**Drops on a Superhydrophobic Hole Hanging On under Evaporation**

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**ABSTRACT:** Drops with larger volumes placed over a superhydrophobic (SH) surface with a hole do not fall through unless they are evaporated to a size that is small enough. This feature offers the ability to preconcentrate samples for biochemical analysis. In this work, the influence of pinning on the behavior of drops placed on a 0.1 mm thick SH substrate with a 2 mm diameter hole as they evaporated was investigated. With 16 µL of water dispensed, the sessile drop component volume was initially higher than that of the overhanging drop component and maintained this until the later stages where almost identical shapes were attained and full evaporation was achieved without falling off the hole. With 15 µL of water dispensed, the volume of the sessile drop was initially higher than that of the overhanging drop component but the liquid body was able to squeeze through the hole after 180 s due to the contact line not having sufficient pinning strength when it encountered the edge of the hole. This resulted in the liquid body either falling through the hole or remaining pinned with an oval-like shape. When it did not fall-off, the liquid body had volume and contact angle characteristics for the sessile drop and overhanging drop components that were reversed. In the later stages, however, nearly identical shapes were again attained and full evaporation was achieved without falling off the hole. The effects of pinning, despite the substrate being SH, offer another path toward achieving practical outcomes with liquid bodies without the need for chemical surface functionalization. Similarities and differences could be seen in the behavior of a sessile drop on a SH plate that was inclined at 30° to the horizontal and evaporated.

**INTRODUCTION**

Superhydrophobic (SH) surfaces offer an attractive means to developing applications because of liquid bodies placed on them having low levels of adhesion¹ and possessing reduced resistance when a liquid flows over them.² The former has been widely harnessed for self-cleaning,³⁻⁵ although this low-adhesion property has also been increasingly explored in applications involving drops to advance biochemical processing and analysis with the advantage of limited sample loss and contamination.⁶⁻¹⁰ In evaporative preconcentration of drops, it is particularly desirable to have the lowest solid–liquid contact area and adhesion possible to minimize entity deposition on the solid substrate. Typically, the drop volumes post evaporation ought to have specific values. Electronic monitoring followed by mechanical intervention allows for this.¹¹ Recently, an autonomous “manhole” approach was demonstrated in lieu, wherein drops with larger volumes when placed over a SH surface with a hole would fall through after being evaporated to a smaller volume.¹² It was revealed, however, that the method worked well with meshed rather than solid surfaces, indicating a strong pinning influence offered by the solid phase at the edge of the hole.

The pinning behavior of sessile drops on tilted surfaces has been well-studied. On a perfectly horizontal surface, large sessile drops can be developed in this manner, where the contact angle θ is typically in the equilibrium state. However, any extent of surface tilt will cause the drop to possess advancing θₐ and receding θᵣ contact angles. With increasing tilt, the drop’s ability to accommodate contact angle hysteresis will eventually be exceeded by gravitational force,¹³ resulting in its detachment and movement on the surface. It has been shown that with onset of tilt the advancing contact line breaches first, leaving the receding contact line to determine the drop’s ability to detach.¹⁴⁻¹⁶ This then allows the ability of the drop to resist movement to be enhanced¹⁷⁻¹⁹ or for the shape to be altered²⁰⁻²¹ (if the surface is hydrophilic) by providing additional pinning modes at the locale of the receding contact line.

In this work, a thin SH solid substrate with a 2 mm hole was prepared. A liquid was then placed directly above the hole, and its characteristics were studied with the onset of evaporation.

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The small thickness (0.1 mm) of the substrate used permitted good side views to analyze the volume and contact angle development of the sessile drop and overhanging drop components more distinctly. The underlying behavior in relation to observable shapes was then characterized using models that depict large to small sessile drops residing on strongly nonwetting surfaces and of drops subjected to gravitational force that cause them to display oval-like forms. The similarities and differences in the behavior of sessile drops placed on surfaces inclined at an angle to horizontal are highlighted.

■ SHAPES OF SESSILE DROPS ON HIGHLY NONWETTING SURFACES

In order for evaporative preconcentration to be effective, drops need to be evaporated from reasonably large volumes.\(^{11,12}\) The shapes of sessile drops on horizontal surfaces have been extensively studied. In the absence of wetting interactions and gravity, drops would form spheres that contact the solid substrate at a single point. When the drop volume is small enough such that the influence of gravity is negligible, wetting interactions will cause drops to spread and produce a semispherical shape. If the volume is large enough, such that gravity cannot be excluded, the drop flattens out such that the shape transitions are gradual and the mathematics that describes the shape of sessile drops is no longer straightforward.

