1 Introduction

Because of their promising applications for micro- and nanofluidic devices, condensation heat transfer systems, friction control, self-cleaning and icephobic functionality, there is currently significant interest in the wetting states on patterned hydrophobic substrates that form the so-called superhydrophobic surfaces. Despite these intriguing and useful applications, the large-scale implementation of superhydrophobic surfaces with robust non-wetting properties has remained challenging because an irreversible wetting transition can occur, destroying a gas-trapping state. For instance, various experiments, theoretical modeling, and numerical simulations have demonstrated that evaporation can naturally induce a wetting transition from an air-trapping Cassie–Baxter state (CB) or the so-called “Fakir” to a completely wetting Wenzel (W) state on superhydrophobic substrates.

Different techniques have been developed in response to prevent the transition to the complete wetting state. These methods vary from altering the geometrical and chemical properties of the surfaces to stimulating substrates with light, heat, electric potential or mechanical vibration. The fabrication of extremely robust superhydrophobic surfaces is still very active. An advantageous CB state, albeit metastable, may be achieved by tuning the aspect ratio and the packing density of the pillars. Hence, finer textures at the nano-scale may be favorable for durable superhydrophobicity. Insofar, only a few studies have been performed to elucidate the influence of the nano-textured surfaces on the wetting behavior of an evaporating droplet. This pioneering work used (hierarchical) nano-grass structures, and the critical conditions for the CB to Wenzel wetting transition using nano-structures have not been concluded.

In this paper, using both theory and experiment, we elucidate the evaporation dynamics, wetting state and transition of small droplets on regular nano-structures. Systematic measurements of the evaporation rate, droplet contact angle and radius, and critical transition points were conducted for various nano-patterns.
to investigate extremely dilute structures and high aspect ratio pillars. Our results highlight the interplay between the geometrical properties and the universality of the critical contact angle at the CB to W wetting transition for both hydrophobic micro- and nano-structured substrates.

2 Experimental

2.1 Sample preparation

To prepare nano-patterned silicon (Si) molds, the surfaces of the (100)-oriented Si wafers were cleaned by sonication in acetone and ethanol at room temperature for 10 and 5 min, respectively. The Si substrates were then placed in the boiling Piranha solution [H₂SO₄/H₂O₂, 4:1 (v/v)] and RCA solution [NH₃/H₂O₂/H₂O, 1:1:5 (v/v/v)] for 1 h each and then rinsed several times with deionized water. The cleaned Si wafers were spin-coated with a photoresist (TMHR ip3650, TOK) and then patterned using I-line projection photolithography (FPA-3000i5+ Stepper, Canon). The designed metal masks with 200 nm or 400 nm square array patterns and a periodicity P (ranging from 800 nm to 2 μm) were applied. After the development of the photoresist, Si micro/nanopillar arrays were formed through inductively coupled plasma dry etching (ICP; MESC Multiplex, STS) with 600 W power and 11.5 W bias power, when two working gases per duty cycle were used (25 sccm of SF₆ for 7 s; 75 sccm of C₄F₈ for 7 s). The height of the Si micro/nanopillar arrays could be tuned by changing the etching time. The height of the Si micro/nanopillar arrays was determined using a long-range microscope and the top-view images at a rate of 0.5 frames per second. The side-view was magnified using a long-range microscope and the top-view images were used to determine the height of the Si micro/nanopillar arrays.

2.2 Experimental setup

Two synchronized cameras were used to record evaporation dynamics, one taking the side-view and the other top-view images at a rate of 0.5 frames per second. The side-view images were magnified using a long-range microscope and the top-view images were used to determine the height of the Si micro/nanopillar arrays.

