

# Transition from Heterogeneous to Homogeneous Regime in Disordered Superhydrophobic Surfaces\*

Corrado Boragno,<sup>†</sup> Francesco Buatier de Mongeot, Daniele Chiappe, Francesco Gagliardi, and Andrea Toma  
*Dipartimento di Fisica, Università di Genova, via Dodecaneso 33, Genova 16146, Italy*

Roberto Felici  
*ESRF, rue Jules Horowitz, Grenoble, France*

Alessandro Garibbo  
*Selex Communications, via Pieragostini 80, Genova 16151, Italy*  
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In Superhydrophobic systems, a spontaneous transition from heterogeneous to homogeneous regime can occur in time. This transition can hinder the sliding motion of a water drop deposited on the surface, then hampering many applications of such coatings. In this paper, we present a detailed study of this phenomenon on a new kind of Superhydrophobic surfaces, characterized by a strong spatial disorder. We demonstrate that disorder can help to prevent the transition, which assumes a peculiar behavior. [DOI: 10.1380/ejsnt.2010.275]

Keywords: Solid-liquid interfaces; Water; Wetting

## I. INTRODUCTION

During the last decade, much effort has been devoted to mimic the extreme hydrophobic properties of various bio-surfaces such as plant leaves or insects wings and legs [1–3]. Many potential applications of artificial Superhydrophobic surfaces are currently under investigation, like for example self-cleaning coating for clothes or glass, antibiofouling paintings, drop transport on lab-on-chip devices and turbulent drag reduction [4, 5]. All these surfaces share two common features: they are made of (or covered by) hydrophobic materials, and are textured at the micron and/or sub-micron scales. Water drops either bounce or roll off these water-repellent surfaces, making liquid deposition almost impossible.

These properties are due to the so-called “fakir effect”: the water drop stays on top of the asperities present on the surface and then air is trapped at the interface. The actual contact area between liquid and solid is very small and then the “adhesion” of the drop to the surface is small too. However, in many artificial Superhydrophobic surfaces, a spontaneous transition from this status (called heterogeneous regime) to an homogeneous regime (where water wets completely the interface) can occur. In the homogeneous regime, the water drop is “impaled” on the asperities and then it cannot further move.

As demonstrated in recent papers [6, 7], this transition is quite fast: in few milliseconds, the contact area becomes completely wet, since the water front can advance at a velocity of 1 m/sec or more. The occurrence of this transition is the major obstacle to the large scale application of Superhydrophobic coatings. In artificial systems, the transition can be induced by structural defects, or by pressure or by the impact velocity of the falling water

drop.

In this contribution, we present a study of this phenomenon done on a new kind of polymeric Superhydrophobic coatings, demonstrating that spatial disorder can help to prevent or at least to retard the transition between the two regimes.

## II. EXPERIMENTAL

The samples have been obtained by a one-step procedure: a film (around 100  $\mu\text{m}$  thick) of poly(dimethyl)siloxane PDMS is spun on a glass piece. PDMS is a transparent elastomeric polymer which exhibits a contact angle of about  $110^\circ$  on a flat configuration. On this film, a polycarbonate membrane with spatially disordered pores is imposed. These membranes are commonly used as filters in biological research. By capillarity, PDMS enters the membrane pores. After a time, the system was cured at a typical temperature of  $80^\circ\text{C}$  for 2 hours. Finally, the PDMS replica was manually detached from the membrane or the membrane was dissolved in chloroform.

We prepared samples using membranes with different pore size, in the range 0.8-8  $\mu\text{m}$ . In the following, only results obtained with 2  $\mu\text{m}$  or 3  $\mu\text{m}$  pore size membranes will be presented.

The optical measurements have been done with a custom system: a video camera, positioned laterally to the sample, allow us to measure the contact angle of a water sessile drop, dispensed onto the sample by a syringe pump. The sample is posed directly onto the support of a digital microscope, by which we measured from the bottom the wetted area. A fast digital camera (1000 fps) was eventually used to measure the impact of a water drop on the surface.

