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**FROM STICKY TO SLIPPERY DROPLETS:
DYNAMICS OF CONTACT LINE DE-PINNING ON SUPERHYDROPHOBIC
SURFACES**

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ABSTRACT

This study explores how surface morphology affects the dynamics of contact line de-pinning of an evaporating sessile droplet on micro-pillared superhydrophobic surfaces. The result shows that neither a liquid-solid contact area nor an apparent contact line is a critical physical parameter to determine the de-pinning force. The configuration of a contact line on a superhydrophobic surface is multi-modal, comprised of both two-phase (liquid-air) and three-phase (liquid-solid-air). The multi-modal state is dynamically altered when a droplet recedes. The maximal three-phase contact line attainable along the actual droplet boundary is found a direct and linear parameter that decides the de-pinning force on the superhydrophobic surface.

Patterned hydrophobic surfaces have attracted much interest for the extreme water repellent property, typically exhibiting high contact angles for water droplets ($>150^\circ$) and called superhydrophobic [1, 2]. Although the apparent contact angles on superhydrophobic surfaces are similar, they can behave either slippery or sticky, differentiated by the pinning phenomena of the moving droplet on the surfaces. One example from nature is the phenomena called the “lotus effect” vs. “petal effect” [3]. On a lotus leaf, a water droplet rolls off very easily with little contact angle hysteresis. Such slippery surfaces have exhibited great applicability in self-cleaning [4], hydrodynamic friction reduction [5], anti-icing [6], anti-corrosion [7], thermal/energy system [8], biotechnology [9], and micro- and nano-devices [10]. Compared to the lotus leaf, a water drop on a petal surface does not roll off even if the petal surface is turned upside down. Such sticky superhydrophobic surfaces have potential applications in spraying/coating [11], ink-jet printing [12] liquid transportation/analysis [13] and microfluidic devices [14]. Therefore, it is of great significance to understand the physical mechanism of the pinning/de-pinning dynamics of a droplet on superhydrophobic surfaces for such tailored applications.

The pinning phenomena of droplets are affected by many surface parameters including chemical heterogeneity, physical structures, and interfacial wetting states [15-19]. As for superhydrophobic surfaces, the influence of surface structures on the droplet pinning has been studied from the perspective of both kinetics and dynamics [20-25]. However, the results are not consistent and the critical factor that would determine the pinning mechanics has not been clearly understood yet. Moreover, the direct mechanism of how the surface structures regulate the de-pinning dynamics on superhydrophobic surfaces has not been revealed much. In this letter, we report an advanced understanding of the pinning/de-pinning mechanism on superhydrophobic

surfaces by investigating an evaporating sessile droplet as a dynamics model, and propose a new physical criterion to evaluate the stickiness/slipperiness of superhydrophobic surfaces from the perspective of surface morphology.

When a droplet evaporates on a substrate, the droplet boundary is initially pinned to the substrate. Therefore, the contact radius of the droplet remains constant while the contact angle gradually decreases. Such a pinning mode then transits to a de-pinning mode with a decrease of contact radius, as illustrated in Fig. 1. The droplet pinning lasts until an initial quasi-equilibrium contact angle reaches a receding contact angle. The unbalanced force due to the change of contact angle reflects the de-pinning force acting on the droplet boundary, which can be expressed as [26]

$$F_d = \sigma (\cos \theta_r - \cos \theta_e), \quad (1)$$

where σ is the surface tension of liquid ($\sigma \approx 72$ mN/m for water at 23°C in this work), θ_r is a receding contact angle, and θ_e is an initial quasi-equilibrium contact angle (Fig. 1).

To study the correlation between the structural parameters of a superhydrophobic surface and the de-pinning force, we prepared a square array of micro-pillars with systematically varied array densities on silicon substrates (Fig. 2) [27]. The micro-pillar patterns have the same diameter (5 μm) and height (25 μm), but different spaces between them (5, 10, 20 and 50 μm). After a Teflon hydrophobic coating, they make liquid droplets sit on the surfaces all in a partial wetting (Cassie) state with the contact angles greater than 150° [28], whereby the liquid-solid contact area fractions vary from 0.20, 0.09, 0.03, to 0.01, denoted as $\Phi 0.20$, $\Phi 0.09$, $\Phi 0.03$, and $\Phi 0.01$, respectively. A polished silicon substrate with a Teflon coating was also tested as a control, denoted as $\Phi 1.00$. Water droplets of ~ 4 μL were evaporated on the surface samples at a room condition (23 \pm 1°C, 32 \pm 1% in humidity, and atmospheric pressure). The profiles of the

