Counterintuitive Wetting Transitions in Doubly Reentrant Cavities as a Function of Surface Make-Up, Hydrostatic Pressure, and Cavity Aspect Ratio

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Surfaces that entrap air underwater serve numerous practical applications, such as mitigating cavitation erosion and reducing frictional drag. These surfaces typically rely on perfluorinated coatings. However, the non-biodegradability and fragility of the coatings limit practical applications. Thus, coating-free, sustainable, and robust approaches are desirable. Recently, a microtexture comprising doubly reentrant cavities (DRCs) has been demonstrated to entrap air on immersion in wetting liquids. While this is a promising approach, insights into the effects of surface chemistry, hydrostatic pressure, and cavity dimensions on wetting transitions in DRCs remain unavailable. In response, Cassie-to-Wenzel transitions into circular DRCs submerged in water are investigated and compared with those in cylindrical “simple” cavities (SCs). It is found that at low hydrostatic pressures ($\approx 50$ Pa), DRCs with hydrophilic ($\theta_o \approx 40^\circ$) and hydrophobic ($\theta_o \approx 112^\circ$) make-ups fill within $10^5$ and $10^7$ s, respectively, while SCs with hydrophilic make-up fill within $<10^{-2}$ s. Under elevated hydrostatic pressure ($P \leq 90$ kPa), counterintuitively, DRCs with hydrophobic make-up fill dramatically faster than the commensurate SCs. This comprehensive report should provide a rational framework for harnessing microtexturing and surface chemistry toward coating-free liquid repellency.

1. Introduction

Robust entrapment of air on surfaces immersed in water is utilized in numerous practical scenarios, such as for reducing frictional drag,[1–3] corrosion,[4] fouling,[5] and icing,[6] and cavitation erosion.[7] These specialized surfaces are typically realized by coating rough or micropatterned surfaces with water-repellent chemicals, commonly perfluorocarbons.[8,9] However, the cost and environmental impact[10] of these coatings, along with their vulnerability to organic fouling,[11] long-term immersion in water,[12,13] heat and chemicals,[14] and abrasion[15] limit their applications. Thus, new approaches for the long-term entrapment of air on submersion in water that does not entirely depend on coatings are needed. In this context, a new class of microtextures has been developed, comprising microcavities that broaden below the inlets such that the cross-section of the space between adjacent cavities spanning cavity inlets and the intervening wall resembles the serp-T shape.[7,16–22] (Figure 1A–C). These bio-inspired[18,21] microtextures are known as doubly reentrant cavities (DRCs), and they can entrap air inside them on immersion in liquids due to their topography, regardless of their surface make-up.[19] In fact, the transition of these air-filled cavities—Cassie-states[24–26] to the fully-filled or the Wenzel-state[27]—depends on a number of factors, such as the compressibility of the trapped air, liquid vapor pressure, capillary condensation, the solubility of the trapped air in the liquid, and the cavity geometry.[20] For instance, when hexadecane (vapor pressure at NTP, $P_v = 0.01$ kPa) was used to immerse silica surfaces adorned with circular DRCs (apparent advancing contact angle on flat silica, $\theta_a \approx 20^\circ$), they robustly entrapped air, which remained intact even after 27 days.[20] In stark contrast, circular SCs of similar chemical make-up, diameter, and pitch as the DRCs got fully-filled by hexadecane within $t \approx 0.2$ s, that is, a factor of $\approx 10^7$ faster (or $10^{10}$% faster). Indeed, these observations are quite exciting because the function, that is, the entrapment of air underwater, can now be realized by the microtexture alone. A variety of materials and techniques have thus been explored toward proof-of-concept demonstrations of this approach, for example, with silica-on-silicon wafers ($\text{SiO}_2$/Si) and photolithography and dry etching,[7,19,22,28–31] perfluoropolyether dimethacrylate and reverse imprint lithography,[32] and polypropylene and crack formation/propagation[33] among others. Thus, there is a growing expectation that this approach would yield greener and low-cost technologies.

Even if a Cassie state is achieved on an intrinsically wetting material, this scenario does not pertain to the global minimum on the thermodynamic energy landscape; in fact, such a system will eventually transition to the Wenzel-state to reach thermodynamic equilibrium.[25,34] However, these wetting transitions could be impeded by kinetic barriers by controlling the micro/nano texture—cavities/pillars, reentrant/simple profile, and

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aspect ratio—and the chemical make-up of the surface.[25,35–39] Thus, for the coating-free approach to be practical, clear insights into the factors and mechanisms that govern the kinetics of Cassie-to-Wenzel transitions are crucial. While wetting transitions in coating-based water-repellent microtextures have been explored extensively,[9,40–46] insights into wetting transitions in coating-free microtextures (DRCs) are largely obscure. In particular, the effects of hydrostatic pressure on wetting transitions have not been explored, despite their obvious practical relevance, for instance, in pipe-flows and marine applications. 

