DYNAMIC WETTING ON SUPERHYDROPHOBIC SURFACES: DROPLET IMPACT AND WETTING HYSTERESIS
Katherine Smyth\textsuperscript{1}, Adam Paxon\textsuperscript{1}, Hyuk-min Kwon\textsuperscript{1}, Tao Deng\textsuperscript{2}, Kripa K. Varanasi\textsuperscript{1,}\textsuperscript{*}

\textsuperscript{1}Department of Mechanical Engineering
Massachusetts Institute of Technology, Cambridge, MA
\textsuperscript{2}GE Global Research Center, Niskayuna, NY

ABSTRACT

We study the wetting energetics and wetting hysteresis of sessile and impacting water droplets on superhydrophobic surfaces as a function of surface texture and surface energy. For sessile drops, we find three wetting regimes on these surfaces: equilibrium Cassie at small feature spacing, equilibrium Wenzel at large feature spacing, and an intermediate state at medium feature spacing. We observe minimum wetting hysteresis not on surfaces that exhibit Cassie wetting but rather on surfaces in the intermediate regime. We argue that droplets on these surfaces are metastable Cassie droplets whose internal Laplace pressure is insufficient to overcome the energy barrier required to homogeneously wet the surface. These metastable Cassie droplets show superior roll-off properties because the effective length of the contact line that is pinned to the surface is reduced. We develop a model that can predict the transition between the metastable Cassie and Wenzel regimes by comparing the Laplace pressure of the drop to the capillary pressure associated with the wetting-energy barrier of the textured surface. In the case of impacting droplets the water hammer and Bernoulli pressures must be compared with the capillary pressure. Experiments with impacting droplets show very good agreement with this simple pressure-balance model.

KEY WORDS: superhydrophobic, wetting, impact, hysteresis

NOMENCLATURE

\begin{itemize}
\item $a$: post width, m
\item $b$: post spacing, m
\item $h$: post height, m
\item $R$: drop radius of curvature, m
\item $\theta$: contact angle
\item $\gamma_{LV}$: liquid-vapor surface energy (N/m)
\end{itemize}

INTRODUCTION

Recent interest in the wetting properties of superhydrophobic surfaces has been intense. Fundamental understanding of liquid-solid wetting interactions is key to designing effective surfaces for applications such as self-cleaning, where it is desirable for impinging water droplets to roll off without wetting the surface, removing dust and debris in the process and thereby eliminating the need for active cleaning\textsuperscript{3}. As illustrated in Figure 1, one metric of performance is roll-off angle, the angle of surface inclination at which a deposited water droplet begins to roll off.

Many surfaces, both natural and synthetic, exhibit favorable roll-off and self-cleaning properties. Naturally occurring surfaces with self-cleaning properties include the leaves of lotus plants (Nelumbo nucifera), which have micro- and nanoscale asperities composed of waxy, hydrophobic material\textsuperscript{1-2}. Researchers have fabricated textured, hydrophobic surfaces through a range of methods to attain low roll-off angles. Methods include electrodeposition\textsuperscript{3}, nanotube growth\textsuperscript{4}, lithography\textsuperscript{5}, and wet etching\textsuperscript{6}. Textured, hydrophobic surfaces induce roll-off by minimizing solid contact with water droplets. The corresponding equilibrium wetting state on textured surfaces where air is trapped beneath the water droplet is known as the Cassie state\textsuperscript{7}, while the equilibrium state in which water homogeneously contacts all available solid surface area is known as the Wenzel state\textsuperscript{8}, as shown in Figure 2. Models based on minimization of total interfacial energy predict wetting state and enable targeted design of surfaces to ensure Cassie wetting. Moreover, reports suggest designing for equilibrium Cassie wetting as a strategy to design robust surfaces that minimize contact angle hysteresis\textsuperscript{9-11}. However, surfaces outside this equilibrium Cassie design space often yield more favorable roll-off behavior.