Bashforth and Adams\(^{22}\) were arguably the first to approximate the shapes of large sessile drops by trying to solve the Young–Laplace equation with hydrostatic effects incorporated via iterative numerical calculations. The basis of this was then used to develop a more simplified model with some geometrical approximations.\(^{23}\) Other models based on spheroids have also been developed.\(^{24–27}\)

For the purposes of explaining some aspects of drop behavior observed here, we adopt a double-spheroid model.\(^ {27}\) This essentially means that if a cross section is taken of the distorted shape, it will comprise two ellipses having a common origin \(O\) and one principal axis length \(a\) (see Figure 1). The solid substrate is located at vertical height \(y_o\) below the origin. The top ellipse has a second principal axis length \(b\), and at the point of intersection of the bottom ellipse with substrate \(C\), its second principal axis length \(c\) can be determined from

\[
c = \sqrt{\frac{y_o^2 a^2}{a^2 - x_o^2}}
\]

(1)

From here, the volume of the liquid drop can be determined by geometry to be

\[
V = \frac{2}{3} \pi a^2 (b + c) - \frac{\pi a^2}{3} c (2c^3 - 3c^2 y_o + y_o^3)
\]

(2)

The apparent contact angle, \(\theta\), can be obtained based on the tangent of the bottom ellipse at \(C\), in which

\[
\theta = \pi - \tan^{-1} \left( \frac{x_o c^2}{y_o a^2} \right)
\]

(3)

■ DROP SHAPE MODEL UNDER A FORCE

When a drop on a substrate is tilted at an angle to the horizontal, the balance of forces that act at the three-phase contact line to keep it in place would need to counteract the resultant gravitational force. This naturally results in a departure from the axisymmetric shape when it is placed on the horizontal. When viewed from its side, the drop will exhibit advancing and receding contact angles. The view from the top alternatively reveals the contact line of the base of the drop being shifted forward in the direction of gravity, whereas its line curvature tends to grow. Attempts to numerically depict this shape have been done using surface energy considerations.\(^ {28}\)

The deformed shape of the drop when viewed in relation to the action of a force resembles an oval. Here, we seek to obtain a model that defines the shape characteristic alone. Equations depicting ovals are often based on modifications made to the standard equation of the ellipse. In the model here, we use one end of the oval as origin \(O\) so that it will be easier to derive the defining parameters without locating the origin within the shape itself (see Figure 2). If point \(P\) along the \(z\) axis is taken to vary cosinusoidally according to angle \(\phi\), we have

\[
OP = m \cos \phi
\]

(4)

and the shape is generated through

\[
OQ = l + m \cos \phi
\]

(5)

where \(l\) and \(m\) are the constants that define it. The coordinates of any point \(Q\) on the deformed drop shape can thus be given by

\[
z = OP + OQ \cos \phi
\]

\[
r = OQ \sin \phi
\]

(6)

If we use constants \(K_i = 2(l + m)\) and \(K_o = 4m\) to replace \(l\) and \(m\), a compact equation of the shape will be made available through

\[
(z^2 + r^2)^2 = K_o z^3 + (K_i - K_o) z r^2
\]

(7)

By evaluating the volume by integration through

\[
V = \pi \int_0^{K_i} r^2 \, dz
\]

we have in the case where \(K_i \neq 0\)
decomposes to a sphere, where \( \text{fi} \) oxides. In the end of the reaction, the substrate was taken out of the solution, \( 1 \) and \( 1.5 \) M \((\text{NH}_4)_2\text{S}_2\text{O}_8\) for 5 min. The samples were then substrates were oxidized in a solution containing 2 M NaOH deionized (DI) water for another 15 min. In the next step, the ethanol (70\% v/v) and acetone for 3 min and subsequently in drill bit operated at 10 000 rpm. First, the samples were horizontal (free from tilting). With the aid of a radiant heater, the drop was again allowed to 

\[
V = \frac{\pi}{2} \left[ \frac{K_1(K_1 + K_2)^3}{6K_2} + \frac{(K_1 - K_2)^3}{60K_2^2} - \frac{(K_1 + K_2)^5}{60K_2^2} \right] - \frac{K_1^3}{6} - \frac{K_1^2K_2}{2}
\]

(8)

In the situation where \( K_2 = 0 \), alternatively, the shape decomposes to a sphere, where \( l \) is twice the radius.

\[
V = \frac{\pi l^3}{6}
\]

(9)

\[\text{Materials and Methods}\]

\[\text{Surface Preparation}\]. The SH substrate used for the main experiment was prepared from copper sheets of thickness 0.1 mm. A 2 mm hole was created on it using a tungsten carbide drill bit operated at 10 000 rpm. First, the samples were polished until they were shiny and then ultrasonicated in ethanol (70\% v/v) and acetone for 3 min and subsequently in deionized (DI) water for another 15 min. In the next step, the substrates were oxidized in a solution containing 2 M NaOH and 1.5 M \((\text{NH}_4)_2\text{S}_2\text{O}_8\) for 5 min. The samples were then allowed to synthesize in an oven at 180 °C for 120 min. At the end of the reaction, the substrate was taken out of the solution, rinsed several times with DI water and ethanol, and then dried with compressed air. The as-obtained product was dried at 180 °C for 2 h to complete the phase transfer from hydroxides to oxides. In the final step, the substrates were silanized using \(1H,1H,2H,2H\)-perfluorodecyl-triethoxysilane (FAS) to obtain a low-surface-energy layer with good corrosion resistance and thermal stability. The substrate was immersed in FAS–ethanol solution for 30 min and finally dried in the oven at 150 °C for 10 min.

