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Hybrid Surface Design for Robust Superhydrophobicity

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Supporting Information

ABSTRACT: Surfaces may be rendered superhydrophobic by engineering the surface morphology to control the extent of the liquid–air interface and by the use of low-surface-energy coatings. The droplet state on a superhydrophobic surface under static and dynamic conditions may be explained in terms of the relative magnitudes of the wetting and ant iwetting pressures acting at the liquid–air interface on the substrate. In this paper, we discuss the design and fabrication of hollow hybrid superhydrophobic surfaces which incorporate both communicating and noncommunicating air gaps. The surface design is analytically shown to exhibit higher capillary (or nonwetting) pressure compared to solid pillars with only communicating air gaps. Six hybrid surfaces are fabricated with different surface parameters selected such that the Cassie state of a droplet is energetically favorable. The robustness of the surfaces is tested under dynamic impingement conditions, and droplet dynamics are explained using pressure-based transitions between Cassie and Wenzel states. During droplet impingement, the effective water hammer pressure acting due to the sudden change in the velocity of the droplet is determined experimentally and is found to be at least 2 orders of magnitude less than values reported in the literature. The experiments show that the water hammer pressure depends on the surface morphology and capillary pressure of the surface. We propose that the observed reduction in shock pressure may be attributed to the presence of air gaps in the substrate. This feature allows liquid deformation and hence avoids the sudden stoppage of the droplet motion as opposed to droplet behavior on smooth surfaces.

1. INTRODUCTION

The development of superhydrophobic surfaces has attracted significant attention over the past decade because of promising applications in hydrophobic windshields, microfluidics-based technologies such as lab-on-chip devices,1,2 microelectromechanical systems (MEMSs), and ice-repellent surfaces.3 Surfaces may be rendered superhydrophobic by carefully engineering the surface topology and controlling the ratio (ϕ) of the top surface area of the pillars to the total base surface area, thereby controlling the extent of the liquid–air interface.4 Either the Cassie (droplet sits on top of the roughness elements) or the Wenzel (droplet uniformly wets the gaps between the roughness elements) state may be the stable state for a droplet placed on the surface, depending on which state corresponds to a lower energy. Dynamic switching from the Cassie to the Wenzel state can be attained by means of electrical actuation,5–9 application of pressure on the droplet, or dropping the droplet from a height.10

In its Cassie state, a droplet on a superhydrophobic surface experiences a high contact angle which reduces its area of contact with the substrate; the contact angle hysteresis (CAH) is very low, resulting in a low slide-off angle.11–14 This property of superhydrophobic surfaces helps reduce the drag force offered to fluid transport and is being studied extensively for microchannel-based and other applications.15

A high contact angle is not the sole criterion that characterizes the superhydrophobicity of a surface. It is important to design surfaces that are sufficiently robust to prevent impalement by droplets when subjected to external force. A higher capillary pressure within the interstices of roughness elements on a surface enhances the stability of the air gaps therein.16,17 Very high contact angles may be obtained by increasing the liquid–air interfacial area when a droplet is placed on the surface, i.e., by increasing the air gap between the roughness elements. However, larger air gaps result in reduced capillary pressure, with a corresponding reduction in the external actuation force required for the Cassie-to-Wenzel transition. The transition to a Wenzel state due to external forces displaces the air gaps with liquid and significantly increases the drag force incurred in transporting a droplet on the surface. Surface designs must therefore be optimized such that they sustain high contact angles with low contact angle hysteresis, without compromising the antiwetting property of the surfaces.

Higher capillary pressures can be achieved by scaling down the feature size of the roughness elements on the surface, as
well as by employing hierarchical roughness structures. However, lower feature sizes render the surface susceptible to a wetting transition, since the hanging curvature allows a droplet to more readily contact the bottom surface. The challenge, therefore, is to design surfaces that enhance the capillary pressure at the level of single roughness elements for a particular feature size. Park et al. reported the use of a cylindrical nanoshell array to generate a superhydrophobic surface, even without the use of a hydrophobic coating. Bahadur and Garimella demonstrated that structured surfaces with noncommunicating craters offered greater resistance to electrowetting-induced droplet transition compared to equivalent, communicating pillared structures.