![Figure 1](image1)

**Figure 1:** Schematic illustrations of contact (left) and roll-off (right) angles of droplets on a solid surface.

![Figure 2](image2)

**Figure 2:** Illustrations of the Wenzel (left) and Cassie (right) wetting states.

We study droplet roll-off on superhydrophobic arrays of lithographically fabricated square posts. To determine wetting state, we measure static contact angles and compare the results to minimum energy predictions for droplets in Cassie and
Wenzel states. Based on these comparisons, we observe three wetting regimes as the distance between posts is increased: equilibrium Cassie at small post spacing, equilibrium Wenzel at large post spacing, and an intermediate state at medium spacing. As expected, Wenzel droplets on surfaces with large spacing do not roll off. However, we observe minimum roll-off angles not on surfaces that exhibit equilibrium Cassie wetting, but rather on surfaces in the intermediate range. We argue that droplets on these surfaces are metastable Cassie droplets whose internal Laplace pressure is insufficient to overcome the energy barrier required to homogeneously wet the textures\textsuperscript{12}. We further argue that these metastable droplets are characterized by lower contact angle hysteresis (CAH) and optimum roll-off properties. We propose a simple pressure balance model and show that transition from the metastable Cassie to equilibrium Wenzel regimes occurs when the Laplace pressure exceeds the capillary pressure associated with the wetting energy barrier, enabling the droplet to force itself between the texture asperities. While some metastable wetting states may be overcome by impact velocity and other sources of significant input pressure\textsuperscript{10,12-13}, it is possible to design metastably wetting surfaces with substantial resistance to wetting pressures that characterize specific applications. These applications would thus benefit from enhanced performance enabled by metastable wetting\textsuperscript{14}.

**EXPERIMENTAL METHODS**

Silicon surfaces of periodic post arrays are prepared via photolithography and then coated with a layer of hydrophobic molecules to impart superhydrophobicity. To attain posts with high aspect ratios, we employ a deep reactive ion etching technique using the Bosch process. To minimize scalloping on the sidewalls, we develop recipes optimizing gas flows and time ratios between gas etch and sidewall passivation. We then coat these surfaces by placing them in an airtight vessel with about 50\textsuperscript{b} of fluorosilane (tridecafluoro-1,1,2,2-tetrahydrooctyl-trichlorosilane, Gelest), evacuating for several minutes to purge ambient air, and then allowing the remaining fluorosilane to equilibrate with the surface for at least two hours.

Contact angle measurements are conducted with the sessile droplet technique using a VCA Optima device. One-microliter droplets of deionized water are deposited onto the surface of interest, photographed, and then analyzed by curve fitting to determine the static contact angle. Occasionally, surfaces were so hydrophobic that droplets did not detach from the dispensing syringe even after being pushed into the surface. In these instances, the syringe is tapped gently while the droplet is in contact with the surface. Roll-off angles are measured using the tilt stage accessory to the VCA Optima device. After dispensing the 1\textsuperscript{L} droplet, the stage is tilted about two degrees per second to a maximum of 88° while the VCA data acquisition software captured four images per second. Analysis of the video yields the frame at which the droplets roll off, and hence the roll-off angle. For experiments that require both contact and roll-off angle measurements, we use the first image from roll-off videos to determine contact angle. The data points for contact angle and roll-off angle are obtained from six measurements per silicon wafer on two different wafers with identical texture.

**RESULTS AND DISCUSSION**

**Sessile Droplets**

To determine the design space of surface texturing for optimum droplet roll-off applications, we measure roll-off angles on a series of post arrays where the post spacing (denoted by \( b \) in Figure 3) is systematically varied. To determine the droplet wetting state, we measure contact angle and compare results to predicted Cassie and Wenzel angles. As expected, we find that droplets in the equilibrium Wenzel state exhibit poor roll-off behavior, clinging to the surface even when tilted vertically. Surprisingly, droplets in the equilibrium Cassie state did not yield the lowest roll-off angles. We find instead that the optimal region is within the equilibrium Wenzel wetting regime, but dewetting pressures originating from surface energy are sufficient to oppose droplet Laplace pressure and prevent liquid infiltration between the posts.

For arrays of posts that are 15\textsuperscript{m} wide and 25\textsuperscript{m} high, an optimal post spacing region exists for droplet roll-off. Measurements are plotted in Figure 4 as a function of post spacing-to-width ratio \( b/a \). For \( b/a \) ratio smaller than 1, 1\textsuperscript{L} droplets do not roll off, as indicated by values of 90°. When the \( b/a \) ratio is about 1.5, droplets begin to roll off, reaching minimum roll-off angles of about 17° at a \( b/a \) ratio of 5. However, for \( b/a \) ratio greater than about 6, droplets do not roll off.

