Spontaneous Breakdown of Superhydrophobicity, Mauro Sbragaglia, Alisia M. Peters, Christophe Pirat, Bram M. Borkent, Rob G. H. Lammertink, Matthias Wessling, and Detlef Lohse, Phys. Rev. Lett. 99, 156001 (2007).

Abstract from the original paper:

In some cases water droplets can completely wet microstructured superhydrophobic surfaces. The dynamics of this rapid process is analyzed by ultrahigh-speed imaging. Depending on the scales of the microstructure, the wetting fronts propagate smoothly and circularly or—more interestingly—in a stepwise manner, leading to a growing square-shaped wetted area: entering a new row perpendicular to the direction of front propagation takes milliseconds, whereas once this has happened, the row itself fills in microseconds (‘‘zipping’’). Numerical simulations confirm this view and are in quantitative agreement with the experiments [1].

Overview

When a surface structure is introduced in a material, the roughness of the material changes wetting behavior of the surface.

Wenzel derived an expression for a contact angle with the microstructured surface as follows:

$$\cos\theta_W = r\cos\theta$$

(θ: contact angle of a surface without microstructures, θ_W : contact angle of a surface with microstructures, r is the ratio of the actual area to the projected area [2])

As a result, a hydrophobic surface (a surface with a contact angle larger than 90°) becomes more hydrophobic, whereas a hydrophilic surface (a surface with a contact angle smaller than 90°) becomes more hydrophilic [3]. Thus, materials with surface structures can show superhydrophobicity (contact angle larger than 150°).

Cassie and Baxter found that if a liquid is suspended on top of microstructures, the contact angle will change to a new value θ_{CB} with the following relation [4]:

$$\cos\theta_{CB} = \varphi(\cos\theta + 1) - 1$$

(φ is the area fraction of the solid that touches the liquid.)

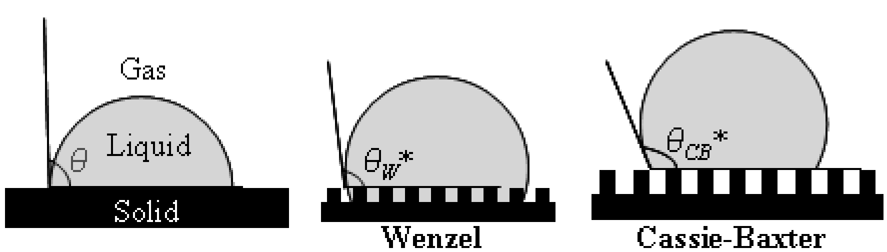

Fig. 1. Schematic diagrams of droplets sitting on surfaces with different wetting behaviors [5].

In some conditions, there is spontaneous transition from Cassie-Baxter (hereafter, CB) state to Wenzel (hereafter W) state as the fluid penetrates into the microstructures and spreads. This CB to W transition can be desirable in many situations including the case that water-repellent structures on leaves keep plants healthy, but make spraying of pesticides inefficient [6].

In this paper, the authors used a periodic structure of square pillars made of styrene-butadiene-styrene (trade name "kraton") by micromolding technique with height h = 10 μm, width w =5 μm, and a gap width a between 2 and 17 μm as shown in the Fig. 2.

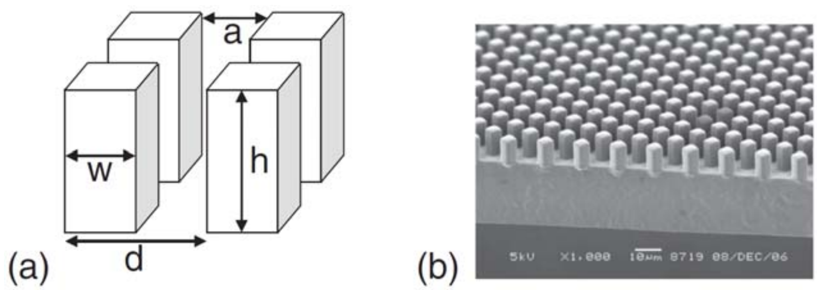

Fig. 2. Sketch and (a) and scanning electron microscope image (b) of the micropatterned substrate [1].

Using this structure, they observed that the CB state spontaneously broke down as shown in the Fig. 3. They also observed that after fluid sunk down, a lateral spreading of fluid developed, which depended on the parameter-gap width (a)-of the microstructured-surface as shown in Fig. 4. They reported that for a large gap width of a = 11 μm, a round shape of the fully wetted area appeared (Fig. 4. (c)), while at smaller gap (a= 5 μm), the propagation fronts reflected the underlying lattice structure (Fig. 4 (b)). It was also reported that at very small spacing (a=2 μm), they did not observe any transition to W state.