Analytical and experimental research has corroborated the strong effect of surface morphology on the impact behavior of a water droplet and its ability to bounce off the surface. Bhushan et al. demonstrated improved water repellence on hierarchical surfaces as compared to single roughness elements. On the basis of the Laplace pressure and the Bernoulli pressure, they formulated an expression for the critical velocity of the droplet beyond which it transitions to a Wenzel state on textured surfaces. Deng et al. developed a pressure-balance model to arrive at a condition for droplet infiltration into the air gaps in the surface structures. They accounted for the water hammer pressure that acts on the surface during droplet impingement. Denser textured surfaces were expected to provide greater capillary pressure and superior resistance to Wenzel wetting of impacting droplets.

The water hammer pressure ($P_{WH}$) was first proposed by Cook as $P_{WH} = \rho c V$, where $\rho$ is the density of the impinging droplet, $c$ the speed of sound in the liquid, and $V$ the velocity of impingement. This expression was validated by Engel through droplet impingement experiments on different substrates and by the use of a Schlieren technique to determine the time dependence of the impact force. He proposed a correction to Cook’s expression, $P_{WH} = kpcV$, where the coefficient $k$ varies depending on the type of the substrate and impact velocity. While the water hammer pressure is relatively well-defined for a flat, rigid surface, it is less well understood during droplet impact on superhydrophobic surfaces.

The focus of present research in this field is not only on the development of surfaces that exhibit superhydrophobic properties, but also on ensuring that they are robust and can maintain the superhydrophobic state against external forces that tend to induce wetting. In this paper, we present and discuss two major findings. First, we show through analysis that hollow square pillars used as roughness elements demonstrate a higher ant iwetting pressure as compared to solid pillars of similar dimensions, both with communicating air gaps. Second, we characterize the hybrid surfaces fabricated in this work in terms of the static contact angle of a sessile droplet and test their robustness with droplet impingement tests. We explain the droplet impingement behavior on the superhydrophobic surfaces using a dynamic pressure model. We then use the experimental results to determine the water hammer pressure during impact. We show the water hammer pressure acting on the superhydrophobic substrate during droplet impingement to be dependent on the surface morphology.

### 2. HYBRID SUPERHYDROPHOBIC SURFACES: DESIGN AND FABRICATION

The intrinsic contact angle, or Young’s contact angle ($\theta_Y$), of a droplet when placed on a smooth surface is given by the relative surface energies of the solid–liquid ($\gamma_{SL}$), solid–air ($\gamma_{SA}$), and liquid–air ($\gamma_{LA}$) interfaces as

$$\theta_Y = \cos^{-1}\left(\frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}}\right)$$

On a structured surface, on the other hand, the droplet contact angle depends on whether it is in a Cassie or a Wenzel state on the substrate; this droplet state can be predicted using an energy minimization approach. A droplet gently deposited on a rough surface that favors the Cassie state energetically stays in the Cassie state with a high contact angle as given by

$$\theta_C = \cos^{-1}(-1 + \phi(1 + \cos \theta_Y))$$

where $\theta_C$ is Young’s contact angle of the droplet on a smooth surface (=120° for a water droplet on a Teflon-coated smooth surface) and $\phi$ is the solid area fraction defined as the ratio of the projected area to the base area of the surface ($\phi = a^2/p^2$), with $a_s$ being the feature size and $p$ the pitch of the pillars (Figure 1a). The apparent contact angle of a droplet in the Cassie state thus depends on Young's contact angle and the solid fraction.

An alternative situation is realized when the droplet homogeneously wets the micropillars and is in the Wenzel state; the contact angle in this case is given by

$$\theta_W = \cos^{-1}(r_m \cos \theta_Y)$$

in which $r_m$ is the roughness given by $r_m = 1 + 4a_hh/p^2$ and $h$ is the height of the roughness elements.

It is possible to obtain two different contact angles (corresponding to the Cassie and Wenzel states) on the same rough surface depending on how the droplet is formed. The important condition for the Cassie state to be the more stable configuration on a superhydrophobic (SH) surface is for the Cassie state of the droplet to have a lower energy than the Wenzel state. That is, the contact angle obtained from the Cassie expression (eq 2) must be smaller than that obtained using the Wenzel expression (eq 3).