Fig. 1 Initial wetting state. (a) A scanning electron micrograph and a schematic representation of the hydrophobic nano-structures, whose geometric parameters are revealed by \( D \), \( P \), and \( r \) in the phase space of surface roughness, \( r \), and the packing fraction of nano-pillars, \( \Phi \), in (d). Using an energetic argument, the phase space shown in (d) can be divided into a stable Cassie–Baxter (CB) state domain (in red) and a stable Wenzel state region (in blue). The previous experimental data by Barbieri et al.\(^{43}\) (\( \square \), \( \bullet \), \( \circ \)) and Jung et al.\(^{23}\) (\( \triangle \), \( \phi \), \( \bigcirc \)) using microstructures are also plotted for a comparison. Due to the different contact angles on the smooth surfaces, \( \theta \), the CB–W separation lines are depicted differently: the lower one for our data using nanostructures (\( \theta = 115^\circ \)) compared to the previous studies (\( \theta = 109^\circ \)). For high roughness surfaces, the initial drop shape always exhibits superhydrophobic states (denoted by the open symbols \( \square \), \( \triangle \), \( \bigcirc \)); for instance, the initial droplet shown in (b), with \( r = 4.92 \) and \( \Phi = 0.20 \), has a contact angle higher than 165°, whereas at low roughness (e.g., in (c), \( r = 1.16 \) and \( \Phi = 0.0079 \)) a Wenzel state (denoted by the filled symbols, \( \bullet \), \( \bigcirc \), \( \triangle \)) is more likely observed. However, by carefully depositing the drop, a metastable Cassie–Baxter state (\( \square \), \( \bullet \), \( \bigcirc \)) with a larger contact angle is also found (e.g., in (c), \( r = 1.16 \) and \( \Phi = 0.0079 \)).
using a fixed focal length lens mounted on an extension tube. Top-view visualisation was used to check drop sphericity. Drop shapes were first extracted from the side-view images using ImageJ software. The drop volume, contact angle, and base radius were measured using an axi-symmetric drop shape analysis (ADSA)13 Matlab code by considering the gravity effect on the Laplace pressure. Instead of the spherical cap model, the ADSA method was used because non-spherical droplet shapes were observed, especially when the droplet size was comparable with the capillary length (see the ESI† for details). The experiments were conducted at 25 °C and 16% relative humidity ($H_a$).

3 Results and discussion

3.1 Wetting state

Fig. 1 summarizes the initial wetting state of a water droplet (of 10 μL) on various hydrophobic nano-structures. Snapshots in Fig. 1(b) and (c) reveal representative initial drop shapes for two nano-structures ($r = 4.93$ and $r = 1.16$, respectively). We observed two distinct wetting behaviours of the initial water droplet on various hydrophobic nano-structures, manifested by two different apparent contact angles, $\theta_{app}$. At contact angles $\theta_{app} > 160^\circ$, the drop rests only on the top of the pillars, while air is trapped beneath. In this so-called Cassie–Baxter state,19 the droplet has hybrid inter-facial gas–liquid and liquid–solid contacts. By contrast, the liquid could completely wet the entire structure forming a smaller $\theta_{app} \approx 120^\circ$, in an impaled or Wenzel state,21 with solely homogeneous liquid–solid contact.

This difference in apparent contact angles arises from the change in the solid–liquid contact area. For a CB drop, the contact angle depends on the solid fraction $\Phi$ and is defined by $\cos \theta_{CB} = \Phi (\cos \theta_\ell + 1) - 1$, obtained with a surface energy argument.19 In contrast, in the Wenzel state the wet area is characterised by the surface roughness $r$, and thus the apparent contact angle is given by $\cos \theta_{app} = r \cos \theta_\ell$, where $\theta_\ell$ is the contact angle measured on the flat surface of the same material.21

The impaled (Wenzel) state makes the surface sticky by increasing the retention forces46 via an increase of the contact angle hysteresis47,48 and contact radius, resulting in a loss of superhydrophobicity.49 The stability of the CB state can be predicted theoretically by comparing the two surface energies.44 The resulting criterion depends on the geometric parameters $r$ and $\Phi$ in relation with $\theta_\ell$, shown by the dashed line in Fig. 1. For given surface properties ($\theta_\ell$), the Cassie–Baxter state will be favorable on patterned surfaces with a high roughness of $r \geq \frac{\Phi - 1}{\cos \theta_\ell} + \Phi$ (i.e., the red area in Fig. 1d). This prediction agrees well with our observations; we always observed a Cassie–Baxter state of the initial drop for greater $r$ (e.g., $\theta_{app} \geq 160^\circ$ for $r = 3.51$ and $r = 4.92$). The Wenzel state is theoretically more favorable for low-roughness surfaces (the blue regime in Fig. 1d).

Indeed, consistent with this prediction, we only observed an initial Wenzel drop in the intermediate range of roughness (e.g., $r = 1.63$ and $r = 1.98$).

