. If the droop is much greater than depth of the cavity,

$$(\sqrt{2}P - D)^2/R \geqslant H, \tag{1}$$

then the droplet will just contact the bottom of the cavities between the pillars, resulting in the transition from the Cassie–Baxter regime to the Wenzel regime. Furthermore, in the case of large distances between the pillars, the liquid–air interface can easily be destabilized due to dynamic effects, such as surface waves which are formed at the liquid–air interface due to gravitational or capillary forces. This leads to the formation of a homogeneous solid–liquid interface.

Single-crystal silicon (Si) was used in this study because it is the most commonly used structural material for micro/nanocomponents [28]. The Si surface was patterned using photolithography to create two sample series, each with nine different pitch values [29]. The pitch is the spacing between the centers of two adjacent pillars. Series 1 has 5 μm diameter and 10 μm height flat-top, cylindrical pillars with different pitch values (7, 7.5, 10,

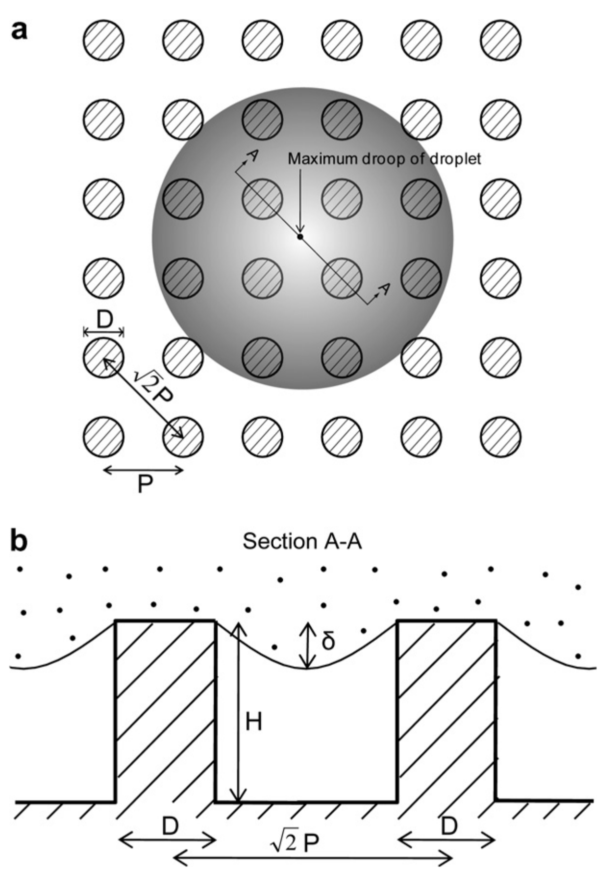

Figure 1. A small water droplet suspended on a superhydrophobic surface consisting of a regular array of circular pillars. (a) Plan view. The maximum droop of droplet occurs in the center of square formed by four pillars. (b) Side view in section A–A. The maximum droop of droplet (δ) can be found in the middle of two pillars that cross diagonally.

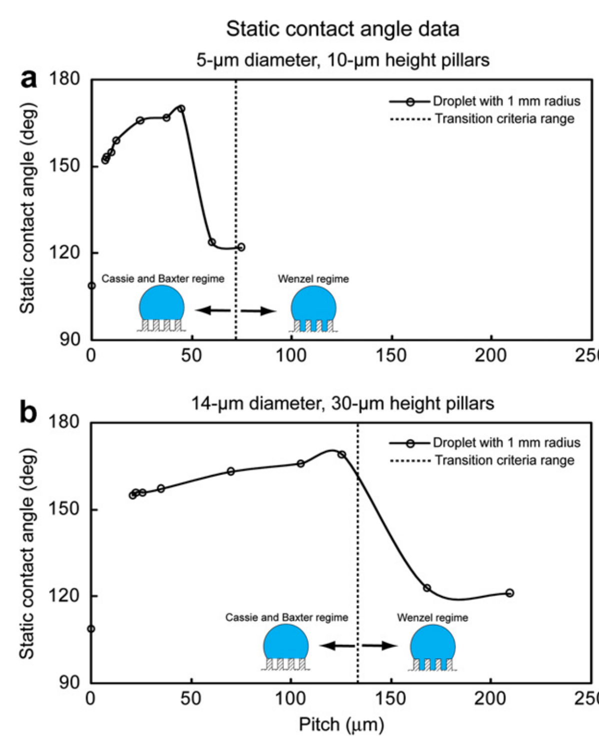

Figure 2. Static contact angle as a function of geometric parameters for two series of the patterned Si with different pitch values coated with PF_3 for a droplet with 5 μl volume. A dotted line represents the transition criteria range obtained using Eq. (1).