The nonwetting Cassie state of an SH surface is attributed to the high capillary pressure ($P_C$) resulting from its small pore structure. The capillary pressure depends on Young’s contact angle ($\theta_Y$) of the droplet on a smooth surface and the capillary perimeter ($L_C$) and area ($A_C$) and is given as

$$P_C = -\gamma_{LA}(\cos \theta_Y)\frac{L_C}{A_C}$$
in which \( \gamma_{LA} \) is the surface tension of the liquid (=0.072 N/m for water). For a structured surface with a solid-pillared pattern as shown in Figure 1a, the capillary pressure takes the form

\[
R_C = -4\gamma_{LA} \cos(\theta) \frac{\phi}{a_o(1 - \phi)}
\]  

The total energy barrier between the two states of a droplet of radius \( R_C \) (assuming the space beneath the droplet to be wetted homogeneously) may be determined by multiplying the energy by the total number of pillars \( n \) beneath the droplet \( n = \pi R_C^2 / \phi \) as

\[
E_C - E_W = -4\gamma_{LA} \cos(\theta) a_o h \frac{\pi R_C^2}{\phi}
\]

\[
= -4\gamma_{LA} \cos(\theta) a_o h (1 - \phi) \pi R_C^2 / \phi^2
\]

\[
= -4\gamma_{LA} \cos(\theta) a_o h (1 - \phi) \pi R_C^2 / \phi^2
\]

The energy barrier between the Cassie and Wenzel states can be overcome by the kinetic energy of the droplet striking such a surface. Under dynamic conditions, additional pressures come into play at the interface: the Bernoulli pressure \( (P_{B}) \), the water hammer pressure \( (P_{WH}) \), and the antiwetting pressure which may exceed the hydrostatic pressure acting on the surface. \( P_{WH} \) acting during the impingement of a droplet on a textured superhydrophobic surface is therefore determined experimentally using a pressure-balance-based approach in the present work, as discussed in a subsequent section.

To prevent the droplet transition to homogeneous wetting of the surface, the antiwetting pressure must exceed the wetting pressure, namely, the sum of the dynamic pressure and the water hammer pressure, i.e., \( P_C > P_D + P_{WH} \). Otherwise, either partial or total infiltration of the air gap by the impinging droplet occurs. Figure 2 illustrates these two possibilities following the impingement of a droplet on a superhydrophobic surface.

The capillary pressure may be enhanced by decreasing the feature size (eq 5). The feature height must exceed a minimum value to avoid a transition to droplet impalement caused by the curved surface of the droplet touching the substrate. Tall, slender pillars would ensure superhydrophobicity, but may not be sufficiently robust. At the microscale, an alternate approach is to modify the surface design to increase the net antiwetting pressure. In the remainder of this section, we describe the design of hollow-pillared hybrid surfaces based on this approach and compare their characteristics in terms of static contact angle and antiwetting pressure with those of surfaces with solid pillars with only communicating air gaps.

The hollow-pillared hybrid surface designed in this work consists of a square array of pillars with square holes at the centers of each of the pillars that serve to trap air in the holes. The rationale is to use both the communicating and noncommunicating air gaps to enhance the antiwetting property of the surfaces. Figure 1b shows the layout of such a surface: \( a_o \) and \( a_i \) represent the outer and inner dimensions of the square pillars, \( b \) is the pitch of the pillars, and \( h \) is the gap between the pillars. In the present study, \( a_o \) is maintained at \( \phi \alpha_o \) for all the fabricated surfaces. For the experimental verification tests, six different substrates are fabricated with varying surface roughness and solid fraction as will be discussed in detail in a following section.

2.1. Static Contact Angle on the Hybrid Structure. The static contact angle that may be achieved with the hollow-pillared hybrid surfaces (Figure 1b) is compared against that with a solid-pillared surface (Figure 1a) of equivalent pillar outer dimension, \( a_o \). The solid fraction \( \phi \) and the surface roughness \( r_m \) of the hybrid surface are given by

\[
\phi = \frac{a_o^2 - a_i^2}{b^2}
\]

\[
r_m = 1 + \frac{4(a_o + a_i)h}{b^2}
\]

The use of the noncommunicating air gaps reduces the solid fraction, thus increasing the apparent contact angle. He et al. formulated an expression for the equilibrium contact angle based on the energy balance between the Cassie and Wenzel states of the droplet. This angle represents the maximum contact angle of a droplet on a particular superhydrophobic surface and for communicating square structures is given by