![Figure 3: Schematic and SEM image of a representative post array. Top and side views of a unit cell illustrate definitions of post width \( a \), spacing \( b \), and height \( h \).](image-url)
To gain insight into droplet wetting state, we first calculate equilibrium contact angles according to the Wenzel and Cassie models. From interfacial energy considerations, it can be shown that the equilibrium contact angle $\theta_w$ in the Wenzel state is given by

$$\cos \theta_w = r \cos \theta_0$$  \hspace{1cm} (1)

where $r$ is the ratio of the total liquid-solid contact area to the surface area projected onto the horizontal plane, and $\theta_0$ is the equilibrium contact angle on a smooth surface of the same material. In our experiments, we measure $\theta_0 = 120^\circ$. For an array of square posts $r$ is given by the following expression:

$$r = 1 + \frac{4(h/a)}{(1 + b/a)^2}$$  \hspace{1cm} (2)

where $h/a$ is the aspect ratio of the posts. In the Cassie state, where water droplets contact both solid and air, the equilibrium contact angle $\theta_C$ is given by

$$\cos \theta_C = f_{SL} \cos \theta_0 - f_{LA}$$  \hspace{1cm} (3)

where $f_{SL}$ and $f_{LA}$ are the area fractions of solid-liquid and liquid-air contact, respectively. For an array of square posts $f_{SL}$ and $f_{LA}$ are given by

$$f_{SL} = \frac{1}{(1 + b/a)^2} ; \quad f_{LA} = 1 - \frac{1}{(1 + b/a)^2}$$  \hspace{1cm} (4)

We then measure the contact angle of droplets on each texture and compare results with theory. Predictions and measurements for arrays of posts are plotted as a function of post spacing-to-width ratio $b/a$ in Figure 5. Predicted contact angles for equilibrium Wenzel wetting (dashed line) fall from $180^\circ$ at $b/a$ of about 1.5 to about $122^\circ$ at $b/a$ of 10 while equilibrium Cassie angles (solid line) rise from about $135^\circ$ to $175^\circ$ for $b/a$ ratios of 0.33 and 10, respectively. Because Cassie and Wenzel curves cross at $b/a$ of about 1.8, energy minimization should favor Cassie wetting for $b/a$ smaller than 1.8 and Wenzel wetting for $b/a$ greater than 1.8. Indeed, measured contact angles (solid circles) are consistent with Cassie wetting for $b/a$ ratios that are less than about 2 and with Wenzel wetting for $b/a$ ratios that are greater than 6. However, in the intermediate spacing regime, measured angles do not agree with either equilibrium wetting state. Droplets in this intermediate state exhibit optimum roll-off behavior and permit direct light transmission between droplet and surface (left image) as opposed to Wenzel droplets (right image), evidence that this intermediate state is Cassie-like.

Persistence of Cassie-like droplets in the equilibrium Wenzel regime indicates that there is an energy barrier\textsuperscript{9,11,15} that maintains the droplet in a metastable state and prevents water from infiltrating into the texture. Hydrophobic materials will resist wetting because there is an associated energy cost. As the air-water interface penetrates deeper into the structures and the water wets a greater solid surface area, the total interfacial energy increases. An effective force required to wet these
surfaces can be calculated by differentiating the energy with respect to the penetration depth. Normalizing by the air-water interfacial area yields the required pressure to force water into the texture, or capillary pressure $P_C$. For a square array of square posts of width $a$ and edge-to-edge spacing $b$, the capillary pressure is given by

$$P_C = \left(\frac{-4 \cos \theta_0}{\left(1 + \frac{b}{a}\right)^2 - 1}\right) \frac{\gamma_{LV}}{a}$$  \hspace{1cm} (5)