A second substrate was prepared with a silicone sheet of 60 \(\mu\)m thickness and with a 2 mm hole created on it using a tungsten carbide drill bit operated at 10 000 rpm. During observations, the two ends of the substrate were pulled apart and kept in position using weights to ensure that the substrate was taut.

A third SH substrate was used for the secondary experiment according to a method previously shown. For this, a copper plate was polished to remove scratches using silicon carbide electrocoated water-proof abrasive paper (KMCA, WET/DRY S85 P600). Prior to use, it was first cleaned using absolute ethanol, allowed to air-dry, and then immersed in a 24.75 mM aqueous solution of silver nitrate (AgNO\(_3\)) for 1 min to form micro- and nanostuctures. Subsequently, it was rinsed with copious amounts of distilled water followed by absolute ethanol before being allowed to air-dry. Once dried, it was immersed in a 1 mM solution of surface modifier \(\text{CF}_3\left(\text{CF}_2\right)_n\text{CH}_2\text{CH}_2\text{SH}\) in absolute ethanol (ethanol with low water content) for 5 min. An impression of 1 mm diameter was created using a pipette tip on the surface. This was to create a hydrophilic circular region that is bounded by superhydrophobicity.

\[\text{Characterization of Surfaces}\]. The SH copper sheet and plate samples were placed on stubs using a conductive adhesive and examined using a scanning electron microscope (SEM, Nova NanoSEM 430; FEI). As the samples were conductive, we were able to use 10 keV for imaging. In the case of the silicone sheet, it was coated with gold prior to imaging. Imaging was done on the Hitachi TM3030 SEM for this sample.

To obtain optical profilometry images of the copper sheet in the vicinity of the hole within, the sample was attached onto a flat silicon surface to serve as reference. This was then placed inside the profilometer (Bruker ContourGT-I), where optical scans were made. Processing and analysis were performed on the instrument’s accompanying software (Contour Elite). Because of the relatively large area to be covered, multiple images were recorded, and the stitching capability was used to create an integrated map over an extended field of view.

\[\text{Drop Shape Measurements}\]. Side views of the drops were recorded using a camera (Moticam 2.0). A bright light-emitting diode lamp with a diffuser was used to provide the lighting for the recordings. The recorded images were then analyzed using processing software (ImageJ and Tracker) to determine the contact angles and their lengths on the solid substrate. To determine the volume, routines in Matlab were written based on eqs 2, 8, and 9.

\[\text{Drop Evaporated on Hole}\]. In the first set of experiments, relatively large drops of deionized water were dispensed on the SH surface such that they sat directly above the hole. Before the drops were dispensed, a spirit level was used to ensure that the substrates were horizontal (free from tilting). With the aid of a radiant heater, the drops were allowed to evaporate. During the process, images of the drops were recorded at specific time intervals to analyze their shape characteristics.

On the basis of the outcome of the first set of experiments, a second set was conducted wherein drop volume was adjusted so that the length of the drop of deionized water on the surface approximated closely with the diameter of the hole. This was found to coincide with a volume of 15 \(\mu\)l of water dispensed. With the aid of a radiant heater, the drop was again allowed to evaporate. Images of the drop were recorded at specific time intervals to analyze its shape characteristics. The experiment was repeated on the silicone surface with hole for comparisons.

An infrared thermometer (Raytek Raynger ST Pro Plus) with 1 °C resolution and 500 ms response time was used to measure the substrate temperature close to the three-phase contact line at four positions spaced 90° apart from each other. The temperature was found to vary by not more than ±1.2 °C from
the mean of 25 °C. This indicated that thermal gradients were not likely to be responsible for any of the behaviors observed. The humidity throughout the experiments was also monitored and found to vary by not more than 2% from the mean of 46%. The experiments were also conducted in an enclosed space to eliminate any forced convection influences.

Drop Evaporated on an Inclined Surface. The SH plate was placed on a modified optomechanical rotary stage (Edmund Optics, 52-572) previously described. The stage has a 1° resolution and permitted a drop to be located on the SH plate substrate at the gimbal position. This circumvents the need to move the camera when different degrees of tilt are applied and also allows the substrate to be tilted over a large angular range. A liquid drop of 20 μL was dispensed on the SH plate in the horizontal position at the location of the circular non-SH region. The plate was then rotated by 30° such that the extent of contact angle hysteresis was as high as possible before any contact line breaching. With the aid of the radiant heater, the drop was allowed to evaporate. Images of the drop were recorded at intervals in time to analyze its shape characteristics.

RESULTS AND DISCUSSION

Figure 3A provides the SEM images of the SH sheet sample. The hierarchical microscale and nanoscale structures (taken at 500 μm from the edge of the hole) are predominantly prismatic. The SEM image of the SH substrate with a circular impression made on it is shown in Figure 3B. Whereas the SH region clearly has hierarchical dendritic microscale and nanoscale structures that permit predominant Cassie wetting, there is clear absence of these structures within the circular impression, which should then allow predominant Wenzel wetting. At the interface between these two regions, there is a distinct separation of the two structure types, indicating a means for a liquid drop resting on the circular impression region to possess high apparent contact angles at the three-phase contact line. Figure 3C provides SEM images of the silicone sheet sample (taken also at 500 μm from the edge of the hole). There is a general lack of hierarchical structures, albeit some scratching of the surface is evident. This is typical of silicone surfaces due to their general softness.