## III. RESULTS AND DISCUSSIONS

In Fig. 1 an image of a sample prepared with a 2  $\mu\text{m}$  membrane is presented. The morphology is character-

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<sup>†</sup>Corresponding author: corrado.boragno@unige.it

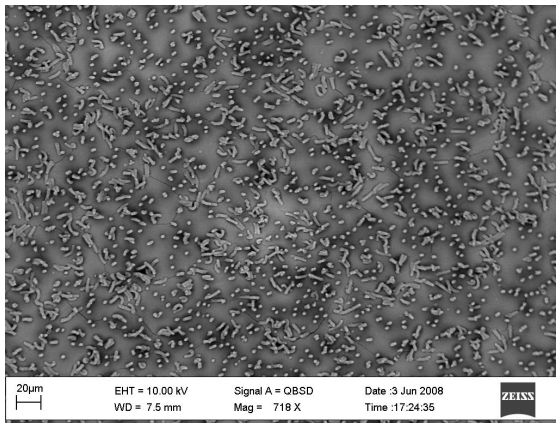


FIG. 1: A SEM image of a 2  $\mu\text{m}$  sample.

ized by pillars, having an height of 10  $\mu\text{m}$ , randomly distributed on the surface. The pillar density is  $2.2 \cdot 10^6 \text{ cm}^{-2}$ .

Looking at the SEM image, we recognize at least three different arrangements of the pillars: some are vertically aligned (covering  $\sim 2.5\%$  of the total area), others are bent towards the surface ( $\sim 8.5\%$  of the total area) or arranged in bundles ( $\sim 5\%$  of the total area). Between asperities, the PDMS surface appears flat ( $\sim 84\%$  of the total area). Many pillars are bent towards the surface because their aspect ratio length/diameter is around 5, a value close to the critical one for PDMS.

The roughness ratio (i.e. the ratio of the actual area of the solid surface to its projection area) can be calculated to be around 1.4, by considering ideal cylinders vertically or horizontally aligned.

When a water drop is dispensed on such a surface, it stays in the heterogeneous regime. The static contact angle is  $166^\circ \pm 1.5^\circ$ . By observing the water drop from the bottom (Fig. 2), we can follow in time the evolution of the wet area, which is zero at the beginning and then enlarges invading all the contact area.

The wet area appears black when observed in reflection mode, as the light originated from the digital microscope illuminator is more effectively transmitted through the sample.

As evidenced in the figure, the wet area evolves in time in an irregular way: starting from one point, the water front proceeds fast in one direction, then it stops for a while, then it restarts along another random direction. Our actual time resolution with the digital microscope is limited to 1 sec, then we cannot measure the real velocity of the water front. The wet area invades all the contact area in a time depending on the particular samples, but which is of the order of 1000 sec. At the end of the process, non-wetted regions are still present at the interface.

At the end of the wetting process, the static contact angle assumes the new value of  $156^\circ \pm 1.5^\circ$ .

The observed transition is quite different from that reported by other authors [6, 7]: in our case, the time needed to complete the wetting process can be long as 1000 sec, while in other cases it is completed in few milliseconds; the wet area in [6, 7] expands in a compact way, i.e. starting in a point it enlarges in all directions with a more or less constant speed, which is in contrast with the

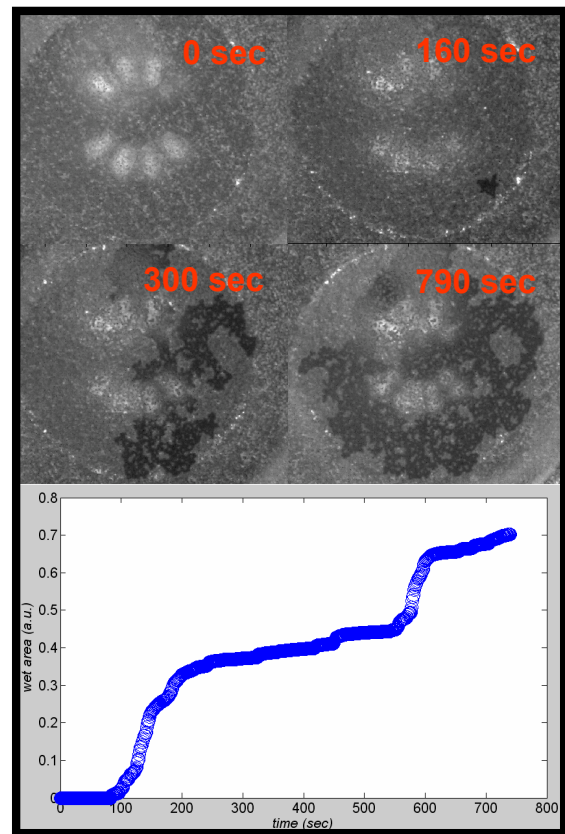


FIG. 2: Top: A series of images acquired with a digital microscope during the transition from the heterogeneous to homogeneous regime in a 2  $\mu\text{m}$  sample. Size view  $600 \times 600 \mu\text{m}^2$ . Bottom: time evolution of the wetted area, normalized to the contact area.

behavior we reported in Fig. 2; finally, we always observed un-wetted regions at the end of the wetting process, while in [6, 7] the interface appears completely wet.