![Figure 2. Schematic illustration of the alternative transition events during droplet impingement on a superhydrophobic surface.](Image)
the same a support the Cassie state of a droplet over a larger range of solid structures than with solid pillars. It is also noteworthy that hybrid pillars angle can be obtained using a hollow-pillared hybrid geometry solid pillars of 159.

varying the pitch Structure.

the capillary pressure of the surface is also di

dependence of the contact angle on the solid fraction for hollow hybrid pillars and solid pillars. The intersection of the Cassie and Wenzel curves represents the equilibrium contact angle.

the contact angle for the Cassie (eq 2) and the Wenzel (eq 3) states with respect to the solid fraction corresponding to both the hollow-pillared hybrid surfaces and the solid pillar structures. The chosen feature dimensions are \( a_o = 20 \mu m \) and pillar height \( h = 32 \mu m \), and the solid fraction \( \phi \) is varied by varying the pitch \( p \). The equilibrium contact angle \( \theta_E \) is the intersection of the Cassie and the Wenzel curves (Figure 3).

The equilibrium contact angle for the hybrid structure is 167.2° and is achieved at \( \phi = 0.049 \); this compares to the values for the solid pillars of 159° at \( \phi = 0.137 \). Thus, a higher stable contact angle can be obtained using a hollow-pillared hybrid geometry than with solid pillars. It is also noteworthy that hybrid pillars support the Cassie state of a droplet over a larger range of solid fractions (\( \phi > 0.049 \)) than do the solid pillars (\( \phi > 0.137 \)) for the same \( a_o \).

2.2. Antiwetting Pressure Offered by the Hybrid Structure. The capillary pressure of the surface is also different for the hollow hybrid pillars proposed here, relative to a solid pillar structure. From eq 4, the capillary pressure for the hybrid surface is

\[
\cos \theta_E = \left[ 1 + \frac{4\phi h}{a_o} (1 - \phi) \right]^{-1}
\]

Thus, the equilibrium contact angle of the droplet on the hollow-pillared hybrid geometry is given by

\[
\cos \theta_E = \left[ 1 + \frac{4\phi h}{(a_o - a_i)} (1 - \phi) \right]^{-1}
\]

Comparing eqs 10 and 11, it may be deduced that for a fixed outer feature size \( (a_o) \), the equilibrium contact angle \( (\theta_E) \) is larger for the hybrid surface. Figure 3 compares the variation of

obtained using the Cassie equation (eq 2) decreases. An increasing solid fraction implies a decrease in air gap size, which results in an increase in capillary pressure. Although this trend can be seen in the cases of both surface geometries, the hybrid surface shows a much higher capillary pressure than the solid pillars for a given contact angle. At a solid fraction of 0.4 (\( \theta_c \approx 143^\circ \)), the capillary pressure \( P_c \) is 14 400 N/m² for the hybrid surface but only 4800 N/m² for the solid pillars. This is an important factor in the design of robust superhydrophobic surfaces for high antiwetting pressure without compromising the high contact angle.

2.3. Fabrication of Hollow-Pillared Hybrid Surfaces. Six hybrid surface samples are fabricated in the present work, with the surface parameters selected such that the Cassie state is the stable configuration for a droplet. The contact angle and the capillary pressure for the six hybrid surfaces are computed from eqs 2 and 12, respectively, to be significantly higher than the values on corresponding solid square pillars of the same pillar outer dimension \( (a_o) \) and pitch \( (p) \). Table 2 summarizes these surface parameters. All the surfaces were fabricated in the Birck Nanotechnology Center at Purdue University. Silicon wafers with a 1 \( \mu m \) oxide layer are used as the substrates. The fabrication process includes spinning of hexamethyldisilazane (HMDS) at 3000 rpm for 10 s followed by spinning photoresist AZ 5214 (MicroChem) at 3000 rpm for 30 s. The wafer is soft-baked at 110 °C for 65 s and exposed for 7 s at a power of 23 mW/cm² (Karl Suss MJB-3 mask aligner). The reversal bake is carried out at 110 °C for 2 min and 40 s, followed by a flood exposure for 60 s. The photoresist is developed using AZ 400K:deionized (DI) water at a dilution ratio of 1:4 for 30 s. The photoresist is used to pattern SiO₂ using reactive ion etching (STS AOE). Subsequently, the photoresist is removed using acetone and methanol cleaning steps, and the patterned oxide layer acts as the etch mask for silicon patterning using a deep reactive ion etch (DRIE) process. A low etch rate of 1.7 \( \mu m/min \) is chosen for anisotropic etching to achieve the design feature size. The DRIE parameters are listed in Table 1.