The optical profilometer trace of the SH sheet around the area of the hole indicated reasonably uniform edges (Figure 4). In addition, the transition area was limited to around 10 μm, which implied a sharp rather than tapered discontinuity. There was also absence of any escarpment due to material build-up. The ability of any contact line to pin is hence dependent solely
on the edges that surround the hole over the thickness of the sheet.

When water drops of 16 μL volume (or larger) were first dispensed over the hole on the SH surface, a prominent overhanging component is visible (Figure 5). This component, with a hemispherical front, forms to counteract the pressure (hydrostatic and Laplace) that develops at the liquid body on top of the substrate. We consider that the liquid body shape

Figure 5. Side views of a 16 μL liquid body deposited on the hole of the SH sheet at various time points during evaporation. The liquid body initially comprises a sessile drop and an overhanging drop component. The former decreases in volume initially until a stage where both subsequently do so in tandem. The liquid body fully evaporates without falling off the hole.

Figure 6. Volumes (A) and contact angles (B) of the sessile and overhanging drop components of the 16 μL liquid body deposited on the hole of the SH sheet at various time points during evaporation. In the case of volume, the sessile drop component can be seen to be reducing throughout, whereas the overhanging drop component increases marginally until around 300 s before it begins reducing in volume. In terms of contact angles, the sessile component is able to maintain a constant value in the first 100 s before decreasing thereafter. The overhanging component has a trend of contact angle values that directly reflect changes in its volume.
changes with the onset of evaporation. In the initial stages, only
the sessile drop component appears to lose volume, proceeding
until around 450 s from the start. After this period, the
overhanging component joins in the process of evaporation,
where volumes of both sessile and overhanging components
contract in sync. An important characteristic to note is that the
liquid body evaporates fully without falling through the hole via
gravity. This happens despite the seemingly small thickness of
the sheet, which should limit the amount of pinning available at
the edge of the hole.

We depict the shape changes quantitatively. The sessile drop
component appears to reduce its size by evaporation in the
manner of a large sessile drop formed on a typical surface. To
confirm this, we tracked the values of \( \theta_a, \theta_r, x, \) and \( \gamma_a \) (Figure 1) to determine the attendant values of \( V \) and \( \theta \) from eqs 2 and 3 respectively. It should be noted that this model begins
to become inaccurate when the drop shape departs markedly from
a hydrophobic characteristic. Hence, at these stages, the volume
of the sessile drop component was determined analytically
using a semispherical model. In the case of the overhanging
drop component, the volume was determined using the
semispherical model throughout.

From the plots of the sessile drop and overhanging drop
volume components with time (see Figure 6A), it can be seen
that the former reduces throughout the evaporation process.
The latter, however, increases marginally until around 300 s
from the start before it also began reducing in the same manner
as the former. The corresponding contact angle plots (Figure
6B) furnish better insights into this. The sessile drop component
showed relatively constant contact angles for the
first 100 s. To accommodate for volume decreases with time,
the contact line would have to move in at a rate such that
volume reduction of the sessile component would exceed the
amount of liquid evaporated. Furthermore, this lack of initial
pinning is at odds with results reported previously of sessile
drops evaporated on solid SH substrates.\(^{36}\) This deviation in
behavior can be accounted for by the overhanging drop
undergoing a volume increase at the same time. Essentially, the
liquid body applied surface energy redistributions via changes
to the overhanging drop to bypass the expected pinning
characteristic.

The mechanics at play can be compared for similarities and
differences with sessile drops on an incline that exhibits
advancing and receding contact lines (indicated by AL and RL,
respectively) and thus having attendant advancing and receding
contact angles \( \theta_a \) and \( \theta_r \) (see Figure 7). In the situation here,
advancing and receding contact lines (indicated by AL and RL,
respectively) can also be identified as shown in Figure 8A. At
the initial stage before evaporation begins, AL resides within the
drop component. The former is strongly pinned, whereas pinning of the latter is
weaker due to its interaction with a flat SH substrate. With the
onset of evaporation, the receding contact line is then able to
move radially inward (toward the center of the hole) to
accommodate the energy changes that ensue. In the process,
the contact angle (which is receding in the context of the entire
liquid body) remained relatively invariant. This should result in
an increasing Laplace pressure because the radii are gradually
reduced (i.e., \( \Delta P = 2/\gamma \)). Yet, this does not cause significant
changes at the advancing contact line. This is due to the known
ability of a liquid to harness the sharp edges located on the
bottom surface of the substrate for added resistance toward any
outward radial spreading (first reported 40 years ago by Oliver
et al.\(^{33}\)). This is attested to by the corresponding increases in
the contact angle (which is advancing in the context of the
entire liquid body) exhibited by the overhanging drop
component (Figure 6B). A major point of difference lies in
the contact angle of the overhanging component being
consistently smaller than that of the sessile drop component
(Figure 6B). This infers strong stability of the liquid body as it
resides on the hole.