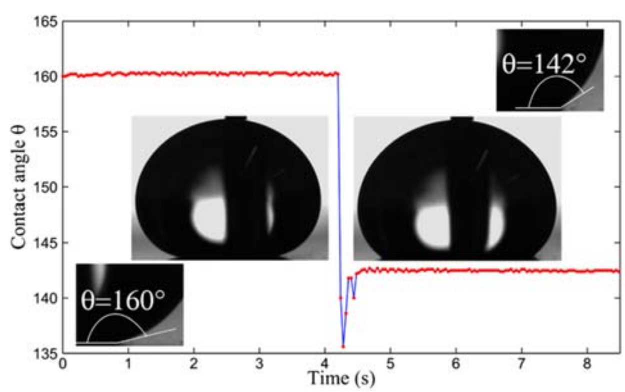

Fig. 3. Transition from the CB to the W state [1].

In this paper, they argued that the transition from CB to W happened because the energy of a droplet on a substrate monotonically increases with the effective contact angle. Thus, when the effective contact angle of CB state is higher than that of the W state, the CB droplet always move towards the W state. This process can have some energy barriers to overcome and the infiltration does not happen at once, but it starts locally. Then, they did numerical analysis of this dynamic process and reported that their numerical calculation results confirmed their explanation and were in quantitative agreement with experimental results.

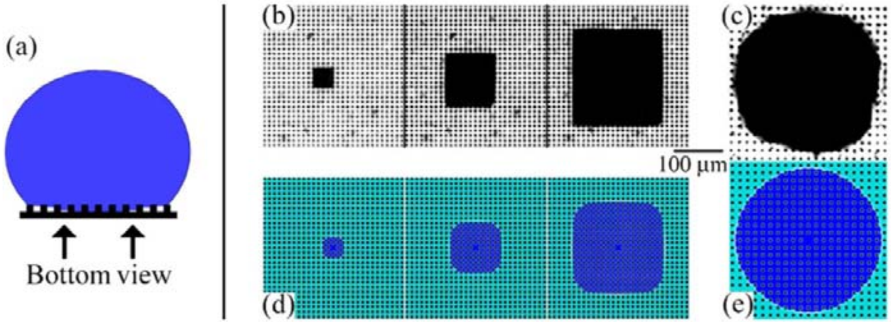

Fig. 4. Bottom views of the front evolution of the transition, as sketched in (a). (b) Three snapshots for the case with a = 5 µm. (c) When a = 11 µm, it resulted in a circular wetted area. (d) and (e) show the results of the corresponding numerical simulations [1].

Comments

Because of my limited understanding, I couldn't follow all their arguments. However, it was very paper and this paper caught my attention because I also observed interesting footprints of wetting behaviors as shown in Fig. 5, which can be related to breakdown of superhydrophobicity. In this case, two samples had the same surface structures, a periodic square array of epoxy cylinders with a diameter of 250 nm with the spacing of 2 µm and height of 8 µm, but different modulus of 1000 MPa and 600 MPa. In this case, the transition probably happened in spite of a very small spacing because the samples had a different geometry and material properties.

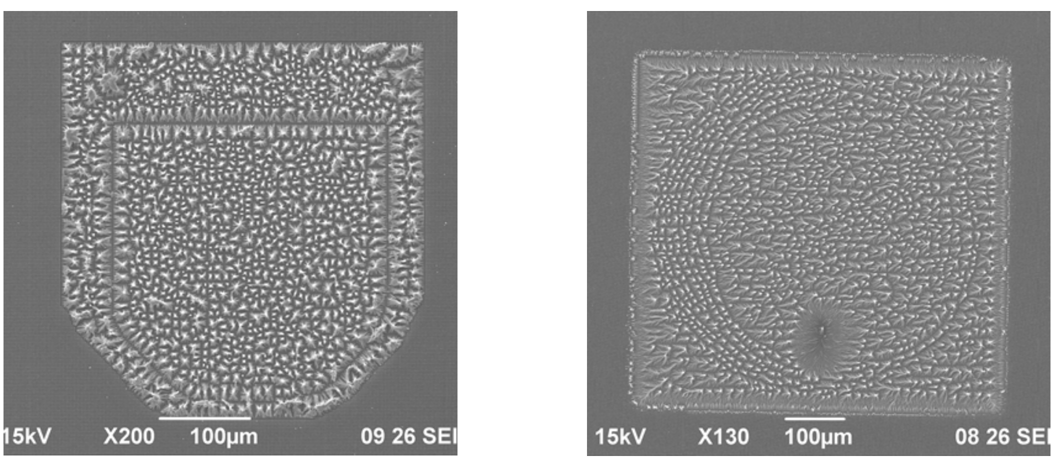

Fig. 5. Scanning electron microscope images of the footprints of wetted area for samples with the same microstructures but different stiffness (a) 1000 MPa (b) 600 MPa.

References

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