In order to explain our results, we hypothesize that spatial disorder plays a crucial role in the Superhydrophobic properties of our samples. In fact, the sample studied in [6, 7] are made of a regular array of pillars, arranged in a square or triangular symmetry. A critical value of the distance between pillars exists to allow the water front to invade the contact area. This value depends on geometry and on the contact angle measured on the pristine material. Applying these concepts to our case, we found that the critical value is around 10  $\mu\text{m}$ ; but looking to Fig. 1, it is recognizable that many pillars have a mutual distance of the same order and moreover that the bended pillars or the bundles can produce a sort of channels with an aperture less than 10  $\mu\text{m}$ .

In this framework, we suggest that the wetting process in our case occurs in the following way: after a water drop is deposited on the surface, it starts to percolate the interface, like described in [7]. But the percolation is hindered by the presence of the bent pillars and of the bundles. When the water front touches the base, also the horizontal wetting proceeds with difficulty, again for the presence of the same obstacles.

This complicate wetting process, quite different from the one observed in regular arrays, requires a long time

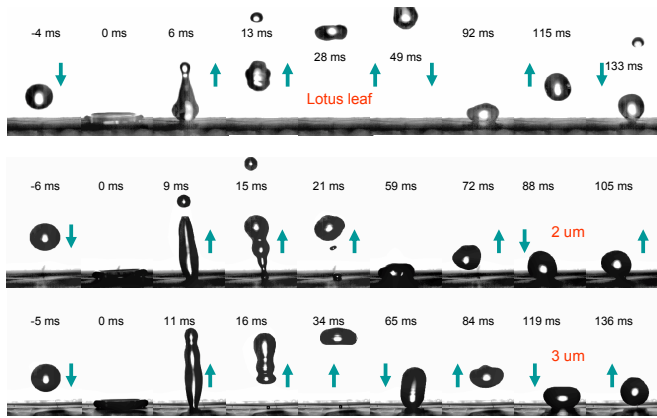


FIG. 3: Drop impact events recorded by a fast camera (1000 fps) on 3 different samples: first row: natural Lotus leaf; second row:  $2\ \mu\text{m}$  sample; third row:  $3\ \mu\text{m}$  sample. The arrows indicate the direction of motion.

to be completed.

If disorder plays an important role in the wetting process, what is its effect on the impact of a water drop?

In Fig. 3 we report a preliminary analysis of such an experiment done on a Lotus leaf (row a) and on two samples, the first done with a pore size of  $2\ \mu\text{m}$  (row b) and the last with a pore size of  $3\ \mu\text{m}$  (row c). The drop velocity is  $0.8\ \text{m/sec}$ . The  $3\ \mu\text{m}$  samples have the same pillars density than the  $2\ \mu\text{m}$  membranes and a morphology quite similar to that reported in Fig. 1, the only difference being that the number of bent pillars is smaller than in the other case. (50% on the  $2\ \mu\text{m}$  membranes, 20% in the  $3\ \mu\text{m}$  membranes).

It is evident that the Lotus leaf presents the best behav-

ior: the water drop bounces four times before to stop on the surface, and it reaches an higher height. In the  $2\ \mu\text{m}$  sample, the drop stops after 2 bounces, while 3 bounces are necessary for the  $3\ \mu\text{m}$  sample. In this last case, a small portion of the drop is impaled on the surface after the first bounce, but it is re-adsorbed at the second bounce.

Roughly speaking, these measurements suggest that now the spatial disorder (more relevant in the  $2\ \mu\text{m}$  sample respect to the  $3\ \mu\text{m}$  one) seems to depress the Superhydrophobic behavior, that is amplified by an higher density of upright pillars. More, the best performance has been measured on the natural system, where a double-roughness (in micro/nano scale) is present [8].

A more detailed study will be necessary to address this important point.

#### IV. CONCLUSIONS

We reported on a study of the Superhydrophobic properties of a new kind of polymeric surfaces, which can be easily produced with a one-step procedure. The spatial disorder which characterizes these surfaces can retard the development of the wetting process during the transition from the heterogeneous to the homogeneous regime, but it seems to be less efficient when a water drop impacts on the surface.

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