12.5, 25, 37.5, 45, 60 and 75 μm), and series 2 has 14 μm diameter and 30 μm height flat-top, cylindrical pillars with different pitch values (21, 23, 26, 35, 70, 105, 126, 168 and 210 μm). The Si chosen was initially hydrophilic, so to obtain a sample that is hydrophobic, a self-assembled monolayer (SAM) of 1,1,2,2-tetrahydroperfluorodecyltrichlorosilane (PF_3) was deposited on the sample surfaces by vapor-phase deposition [29]. The effect of static contact angle and contact angle hysteresis (i.e. the difference between advancing and receding contact angles) has been studied previously for patterned surfaces coated with PF_3 [20].

The proposed transition criterion (Eq. (1)) was applied to experimental results for a droplet with a 1 mm radius (5 μl volume) on the patterned Si with different pitch values coated with PF_3 [20]. The capillary length, defined as $k^{-1} = \sqrt{\gamma/g\rho}$, where γ is the surface tension, ρ is the liquid density and g is the gravity, is 2.7 mm for water. Since this size of water droplet is less than the capillary length, effects other than gravity may govern the deformation. In our analysis we assume that the effect of gravity is negligible. The contact angles on the prepared surfaces are plotted as a function of pitch between the pillars in Figure 2. A dotted line was drawn to represent the range of transition criteria obtained using Eq. (1). The flat Si coated with PF_3 has a static contact angle of 109°. As the pitch increases up to 45 μm for series 1 and 126 μm for series 2, the static contact angle first increases gradually from 152° to 170°. Then, the contact angle starts decreasing sharply. As predicted from the transition criterion (Eq. (1)), the decrease in contact angle at higher pitch values is due to the transition from composite interface to solid–liquid interface. In series 1, the value predicted from the transition criteria is a little higher than the experimental observations. However, in series 2, there is a good agreement between the experimental data and the theoretically predicted values for the transition from the Cassie–Baxter regime to the Wenzel regime.

To prove the validity of the transition criterion in terms of droplet size, the critical radius of droplets deposited on the patterned Si with different pitch values coated with PF_3 is measured during evaporation. For each experimental run, the process of droplet evaporation was recorded by a digital camcorder (Sony, DCRSR100) with a 10 × optical and 120 × digital zoom. Frame-by-frame advancement of the camcorder gave a resolution of 0.03 s. An objective lens placed in front of the camcorder gave a total magnification of 10–20×. Droplet diameters as small as a few hundred microns can be recorded. Droplets were gently deposited on the substrate using a microsyringe and the whole process of evaporation was recorded. Evaporation starts immediately after the deposition of the droplets. To find the dust traces remaining after droplet evaporation, an optical microscope with a CCD camera (Nikon, Optihot-2) was used. All measurements were made in a controlled environment at 22 ± 1 °C and 45 ± 5% RH.

Figure 3 shows a water droplet on a patterned Si surface coated with PF_3 before and after the transition. The light passes below the left droplet, indicating that air pockets exist, so that the droplet is in the Cassie–Baxter state. However, an air pocket is not visible below the bottom right droplet, which must therefore be in the Wenzel state. There is an abrupt increase in the "foot" part of droplet with an apparent increase in the radius of the droplet, which can be interpreted as an abrupt increase in the solid–liquid surface area. This could result from the droplet being impaled on the patterned surface, which would be characterized by a smaller contact angle. Figure 4 shows the radius of the droplet as a function of geometric parameters for the experimental results (circle) compared with the transition criterion from the Cassie–Baxter regime to the Wenzel regime (solid lines) for two series of patterned Si with different pitch values coated with PF_3. It is found that the critical droplet radius where the transition occurs is indeed in good quantitative agreement with our predictions. The critical droplet radius increases with the geometric

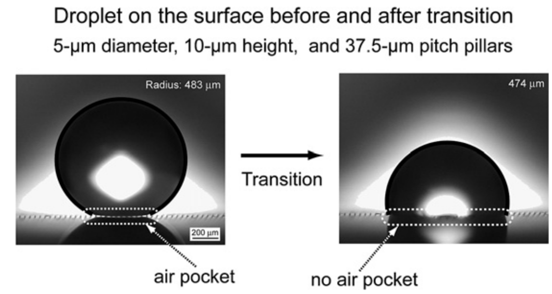

Figure 3. Water droplet on patterned Si surface coated with PF_3. Before the transition, an air pocket is clearly visible at the bottom area of the droplet, but after the transition, an air pocket is not found at the bottom area of the droplet.