where $\gamma_{LV}$ is the air-water surface energy. Hydrophobic materials have values of $\theta_0$ that exceed $90^\circ$, resulting in positive values of $P_C$ corresponding to pressures that resist water penetration. Conversely, textures of hydrophilic materials ($\theta_0 < 90^\circ$) have negative $P_C$ values, consistent with the tendency of hydrophilic capillaries to draw water in. For water and air, $\gamma_{LV} = 0.072 \text{ N/m}$. Because our model surfaces are periodic with well-defined posts, given the intrinsic surface energy of a smooth surface of the same composition, we can then calculate capillary pressures exactly for each texture.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{Calculated dependence of capillary and Laplace pressures for 1 $\sim \mu$m water droplets as function of post spacing-to-width ratio. Laplace pressure (solid line) surpasses capillary pressure for 15 $\sim \mu$m-wide posts (dashed line) at b/a ratio of 5.5. For comparable spacing-to-width ratio, capillary pressure for 3 $\sim \mu$m-wide posts (dotted line) always exceeds Laplace pressure.}
\end{figure}

Wetting state is determined not only by the energy level of each state, but also the accessibility of each state. Because our droplets are placed on top of the textures and thus begin in a Cassie-like state, the energy landscape between this initial state and the lowest energy state will determine whether droplets can minimize total interfacial energy. The slope of the energy barrier is proportional to the capillary pressure, which will resist wetting and thus impede Cassie-to-Wenzel transitions. Calculated pressures for posts that are 15 $\sim \mu$m in width are plotted in Figure 6 as a function of the ratio between post spacing and post width (dashed line). Capillary pressure decreases as the post spacing increases because there are fewer posts to wet per unit area. In the absence of external impulses, Laplace pressure

$$P_L = \frac{2 \gamma_{LV}}{R}$$

where $R$ is the droplet radius, is the driving force that facilitates wetting transitions. As shown in Figure 6, at a critical spacing-to-width ratio of about 5.5, the dashed line representing the capillary pressure for 15 $\sim \mu$m posts intersects the solid line representing the Laplace pressure. At larger values of post spacing, we expect Laplace pressure to overcome capillary pressure and allow droplets to transition to their equilibrium Wenzel state. This prediction is in agreement with the contact angle measurements of Figure 5 in which contact angles transition to predicted Wenzel values beyond the critical post spacing. The above prediction is further validated by the roll-off angle measurements of Figure 4 in which droplet roll-off angles decrease with spacing and reach minimum values on surfaces with spacing ratios that are slightly narrower than the critical spacing ratio. This is because droplets on these surfaces exist in Cassie state (ranging from equilibrium to metastable states) and therefore experience continuous reduction in contact-line pinning as the spacing ratio is increased. However, beyond the critical spacing, droplets do not roll-off as they transition into the Wenzel state and experience substantial increase in contact-line pinning. Therefore, this simple pressure balance model can predict whether surfaces will enable metastable wetting and optimal roll-off performance or equilibrium Wenzel wetting and poor roll-off characteristics.

Because pressures that force fluid into textures are not limited to Laplace pressures, it is desirable to design textures with higher capillary pressures to resist homogeneous wetting. For example, moving droplets exert dynamic pressures that can far exceed Laplace pressures. As given in (5), simply scaling down the feature size increases capillary pressure. For an array of square posts capillary pressure does not depend on feature height. However, shrinking in the lateral dimensions increases the capillary pressure because the differential vertical surface area of posts increases. For example, shrinking a post array by a factor of two is equivalent to cutting each post into four smaller posts, effectively doubling the differential vertical surface area. Calculations for capillary pressure of arrays of posts that are 3 $\sim \mu$m in width are plotted in Figure 6 (dotted line). Indeed, for a given post spacing-to-width ratio, pressures for the arrays of 3 $\sim \mu$m posts are larger than those of the 15 $\sim \mu$m posts. An estimate for the critical spacing ratio at which the transition from Cassie to Wenzel state would occur can be obtained by equating the capillary and Laplace pressures given by (5) and (6), respectively, and solving for the critical spacing ratio $(b/a)_c$ as

$$\left(\frac{b}{a}\right)_c = \sqrt{1 - (2 \cos \theta_0) \frac{R}{a} - 1}$$

(7)
Using the above equation, we predict the Cassie-to-Wenzel transition of a 1 μL droplet on a superhydrophobic surface with square array of 3 μm posts to occur at a spacing ratio of about 13.4. A plot of the critical spacing ratio versus the feature size (Figure 7) shows that the design constraints on the spacing can be relaxed by designing for smaller feature sizes and vice versa.