evaporating droplets, including the contact angle and contact radius, were first measured with a goniometer system. Fig. 3 shows the initial and receding contact angles of a water droplet on each surface, and the resultant de-pinning forces calculated according to Eq. (1), with respect to the liquid-solid contact area fraction (Φ). The result shows that the de-pinning force declines dramatically with the decrease of the liquid-solid contact area. It even approaches zero on the $\Phi 0.01$ sample. However, the decrease rate is not linear with respect to the contact area (Φ). Moreover, on $\Phi 0.20$ and $\Phi 0.09$ samples, the de-pinning forces are greater than that on a planar surface ($\Phi 1.00$), despite the less liquid-solid contact area. It indicates that superhydrophobic surfaces can cause larger de-pinning force than a planar surface and the liquid-solid contact area fraction (Φ) is not a direct (linear) factor that determines the de-pinning force.

We further utilized a reflection interference contrast microscopy (RICM) technique to directly observe the droplet contact line and the liquid-solid interface (Fig. 4) [29]. For this experiment, transparent surface samples were prepared on polydimethylsiloxane (PDMS) substrates by replication [27]. Unlike the macroscopic apparent droplet boundary typically viewed as a simple circle, the RICM image reveals that the microscopic actual droplet boundary on the superhydrophobic surfaces is rugged and constituted by two parts: two-phase (liquid-air) and three-phase (liquid-solid-air) contact lines. During the evaporation process, the three-phase contact line at the droplet boundary is dynamically distorted [15]. Figs. 5(a-j) show the evolution of the actual droplet boundary during the evaporation. In the beginning, the three-phase contact line on most pillars occupies about 3/4 of the circular pillar perimeter (e.g., Pillars B and C in Fig. 5(a)). However, on the pillars where the droplet boundary veers off its direction across them (e.g., Pillar A in Fig. 5(a)), the three-phase contact line elongates until it covers the whole periphery of the pillars. Then (e.g., after 420 seconds in Fig. 5(b)), the three-phase contact line

begins to recede crossing the top surface of the pillars and eventually detaches. Figs. 5(c-j) show the sequential de-pinning progress of the three-phase contact line from Pillar A to B to C [30]. Fig. 5(k) summarizes the transitional progress in terms of the normalized length ratio of the three-phase contact line to the circular pillar perimeter. For Pillar A, the normalized value remains constant during the pinning mode and then gradually decreases after de-pinning. For Pillars B and C, it increases slowly in most of the pinning period, and then rapidly increases to the maximum (approximately unity, i.e., being equal to the circular perimeter of the pillar top) at the transition point from the pinning to de-pinning mode. After de-pinning, it abruptly drops to zero. Based on the observation that the onset of de-pinning occurs when the three-phase contact line reaches the maximum, we correlated de-pinning force to the maximal three-phase contact line. To account for varying droplet sizes, a maximal three-phase contact line normalized for an apparent droplet boundary is defined as,

$$\delta = \frac{\sum_{i=1}^n l_i}{L_{boundary}}, \quad (2)$$

where n is the total number of the solid protrusions along the actual droplet boundary, l_i is the length of maximal three-phase contact line on the individual solid protrusion at the boundary, and $L_{boundary}$ is the length of the macroscopic apparent droplet boundary (i.e., $2\pi R$). On the micro-pillared superhydrophobic surfaces, the maximal three-phase contact line on each circular pillar reached nearly equal to the perimeter of the top surface. In such a case, the normalized maximal three-phase contact line (δ) is reduced to

$$\delta = \frac{\pi d}{\lambda}, \quad (3)$$

where d is the diameter of a circular micro-pillar, and λ is the pitch between pillars. According to this analysis, the normalized maximal three-phase contact line (δ) for pillar-type structures is determined by the pitch between solid pillars (λ) and the perimeter of each pillar (πd).