For even lower roughness ($r = 1.16$ and $r = 1.31$), corresponding to the stable Wenzel regime (marked in blue in Fig. 1d), if no precautions were taken during the drop deposition a Wenzel state was more likely to be observed. However, by using a needle and a slow approach we were able to deposit a Cassie–Baxter drop. This metastable CB state, also reported on other micro-structures,23,24,49 is unstable and undergoes a transition to the Wenzel state during the evaporation of a water droplet. Below, we focus on the results of such wetting transition and drop morphology during evaporation.

3.2 Evaporation dynamics

Fig. 2 shows our results for the contact radius and angle evolutions of evaporating water droplets on nano-structures, for the two different initial states: air-trapping CB and complete wetting Wenzel state (denoted in red and blue, respectively in Fig. 2). We found that drops exhibit similar behaviours regardless of the nano-structures and initial wetting states. In general, at the early stage the contact line is pinned, while the contact angle decreases due to the decreasing volume and hence the height during evaporation. Once the contact angle reaches the receding contact angle ($\approx 155^\circ$ for the Cassie–Baxter state and $\approx 90^\circ$ for the Wenzel state), the contact radius starts decreasing, while maintaining a nearly constant contact angle. Finally, at the end of the evaporation, the contact radius and angle decrease simultaneously. These three sequential stages of evaporation dynamics are known as the constant contact radius (CCR), constant contact angle (CCA), and mixed mode (of CCR and CCA),50,51 which have been observed during drop evaporation on flat50,52 and micro-structured53–55 surfaces. A CB droplet evaporates mostly in the CCA mode due to the small contact angle hysteresis. Whereas, for impaled drops, the CCR mode is longer, lasting for almost the entire evaporation in the intermediate roughness range.

A classical theory that models the evaporation rate of a sessile water drop is based on diffusive transport of saturated vapor along the top droplet surface to the ambient air56 (see the ESI†). We compare in Fig. 3 our experimental results using hydrophobic nano-structures with the theoretical prediction (dashed line) without the consideration of roughness $r$. The comparative quantity is a dimensionless mass flux rate, $M = \frac{M}{R_b D (c_s - c_\infty)}$ derived from the vapor-diffusion model, where $R_b$ is the base radius, $D$ is the water vapor diffusion coefficient in air, $c_s$ is the saturated vapor concentration, and $c_\infty$ is the vapor concentration at infinity (see the ESI† for the details). Regardless of the nano-patterned surfaces, experimental data collapse, corroborating the theory that the evaporation rate only depends on the contact angle. Nevertheless, the classical theory based on a pure diffusion process slightly overestimates the evaporation rates measured on nano-patterned surfaces. This observation is in agreement with a recent study showing that drops evaporate more slowly on superhydrophobic surfaces.57 This discrepancy has been attributed to the evaporation cooling effect. At a high contact angle, the contact radius becomes small, limiting the heat flux between the substrate and drop. Consequently, the droplet becomes colder, which in
turn results in a decrease of saturated vapor concentration and hence a slower evaporation. Based on the numerical simulation of the temperature field during the evaporation, a correction factor has been introduced in the classical theory of droplet evaporation to account for the drop cooling.\textsuperscript{58} Our experimental data show a better agreement with the latter model (see Fig. 3). For contact angles higher than 150\degree, we noticed that the discrepancy increases significantly, and the experiments show a lower evaporation rate. This discrepancy may be attributed to the assumption of a spherical drop used by the theory\textsuperscript{56,58} and the deviation of the drop shape from a spherical cap at such a high contact angle, observed in the experiments (see the ESI\textsuperscript{†} note).

3.3 Cassie–Baxter to Wenzel wetting transition

For droplets initially in the CB state, sudden changes in the contact radius and contact angle are observed, while the droplet undergoes a transition to an impaled, i.e. complete wetting, state (see Fig. 4a). At this wetting transition, these changes arise due to liquid penetration into the nano-structures, thereby destroying superhydrophobicity. As a consequence, designing robust water repellent surfaces requires an insightful understanding of this wetting transition. A supporting movie illustrating the CB to W wetting transition corresponding to the data in Fig. 4 is provided (see the ESI\textsuperscript{†} movie and info).