In response, we apply a broad set of techniques to gain high-resolution insights into Cassie-to-Wenzel transitions in circular DRCs immersed in water as a function of surface chemistry, cavity dimensions, and hydrostatic pressure, and compare their performance with that of commensurate simple cavities (SCs). We also model the time- and pressure-dependent wetting transitions inside the cavities to pinpoint the governing factors and mechanisms.

2. Results and Discussion

We realized arrays of DRCs and SCs on SiO$_2$/Si wafers using microfabrication protocols that we have reported recently[19–21,47] (Figure 1). Briefly, we utilized photolithography, dry etching of Si and SiO$_2$ layers, and thermal oxide growth, to carve arrays of circular DRCs with diameter, $D = 200 \mu$m, center-to-center distance, pitch, $L = 212 \mu$m and depth, $H \approx 53 \mu$m. We also microfabricated arrays of SCs onto SiO$_2$/Si wafers, with identical $D$, $L$, and $H$, to discern the advantages/drawbacks of the DRCs profile over the SCs. The cavities were hexagonally-packed, to maximize the liquid–vapor interfacial area and minimize the liquid–solid contact. The surface roughness, defined as the real surface area divided by the projected surface area, for DRCs and SCs were similar and equal to $Ra = 1.9$. Next, we define the liquid–solid area fraction, $\phi_{LS}$, as the real liquid–solid area normalized by the projected area. For example, if water fully penetrates the microtexture (the Wenzel state), $\phi_{LS} = Ra = 1.9$. We also define the liquid–vapor area fraction, $\phi_{LV}$, as the real liquid–vapor area normalized by the projected area. For example, right after DRCs entrap air on immersion in water, the liquid–vapor fraction, $\phi_{LV} = 0.81$ and $\phi_{LS} = 0.24$ (Table 1, Section S1, Supporting Information).

In addition to the high-precision microfabrication, SiO$_2$/Si wafers enabled us to specifically control their chemical make-up. For instance, we could render them i) superhydrophilic by an oxygen plasma-treatment (Figure 2A); ii) hydrophilic by piranha treatment followed by a specific protocol for storage[20] (Figure 2B); iii) hydrophobic by silanation with perfluordecytrichlorosilane (FDTS) using a molecular vapor deposition technique[48] (Figure 2C). The apparent contact angles of water drops on smooth SiO$_2$/Si samples after surface treatments (i), (ii), and (iii) were $\approx 0^\circ$, $40^\circ$, and $112^\circ$, respectively (Table S1, Supporting Information). Following the nomenclature proposed by Marmur et al.,[49] we consider these angles to be the actual contact angles ($\theta_o$) for our theoretical analysis (Section S1, Supporting Information). We measured the advancing and receding (at 0.2 $\mu$L s$^{-1}$) contact angles of water drops on surfaces adorned with arrays of DRCs and SCs with those chemical make-ups (Table 1). We found that the plasma-treated SCs and DRCs got spontaneously filled (Wenzel-state) due to the liquid imbibition along the walls and rapid capillary condensation, respectively, which we describe in detail while discussing the outcome of immersing them in water. The non-zero apparent contact angles of water on these microtextured surfaces were due to the edge-effect that hinders the spreading of liquid despite the...
surfaces’ superhydrophilicity (Table 1). For pristine silica surfaces with $\theta_0 = 40^\circ$, water penetrated almost 30% of the depth of SCs, and, in contrast, DRCs stabilized the air–water interface at the inlet of the cavities and robustly entrapped air. In either case, apparent contact angles were in the range, $\theta_A = 135^\circ$. Due to the presence of a continuous solid–liquid–vapor interface in SCs and DRCs, the receding contact angles were $\theta_R \approx 0^\circ$ (Table 1). FDTS-grafted SCs and DRCs exhibited superior repellence to water drops, characterized by $\theta_A \geq 150^\circ$ and $\theta_R = 100^\circ$.

Table 1 lists the advancing and receding contact angles of all the microtextured surfaces investigated in this study.

As microtextured surfaces are immersed in water, the entrapped air gets nearly saturated with water vapor. Thus, it is crucial to understand how the capillary condensation of water varies as a function of the chemical make-up of the surface. To this end, we exposed the abovementioned silica surfaces with DRCs to high relative humidity at temperatures below the dew point using an environmental scanning electron microscope. In accordance to the literature on dew nucleation, we observed the formation of (i) thick water films inside DRCs with the superhydrophilic surface make-up (Figure 2D), (ii) discrete water drops in the hydrophilic case (Figure 2E), and (iii) a lower number of discrete water drops in the hydrophobic case (Figure 2F). These trends have profound consequences on the underwater wetting transitions at low hydrostatic pressures (<100 Pa) that we present in the following section.