It is noteworthy that after the initial 100 s the contact angle
of the sessile drop component started to decrease, in the same
manner as its volume, to values that are significantly below 90°
(see Figure 7B). It has been previously argued that the surface
energy of any liquid on a real SH surface is distributed
according to the Cassie–Baxter and Wenzel components.\(^{32}\) It is
plausible that with the onset of evaporation the ratio of latter
may increase over the former, which may then allow for a
sessile drop that initially exhibited predominant Cassie–Baxter
behavior to transition toward a more predominant Wenzel
character. A quantitative analysis to determine this in the
current context will be challenging as the surface structures are
hierarchical.

Beyond the first 100 s, the contact angle of the overhanging
drop component continued to increase until the 300 s time
point, after which it exhibited a reducing trend in a similar
fashion as that of the sessile drop. This reversal is marked by a
slowdown in the contact angle reduction rate of the sessile drop
component (at time points from 300 to 400 s). This phenomenon
is attributed to the inability of the liquid body to
shift mass toward the overhanging drop component indefinitely
for surface energy adjustments. Once a tipping point is reached
(at the 300 s time point), the movement of AL (Figure 8A) slows down to allow both the sessile drop and
overhanging drop components to reduce their volumes in
tandem to respond to the mass loss from evaporation.

Clearly, RL in Figure 8A must reach the edge of the hole at
some stage where it starts to encounter much stronger pinning.
With an inability of RL now to move at this point, the onset
of evaporation then causes the contact angle of the sessile
component to reduce more significantly. The situation of RL
reaching the edge of the hole is supported by observations at
the 400 s time point, where a change in the contact angle
reduction rate of the sessile drop component is discernible
(Figure 8B). In the process, the contact angle was reduced by
43° from its starting condition and its value at 90° at the 400 s
time point. This logically should lead to a Laplace pressure
reduction that ought to cause the advancing contact line to
commence reversing its earlier adjustment. This is indeed
observed in the contact angle versus time plot for the
overhanging component (Figure 6B). Intriguingly, this will eventually reach a stage where the advancing and receding contact lines will almost merge as one along the edge of the hole. From this stage onward, the top and bottom liquid bodies should have almost similar surface energies, leading to a propensity for both entities to adopt identical shapes. This is apparent in the image corresponding to the 510 s time point (Figure 6). As evaporation progresses with more volume loss, the liquid body should progress toward a stretched thin film state over the hole. However, rupture often occurs before this takes hold. From 20 repetitions at 16 μL volume, there were no instances in which the drop was able to fall through the hole. In addition, similar characteristics were observed with liquid volumes from 16 to 25 μL. We have included the sequence of images of the evaporation of a 25 μL drop as Supporting Information.

When 15 μL drops are directly placed over the hole on the same SH sheet, a strong overall departure from the earlier behavior is observed (Figure 9). As in the previous case, only the sessile drop component appears to lose volume up to around 180 s from the start. At the 180 s stage, the liquid body undergoes a dramatic change in shape as it seemingly attempts...
to “squeeze” through the hole, causing the overhanging component to extend downward and the overall shape to be oval-like. This results in two outcomes. In the first, the liquid body falls completely from the hole (as per the manhole effect previously reported \(^\text{12}\)). In the other, depicted in the remaining image—time sequences of Figure 9, the overhanging component starts to contract progressively. The occurrence of either is counterintuitive because a smaller volume was used at the start (i.e., 15 \(\mu\)L instead of 16 \(\mu\)L). The end phase mimics the behavior uncovered in the previous case, where identical liquid shapes form and progress to being fully evaporated without falling through the hole.

To better understand the mechanics, it will be necessary to break the analysis into stages. The first stage, which takes place over the first 180 s, follows in the same vein as the sessile and overhanging drop volume and contact angle trends (Figure 10A) with the 16 \(\mu\)L case. A noteworthy difference lies in the contact angle of the sessile drop component, reducing almost right from the outset (Figure 10B). This departure is accounted for by the lower contact angle that it first exhibited (120° instead of 140°), which meant that it possessed a higher Wenzel energy content. In addition, the initial volume and contact angle of the overhanging component remained 1.2 \(\mu\)L and 60°, respectively, at the start. This meant that the sessile component needed to adopt lower contact angles because its volume was relatively smaller than that previously. Apart from this, the overall mechanics for this stage follows that described previously through Figure 8A.

The second stage occurs when the contact line of the sessile drop component reaches the edge of hole (at 180 s). The plots of volume against time (Figure 10A) show a sudden exchange in behavior for the sessile and overhanging components. This now resulted in the volume of the overhanging component and its rate of reduction with evaporation being higher than those of the sessile component. Hence, the mechanics depicted in Figure 8A reverts instead to that described in Figure 8C for this stage. This can be accounted for by the relatively small reduction in the contact angle (10°) of the sessile drop component to 110° (instead of 90°) at the 180 s time point. Without the contact line being able to attain as strong a pinning strength when it encounters the edge of hole as previously, the liquid body then encounters less resistance to squeeze through the hole. The prevailing pinning strength when this happens then dictates whether the liquid body detaches fully or stays at the hole. It is interesting to note that the 15 \(\mu\)L volume is limiting, as attempts to dispense 14 \(\mu\)L resulted in the liquid body falling right through.