After DRIE etching, the oxide layer is removed using a buffered oxide etch. The structures are subsequently spin-coated with 0.2% Teflon AF1600 (DuPont, Wilmington, DE) in FC77 solution at 1500 rpm for 30 s, resulting in a conformal coating of ~50 nm. The substrates are then baked at 90 °C for 45 min. Scanning electron microscopy (SEM) images of the hollow-pillared hybrid surfaces before spinning Teflon are shown in Figure 5.

Figure 3. Dependence of the contact angle on the solid fraction for hollow hybrid pillars and solid pillars. The intersection of the Cassie and Wenzel curves represents the equilibrium contact angle.

Figure 4. Variation of the contact angle and capillary pressure with the solid fraction for the hollow-pillared hybrid surface and the solid-pillared surface.
3. EXPERIMENTAL SETUP

The capillary length of a water droplet defined as \( (\gamma/\rho g)^{1/2} \) is 2.7 mm. For droplet diameters smaller than this length, the flattening effect of gravity on the droplet may be neglected and a spherical geometry assumed. A 3 \( \mu \)L deionized water droplet is used for the static contact angle measurements such that the length scale (diameter) is approximately 1.79 mm and is less than the capillary length. A goniometer (model 290 Ramehart) is used for imaging the droplet and determining its contact angle using a circular-fit algorithm. The spherical symmetry of the droplet allows for such a fit to determine the contact angle. The droplet impingement experiments are carried out with a droplet of 4.5 \( \mu \)L volume. Figure 6 shows a schematic diagram of the experimental setup used for the droplet impingement experiments. The images are recorded using a high-speed camera (Photron 1024 PCI) at 3000–3750 fps. Each experiment is carried out at least three times.

The reported droplet static contact angle is obtained as the average of the contact angles measured at different locations on the substrate. The droplet behavior upon impingement on the hybrid surfaces is seen to be extremely repeatable, mainly because of the precise control of the impingement settings and the uniformity of the fabricated substrates. For droplet impingement experiments, representative results are presented in terms of the contact angle and the droplet-wetted diameter. Image processing is done using an in-house Matlab\textsuperscript{33} code and Image J software (an image processing program available from the National Institutes of Health).

4. RESULTS AND DISCUSSION

4.1. Static Contact Angle. The static contact angles for the six test surfaces, measured using a circular curve-fit algorithm to the goniometer images, are summarized in Table 3. The experimental values of the contact angle lie within 96–103% of the theoretically predicted values (from eq 2), showing a reasonably good match. The reported static contact angles are averaged over four sets of experiments. All the fabricated hollow-pillared hybrid surfaces support high contact angles in the range of 153.4–157°.

4.2. Droplet Impingement. As discussed in an earlier section, the wetting transition upon impact is determined by the relative magnitudes of the Bernoulli pressure \( (P_D) \), water hammer pressure \( (P_{WH}) \), and capillary pressure \( (P_C) \). When a droplet of water impinges on a surface from a height of 50 mm

![Figure 5. SEM images of four representative hollow hybrid superhydrophobic surfaces fabricated in the present work: (a) surface 1, (b) surface 3, (c) surface 4, and (d) surface 5.](image)

![Figure 6. Schematic diagram of the experimental setup for the droplet impingement experiments.](image)
Table 3. Predicted and Measured Values of the Static Contact Angle for Hollow-Pillared Hybrid Surfaces

<table>
<thead>
<tr>
<th>surface</th>
<th>contact angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>163.5 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>160.9 ± 0.9</td>
</tr>
<tr>
<td>3</td>
<td>157.7 ± 0.5</td>
</tr>
<tr>
<td>4</td>
<td>154.7 ± 1.1</td>
</tr>
<tr>
<td>5</td>
<td>152.3 ± 0.2</td>
</tr>
<tr>
<td>6</td>
<td>149.7 ± 0.5</td>
</tr>
</tbody>
</table>

with $a_w = 20 \mu m$ and $\phi = 0.1$, these pressures take magnitudes of $P_C = 1934 N/m^2$, $P_a = 491 N/m^2$, and $P_{WH} = 296740 N/m^2$ (obtained using $k = 0.2$ in the expression for $P_{WH}$). The water hammer pressure so predicted is orders of magnitude higher than the wetting pressures, and the wetting transition would be expected to occur at a droplet impingement height as small as $\sim 2 \mu m$. In the experiments, however, it is observed that the wetting transition for superhydrophobic surfaces of this geometry occurs when the impingement height is in the range of tens of millimeters. It is clear that the expression for predicting $P_{WH}$ must be modified.