Fig. 6 shows the de-pinning force drawn for the new surface parameter δ on both the superhydrophobic surfaces and a planar hydrophobic surface. The result shows that the de-pinning force exhibits good linearity with δ . On a planar surface ($\Phi 1.00$), the δ is equal to unity since the length of maximal three-phase contact line is the same as the perimeter of a droplet boundary. On superhydrophobic surfaces, when δ is greater than unity, such as for the $\Phi 0.20$ and $\Phi 0.09$ samples, a higher de-pinning force is observed than that on a planar hydrophobic surface. It suggests that the micro-pillared superhydrophobic surfaces of $\delta > 1$ behaves as a stickier surface than a planar hydrophobic surface. On the contrary, if δ is less than unity, such as $\Phi 0.03$ and $\Phi 0.01$ samples, a lower de-pinning force is measured on the superhydrophobic surfaces, suggesting that the micro-pillared superhydrophobic surfaces of $\delta < 1$ turn to be slippery compared to a planar hydrophobic surface. McCarthy et al. have commented the importance of three-phase contact line and its pinning effect on contact angle hysteresis (the difference between advancing and receding contact angles) [23-25]. However, the three-phase contact line referred in their study represents a static and apparent one, instead of a dynamic and actual three-phase contact line. Such static and apparent surface parameters are inappropriate to understand the dynamic behaviours of the contact line de-pinning on the superhydrophobic surfaces that impose the multi-modal multi-phase boundary conditions. Therefore, no direct (linear) correlation between the surface structures and surface stickiness could be revealed in their study. For comparison, we examined their experimental data [23] in terms of our new parameter δ , which is also plotted in Fig. 6. Then, they now show a good linear correlation between the de-pinning

force and δ . This further confirms and validates the linear dependency of the de-pinning force on the new parameter δ . In Fig. 6, the different slopes fitted to the data reflect the different intrinsic surface property (e.g., initial and receding contact angles) of the hydrophobic coatings used in the works (Teflon coating was used in this work, while dimethyldichlorosilane in Öner's experiment).

On the other hand, McHale et al. reported no significant change in the contact angle hysteresis, when the contact perimeter of the liquid-solid interface was varied but the effective contact area of the liquid-solid interface was held constant. Based on the observation, they concluded that the contact angle hysteresis should be a consequence of the effective contact area between liquid and solid [20, 21]. However, such conclusion cannot explain the results exhibited in this study, that the de-pinning forces can be even greater on certain superhydrophobic surfaces (i.e., $\Phi 0.20$ and $\Phi 0.09$ samples) than that on a planar surface (i.e., $\Phi 1.00$). We also analysed their data [20, 21] in terms of the new parameter δ . We found that their surface samples were made to have the same δ value accidentally. According to the new criterion discovered in this study, the surface morphologies that have the same δ value should result in the same de-pinning force and so for the contact angle hysteresis. Thus, the experimental results of McHale et al. [20, 21] also turn out to agree with the new linear criterion to δ . All these results support that the normalized maximal three-phase contact line along the actual droplet boundary of multi-modes is the direct (linear) factor determining the pinning/de-pinning dynamics on the superhydrophobic surfaces rather than other parameters describing the surface and interfacial morphology such as static or apparent contact line and contact area.

By investigating the geometric profile and contact interface of an evaporating sessile droplet on micro-pillared superhydrophobic surfaces, this study reveals the dynamic mechanism

of the contact line de-pinning of receding droplets and its direct correlation to the surface morphology of superhydrophobic surfaces. The de-pinning force, which drives the movement of droplet boundary, is found to display a linear correlation with the normalized maximal three-phase contact line at the droplet boundary, which depends on the morphology of the surface structures. This new insight paves the way to better understand the outstanding problem of interfacial wetting, adhesion, and frictional properties on textured surfaces, such as pinning, slip, and contact angle hysteresis. Not only for droplet dynamics, the de-pinning of the three-phase contact line is also of significant importance in the friction reduction in continuous flows. The contact line de-pinning facilitates the separation of the liquid flow from the solid surface so that it can provide more air fraction on the surface and result in an enhanced slip and friction reduction [31]. Another example is unidirectional wetting/pinning/spreading phenomena on patterned surfaces [18, 19]. The new surface parameter revealed in this study will benefit the understanding of such phenomena from the perspective of anisotropic maximal three-phase contact line, as well as the function of other anisotropically textured surfaces in nature, such as the legs of water strider, wings of butterfly, and leaves of plant [32]. Such advanced understanding of the dynamics of contact line de-pinning on structured surfaces can offer essential guidelines for the engineering of versatile superhydrophobic surfaces that can regulate their slipperiness/stickiness tailored to particular and customized applications with broader impact.

