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THE ZIPPING WETTING DYNAMICS AT THE BREAKDOWN OF SUPERHYDROPHOBICITY

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Summary Under some conditions water droplets can completely wet micro-structured superhydrophobic surfaces. The *dynamics* of this rapid process is investigated with ultra-high-speed imaging. Depending on the scales of the micro-structure, the wetting fronts propagate smoothly and circularly or – more interestingly – in a *stepwise* manner for a smaller periodicity of the microstructure. The latter phenomenon leads to a growing *square-shaped* wetted area: liquid laterally enters a new row on a slow timescale of milliseconds, once it happens the row then fills itself towards the sides in microseconds (*"zipping"*).

INTRODUCTION

Micro-structured materials can exhibit superhydrophobic behaviour with effective contact angles of 160^o and even higher. These large contact angles lead to a prominent low friction mechanism (the so-called Lotus effect), thereby providing a wide range of useful and interdisciplinary applications. The Cassie's law [1] describes such a state of composite wetting (also called "Cassie Baxter" state): an effective contact angle for the droplet is determined by surface heterogeneities, i.e. surface posts alternating with air pockets trapped below the droplet (Fig. 1a-b). In some cases, this superhydrophobicity can break down [2]. After some initial infiltration the fluid can spread and the droplet impregnates through the micro-structure, yielding the smaller contact angle of the so-called "Wenzel state" [1] (Fig. 1 d-e, c). Despite good understanding and extensive applications of a pure Cassie-Baxter or a pure Wenzel state, the detailed dynamics and physical mechanism of Cassie-Baxter to Wenzel transition are challenging research topics and still remain puzzling [2, 3]. In this paper, the details of the transition are studied from the experimental, numerical, and theoretical point of view. Micro-structured surfaces with regular arrays of posts are used and allow a quantitative understanding of the transition in terms of the geometry [4] and liquid-solid interactions [5].

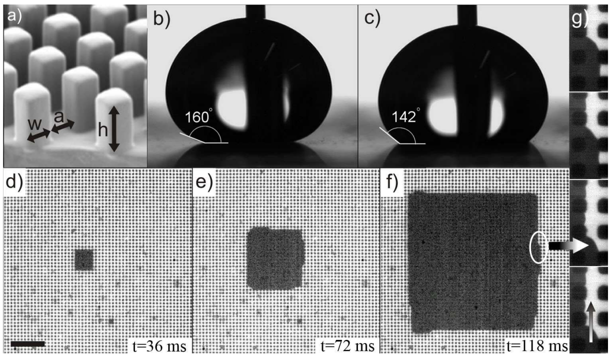

Figure 1. Our experimental observation of the fast transition from a Cassie-Baxter to a Wezel state. A drop deposited on a micro-patterned surface (shown in (a)) can stay suspended with air pockets trapped in the grooves underneath the liquid, revealed in (b). At some point the Cassie-Baxter state spontaneously breaks down, resulting in a lower contact angle shown in (c). The drop then homogeneously wets the substrate—indicated by the dark areas in (d) from a bottom view. The bar in (d) marks a length scale of $100\mu m$. (d)-(f) are the snapshots of the fast dynamics of this transition in a stepwise manner in milliseconds. The detailed *zipping* process of (f) is enlarged in (g), filling in microseconds.

RESULTS AND DISCUSSION

Experiments

We measured the filling dynamics during the breakdown of the Cassie-Baxter state with a tiny droplet of Milli-Q water deposited on micro-structured hydrophobic surfaces. The substrates consist of square pillars arranged on a regular square lattice with height $h = 10\mu m$, width $w = 5\mu m$, and an inter-spacing a between the pillars varying from 2 to 26 μm (see Fig.1a). These micro-patterns are precisely fabricated through a micro-molding technique. The substrates used are thin translucent polymer films, including a block-copolymer,"kraton" (styrene-butadiene-styrene) and a rubbery polymer, PDMS (polydimethylsiloxane). The observations are performed from the bottom of the film via an inverted optical microscopy (see Fig.2a). When water impregnates between pillars, the image color turns to filled black. A high speed camera was used, mostly with a sampling rate of $10\ 000$ fps, to capture the rapid filling dynamics of the transition.