To further validate our pressure balance model in predicting wetting behavior, we repeat contact and roll-off angle measurements for similar arrays of posts that are now 3 μm in width and 10 μm in height. In Figure 8, we plot measured contact angles (solid circles) and predictions for Cassie (solid line) and Wenzel (dashed line) wetting as a function of post spacing-to-width ratio. At a b/a ratio of about 2.8, theoretical Cassie and Wenzel curves cross, indicating equilibrium Cassie wetting for b/a less than 2.8 and equilibrium Wenzel wetting for b/a values greater than 2.8. However, measured contact angles increase with spacing-to-width ratio. This trend is consistent with predictions for Cassie wetting, but opposite to that of Wenzel wetting. Unlike the system with 15 μm-wide posts, measured contact angles do not drop to Wenzel values at high spacing-to-width ratios. Moreover, as shown in Figure 9, roll-off angles continue to decrease as post spacing increases and reach values as low as 4° for b/a of 10. This suggests that droplets on surfaces outside the equilibrium Cassie regime (b/a > 2.8) do not transition into the Wenzel state but rather exist in the metastable Cassie state, and therefore exhibit continual reduction in contact-line pinning and decreasing roll-off angles as the spacing ratio is increased. These observations are consistent with our prediction from (7) that for 3 μm posts equilibrium Wenzel wetting will not be attained for spacing ratios that are less than 13.4. Therefore, as the spacing-to-width ratio increases, the Cassie contact between droplet and solid decreases resulting in continually increasing contact angle and decreasing roll-off angle. These conclusions are further validated by wetting experiments conducted on 10 μm posts as described in the Appendix.
Droplet Impingement

To design superhydrophobic surfaces for application onto products such as windshields or aircraft engines, one must consider the effect of impinging water droplets. These droplets can travel at elevated velocities and exert high pressures onto surfaces upon impact. To ensure that superhydrophobic surfaces maintain functionality in specific applications, it is crucial to prevent water infiltration into textures. This requires the texture-dependent capillary pressure to exceed the droplet impact pressures. At the instant of impact a shock wave is set up in the droplet, giving rise to the so-called water hammer impact pressures. At the instant of impact, the pressure given by the water hammer pressure is around 0.9 Mpa.

\[ P_{WH} = 0.2 \rho CV \]  

where \( \rho \) is the density of the liquid, \( C \) is the speed of sound in the liquid, and \( V \) is the velocity of the droplet. After the instant of impact, the wetting pressures drop to the familiar Bernoulli pressure given by

\[ P_B = \rho V^2 / 2 \]  

This sequence of events is schematically shown in Figure 10.

Figure 10: Sequence of events during droplet impact

The water hammer pressure is significantly higher than the Bernoulli pressure. For example, for a droplet impinging on a surface at 3 m/s, the water hammer pressure is around 0.9 MPa when compared to a Bernoulli pressure of about 4.5 kPa. To facilitate complete droplet recoil and prevent droplet infiltration, the surface texture of the superhydrophobic surface should be designed such that the capillary pressure \( P_C \) exceeds both the water hammer and Bernoulli pressures. When the capillary pressure is smaller than Bernoulli and water hammer pressures, the droplet infiltrates the texture and remains pinned to the surface. However, when the capillary pressure is greater than Bernoulli pressure but lower than the water hammer pressure, partial pinning of the droplet should occur. These conditions are summarized in the following equations

\[ P_C < P_B < P_{WH} - \text{complete infiltration and pinning} \]
\[ P_B < P_C < P_{WH} - \text{partial pinning} \]
\[ P_B < P_{WH} < P_C - \text{complete recoil} \]  

To validate our model, we conduct several droplet impact experiments with droplets impinging a surface with a velocity \( V \sim 3 \text{m/s} \) and capture the impact phenomenon on a high-speed camera. The texture parameters such as feature size, spacing, and aspect ratio are systematically varied. Here, we present results of droplet impact on four different surfaces to validate our pressure balance model (10). These surfaces are: 15 micron posts with edge-to-edge spacing of 150 microns, 15 micron posts with edge-to-edge spacing of 5 microns, nano-porous surface with average pore size of \( \sim 38 \text{nm} \) and pore-to-pore spacing of \( \sim 10 \text{nm} \), and a hierarchical surface with nanodendrites (100nm) on microposts (3microns). The capillary pressures for these surfaces can be calculated to be 80 Pa, 12 kPa, and 3.8 MPa, and 0.92 MPa respectively. The photographs of the impact event are shown in Figure 11 along with the SEM images of the different surfaces. These results are in excellent agreement with our predictions.