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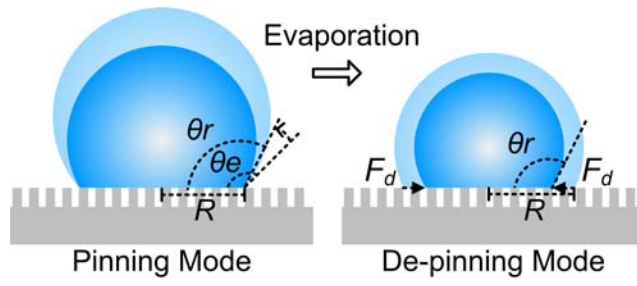


FIG.1. The pinning and de-pinning phenomena of an evaporating droplet on a patterned superhydrophobic surface in a partial wetting (Cassie) state [28]. A pinning mode transits to a de-pinning mode during the evaporation process under the effect of a de-pinning force (F_d). θ_e is an initial quasi-equilibrium contact angle, θ_r is a receding contact angle, and R is the contact radius of the droplet.

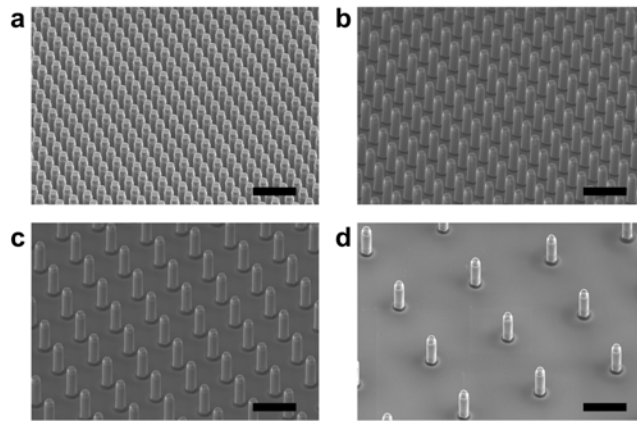


FIG.2. Scanning electron microscopy images (45° tilted view) of the micro-pillared superhydrophobic surfaces. The liquid-solid contact area fraction in a partial wetting (Cassie) state varies from (a) 0.20, (b) 0.09, (c) 0.03, to (d) 0.01. Scale bars are $30\ \mu\text{m}$.

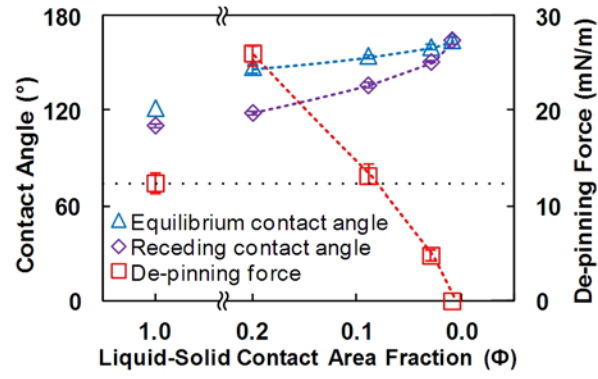


FIG.3. The initial quasi-equilibrium contact angles (θ_e), the receding contact angles (θ_r), and the de-pinning forces (F_d) on the patterned superhydrophobic surfaces (Φ 0.20, Φ 0.09, Φ 0.03, and Φ 0.01) and a planar hydrophobic surface (Φ 1.00).

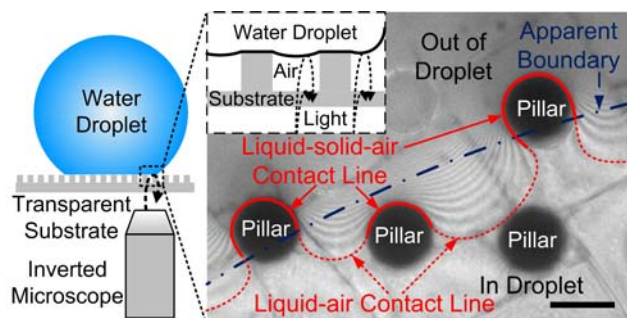


FIG.4. The multi-modal droplet boundary on a pillar-patterned superhydrophobic surface. The droplet boundary is observed from the backside of a transparent superhydrophobic substrate by using reflection interference contrast microscopy (RICM). The light reflected from the liquid-air interface and the substrate forms the interference fringe, which indicates the profile of liquid-air interface and locates the actual droplet boundary. This actual droplet boundary is different from the apparent boundary (drawn with the alternated long and short dash line), and is constituted by the three-phase (liquid-solid-air) contact line (shown by the solid line) and the two-phase (liquid-air) contact line (shown by the dash line). Scale bar is 20 μm .

