

Condensation and Wetting Transitions on Microstructured Ultrahydrophobic Surfaces

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On rough surfaces, two distinct wetting modes can appear. These two states are usually described by the theories of Cassie (drops suspended on top of roughness features) and Wenzel (drops impaled on roughness features). Whereas the wetting transition from the Cassie to the Wenzel state has been relatively well studied both experimentally and theoretically, the question of whether metastable Wenzel drops exist and how they transition to the Cassie state has remained open. In this work, we study the wetting behavior of microstructured post surfaces coated with a hydrophobic fluoropolymer. Through condensation, the formation of metastable Wenzel droplets is induced. We show that under certain conditions drops can transition from the Wenzel to the Cassie state.

Introduction

When the wetting behavior of real surfaces is described, surface roughness is a key factor. Different wetting modes have been observed to exist, depending on (i) the surface chemistry and (ii) the roughness size and topography. In the Cassie state, the interplay of these two parameters is such that drops are suspended on top of the roughness features, with air trapped underneath (Figure 1a). Assuming a contact angle (CA) of 180° on air, the static CA of such a drop is described by¹

$$\cos \theta_r = \phi \cos \theta_e + \phi - 1 \quad (1)$$

where θ_r is the CA on the rough surface, θ_e is the equilibrium CA on the smooth surface, and ϕ is the fraction of the drop footprint area in contact with the solid (the solid fraction). In contrast to the Cassie state, the Wenzel state is characterized by an impalement of the drop on the roughness features (Figure 1b). The CA on the rough surface for this configuration is given by²

$$\cos \theta_r = r \cos \theta_e \quad (2)$$

where r is the roughness factor denoting the factor by which the area of the rough surface is increased compared to the area of the smooth surface. Equations 1 and 2 are sometimes combined into a more general form:³

$$\cos \theta_r = r\phi \cos \theta_e + \phi - 1 \quad (3)$$

It has been emphasized that both the Cassie and Wenzel models are approximations that become better as the drop size increases compared to the size scale of the roughness features.^{3,4} In the following text, we will use the terms “Cassie drop” and “Wenzel drop” for drops that are suspended or impaled, respectively.

In some studies, both Cassie and Wenzel wetting states have been observed to occur on one and the same surface.^{5–10} Which state appears generally depends on how drops are deposited. This effect has been studied in particular for surfaces decorated with micromachined posts, which have recently gained importance

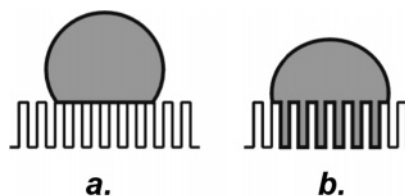


Figure 1. (a) Drops in the Cassie state rest on top of the roughness features, with air trapped underneath. (b) Drops in the Wenzel state are impaled on the roughness features.

as model systems for the wetting of rough surfaces.^{5–9,11–14} If such surfaces are endowed with a suitable hydrophobic surface chemistry, then drops remain in the Cassie mode, easily rolling around if the substrate is only slightly tilted (ultrahydrophobic behavior). It has been shown that on some of these artificial ultrahydrophobic surfaces, drops can transition from the Cassie to the Wenzel state if mechanically pressed or dropped from some height.^{5–8} Also, experiments indicate that the condensation of water onto ultrahydrophobic surfaces usually gives rise to the formation of Wenzel or combined Cassie–Wenzel drops.^{8–10} It is interesting that even the leaf of the lotus plant is not resistant to liquid invasion through condensation.^{15,16} In the Wenzel state, drops are strongly pinned; they cannot move around easily. The ultrahydrophobic properties of the surface are thus lost, a scenario that is highly undesirable for the practical application of such materials.

The coexistence of multiple wetting states on one surface immediately leads to the question of the thermodynamic stability of these states. As a general criterion, it has been found that the Wenzel state is lower in energy than the Cassie state if, for a