The volume exchange behavior is also demonstrated by the contact angles (see Figure 10B). Because of the reversal in volume compositions, the roles of the sessile and overhanging drop components are also swapped. Interestingly, this imbues the same ability for the sessile drop component to first increase its contact angle before reducing it later during evaporation. This feature was available only for the overhanging drop component in the 16 \(\mu\)L case. These results imply that surface energy adjustments via contact angle increase and decrease are reserved for the smaller liquid body component. This is reasonable because smaller liquid bodies tend to be less energetically stable than larger versions.

Once the condition of both contact angles reducing with time is established, the mechanics reverts back to the situation depicted in Figure 8B, where the liquid body eventually evaporates away fully. It is compelling at this juncture to note that the contact line pinning effects that hold the liquid in place
(i.e., at 180 s) rely on a surface area (at the edge of the hole) that takes up barely 2.9% of the total surface area of liquid. If the circumference is attributed instead to the liquid body being able to “hang-on” to the substrate via the hole, this equates to it having a pinning retention capacity of 0.0148 N/m without the need to alter the micro- and nanostructure compositions that typically would allow it to assume a more predominant Wenzel wetting to do so. This represents about one-fifth the surface tension of water (0.0728 N/m). It is noteworthy that in using 15 μL, the liquid body dispensed did not fall through 14 times out of 20 repetitions made. The distribution of falling and nonfalling occurrences was also random, leading us to conclude

Figure 11. Side views of a 15 μL liquid body deposited on the hole of the silicone sheet at various time points during evaporation. The overhanging drop component was not as noticeable from the outset, and the liquid body evaporated fully on the surface without ever falling through the hole. The ability of drops to fall through or dangle from the hole with evaporation appears limited to cases where strong Cassie wetting occurs.

Figure 12. Sequence of images showing a sessile drop originally placed on a horizontal SH plate, then tilted at an angle of 30°, and then evaporated over time. The amount of hysteresis and contact area on the substrate is reduced with evaporation. There are similarities and differences in shape changes of the liquid body on the SH hole.

Figure 13. Contact angle (A) traces of the 20 μL drop placed on the SH plate tilted at 30° to the horizontal. With the onset of evaporation, the advancing and receding contact angles decreased and increased, respectively. The liquid length on the substrate (B) reduces with evaporation as the advancing contact line achieves its nonbreaching condition. In this process, the receding contact line position was invariant.
that the pinning behavior leading to drop hanging was purely stochastic.

These findings have important implications in the reported use of evaporative preconcentration to assist in the detection of low concentrations of nanoparticles in solutions while limiting the effect of contamination (from other stray particulates in the environment) using SH substrates. In using SH mesh substrates with holes, it is possible to conduct this with multiple drops, combining those that have fallen off (the liquid drop fall-off assured because cross-sectional pinning area being minimized), and then repeating the process. This will result in a final drop that will have a much higher concentration of nanoparticles available for detection. It is conceivable that at the stage prior to measurement, it should be possible to obtain the highest nanoparticle concentration in the solution possible if the drop following evaporation did not fall-off (the presence of a hole still needed to minimize liquid—solid contact). In this situation, knowledge of the condition where the lowest drop volume can be dispensed without it falling off the hole would be useful.

When 15 μL of DI water was dispensed on the silicone substrate (with hole, the overhanging component was not clearly observable (Figure 11). With evaporation, the drop altered its shape without any apparent effects offered by the hole and eventually evaporated off fully on the substrate without falling off.

The liquid body beyond the 180 s time point with the SH substrate has advancing contact angles that are larger than the receding contact angles, which is akin to the situation of drops being tilted on inclines. To develop a comparison, a secondary experiment involving a second substrate with hydrophilic and SH features was conducted with a 20 μL drop placed on it. The substrate was then inclined at an angle of 30° to the horizontal and then allowed to evaporate. The stage at which the overhanging component of the liquid body retracts can be equated to the behavior of a sessile drop illustrated under this condition. Clearly, when the substrate is inclined to the horizontal, the advancing and receding contact angles are differentiated due to hysteresis, leading to a “leaning over” behavior at the front end (Figure 12). This is aided to some extent by the ability of AL but not RL to breach initially, similar to situations that were reported previously. With evaporation, this contact angle disparity reduces and AL gradually restores back toward its condition before evaporating. From the quantitative plots of advancing and receding angles with time (Figure 13A), it can be seen that the rate with which the advancing contact angle reduces is somewhat similar to the rate at which the receding contact angle increases. This is markedly different from the case when 15 μL was placed on the SH sheet with a hole and at the stage where the overhanging component dominates (Figure 10B). It is also noteworthy that the liquid length in contact with the solid reduces significantly with evaporation (Figure 13B) and the situation where AL moves relatively toward RL gives the impression of gravity being defied. This behavior appears similar to the case when the overhanging drop component dominates with 15 μL placed on the SH sheet with a hole.

