Spontaneous Breakdown of Superhydrophobicity

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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.

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Microstructured materials can show a superhydrophobic behavior with effective contact angles of 160° and beyond (“Lotus effect”). For many applications this effect is wanted: when a liquid droplet is deposited on microtextured hydrophobic surfaces, it can bead off completely and wash off contaminations very efficiently [1–5]. Superhydrophobic materials are now used for a wide series of applications in medicine, coatings, self-cleaning, textiles, and microfluidics [6–9]. However, under certain conditions, the superhydrophobicity (“Cassie-Baxter state” [10], hereafter CB) spontaneously breaks down [11,12]: fluid enters in between the microstructures and spreads, resulting in a smaller contact angle (“Wenzel state” [13], hereafter W). In many cases this transition from the CB to the W state is highly desirable. For example, water-repellent layers on leaves keep plants healthy, but also complicate spraying crops effectively with pesticides [14]. Other examples are heterogeneous porous catalysts, where superhydrophobicity is an unwanted effect as it reduces the contact area [15] (see Fig. 1).

The objective of this Letter is to characterize and analyze the dynamics of the spontaneous breakdown of superhydrophobicity in terms of geometry, wetting, liquid-gas surface tension σ_{lg} , and the liquid viscosity η .

The fabrication of highly precise and controllable microstructured surfaces becomes possible through a micro-molding technique [16]. As material, we chose a solution of styrene-butadiene-styrene (a block copolymer commercially available as “kraton”) dissolved in toluene. Kraton is used because thin layers are easily removable from the mold. The thickness of the resulting translucent film is only $\sim 40 \mu\text{m}$, allowing for optical imaging of the CB to W transition through the bottom of the film.

For the experiments presented here we chose a regular, periodic structure of square pillars with height $h = 10 \mu\text{m}$, width $w = 5 \mu\text{m}$ (both kept fixed for all our experiments), and as control parameter a gap width a

between 2 and $17 \mu\text{m}$. The wavelength $d = w + a$ of the regular square lattice is thus between 7 and $22 \mu\text{m}$ (see Fig. 2).

Water droplets are deposited on the surface with a syringe pump at a very low flow rate ($5 \mu\text{l/min}$) from an outlet of a vertical thin tube (outer diameter 0.158 mm). The outlet is set parallel to the flat film, 2 mm above it. A typical droplet grows slowly and reaches the dry surface within a minute. Then the flow is stopped and a (meta)stable drop in the CB state (contact area $\sim 1 \text{ mm}^2$) is observed. For the chosen microtextured surfaces the (effective) contact angle in the CB state is $\theta \sim 160^\circ$, while for a smooth surface made of the same material it is $\theta \sim 100^\circ$.

At some point the CB state can spontaneously break down (Fig. 1).

FIG. 1 (color online). Transition from the (meta)stable CB to the W state. A drop softly deposited on a micropatterned surface can stay suspended with air pockets trapped in the grooves underneath the liquid (left). At some point the CB state spontaneously breaks down. The drop then homogeneously wets the substrate, resulting in a lower contact angle (right).

FIG. 2. Sketch (a) and scanning electron microscopy picture (b) of the micropatterned substrate. The geometrical dimensions of the pattern are the pillar height $h = 10 \mu\text{m}$, the pillar width $w = 5 \mu\text{m}$ (both kept fixed for all experiments), and the gap width a , which is varied between 2 and $17 \mu\text{m}$. The wavelength d of the pattern is $d = a + w$. In (b) we have $a = 5 \mu\text{m}$. Typical equilibrium contact angles for a smooth surface made up of the same material are $\theta \sim 100^\circ$.

The extremely rapid filling process towards the W state is recorded from the bottom of the film [see Fig. 3(a) for a sketch] with a microscope and a high-speed imaging system (Photron Ultima APX-RS), using frame rates in the range between 4000–50 000 fps. In Fig. 3 the *large scale* time evolution of the filling process is shown. After fluid sinks down at a certain point, a lateral spreading develops which sensitively depends on the parameters characterizing the microtextured surface: while for large gap width $a = 11 \mu\text{m}$ a round shape of the fully wetted area is emerging [Fig. 3(c)], at smaller $a = 5 \mu\text{m}$ the propagating fronts reflect the structure of the underlying square lattice, leading to a square-shaped wetted area [Fig. 3(b)]. At even smaller $a = 2 \mu\text{m}$ we never observed any transition to the W state.