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given surface roughness, the equilibrium CA on the surface, θ_e , is lower than a critical CA, $\theta_{e,crit}$.^{7,17} $\theta_{e,crit}$ follows from equating the Cassie and Wenzel equations:

$$r \cos \theta_{e,crit} = \phi \cos \theta_{e,crit} + \phi - 1 \quad (4)$$

Thus if $\theta_e < \theta_{e,crit}$, a Cassie-to-Wenzel transition can be seen as a transition from a metastable state to a state of thermodynamic equilibrium. Patankar has shown that on a post surface the metastable Cassie state is stabilized by an energy barrier for hydrophobic solids (i.e., if $\theta_e > 90^\circ$).¹⁸ He computed an increase in interfacial energy as a drop was slowly impaled onto the posts. Energy was then regained as the drop made final contact with the bottom of the post surface. Ishino et al. reached similar conclusions, considering different pathways for the transition and presenting phase diagrams.¹⁹ An attempt to quantify the size of the energy barrier has recently been made by Bartolo et al.²⁰ These authors suggested that the meniscus between two posts is curved downward during the transition process and emphasized the importance of looking at the Laplace pressure within the drop. Liu et al. calculated the pressure difference necessary for a drop to transition from the Cassie to the Wenzel state on a model surface composed of microscale spheres.²¹ In theoretical work, Zheng et al. put forward a possible shape of the meniscus during the transition and computed the critical hydraulic pressure for the transition to occur.²² Several simulations confirm the existence of combined Cassie–Wenzel drops on post surfaces and predict transitions from the Cassie to the Wenzel state.^{23,24}

The existence of metastable Cassie states is well documented, and work has been done to elucidate the mechanisms governing the Cassie-to-Wenzel transition. However, it is presently less clear if the opposite is possible (i.e., if metastable Wenzel states occur and, in particular, if Wenzel-to-Cassie transitions are possible).²⁵ In this work, we attempt to answer this question by looking at the wetting behavior of water on silicon post surfaces coated with a hydrophobic fluoropolymer. Under normal circumstances, these surfaces are wetted exclusively in the Cassie mode, exhibiting strong ultrahydrophobic properties. However, through condensation, the formation of drops in the Wenzel state can be induced. We study the behavior of these Wenzel drops during growth and coalescence with other drops.

Experimental Section

Silicon post surfaces were prepared using micromachining techniques and coated with a hydrophobic fluoropolymer (poly-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecylacrylate)-*co*-4-methacryloyloxybenzophenone) (PFA-*co*-MABP). The detailed fabrication procedure can be found in previous publications.^{26–28} In the surface-modification process, a thin (~ 10 nm) polymer film is covalently attached to the substrate. The geometry of the microstructured silicon surface is thus not changed by the polymer layer. The contact angle of water on smooth layers of PFA-*co*-MABP is $\theta_e = 118 \pm 3^\circ$. The geometry of the post surfaces was quadratic (Figure 2). We prepared one surface where both the post spacing

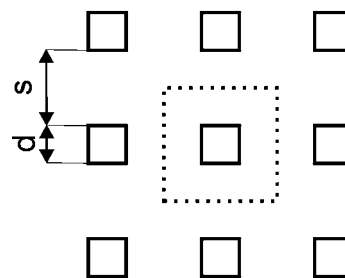


Figure 2. Schematic depiction of the geometry of our post surfaces. The unit cell is indicated.

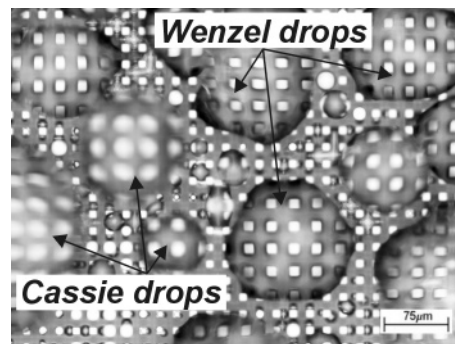


Figure 3. Combination of drops in the Cassie and Wenzel states on a post surface. The Cassie drops can be distinguished from the Wenzel drops because (i) they are spherical whereas the Wenzel drops follow the post structure and (ii) the Cassie drops rest on top of the posts; they are closer to the microscope objective and appear blurred if the microscope is focused on the Wenzel drops.

s and post width d were $8 \mu\text{m}$. On the second surface, s was $8 \mu\text{m}$, and d was $4 \mu\text{m}$. On both surfaces, the posts were $40 \mu\text{m}$ high. Condensation experiments were performed by placing the samples on a custom-built Peltier cooling stage. The temperature was set to $2 \pm 0.1^\circ\text{C}$, and water was allowed to condense onto the surface from the ambient atmosphere ($T = 23^\circ\text{C}$, relative humidity $\approx 70\%$ in an air-conditioned clean-room environment). The progress of the condensation process was monitored from above with a Zeiss optical microscope.