In previous studies, the transition is assumed to be triggered by the inter-pillar interface bending. As the drop evaporates, the Laplace pressure increases (as the drop curvature ($\propto 1/R$) increases), and this causes the bending of the air–liquid interface beneath the drop (between the solid pillars).\textsuperscript{22,24,59} By denoting the maximum interface bending as $\delta$, local curvature between two pillars scales as $\delta I^2$ with $I$ being the inter-pillar spacing. Equating this curvature with the drop, one yields an estimation of the deformation $\delta \sim L^2/\delta I$. The transition may take place if the liquid touches the structure bottom ($\delta = H$), or if the contact line starts to slide on pillar sides toward the bottom, i.e. if the local contact angle overcomes the advancing contact angle $\theta_a$. Both scenarios lead to a critical drop radius: $R^* \sim L^2/H$ for the “touch-down” and $R^* \sim L/|\cos \theta_a|$ for the sliding model. Following these models, by using nano-patterned surfaces, we may be able to lower these critical radii to $\approx 4 \mu$m and hence should extend the range of the superhydrophobic state to extremely small drops. However, our experimental critical radii were found to be between 100 and 500 $\mu$m (see Fig. 4a), different from the predictions using the above models.
Based on the surface energy calculation as an alternative approach, we derived another criterion which is able to account for our own experimental results on nano-structures and the former results using micro-structures. We compared the surface energy of each (CB or Wenzel) state and accounted for the change in the contact angle during evaporation. According to this method, these surface energies at the Cassie–Baxter (CB) and Wenzel (W) states are expressed as:

\[ E_{CB} = S_b(\gamma_{lg}r + \gamma(1 - \Phi(1 + \cos \theta))) + \gamma S_c, \]

\[ E_W = S_b(\gamma_{lg}r - \gamma r \cos \theta) + \gamma S_c, \]

where \( S_b \) is the base surface area, \( S_c \) is the surface of the spherical cap, \( \gamma_{lg} \), \( \gamma_{gs} \), and \( \gamma \) are the surface tension of the liquid–solid, gas–solid and gas–liquid interfaces, respectively. The detailed derivation can be found in the Appendix.

Fig. 4b shows the evolution over time of the difference between Wenzel and Cassie energies, \( \Delta E = E_W - E_{CB} \), for the surface with \( r = 1.16 \). At the beginning of the evaporation, the surface energy of a Cassie–Baxter drop is lower and thus stable; indeed, we observed a higher contact angle while the drop sits on the pillar top. During the evaporation, \( E_{CB} \) decrease slightly faster than the Wenzel one, \( E_W \), resulting in a decrease of the energy difference. Subsequently, when the Cassie–Baxter and Wenzel states have the same energy (\( \Delta E = E_W - E_{CB} = 0 \)), the wetting transition takes place (e.g., after 945 s in Fig. 4b). The proposed model is able to predict the transition for hydrophobic nano-structures, while the two aforementioned models significantly under-predict the critical value, suggesting the universal character of this approach. To validate this universality, we compare our theoretical results with various experimental findings, using a variety of geometric parameters for micro-structures. To this end, we first derive a simple criterion based on the surface energy model. As shown in Fig. 4b, the wetting transition occurs at the critical contact angle \( \theta_C \) when \( \Delta E = 0 \), which can be expressed as:

\[ \cos \theta_C = \Phi - \frac{1}{r - \Phi}, \]

implying that the wetting transition happens at a critical contact angle that universally depends on the geometric parameters of the micro- or nano-patterns.

We now compare, in Fig. 5, this criterion with our experiments using nano-structures (\( \Phi \)) and ten other studies found in the literature using a wide variety of micro-patterned substrates. Regardless of the structure or the material, our critical condition is in good agreement with experimental data, demonstrating its universality. The surface energy calculation is a first-order approximation without considering the energy associated with the (pinned) contact line, and thus a small deviation of the various experimental data from the prediction exists. Several factors can also contribute to this discrepancy: imperfect (square or cylindrical) pillar shapes, pinned contact lines, small chemical contamination, different models used for calculating the contact angle, and the measurement uncertainty stems from the contact radius or/and droplet height. We carried out error analysis and noticed that a 10% measurement uncertainty in the contact radius and droplet height (of \( \approx 20 \) μm) can contribute to a \( \approx 8\% \) error in the contact angle.