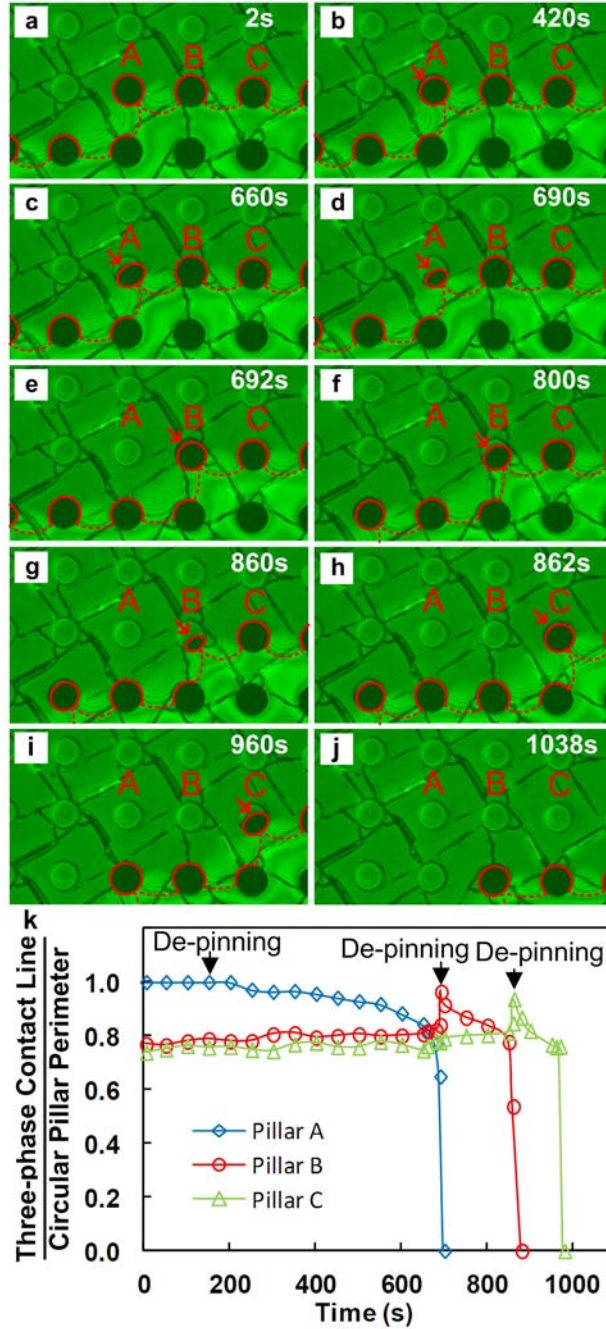


FIG.5. The evolution of the actual boundary of an evaporating droplet on a micro-pillared superhydrophobic surface. The RICM images (a-j) show the sequential de-pinning progress from Pillars A (a-d), B (e-g), and C (h-j), indicated by the arrows. The three-phase (liquid-solid-air) and the two-phase (liquid-air) contact lines on the droplet boundary are shown by the solid and dashed lines, respectively. (k) shows time history analysis of the normalized length ratio of the three-phase contact line to the circular pillar perimeter. It indicates that the de-pinning from each pillar initiates when the three-phase contact line reaches the maximum.

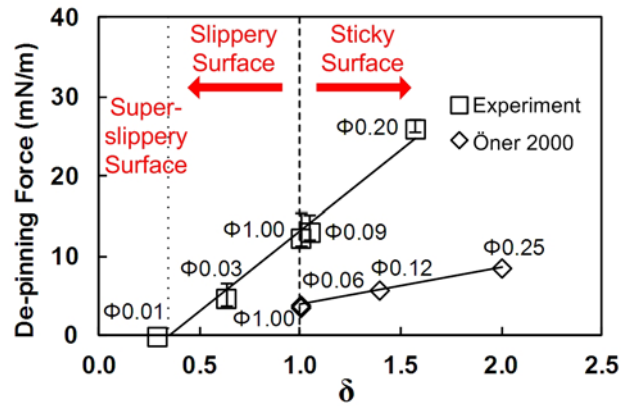


FIG.6. The linear correlation between the de-pinning force and the normalized maximal three-phase contact line (δ) at the droplet boundary. Linearly depending on the surface parameter δ , the superhydrophobic surfaces behave as sticky, slippery, or super-slippy surfaces, compared to a planar hydrophobic surface. The result from Öner et al. [23] has been analyzed [33] with the new parameter δ for comparison.