The droplet impingement experiments not only assess the robustness of the air gaps of the fabricated hollow-pillared hybrid surfaces, but also aid in understanding the mechanics of the impingement-induced droplet transition on the superhydrophobic surfaces. Experiments were carried out by carefully incrementing the height of impingement in steps of 5 mm until a height was reached at which a part of the droplet goes into the Wenzel state on the surface. The velocity corresponding to this occurrence is termed the critical velocity. In the following sections we describe the dynamics of the droplet upon impingement on the hybrid surfaces and propose a modified expression for predicting the water hammer pressure.

4.2.1. Droplet Dynamics. This section describes the dynamics of droplets impinging on superhydrophobic surfaces during completely nonwetting (Figure 2a) and partial wetting (Figure 2b) impact. A droplet of volume $\sim 4.5 \mu L$ was used in all the impingement experiments. The relative importance of the kinetic energy of the impinging droplet and the surface tension force may be compared using the Weber number, defined as $We = \rho V^2 R / \gamma_{LA}$, where $R$ is the radius of the droplet. The Weber number in our experiments varies between 2.7 and 27.3.

The behavior of the droplet upon impact can be analyzed in terms of two main stages. In the first stage, the droplet interface advances to attain the maximum wetted diameter. During this phase, the kinetic energy of the droplet is stored as deformation energy in the droplet. The first stage (advancing phase) is an inertia-driven phenomenon; in the second stage (receding phase), the droplet retracts and the stored energy helps it rebound off the surface. Complete retraction and detachment of the droplet from the superhydrophobic surface is possible only when the air gap within the structures retains its integrity during impact; this is the basic test for water repellence of a surface. In this nonwetting case the pressure of the air gap prevents the droplet from going into a Wenzel state and the droplet reaches almost the same maximum wetted diameter ($\sim 1.85$ times the initial diameter of the droplet) for both wetting (surface 1) and nonwetting (surface 3) impact. This may be attributed to the extremely small fraction of the droplet penetrating the air gap compared to illustrate the dynamics of transition of the droplet to the Wenzel state upon impact. Instantaneous images during the droplet impact process are included as insets in the figure; surfaces 1 and 3 are chosen for inclusion in the figure as they display the minimum and the maximum capillary pressures, respectively, of the six test surfaces designed. For an impingement velocity of $V = 0.99 m/s$, the droplet undergoes a nonwetting impact on surface 3 and a Wenzel transition occurs on surface 1. The time period from $t = 0 ms$ to $t = 2.667 ms$ corresponds to the advancing phase of the droplet. The effect of the Cassie-to-Wenzel transition on the advancing phase of the droplet (i.e., until the droplet reaches its maximum wetted diameter) is negligible. The droplet reaches almost the same maximum wetted diameter ($\sim 1.85$ times the initial diameter of the droplet) for both wetting (surface 1) and nonwetting (surface 3) impact. This may be attributed to the extremely small fraction of the droplet penetrating the air gap compared...
to the volume of the droplet for impact on all six surfaces. In the case of surface 1, for an impingement height of 50 mm, the transition occurs over an area with radius \( \sim 0.72 \text{ mm} \) (Figure 8), and assuming complete transition occurs over this area, the volume of displaced air is 0.048 mm\(^3\), which is approximately 1% of the total volume of the droplet.