It is interesting to note that while previous models predicted a critical contact radius, our approach leads to a critical contact angle reflecting the difference in the underlying mechanism.
triggers the wetting transition. Some data using microstructures of \( P > 50 \mu m \) in Fig. 5 are consistent with the predictions by the touch-down/sliding criteria as well as our model, implying that both mechanisms may play a role in triggering the CB to W transition. However, for nanostructures and some microstructures of smaller \( P < 50 \mu m \) the touch-down/sliding model appears to underestimate the transition. We think that for smaller pillars, contact line pinning and imperfectly shaped pillars likely play a significant role, and these influences should be taken into account and remain an open question.

This new criterion, moreover, revises the way of maintaining a metastable CB state. Previous studies suggest that a reduction of the inter-pillar spacing would extend the CB state to small drops (via \( R^* \sim \sqrt{H/\phi} \) or \( u/\cos \theta_u \)); however, these predictions were not observed for nano-patterned pillars. In contrast, for extending the gas-trapping CB state, our new finding suggests a minimisation of \( \theta \), and hence \( \frac{(\Phi - 1)(r - \Phi)}{r - \Phi} \), by exploiting eqn (3).

### 4 Conclusions

In summary, for the first time we carried out systematic sets of theoretical and experimental examinations of the dynamic wetting transition from a Cassie–Baxter to a Wenzel state during drop evaporation on nano-structured surfaces. Surprisingly, the downscaling of structures to the nanoscale does not sustain the stability of superhydrophobicity, which was expected by previous analyses. We extended a previous model using the surface energy to derive a new and universal criterion that is able to account for our experimental results (using nano-structures) and various data (with micro-structures) in the literature. From this unifying criterion, we see that the CB to Wenzel transition can occur even at a high contact angle (\( \approx 150^\circ \)) for hydrophobic structures with both low roughness and solid fraction. In contrast, the transition to an impalement state is expected at a lower contact angle (\( \approx 100^\circ \)) when the roughness and/or the solid fraction increases. Consequently, increasing roughness is a powerful way to extend the CB state of water drops on hydrophobic micro/nano-structures during evaporation.

### Appendix

The surface energy associated with the Cassie–Baxter state on a patterned surface can be expressed as:

\[
E_{CB} = \gamma_{sl}N\pi D^2/4 + \gamma_{sg}N\left(\pi DH + P^2 - \pi D^2/4\right) + \gamma_{R}N(P^2 - \pi D^2/4) + \gamma_{sC},
\]

where \( H \) is the pillar height, \( D \) is the pillar diameter, \( P \) is the lattice periodicity, \( N = \pi P^2/4P^2 \) is the number of asperities under the drop, \( S_c \) is the surface of the spherical cap, \( S_b \) is the base surface and \( \gamma_{sl}, \gamma_{sg} \) and \( \gamma \) are the surface tension of the solid–liquid, solid–gas and liquid–gas interfaces, respectively. Using the definition of \( N \), the surface energy for a Cassie–Baxter droplet on hydrophobic nano-structures, \( E_{CB} \), can be calculated using the roughness \( r \) and the solid fraction \( \Phi \):

\[
E_{CB} = S_b(\gamma_{sl}(\Phi + \gamma_{sg}(r - \Phi)) + \gamma(1 - \Phi)) + \gamma_{sC},
\]

and \( E_W \), the surface energy of a Wenzel droplet is given by the following equation:

\[
E_W = N\gamma_{sl}(\pi DH + P^2) + \gamma_{sC} = S_b\gamma_{sl}r + \gamma_{sC}.
\]

The contact angle \( \theta \) varies during evaporation, implying the change in the relationship between surface tensions. We use the Young–Dupré equation, \( \gamma_{sl} = \gamma_{sg} - \gamma \cos \theta \), by assuming (quasi-)force equilibrium in the horizontal direction during slow evaporation, and simply the surface energies for the two states in the following equations:

\[
E_{CB} = S_b(\gamma_{sg}r + \gamma(1 - \Phi(1 + \cos \theta))) + \gamma_{sC},
\]

\[
E_W = S_b(\gamma_{sg}r - \gamma r \cos \theta) + \gamma_{sC}.
\]

### References