Results and Discussion

Metastable Wenzel State. If drops are deposited onto the post surfaces from above, they remain in the Cassie mode, easily rolling around (ultrahydrophobic behavior). This Cassie mode is actually very robust: drops cannot be induced to transition to the Wenzel state through pressing or dropping them from some height. Drops released from too high above the surface (> 15 cm) have a strong tendency to disintegrate into smaller Cassie droplets upon impact. The condensation of water onto our surfaces, however, leads to the formation of small droplets in between and on top of the posts. Over time, these drops grow and coalesce, leading to the formation of combined Cassie–Wenzel drops (i.e., drops that are partially in the Cassie and partially in the Wenzel state). It is possible to differentiate between the Cassie and Wenzel regions of these drops because in the Cassie state drops have a tendency to assume a more or less spherical shape whereas the drop footprint is distorted in the Wenzel regions (Figure 3).

Analyzing the energy of the Cassie versus the Wenzel state, we find the following: For our post geometry, the critical CAs as derived from eq 4 are 98° ($d = s = 8 \mu\text{m}$) and 100° ($d = 4 \mu\text{m}$, $s = 8 \mu\text{m}$), respectively. The CA on the fluoropolymer coating is $\theta_e = 118 \pm 3^\circ$, which is higher than the critical CA, $\theta_{e,crit}$, for both surfaces. This indicates that the Cassie state is energetically favored compared to the Wenzel state: Wenzel

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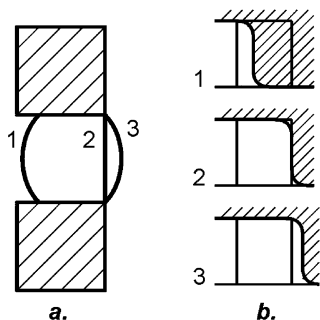


Figure 4. Receding motion of the meniscus in a region where the wetting mode of the post changes from the Cassie to the Wenzel state: (a) from above and (b) side view. Stage 1: movement in the channel between two posts. Stage 2: pinning on the post corners. Stage 3: meniscus is deformed and curves to the right but cannot dewet from the posts because θ_{rec} is not reached on the right side of the posts.

drops formed through condensation must be metastable. Consequently, this is also true for combined Cassie–Wenzel drops because these drops could lower their energy by switching to the Cassie state over their entire footprint area. What is now the nature of the energy barrier preventing these drops from immediately transitioning to the Cassie mode? In the following text, we discuss a possible explanation.

We consider a drop that is partially in the Cassie and partially in the Wenzel state. It seems plausible that a Wenzel-to-Cassie transition of those parts of the drop that are in the Wenzel state would start from the boundary where the wetting mode of the drop changes from Cassie to Wenzel. Figure 4 shows in detail how such a dewetting from the post structure might take place: (1) The meniscus is moving inside the groove between two posts. The shape of the meniscus is curved in order to satisfy the equilibrium CA on the side walls of the posts. In the side view, the meniscus is also curved in order to satisfy the CA on the bottom of the surface and to provide for a smooth transition to the liquid mass lying on top of the post structure. (2) As the post edges are reached, the receding meniscus is pinned on the 90° corner. (3) The meniscus cannot move over the front of the posts before the receding CA is not reached with respect to this plane. This would require a considerable deformation of the meniscus between the posts. However, strong deformations of the meniscus correspond large deviations from the average curvature of the drop surface. They are thus countered by the Laplace pressure. It therefore seems likely that the movement of the meniscus would be stopped at this point. Interestingly, this naïve model is supported by experimental results: if we look in detail at the Cassie–Wenzel boundary of combined Cassie–Wenzel drops, we indeed find that the meniscus is almost always resting on the Wenzel side of a row of posts (as in Figure 5). This suggests that pinning in fact takes place as suggested in Figure 4.

The model detailed above takes into account the microscopic movement of the contact line and emphasizes the importance of pinning effects on roughness features. It thus provides an intuitive explanation of why an energy barrier for a Wenzel-to-Cassie transition can be expected. In the following text, we show that under certain circumstances this energy barrier can be overcome, making Wenzel-to-Cassie transitions possible. The mechanisms described below were observed on both post surfaces.