The extent that the sessile drop on the incline is able to restore from its forward leaning over shape behavior is naturally more limited if no breaching of AL occurs. Much of this is caused by the need for some liquid—solid interface area to exist, which is taken up substantially by the distance separation between AL and RL (see Figure 7). This is in contrast to the case when the drop is placed on the hole, which, because of the small thickness of the sheet, meant that AL and RL are almost merged. The circumference of the hole then contributes more strongly to the liquid—solid interface area requirement despite it retaining a Cassie wetting state. It should also be noted that the manner in which sessile drops with high contact angles are being constrained on inclines makes them less stable, imbuing them with a propensity to resonate when periodic or stochastic perturbations are introduced. We have noticed a similar resonant motion with perturbations, which may be linked to the geometry and composition of the liquid body. This offers avenues to reveal information about the properties of liquid samples.

A cardinal point to raise here is that unlike the case of the sessile drop on an incline, where pinning is afforded by hydrophilic regions (with the SH regions merely serving to increase the contact angles), the capability of the substrate with a hole to sustain the liquid body is provided solely by pinning at the edges of the orifice notwithstanding the material makeup being entirely SH. This affords a new paradigm to how wetting characteristics using SH surfaces can be harnessed. In numerical microscopic-scale studies conducted on regularly spaced pillars, the distances between them have been found to be strongly responsible in ascertaining whether overall Cassie or Wenzel wetting can be attained. This is seemingly attractive in that wetting characteristics can be tuned by changing this parameter alone. More recently, however, the effect played by evaporation in altering these characteristics has been reported. Because evaporation cannot be avoided or easily controlled in most real-world situations, the reliance on Cassie or Wenzel wetting changes via the former strategy can be limiting. In addition, the generation of surfaces using regular microposts will generally be too expensive to be usable in many real-world applications.

The work here provides evidence that interventions at a more macroscopic scale (more specifically with millimeter size scale holes) hold the key to liquids attaining retention characteristics despite the inherent surface wetting characteristics remaining predominantly Cassie in nature. We contend that further investigations along this vein hold promise to being able to better tailor SH surfaces for various practical applications. Such an endeavor has some similarities with a previous report using pinning to create highly deformed shapes, albeit in that case the surface has to be inherently hydrophilic to start with.

CONCLUSIONS

Liquid of different volumes dispensed onto a 0.1 mm thick SH sheet with a 2 mm hole exhibited different characteristics with evaporation. When 16 μL of water was dispensed, the volume of the sessile drop was initially higher than that of the overhanging drop component and consistently maintained this behavior until the later stages where both assumed almost similar volumes and evaporated fully without falling off the hole. In contrast, when 15 μL of water was dispensed, the volume of the sessile drop was initially higher than that of the overhanging drop component until a stage (at the 180 s time point) when sudden changes occurred due to the contact line not having sufficient pinning strength when encountering the edge of the hole. This caused the liquid body to squeeze through the hole, resulting in either its detachment from the hole or its pinning by the edges into an oval-like shape. In the latter case, the liquid body assumed reversed volume and contact angle characteristics for the sessile drop and over-
hanging drop components compared with those for the 16 µL drop volume case. In the later stages, both sessile and overhanging components again assumed almost similar volumes and evaporated fully without falling off the hole. This behavior was not observed with a hydrophobic substrate (silicone) with an equal size hole. Experiments with a sessile drop on a SH plate inclined at 30° to the horizontal and evaporated indicated shape characteristics that had similarities and differences with the results obtained from those of the 15 µL drop volume dispensed on the SH sheet with a hole.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01114.

Side views of a 25 µL drop dispensed on a super-hydrophobic substrate with hole under the onset of evaporation (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Cao, M.; Guo, D.; Yu, C.; Li, K.; Liu, M.; Jiang, L. Water-repellent properties of superhydrophobic and lubricant-infused “slippery” surfaces: A brief study on the functions and applications. *ACS Appl. Mater. Interfaces* 2016, 8, 3615–3623.

(2) Hof, B. Fluid dynamics: Water flows out of touch. *Nature* 2017, 541, 161–162.

(3) Bhushan, B.; Jung, Y. C.; Koch, K. Self-cleaning efficiency of artificial superhydrophobic surfaces. *Langmuir* 2009, 25, 3240–3248.

(4) Yu, M.; Chen, S.; Zhang, B.; Qiu, D.; Cui, S. Why a lotus-like superhydrophobic surface is self-cleaning? An explanation from surface force measurements and analysis. *Langmuir* 2014, 30, 13615–13621.

(5) Zhang, X.-S.; Zhu, F.-Y.; Han, M.-D.; Sun, X.-M.; Peng, X.-H.; Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 10769–10775.

(6) Di Mundo, R.; Nardulli, M.; Milella, A.; Favia, P.; Agostino, R.; Gristina, R. Cell adhesion on nanotextured slippery superhydrophobic surfaces. *Langmuir* 2015, 31, 4924–4932.