A strong influence of the surface type on droplet behavior upon impact is seen, however, during the retraction phase. On surface 3, the droplet retracts and detaches from the surface at \( t = 11.33 \) ms (Figure 8). Okumura et al.\(^{34}\) proposed that the contact time (the total time of contact of the droplet with the surface) for a nonwetting impact is given by a characteristic time scale based on a balance between inertia and capillarity as \( t = (2.6 \pm 0.1)(pR^2/p)^{1/2}\). This characteristic time scale for the droplet in the present work is 10.1 ms. The slightly larger contact time observed with surface 3 may be attributed to the hysteresis of the surface.\(^{39}\) It can be seen from Figure 8 that the droplet behaves more or less alike on both surfaces 1 and 3 until \( t = 8 \) ms. The wetted diameter of the droplet on surface 1 beyond \( t = 8 \) ms remains constant; thus, the corresponding wetted diameter gives the length scale over which droplet transition occurred during impingement. Beyond this time, the droplet continues to retract with diminishing wetted diameter on surface 3, but is stuck indefinitely on surface 1. The inability of the droplet to recover from the Wenzel state induced due to impingement shows that there is extremely high resistance involved in detaching the droplet from the surface once it goes to its Wenzel state. This can be explained in terms of the energy expended in the transition process relative to the energy required for the subsequent reverse transition (from the Wenzel to Cassie state). During droplet impingement, part of the energy of the droplet is expended in overcoming the energy barrier between the Cassie and the Wenzel states of the droplet and the other part is utilized in spreading and subsequent retraction of the droplet interface.

The energy barrier for hollow-pillared hybrid surface may be determined from a modified form of eq 7:

\[
E_C - E_W = -4\pi\gamma_{LA}(\cos \theta_0)(a_o + a_i)\frac{hR_C^2}{p^2} = -4\pi R_C^2\gamma_{LA}(\cos \theta_0)\frac{h}{(a_o - a_i)}
\]

Corresponding to a droplet impingement height of 50 mm, a portion of the droplet (of contact radius 0.72 mm) undergoes Wenzel transition on surface 1 as discussed earlier. The energy expended for this transition is 0.125 \( \muJ \), which is only a small fraction of the total energy of the droplet \( (E_K = 2.21 \muJ) \). The inability of the droplet to retract to the Cassie state once transition has occurred highlights the effect of nonconservative dissipation forces acting during reverse transition.\(^{30}\) In contrast, the droplet has a nonwetting impact on surface 3, which means that the dissipative energy loss occurs only on top of the pillars and, hence, the entire droplet is able to bounce off the surface. The energy required for the Wenzel-to-Cassie reverse transition is much higher for the hollow-pillared hybrid surfaces than for the solid pillars, owing to the increased roughness \( (r_m) \) in the former.

Another characteristic distinguishing Cassie and Wenzel impact is the instantaneous contact angle of the droplet during the advancing and the receding phases (Figure 8). On surface 3, the droplet maintains a very high contact angle during its entire period of contact with the surface. On surface 1, however, the contact angle decreases beyond \( t = 8 \) ms, while the wetted diameter remains unchanged as the droplet remains partially in a Wenzel state. The oscillation observed in the contact angle beyond this time is a result of the attempt by the droplet to overcome the dissipative forces.

4.2.2. Pressure Balance. As discussed above, droplet impact on the hybrid surfaces fabricated for this work remains nonwetting for impingement velocities that are lower than the critical velocity. At the critical velocity, a part of the droplet goes into the Wenzel state and remains stuck to the surface. Once the impingement velocity exceeds the critical value and the effective wetting pressure exceeds the capillary pressure, the stability of the air gap in the superhydrophobic surface is compromised and drastic changes in the droplet characteristics are observed, primarily during the retraction phase of the droplet. Figure 9 illustrates the critical-velocity limit for surface 5. For the geometrical parameters of surface 5, the critical velocity is experimentally determined to be 1.37 m/s.

While expressions for \( P_{C} \) and \( P_{D} \) are available in the literature, the water hammer pressure \( P_{WH} \) for structured surfaces is less well quantified. The impact dynamics change in the presence of superhydrophobic surfaces. In the present work, careful experimental observation helps deduce the dependency of the water hammer pressure on different factors. The critical velocity corresponding to each surface is determined experimentally. The coefficient of water hammer pressure \( (P_{WH} = k_pV) \) is then determined for each of the hollow hybrid surfaces on the basis of the critical velocity for the Cassie–Wenzel transition.
The theoretically calculated capillary pressure $P_C$ applies. We assume that the effect of the step size of 5 mm used during impingement experiments is negligible in calculations of the coefficient. Table 4 lists the critical velocity and the value of the coefficient $k$ in the definition of $P_{WH}$ corresponding to each of the surfaces. It is observed from these results that this coefficient is in fact not a constant, but is rather a function of the capillary pressure of the surface. The coefficient varies almost linearly with respect to capillary pressure as shown in Figure 10.

