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Research paper

Contact angle and impinging process of droplets on partially grooved hydrophobic surfaces

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HIGHLIGHTS

- We investigate droplet resting and impinging on partially grooved PDMS surface.
- The contact angle parallel to grooves is larger than the perpendicular one.
- An impinging droplet would recoil faster in the direction parallel to grooves.
- More groove area or smaller droplet will make the anisotropy more significant.

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ABSTRACT

Wetting states of droplets on partially micro-grooved surfaces were investigated. Grooves were fabricated using soft lithography and the width of the grooves was smaller than the droplet diameter. On the partially micro-grooved surfaces, the apparent contact angle parallel to the grooves is larger than the one on the smooth surface, while the microstructures have little effect on the contact angle perpendicular to the grooves. Increasing the fraction of the grooved area and the surface energy of the surface will result in a more anisotropic droplet. When a droplet impinged upon these partially grooved surfaces, the spreading process was similar to that on a smooth surface. However, the recoiling process was found to be quite anisotropic. The grooves enhanced the recoiling velocity in the direction parallel to the grooves while hindering the recoiling process in the perpendicular direction. The recoiling process will become more anisotropic by increasing the fraction of the grooved area. The effect of the grooves on both the contact angle and the impinging process is independent of the groove width scale and is only dependent on the fraction of the grooved area in the Cassie state.

1. Introduction

Superhydrophobic surfaces, which are composed of low surface energy materials and micro/nano scale structures, have many useful properties and applications: water repellency [1], self-cleaning [1–3], drag reduction [4–7], anti-icing [8,9], enhancing condensation heat transfer [10,11], biomolecular manipulation at surface/interface [12–15], etc. When a droplet rests on a superhydrophobic surface, equations based on the Wenzel and the Cassie models [16,17] have been widely used to analyze the apparent contact angle. The Wenzel model refers to the wetting state that the liquid were trapped in the microstructures, and the apparent contact angle (θ_W) is related to the contact angle on the smooth surface (θ) in the manner: $\cos\theta_W = r\cos\theta$, where r is the roughness factor. In the Cassie model, the fluid is supported by the peaks of the roughness resulting in the air–water interfaces in the cavities, and the apparent contact angle (θ_C) is $\cos\theta_C = -1 + \varphi_s(1 + \cos\theta)$, where φ_s is the solid fraction. However, strict limits cannot be ignored for these two equations which can only be used to analyze isotropic surfaces [18–23]. It is eventually the small contact line rather the contact area that determines the apparent contact angle [18,19]. When a droplet rests on a grooved surface, the surface is anisotropic and the apparent contact angle varies along the contact line [22,24–26]. Neither the Wenzel nor the Cassie model is suitable to

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be used any longer. Chen et al. [24] and Zhao et al. [26] studied the droplet on a fully grooved surface. They showed that the apparent contact angle parallel to the groove direction was smaller than the one perpendicular to the grooves, and both of them were larger than the intrinsic value. This observation was attributed to the fact that the droplet would be squeezed and pinned in the direction perpendicular to the grooves while being stretched in the parallel direction. Choi et al. [27] observed the three-phase contact line on the grooved surfaces using an electron microscope with non-volatile organic liquids. Their experimental studies illustrated that the differential area fraction of the solid substrate was the most important factor to determine the apparent advancing and receding contact angles. The distortion of the three-phase contact line is not the key factor that leads to the differences between Cassie's prediction and the measured values.

The impingement of a droplet on superhydrophobic surfaces is also well studied [8,23,28–30]. When a droplet impinges on a superhydrophobic surface, it spreads rapidly to the maximum diameter, and then recoils. During the recoiling process, a vertical jet forms when the kinetic energy is large enough to overcome the gravitational potential energy. In the end, the droplet would rebound from the surface. The contact time can be estimated by $t = (2.6 \pm 0.1)\ (\rho R_0^3/\gamma)^{1/2}$, is independent of the impinging velocity, where t, ρ, R_0 and γ represent the contact time, the density of the liquid, the droplet radius, and the gas–liquid surface tension, respectively [31,32]. Pearson et al. [33] conducted a series of experiments on the grooved hydrophobic surfaces with a wide range of Weber numbers ($We = (\rho R_0 V_i^2)/\gamma$, where V_i is the impinging velocity of the droplet). The droplet would splash at high imping velocity whereas vertical jets were observed to rebound from the surface at low impinging velocity. In their experiments, the maximum spreading diameter parallel to the grooves is larger than the one perpendicular to the grooves. Kannan et al. [28] reported that the droplet would spread slower in the perpendicular direction on the grooved surface.