(7) Vuong, T.; Cheong, B. H.-P.; Huynh, S. H.; Muradoglu, M.; Liew, O. W.; Ng, T. W. Drop transfer between superhydrophobic wells using air logic control. *Lab Chip* 2015, 15, 991–995.

(8) Shao, F.; Ng, T. W.; Liew, O. W.; Fu, J.; Srithar, T. Evaporative preconcentration and cryopreservation of fluorescent analytes using superhydrophobic surfaces. *Soft Matter* 2012, 8, 3563–3569.

(9) Sun, Q.; Aguila, B.; Verma, G.; Liu, X.; Dai, Z.; Deng, F.; Meng, X.; Xiao, F.-S.; Ma, S. Superhydrophobicity: Constructing homogeneous catalysts into superhydrophobic porous frameworks to protect them from hydrolytic degradation. *Chem* 2016, 1, 628–639.

(10) Moita, A. S.; Laurêncio, C.; Ramos, J. A.; Prazeres, D. M. F.; Moreira, A. L. N. Dynamics of droplets of biological fluids on smooth superhydrophobic surfaces under electrostatic actuation. *J. Bionic Eng.* 2016, 13, 220–234.

(11) Cheong, B. H.-P.; Muradoglu, M.; Liew, O. W.; Ng, T. W. Concentrating nanoparticles in environmental monitoring. *Environ. Toxicol. Pharmacol.* 2015, 40, 187–190.

(12) Chung, D. C. K.; Huynh, S. H.; Wang, S.; Jiang, X.; Liew, O. W.; Muradoglu, M.; Ng, T. W. Superhydrophobic manhole for drops. *J. Mater. Chem. A* 2017, 5, 914–918.

(13) Dussan, V., E. B. On the Ability of Drops or Bubbles to Stick to Non-horizontal Surface of Solids. Part 2. Small Drops or Bubbles Having Contact Angles of Arbitrary Size. *J. Fluid Mech.* 1985, 151, 1–20.

(14) Ling, W. Y. L.; Ng, T. W.; Nelder, A.; Zheng, Q. Sliding variability of droplets on a hydrophobic incline due to surface entrained air bubbles. *J. Colloid Interface Sci.* 2011, 354, 832–842.

(15) Tadmor, R.; Chaurasia, K.; Yadav, P. S.; Leh, A.; Bahadur, P.; Dang, L.; Hoffer, W. R. Drop retention force as a function of resting time. *Langmuir* 2008, 24, 9370–9374.

(16) Zhang, X.-S.; Zhu, F.-Y.; Han, M.-D.; Sun, X.-M.; Peng, X.-H.; Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(17) Tsai, P. A. Universal wetting transition of an evaporating water droplet having contact angles of arbitrary size. *Soft Matter* 2015, 11, 568–577.

(18) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(19) Li, Y.; Wu, H.; Wang, F. Effect of a single nanoparticle on the contact line motion. *Langmuir* 2016, 32, 12676–12685.

(20) Roura, P.; Fort, J. Equilibrium of drops on inclined hydrophilic surfaces. *Phys. Rev. E* 2001, 64, No. 011601.

(21) Dussan, V., E. B. On the Ability of Drops or Bubbles to Stick to Non-horizontal Surface of Solids. Part 2. Small Drops or Bubbles Having Contact Angles of Arbitrary Size. *J. Fluid Mech.* 1985, 151, 1–20.

(22) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(23) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(24) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(25) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(26) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(27) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(28) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(29) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(30) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(31) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.

(32) Zhang, H.-X. Self-cleaning poly(dimethylsiloxane) film with functional micro/nano hierarchical structures. *Langmuir* 2013, 29, 849–855.
on hydrophobic micro- and nano-structures. *Soft Matter* 2017, 13, 978–984.

(33) Mettu, S.; Chaudhury, M. K. Vibration spectroscopy of a sessile drop and its contact line. *Langmuir* 2012, 28, 14100–14106.

(34) Korenchenko, A. E.; Malkova, J. P. Numerical investigation of phase relationships in an oscillating sessile drop. *Phys. Fluids* 2015, 27, No. 102104.

(35) Chong, M. L. H.; Cheng, M.; Katariya, M.; Muradoglu, M.; Cheong, B. H.-P.; Zahidi, A. A. A.; Yu, Y.; Liew, O. W.; Ng, T. W. Liquid body resonance while contacting a rotating superhydrophobic surface. *Eur. Phys. J. E: Soft Matter Biol. Phys.* 2015, 38, 119.

(36) Zheng, Q.-S.; Yu, Y.; Zhao, Z.-H. Effects of hydraulic pressure on the stability and transition of wetting modes of superhydrophobic surfaces. *Langmuir* 2005, 21, 12207–12212.

(37) Papadopoulos, P.; Mammen, L.; Deng, X.; Vollmer, D.; Butt, H.-J. How superhydrophobicity breaks down. *Proc. Natl. Acad. Sci. U.S.A.* 2013, 110, 3254–3258.

(38) Cheng, D. F.; McCarthy, T. J. Using the fact that wetting is contact line dependent. *Langmuir* 2011, 27, 3693–3697.