CONCLUSIONS

We demonstrate that metastable Cassie droplets have superior roll-off properties when compared to equilibrium Cassie and Wenzel droplets. By systematically increasing the spacing between posts, we show that droplet wetting regime transitions from equilibrium Cassie to metastable Cassie and finally to equilibrium Wenzel regime. We propose a simple pressure balance model that predicts the transition from metastable Cassie to equilibrium Wenzel wetting. Measurements on textured hydrophobic surfaces with varying post spacing and size show good agreement with the model. In many cases, the metastable regime occupies a significant region of design space and we show that this additional design space can be utilized. One can thus exploit metastable wetting not only to improve roll-off behavior, but also to relax design constraints on specific physical systems. Our work indicates that the design of superhydrophobic surfaces for optimum roll-off properties is characterized by a trade-off between the need for high capillary pressures to maintain droplet metastability (denser texture) versus the requirement for low contact line pinning to minimize contact angle hysteresis (sparser texture). We demonstrate that this trade-off can be circumvented by the use of smaller feature sizes. Our analysis and experiments show that similar textures with smaller feature length scales offer more capillary pressure to resist wetting, consistent with the analysis of Liu et.al. This further extends the metastable regime and provides an additional barrier against droplets that wet with greater pressures, such as falling raindrops and water droplets impacting moving surfaces. Smaller textures also offer a geometric advantage, as they restrict the size of droplets that can fit in between the textures. For example, droplets encountered during flight in aircraft engine applications can move as fast as 60m/s relative to the aircraft and are often smaller than 20mm in diameter. In this important application, wetting dynamics and freezing kinetics are also of concern. Nevertheless, our work validates a simple picture based on pressure balance that provides a framework for the predictive design of surfaces with optimal water-repellant and droplet shedding properties for many applications (such as dropwise condensation, deicing, etc.).
Figure 11: Dynamic interactions of 1mm diameter droplets with a variety of surfaces captured using a high-speed camera\textsuperscript{20} (a) Microtextured surface consisting of 15\textmu m posts spaced apart by 150\textmu m – droplet does not recoil (b) Partial recoil on microtextured surface consisting of 15\textmu m posts spaced apart by 5\textmu m (c) Hierarchical texture comprising of 3\textmu m posts with 100nm dendritic structures causes complete recoil and shedding (c) Metaloxide nanoporous surface with \textapprox 38 nm pores results in complete drop recoil and shedding.

Appendix: Further wetting measurements

The following plot shows systematic roll-off angle measurements on a superhydrophobic array of 10\texttimes m square posts with varying width. These results show that the drops do not transition into Cassie consistent with the pressure balance model discussed earlier. As in the case of 3\texttimes m posts the roll-off angle continually decreases with post spacing indicating that the drop is in Cassie state and the contact line pinning reduces as the post spacing is increased consistent with prior observations. All of these results (15\texttimes m, 10\texttimes m, and 3\texttimes m posts) clearly validate our simple pressure balance model and can be used for design of metastably wetting, easy drop-shedding surfaces.

Figure 12: Dependence of roll-off angle of 6\texttimes L water droplets on the $b/a$ ratio of square posts that are 10\texttimes m wide and 10\texttimes m high. Roll-off angles (solid circles) decrease monotonically as the $b/a$ ratio increases, further evidence that the droplets do not transition to the Wenzel state, even at the maximum tested ratio. The insets show typical dense and sparse textures with spacing ratios $b/a=0.5$ and $b/a=7.5$. 
Acknowledgements

We thank Dr. Margaret Blohm and the Nanotechnology Program at GE Global Research Center for support. The MIT authors also thank MIT Energy Initiative and Reed Award for support.

References