The wetting characteristics of droplets on the fully grooved surfaces have been studied extensively, while it has been barely studied on the partially grooved surfaces. Here the partially grooved surfaces refer to the surfaces on which the width of the grooved area is much smaller than the droplet diameter. This kind of surface is very common in nature, e.g., scars on a smooth surface, a thin gap between two objects and so on. In this paper, the partially grooved hydrophobic surfaces were fabricated using soft lithography. A fully grooved surface and a superhydrophobic surface with isotropic microstructures were also tested for comparison. First, we analyzed the difference of the apparent contact angles in the directions parallel and perpendicular to the grooves. Then, we investigated the spreading and recoiling processes of an impinging droplet on these surfaces using a high speed camera.

2. Experiment and simulation method

2.1. Fabrication of the surfaces

The micro-grooved surfaces were fabricated from Sylgard 184 PDMS(Dow Corning) using standard soft lithography technique. First, photomasks with desired groove patterns were designed and printed on high-resolution transparency at 5080 dpi. The transparency was then served as a mask for contact photolithography. The positive photoresist (S1813, MICROPOSITTM photoresist, Shipley Co.) was spin coated on silicon wafer (100). The photomask was aligned in close contact with the wafer and an ultra-violet light source was used to expose the photoresist (model 100UV30S1, Karlsus Inc.). The exposed photoresist was dissolved in a solution of MICROPOSIT 351 developer (J. T.Baker Co.) with water in a 1:4 ratio. Patterned groove ribs with depth 30 μm, were left on the wafer and served as a mold. Liquid pre-polymer PDMS with curing agent (5:1 weight ratio) was cast onto the master. The PDMS was cured in an oven at 70 °C for 7 h. A fresh PDMS stamp with features opposite to the master was fabricated by peeling the PDMS stamp off the master substrate. More details about this technique can be found in Refs. [4,34,35] .

The smooth PDMS surface is hydrophobic with contact angle 101.8°, and the advancing and receding contact angles are 110° and 64°, respectively. The grooved PDMS is shown in Fig. 1. On the partially grooved surface, rather than introducing grooves to the entire surface, only a small area was grooved. Two groups of partially grooved surfaces were fabricated. In the first group, between two and thirty two grooves, 50 μm wide (w) and spaced 50 μm (s) apart, were introduced in the PDMS, and the width of the overall grooved area ($n(w + s)$) varied from 0.2 mm to 3.2 mm, where n is the groove number. In the other group, the width of the grooved area was kept constant: $n(w + s) = 800$ μm and two to ten grooves were introduced in the PDMS with width (w) and spacing(s): $w = s = 200$ μm, 100 μm, 67 μm, 50 μm, 40 μm, respectively. A fully grooved surface with grooves 50 μm wide, spaced 50 μm apart was also fabricated. The depth of the grooves (h) is 30 μm for all grooved surfaces.

An isotropic surface coated by a commercial superhydrophobic coating, Ultra-Ever Dry [36], was also made for comparison. Two components were used: a bottom coating and a top coating. The bottom coating was first sprayed on a glass slide and dried for 3 h. Then the top coating was sprayed and dried 3 h at 20 °C. The microstructures of the coated surface are shown in Fig. 1d. The surface is coated with micro particles with diameter ~35 μm and the average height of the structures is ~20 μm. The coating is extremely superhydrophobic, with the contact angle over 160° and contact angle hysteresis <2°.

2.2. Experimental method

The contact angle in the direction perpendicular ($CA_{\perp}$) and parallel ($CA_{\parallel}$) to the grooves were measured using telescopic goniometer with a Gilmont syringe. The fluid was Deionized water. In the experiments, the droplet was released 5 mm above the surface. Measurements were conducted at least 5 times.

Here we also applied Surface Evolver, a public domain software package written by Brakke [24,25,37], to investigate the equilibrium shape of the droplet on the partially grooved surfaces. The Surface Evolver is based on minimizing the free energy of the system to obtain the equilibrium drop shape and has been widely used to analyze the fluid interface [24,38]. The volume is constant without considering contact angle hysteresis. All lengths were scaled by the capillary length, $L_c = \sqrt{\gamma/(\rho \cdot g)} = 2.7$ mm (volume were scaled by L_c^3), where g is the acceleration due to gravity. More details can be found in the supporting information and ref [24].

A series of experiments have been performed to see how the droplet spreads and recoils on the grooved PDMS surfaces. The schematic diagram of the experimental apparatus is shown in Fig. 2. A 1024 × 1024 high speed camera (MotionXtra NX-4) equipped with a 50 × microscope lens was used to observe the impinging process with two different camera views: the bottom view captured by the camera placed under the surface; the side view captured by the camera placed beside the surface horizontally. The recording rate was 3000 fps, and exposure time was 333 μs. A LED lighting source was placed right behind the droplet and faced the lens. The distance between the droplet and the microscope lens was 28 mm. At this distance, the lens could focus