Theory and Phenomenology

After a liquid infiltration between the pillars, an energy argument can be established to introduce a critical length-scale ratio of the gap/height value, $(\frac{a}{h})_c$, above which the filling takes place. The theory is based on a balance of the energy gained by the reduction of the liquid-gas interface on the top of the pillars and the energy lost in the wetting of the microstructure, finally resulting in

$$\left(\frac{a}{h}\right)_c = \frac{2}{\cos\theta + 1} - 2$$

with θ the wetting angle on the flat surface of the same material. When the control parameter a/h approaches this critical value $(\frac{a}{h})_c$ the fluid front propagating from the Cassie-Baxter to the Wenzel state experiences a slowing down: the main front is almost stopped in between the pillars. In this regime the filling mechanism is observed to be a zipping that liquid fills the structured material perpendicular to the direction of the main front, revealed in Fig.1 g. This zipping-wetting front reflects the geometrical arrangement of the pillars, as shown in Fig.1 d-f. In the other limit, when a/h is much larger than the critical value, a smoother propagation is observed: the filling front is faster and is able to fill the micro-structure with the development of a circular wetting front (see Fig.2) [2].

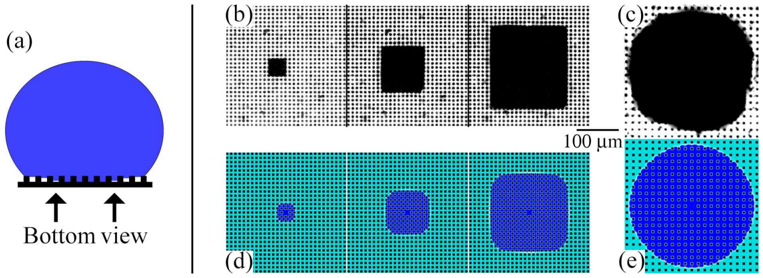

Figure 2. (color) Bottom views of the front evolution of the transition, as sketched in (a). In (b) three snapshots for the case with $a = 5\mu m$ are shown, leading to square-shaped wetted area. In (c) a circular wetted area for $a = 11\mu m$. Figures (d) and (e) show the corresponding simulation results by the Lattice Boltzmann method with $a = 5\mu m$ and $11\mu m$, respectively.

Numerical Simulations

We performed numerical simulations with a three-dimensional (3D) lattice Boltzmann algorithm for single component multiphase fluids to understand the fast transition observed experimentally [6]. Geometrical structures and wetting properties are parametrized according to the experimental values. Consistent with the experimental observations, simulation results show spherical wetted areas in the large a/h case whereas square-shaped wetted areas for smaller values of a/h (Fig.2). The pathway of the single zipping filling shown in Fig. 1 g is also reproduced in these simulations [2]. In using the mesoscale algorithm, one has no need to track the moving interfaces when simulating multiphase flows. Thus, these numerical simulations offer insight into the zipping-wetting dynamics, which is a 3D complex problem involving multiple timescales [2].

CONCLUSIONS

We have experimentally, numerically, and theoretically revealed the origin of zipping wetting behavior at the breakdown of superhydrophobicity, namely, the existence of two different timescales. We observed that the wetting process starts locally from a single point and then proceeds laterally. Close to a critical point the front propagation slows down due to viscous effects, and zipping wetting is observed. As a consequence, the front propagates in a stepwise manner and square-shaped wetted areas emerge. Ongoing extension of this work includes the investigation of scaling relations for the wetting front velocity and the effects of geometry (i.e., a, h, w, pillar shapes, and micro-patterns) and the wetting properties.

References

[1] A. B. D. Cassie and S. Baxter, *S. Trans. Faraday Soc.* **40**, 546-551 (1944); R. N. Wenzel, *Ind. Eng. Chem.* **28**, 988-994 (1936).
[2] M. Sbragaglia, Alisia M. Peters, Christophe Pirat, Bram M. Borkent, Rob G. H. Lammertink, Matthias Wessling, and Detlef Lohse.: Spontaneous Breakdown of Superhydrophobicity. *Phys. Rev. Lett.* **99**:156001 (2007); C. Pirat, M. Sbragaglia, A. Peters, B. Borkent, R. Lammertink, M. Wessling and D. Lohse, submitted (2008).
[3] S. Moulinet and D. Bartolo.: Life and Death of a Fakir Droplet: Impalement transitions on superhydrophobic surfaces. *Euro. Phys. E* **24**:251–260 (2007).
[4] T. Cubaud and M. Fermigier, *Europhys. Lett.* **55**, 239-245 (2001).
[5] Courbin et al., *Nature Materials* **6**,661-664 (2007).
[6] R. Benzi, L. Biferale, M. Sbragaglia, S. Succi, and F. Toschi, *Phys. Rev. E* **74**, 021509 (2006).