![Figure 10](image1.png)

**Figure 10.** Dependence of the coefficient of water hammer pressure on the capillary pressure (corresponding to the six hybrid test surfaces in the present work). Experimental results from refs 35 and 36 for solid-pillared surfaces are also included.

Kwon et al.\textsuperscript{35} showed that a Cassie-to-Wenzel transition can be induced due to water hammer pressure acting during pendant-drop deposition on a superhydrophobic surface. Wu et al.\textsuperscript{36} carried out impingement experiments on superhydrophobic surfaces with different geometric parameters to demonstrate that the Cassie–Wenzel transition can lead to self-propelled movement of the droplet against the wettability gradient (due to the unbalanced interfacial forces). They reported the critical velocity of impingement for the different test surfaces (cylindrical pillars with fixed pillar diameter and height and varying pitch). We determine the capillary pressure on the basis of the geometrical parameters of the surfaces used by Wu et al.\textsuperscript{36} Substituting these values of critical impingement velocity and the capillary pressure in eq 14, we calculate the coefficient of water hammer pressure ($k$). The data points evaluated are included in Figure 10 to place our experimental results in context with the literature. Even with a surface geometry different from that considered in the present work, these results from the literature follow a similar trend.

This dependence of the water hammer pressure coefficient on the capillary pressure may be explained considering the morphology of the superhydrophobic surface, which is a combination of solid surfaces and air gaps. When a droplet impinges on a flat surface, its motion in the direction of fall is immediately arrested, resulting in a shock pressure. However, in the case of structured surfaces, the droplet experiences a heterogeneous impact. While the droplet comes to a sudden stop on the solid parts of the surface, it is still free to deform into the air gaps so that its overall deceleration is gradual. The shock developed is thus alleviated compared to that of a flat surface, and this results in the much smaller observed coefficient of $P_{WH}$ (ranging from $k = 0.1408 \times 10^{-2}$ to $k = 0.2334 \times 10^{-2}$ for the hybrid surfaces in this work compared to $k = 0.2$ on a flat surface for moderate impingement velocities of approximately 8 m/s\textsuperscript{26}).

In the limiting case ($V = V_{critical}$), the pressure balance may be written as

$$P_C - (k\rho cV)P_C - \frac{1}{2}\rho V^2 = 0$$

Equation 15 shows a quadratic dependence of the critical velocity on the capillary pressure, which is also illustrated by the experimental results as well as those from Wu et al.\textsuperscript{36} in Figure 11.

![Figure 11](image2.png)

**Figure 11.** Quadratic dependence of the critical velocity with respect to the capillary pressure for the superhydrophobic surfaces studied and for those from Wu et al.\textsuperscript{36}

This finding of the dependence of water hammer pressure on the surface morphology and capillary pressure could potentially contribute significantly to the design of superhydrophobic surfaces for practical applications. Experimental measurement of the impact forces during droplet impact on textured superhydrophobic surfaces would help in further understanding the physics of impingement-induced wetting and droplet retraction.

5. CONCLUSION

Hollow-pillared hybrid surfaces consisting of both communicating and noncommunicating air gaps are designed for enhancement of the antiwetting pressure during droplet impact. The energy barrier of the superhydrophobic surfaces is represented...
in terms of the capillary pressure of the air gaps. The design could be further improved by decreasing the feature size, which would result in enhanced capillary pressure and air gaps of greater robustness. An additional pressure, namely, the water hammer pressure, is demonstrated to play an important role during droplet impingement; however, the water hammer pressure coefficient is much smaller than for impingement on a rigid flat surface. Furthermore, the coefficient is predicted to be a function of the surface morphology and hence of the capillary pressure; the critical velocity (which is the velocity of the droplet at which the droplet just goes to a Wenzel state upon impingement) is observed to exhibit a quadratic relationship with the capillary pressure.

Precise measurement of the impact forces is required to further validate the experimental observations and to obtain a precise value for the water hammer pressure coefficient. Results from this study offer a better understanding of impact dynamics that can aid in the improved design of surfaces that can avoid the Wenzel transition under impinging droplets.

■ ASSOCIATED CONTENT

Supporting Information

Videos showing droplet impingement from a height of 50 mm on surface 4 (experiment corresponding to Figure 7) and on surface 1 demonstrating the nonwetting and wetting impacts, respectively. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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■ REFERENCES