Transition through Growth and Coalescence. The condensation of drops has been well studied for smooth surfaces^{29–35}

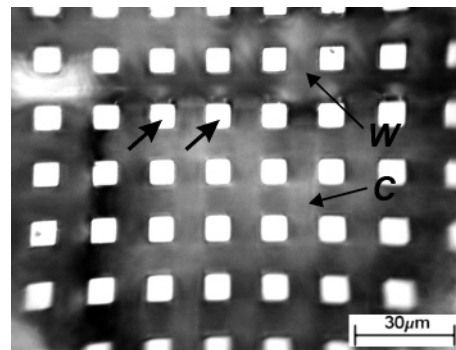


Figure 5. Image of a combined Cassie–Wenzel drop. W indicates parts of the drop that are in the Wenzel mode, and C indicates parts of the drop that are in the Cassie mode. Both areas are separated by a region where the meniscus reaches down from the top to the bottom of the post surface. The meniscus can be observed to lie on the Wenzel side of the drop (i.e., the liquid is unable to dewet from the back side of the posts; this effect is especially pronounced on posts indicated by arrows).

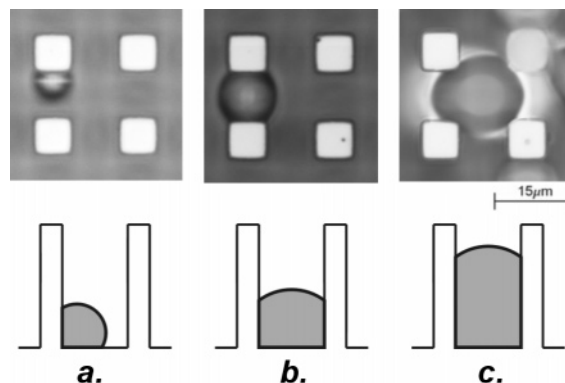


Figure 6. Evolution of drops inside the post structure with a suggested side profile. (a) Stage 1: a droplet is formed in a convex corner. (b) Stage 2: the drop grows to bridge the area between two posts. (c) Stage 3: further drop growth leads to drops that are in contact with four posts. The post in the upper right corner has a fuzzy appearance because a droplet has condensed on top of it. Note that the drawings are not to scale. In reality, the posts are even taller.

but studied to a lesser extent for microstructured ultrahydrophobic surfaces.^{8–10,36} On rough surfaces, we observe that drops form preferably in convex corners because in this configuration the liquid–air interfacial area of the drops is minimized. This behavior is illustrated in Figure 6a (stage 1). The drop continues to grow through condensation, eventually making contact with the opposite-lying post (stage 2, Figure 6b). Further growth and/or coalescence with neighboring drops of the same kind results in drops that are centered between four posts (stage 3, Figure 6c). These drops then grow upward as well as in the lateral direction. We note that for these microscopic droplets the critical angles as computed from eq 4 are only approximations.

In our experiments, it was observed that if such a drop-formation process took place underneath an already existing Cassie drop then the newly formed drop was able to make the transition to the Cassie state shortly after stage 3 in the drop evolution was reached. It is probable that at some point the growing drop makes contact with the Cassie drop lying above it (Figure 7a). We note that, at this stage, the drop is very elongated

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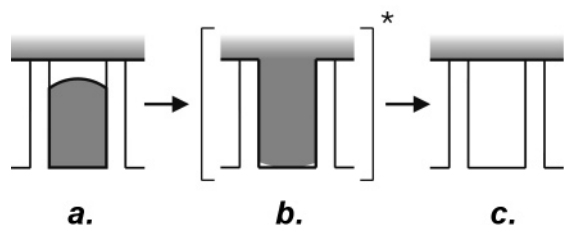
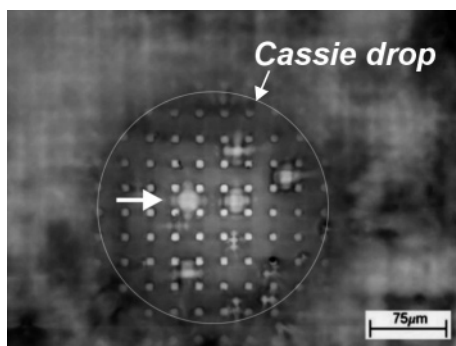
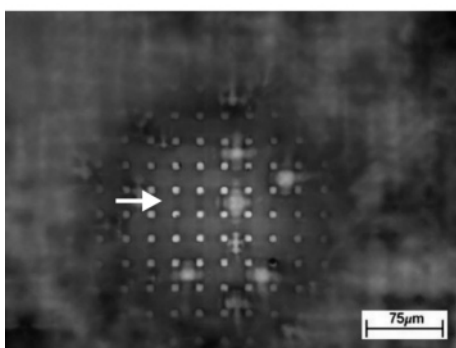


Figure 7. Transition through growth and coalescence. (a) A small drop grows upward toward a larger Cassie drop lying above it. (b) The small drop makes contact with the Cassie drop. The asterisk denotes the fact that this is an unstable high-energy state that cannot be observed experimentally. (c) The small drop has completed the transition to the Cassie state.



a.



b.