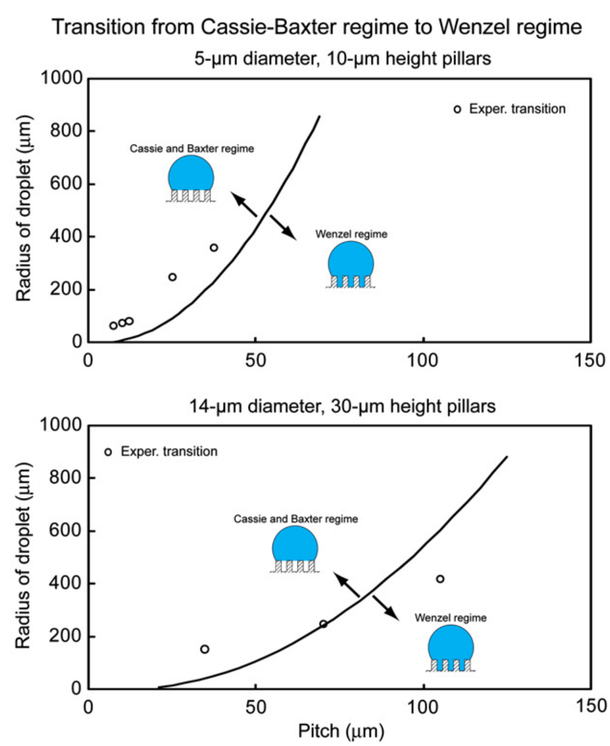

Figure 4. Radius of droplet as a function of geometric parameters for the experimental results (circle) compared with the transition criterion from the Cassie–Baxter regime to the Wenzel regime (solid lines) for two series of the patterned Si with different pitch values coated with PF_3.

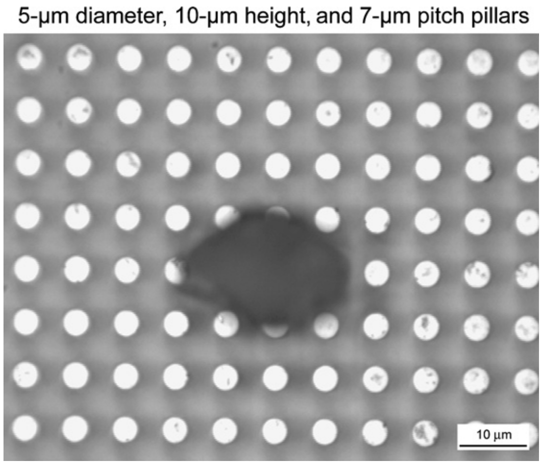

Figure 5. Dust trace remaining after droplet evaporation for the patterned Si surface on which the transition was not found during the process of droplet evaporation.

parameter (pitch). For surfaces with small pitch, the critical droplet radius can become quite small. Based on this trend, one can design superhydrophobic surfaces, even for small droplets.

Another approach using dust mixed in water was studied to verify the transition. Figure 5 presents the dust trace remaining after evaporation of a droplet of 1 mm radius (5 μl volume) on patterned Si with 5 μm diameter, 10 μm height and 7 μm pitch pillars. The dust particles remained on only a few pillars at the end of the evaporation process. The transition occurred at a droplet radius of about 20 μm and the dust particles left a footprint of about 25 μm. From Figure 4, on the patterned Si surface with 5 μm diameter and 10 μm height, the transition does not occur for pillars with less than about 5 μm pitch. These predictions are consistent with experimental observation. In the literature, it has been shown that on superhydrophobic natural lotus, the droplet remains almost entirely in the Cassie–Baxter regime during the evaporation process [30]. This indicates that to achieve superhydrophobicity the distance between the pillars should be minimized in order to improve the ability of the droplet to resist sinking.

In conclusion, we have investigated by studying evaporation that droplet size influences the transition from the Cassie–Baxter regime to the Wenzel regime on patterned surfaces with various distributions of geometrical parameters. As the distance between pillars on the surface was reduced with respect to droplet size, it was found that the droplet remains at the top of the pillars throughout the evaporation process, maintaining a strong superhydrophobic surface even when the droplet size is comparable to the distance between pillars. We have proposed a transition criterion based on water droplet size. The experimentally observed critical radius of droplet where the transition occurs is indeed in good quantitative agreement with our proposed criterion for the patterned Si. This indicates that the distance between the pillars should be reduced enough to improve the ability of the droplet to resist sinking, thereby enabling the surface to retain its superhydrophobicity.

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