For the wetting cases, the velocity of front propagation drastically depends on the gap width a (see Fig. 4): for $a = 11 \mu\text{m}$ we measure a mean velocity $v \sim 700 \text{ mm/s}$, 2 orders of magnitude faster than the case with $a = 5 \mu\text{m}$, where $v \sim 7 \text{ mm/s}$. Moreover, in the latter case the front

FIG. 3 (color online). Bottom views of the front evolution of the transition, as sketched in (a). In (b) three snapshots for the case with $a = 5 \mu\text{m}$ are shown, leading to a square-shaped wetted area. In (c) it is $a = 11 \mu\text{m}$, resulting in a circular wetted area. (d) and (e) show the results of the corresponding numerical simulations with the lattice Boltzmann method with $a = 5$ and $11 \mu\text{m}$, respectively. The infiltration point has been centered in the figure but is not located in the center of the droplet's base: its dependence on local energy barriers can, indeed, produce uncertainty in its location.

propagates in a stepwise manner [Fig. 4(a)], and fronts at different positions on the sample or in different directions show a remarkable variation in their velocity (“dispersion”).

For the more striking case of the square-shaped wetted area ($a = 5 \mu\text{m}$) we show details of the wetting dynamics in Fig. 5(a). The front is here advancing from top to bottom and is slowing down while wetting occurs in a *zipping* manner: the time scale of the front for entering a new row is slow as already shown above [Fig. 4(a)], namely, typically $d/v \sim 1.4 \text{ ms}$, and the time scale for the filling of the once entered row itself is about 2 orders of magnitude faster, $\sim 0.01 \text{ ms}$.

In order to better reveal the physics of the wetting mechanism, we performed numerical simulations with a three-dimensional lattice Boltzmann algorithm [17] for single component multiphase fluids. Wetting properties with surface tension are introduced as explained in [18], leading to wetting angles comparable with those in the experiments. Geometrical structures are reproduced with the same aspect ratio as in the experiment. Similarly, in the large gap-width case $a = 11 \mu\text{m}$ (nearly) spherical wetted areas are observed [Fig. 3(e)], whereas in the case $a = 5 \mu\text{m}$ we observe square-shaped wetted areas; see Fig. 3(d). Also the zipping wetting behavior is reproduced in these simulations for $a = 5 \mu\text{m}$ [see Fig. 5(b)]. When repeating the simulations with a gap width $a = 2 \mu\text{m}$, we do not observe any lateral infiltration of the substrate and the CB state remains stable, again, just as experimentally observed.

How to explain the transition from CB to W ? The energy of a droplet in equilibrium on a substrate is monotonically increasing with the effective contact angle [12]. As a result, when the CB effective contact angle is higher than the W one, we would argue that the CB droplet always collapses

FIG. 4 (color online). Wetting front evolution for micropatterned surfaces with different gap width a . We show a case where $a = 5 \mu\text{m}$ (a) and a case where $a = 11 \mu\text{m}$ (b). In both cases, nine different experiments were carried out with the same sample. The position of the front has been normalized with respect to the pattern wavelength $d = a + w$, and time has been made dimensionless with t_0 as in Eq. (4). Note the difference in front speeds v in the two cases: in the small wavelength case (left) a *critical slowing down* ($v \sim 7 \text{ mm/s}$) induces large dispersion and *zipping* is revealed. The large wavelength case (right) is less dispersed and much faster, reaching velocities of $v \sim 7 \times 10^2 \text{ mm/s}$.

towards the W state. Anyhow, intermediate states with higher energy can be encountered [12]: they represent energy barriers to overcome, and work has to be done in order to induce the transition [3,12]. The bottom-view observations reveal that the microstructured surface is not wetted all at once, but the infiltration starts locally. In our case, this happens spontaneously after a few seconds, whereas in other cases (i.e., larger h) the infiltration can take longer and one may want to trigger it. Once the transition has started, how is it possible to theoretically understand the shape of the wetted area, the zipping, and the different involved time scales? For the dynamics of liquid moving in between the posts, both the free surface and wall interactions play a role. A small advancing displacement $dx \ll a$ of the interface within the posts would take place in favor of a gain in surface energy due to the reduction of liquid-gas interface ($\sigma_{lg}adx$) on the top of the pillars. This is a *pulling* mechanism for the transition that must be balanced with the energy *loss* to wet a small portion of hydrophobic wall ($\sigma_{lg}(2h+a)dx \cos\theta$, $\cos\theta < 0$). The overall energy gain is

$$dE_s = \sigma_{lg}adx + \sigma_{lg}(2h+a)dx \cos\theta. \quad (1)$$

The limit $dE_s \rightarrow 0$ characterizes a critical contact angle θ_c for the wetting properties above which the liquid can spread horizontally through the posts. For square posts and square geometry it is equal to

$$\cos\theta_c = -1 + \frac{2h}{2h+a}. \quad (2)$$

Note that in this equation there is no reference to the width w of the posts because we describe the horizontal filling, different from a simultaneous vertical collapse [1,12]. With this critical value, the energy gain (1) can be rewritten as

$$dE_s = \sigma_{lg}adx \left(1 - \frac{\cos\theta}{\cos\theta_c}\right), \quad (3)$$

where for $\cos\theta < \cos\theta_c$ no favorable propagation is expected, while in the other case, when $\cos\theta_c < \cos\theta < 0$, the propagation is energetically favored. For the two analyzed cases $a = 5$ and $11 \mu\text{m}$ we obtain $\theta_c = 101.54^\circ$ and 110.78° , respectively. As $\theta = 100^\circ$ for water on flat krypton, we thus understand that for gap widths smaller than $a = 4.2 \mu\text{m}$ the propagation to the W state is energetically not possible.