Figure 8. Transition of microscopic Wenzel drops. (a) A small Wenzel drop has formed underneath a Cassie drop (indicated by the arrow). This drop is in contact with four posts only. (b) The drop has been drawn into the Cassie state.

in the z direction. (The post height is $40\ \mu\text{m}$, but the post spacing is only $8\ \mu\text{m}$.) Both drops coalesce, forming an energetically unstable transitory state (Figure 7b). Dewetting from the Wenzel state takes place immediately (Figure 7c). In Figure 8a, a microscopic Wenzel drop lying underneath a Cassie drop is shown. A few time steps later, the drop has been drawn upward into the Cassie state (Figure 8b). We speculate that a transition becomes possible in this situation for two reasons: First, the coalescence of the microscopic drop with the Cassie drop lying above it imparts kinetic energy into the system through the elimination of liquid–air interfacial area. This energy can be directed toward overcoming the energy barrier. Second, it can be assumed that pinning on post corners plays a less important role here because the droplet is in contact with only four posts. Pinning as described in Figure 3 is thus not possible. The influence of gravity on the transition can be safely neglected: at the size scale in question here, surface forces are dominant.

The drop shape in different stages of development was studied using the numerical algorithm Surface Evolver. The Surface

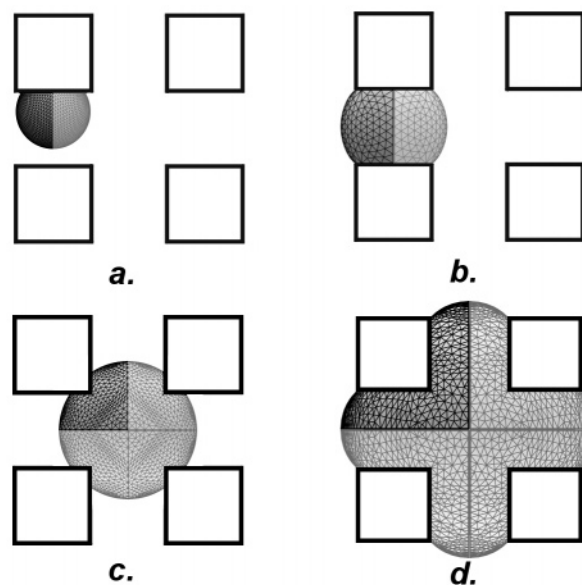
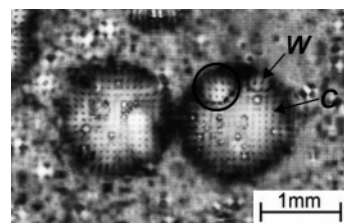
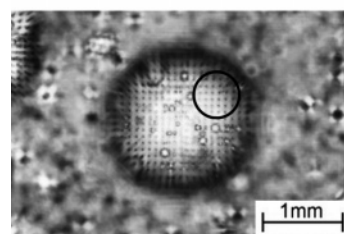


Figure 9. Simulation of the droplet evolution during condensation. For each development stage, the shape of the surface of a drop of given volume was computed. The post width was $8\ \mu\text{m}$. (a) Stage 1: drop in contact with one post. (b) Stage 2: drop in contact with two posts. (c) Stage 3: drop in contact with four posts, drop height = $10\ \mu\text{m}$. (d) A drop in contact with four posts has grown to a height of $35\ \mu\text{m}$.



a.



b.

Figure 10. Coalescence of two combined Cassie–Wenzel drops. (a) Before the coalescence event: The black circle indicates a Wenzel region in the right drop, as does the index W. Index C denotes the Cassie part. (b) After the coalescence event, a region of the drop that was in the Wenzel state is now in the Cassie state.

Evolver is a simulation tool that employs a gradient descent method to compute the equilibrium shape of a surface under the influence of quantities such as surface tension and gravity.^{37,38} Figure 9 shows top views of the simulated drop shapes for development stages 1 (Figure 9a), 2 (Figure 9b), and 3 (Figure 9c,d). Good agreement with the experimental observations (Figures 6 and 8) is found. In Figure 9c, the drop volume is 1 pL. The resulting droplet has a height of $10\ \mu\text{m}$. The drop shape in Figure 9d is analogous to the situation shortly before the drop reaches the top of the post surface: for a volume of 10 pL, the extension of the drop in the z direction is now $35\ \mu\text{m}$.

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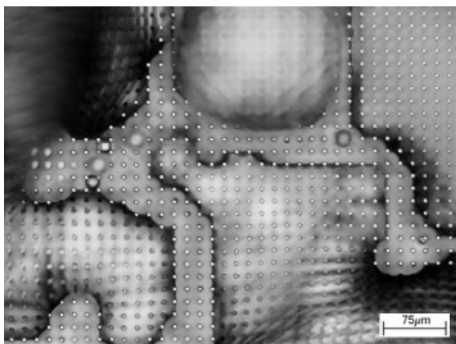


Figure 11. Wenzel regions of drops penetrate the post structure over large areas, forming flat “tongues” of liquid. Note that the drop boundaries follow the post structure.

Transition upon Coalescence. Figure 10a shows two combined Cassie–Wenzel drops lying next to each other. These drops continue to grow through condensation. Eventually, they will coalesce. In Figure 10a, we focus our attention on a region of the drop that is in the Wenzel mode (indicated by a circle). We notice that after the coalescence event (Figure 10b) this part of the new drop is no longer in the Wenzel mode. A transition from the Wenzel to the Cassie state has taken place. The coalescence of drops on solid surfaces is a complex problem and a research topic of its own.^{39–43} Without going into detail here, we can state that coalescence is a very dynamic process in the course of which considerable amounts of liquid can be displaced. It is probable that because of this dynamism enough energy is present in the system for this part of the droplet to overcome the energy barrier separating the Wenzel from the Cassie state. A transition becomes possible.

No Transition. For some drops, no transitions or only partial transitions were observed. This means that not all of the larger Wenzel drops (such as those shown in Figure 3) can make the transition to the Cassie state even if they coalesce with neighboring Cassie drops. In this case, the energy available during the coalescence event is not sufficient to trigger a transition over the whole droplet area. Also, in the long-term limit of the condensation process, large combined Cassie–Wenzel drops with large sections in the Wenzel mode are formed. As the water resting on top

moves around in the course of coalescence events, flat “tongues” of liquid penetrating the post structure are left behind (Figure 11). These tongues cannot move because they are very strongly pinned inside the post structure: the CA hysteresis is extremely high in this case. Interestingly, this can lead to drops that exhibit various CAs in different places, depending on the wetting state in the respective drop region.

Conclusions

We have investigated the behavior of water drops on silicon post surfaces coated with a hydrophobic fluoropolymer. It has been found that condensation leads to an invasion of the surface roughness by water and to the formation of Wenzel and combined Cassie–Wenzel drops. Drops in the Wenzel state on such fluorinated surfaces are energetically metastable. It is shown that a transition from this metastable Wenzel state to the thermodynamically stable Cassie state is possible in two cases: (i) For microscopic droplets that are in contact with four posts only. These drops grow upward through continued condensation until they have filled the entire volume between the four posts. If, at this stage, the drop comes into contact with a Cassie drop, coalescence occurs, and the pinning forces are overcome, resulting in a drop that is in the Cassie state. Wenzel drops in other configurations (i.e., in contact with more than four posts) experience stronger pinning and do not transition to the Cassie state through this mechanism. (ii) If the coalescence of macroscopic drops results in a dynamic movement of liquid that allows energy barriers to be overcome. In this case, the size of the area over which the transition occurs critically depends on the strength of the pinning.

When a large number of drops is evaluated, it becomes evident that Wenzel-to-Cassie transitions are possible in principle but that dewetting from the Wenzel state does not happen quantitatively. Our results seem to indicate that, on rough surfaces, pinning of the meniscus on roughness features will in many cases lead to a trapping of drop parts or entire droplets in the Wenzel state. The state of thermodynamic equilibrium is thus not always reached. Pinned drops exhibit increased CA hysteresis and roll off of the surface less easily. Consequently, a surface that shows very good ultrahydrophobic properties against large, conventionally deposited drops is much less hydrophobic against drops obtained through condensation. As a result of the different wetting states, the observed CA varies from drop to drop, sometimes even within a single drop, making the specification of “the” CA on the surface rather meaningless. In such a situation, a more detailed discussion of the wetting situation is required.

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