We can also understand the critical slowing down of the front close to the critical angle θ_c (Fig. 4). Therefore we have to identify the relevant time scale τ for the system and quantify its fluctuations with respect to the geometry. To do so, we estimate the energy cost in terms of dissipation and compare it with the change in surface energy of Eq. (3). With the small dimensions under consideration, flows can be regarded as laminar and viscous dissipation is dominant

as compared to flow inertia. A simple estimate for the rate of viscous dissipation per unit volume in a fluid with viscosity η is $\epsilon \approx \eta \dot{\gamma}^2$ [19], with $\dot{\gamma} \sim 1/\tau$ the characteristic shear rate. If we integrate it over the small volume $dV = ahdx$ and time lag τ , we obtain the viscous contribution for the energy as $dE_d \approx \epsilon \tau dV = \eta ahdx/\tau$. Balancing dE_s in Eq. (3) with dE_d , we deduce the time scale

$$\tau = \frac{t_0}{(1 - \frac{\cos\theta}{\cos\theta_c})} \quad (4)$$

with $t_0 = \eta h/\sigma_{lg} \sim 10^{-7}$ s for typical values of η , σ_{lg} , and $h = 10 \mu\text{m}$. Equation (4) reveals the origin of the critical slowing down of the front propagation, its dispersion, and the appearance of zipping: if $\theta \sim \theta_c$, the time scale τ of front propagation *diverges* as $\tau \sim 1/|\theta - \theta_c|$. Around this *critical point*, a small uncontrollable variation (imperfections of the microstructure, dust deposit) in the local wetting angle translates into a huge dispersion in the time scales, which is consistent with the experimental observation shown in Fig. 4(a). A flat front is slowly allowed to proceed further, and entering a new row perpendicular to the direction of the front can take up to milliseconds, whereas once this has happened, the row itself is filled on a faster time scale (zipping). In this way a square-shaped propagating wetting pattern emerges (see the case with $a = 5 \mu\text{m}$ in Fig. 3(b) where $\theta_c \sim 101.54^\circ$ and $\theta \sim 100^\circ$).

On the contrary, when approaching the other limit $\cos\theta/\cos\theta_c \ll 1$ [as in Fig. 3(c), where $\theta \sim 100^\circ$ and $a = 11 \mu\text{m}$, implying $\theta_c \sim 110.78^\circ$] the dynamics becomes more and more determined by the time scale t_0 itself [see Fig. 4(b)] and the propagation through the posts is expected to be smooth. In this limit it is the pure pulling mechanism of surface tension in Eq. (3) that dominates the spreading dynamics and is prevalent over wall effects [20]. For this reason, the geometrical properties of the lattice do not emerge and the front assumes an almost circular shape.

In conclusion, we have experimentally, numerically, and theoretically revealed the origin of zipping wetting behavior at the spontaneous breakdown of superhydrophobicity. We observed that the wetting process starts locally from a single point and then proceeds laterally, depending on a critical contact angle.

Close to this critical point the driving energy for the lateral filling reduces, the front propagation slows down through viscous effects, and zipping wetting is observed. As a consequence, the front propagates in a stepwise manner and square-shaped [21] wetted areas emerge. Although we have observed the origin of this zipping process, its dynamical details have not been characterized here and will be the object of a forthcoming paper [22].

The critical contact angle [Eq. (2)] can be calculated from the geometrical properties of the microtextured ma-

FIG. 5 (color online). The lateral zipping mechanism (left to right) close to the critical point ($\theta \sim \theta_c$). (a) Snapshots of the zipping mechanism recorded in an experiment with $a = 5 \mu\text{m}$ with the front propagation from top to bottom. (b) The results are also compared with snapshots from numerical simulations. (c) Numerical results for the front propagation (lines) in the lateral zipping process close to the critical point. From top to bottom we show the following cases: $\cos\theta/\cos\theta_c \sim 0.868, 0.890, 0.927, 0.945, 0.971$. The geometrical aspect ratio for the simulations is chosen to be the same as in the experiment with $a = 5 \mu\text{m}$, whose typical outcomes are also reported ($\circ$).

terial and is consistent with our experimental and numerical findings.

Our results are useful for the design and fabrication of microstructured surfaces with certain wetting properties: for given hydrophobic material and liquid, the post height and the gap width can simply be calculated to obtain some desired critical contact angle.

The next step will be to control the time scale of the local initiation point, characterize the dynamics of the zipping process, and extend our analysis to more complicated micropatterned structures, including three-dimensional ones.

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