### 2.1. Wetting Transitions in DRCs and SCs with Superhydrophilic Surface Make-Up ($\theta_0 \approx 0^\circ$)

Using high-speed imaging, we investigated wetting transitions on arrays of DRCs and SCs with superhydrophilic make-up (Figure S4, Supporting Information). Surfaces were placed inside glass petri-dishes and water was introduced from one side at the rate of 2 mL min$^{-1}$, leading to a uniform water

Table 1. Summary of all the measurements performed in this study. Actual apparent (or intrinsic) contact angles ($\theta_0$), advancing contact angles ($\theta_A$), receding contact angles ($\theta_R$), predicted contact angles ($\theta_{Pr}$), cavity-filling times ($t_{\text{filling}}$) on immersion, and breakthrough pressures ($P_b$). For the $\theta_0 = 40^\circ$ case, the data were taken from ref. [20].

| Make-up               | Superhydrophilic ($\theta_0 \approx 0^\circ$) | Hydrophilic ($\theta_0 = 40^\circ$) | Hydrophobic ($\theta_0 = 112^\circ$) |
|-----------------------|-----------------------------------------------|-------------------------------------|--------------------------------------|
|                       | Cavity SCs | DRCs | SCs | DRCs | SCs | DRCs | SCs | DRCs |
| $\theta_A$            | 73° ± 3° | 135° ± 3° | 118° ± 4° | 139° ± 3° | 153° ± 2° | 153° ± 2° |
| $\theta_R$            | 0°       | 0°   | 0°   | 0°   | 100° ± 2° | 100° ± 2° |
| $\theta_{Pr}$         | 90°      | 90°   | 118°  | 128°  | 151°  | 151°  |
| $\phi_{LV}$           | 0        | 0     | 0.43 | 0.24 | 0.19 | 0.19 |
| $\phi_{LS}$           | 1.9      | 1.9   | 0.43 | 0.24 | 0.19 | 0.19 |
| $t_{\text{filling}}$  | 55 ms    | 30 s  | 2 days | 9 days | 82 days | 214 days |
| Mode of filling       | Liquid imbibition | Capillary condensation | Liquid imbibition | Air diffusion and capillary condensation | Air diffusion and capillary condensation | Air diffusion and capillary condensation |
| $P_b$ (kPa)           | 0        | 0     | 0    | 102 ± 1 | 169 ± 1 | 103 ± 2 |

Figure 2. Contact angles and condensation patterns on smooth and flat silica with different surface make-ups probed via contact angle goniometry and environmental scanning electron microscopy, respectively. Contact angles of sessile water drop on the flat silica surface with A) oxygen plasma-treated; B) pristine silica; C) perfluorodecyltrichlorosilane (FDTS) grafted. D–F) Environmental scanning electron micrographs of capillary condensed water on silica surfaces as a function of their chemical make-up as listed in (A–C), respectively; the relative humidity was ~99%. Panel (D) also depicts through its inset the capillary condensed water in the spacing between the DRC edge and the cavity wall.
column of height \( z \approx 5 \) mm above the sample (hydrostatic pressure, \( P = 49 \) Pa). The advancing water meniscus was stabilized at the DR edges and air was entrapped inside the cavities. In this configuration, DRCs were nearly saturated with water vapor, which led to the formation of continuous wetting films onto the superhydrophilic cavity surface\(^{[31]}\) (Figures 2D and the inset and Figure 3A–H). As the condensed water-layer touched the meniscus stabilized on top, a bubble manifested on top, which rises upward due to its buoyancy and lack of pinning forces at the water–silica–air interface. E, F) A schematic representation of Cassie-to-Wenzel transition in DRCs filling sequence shown in (A–D); I–L) Filling dynamics in simple cavities, water imbibed into the cavity and filled it from bottom to top by displacing all the air. M–P) Schematic representation of SCs filling sequence shown in (I–L).

In contrast, when the water meniscus approached SCs with the superhydrophilic make-up, it surrounded their perimeters and imbibed inward along the walls, filling them bottom-upward. There was no Cassie-state in this wetting transition, and the imbibition happened within <50 ms, without any bubbles (Figure 3I–P; Movie S2, Supporting Information). Curiously, SCs met the same fate as those of the DRCs, but via an entirely different pathway.

2.2. Wetting Transitions in DRCs and SCs with Hydrophilic Surface Make-Up (\( \theta_o \approx 40^\circ \))

Similarly to the superhydrophilic case above, hydrophilic DRCs entrapped air inside them under a water column of height \( z \approx 5 \) mm (hydrostatic pressure, \( P = 49 \) Pa). As the cavities got near-saturated with the water vapor, drop-wise condensation occurred on the cavity walls and floor (Figure 2E and Figure S5,
Supporting Information). However, unlike the superhydrophilic DRCs, the entrapped air in the hydrophilic case did not escape as bubbles. We estimated the ratio between the pinning force and buoyancy to be, $F_{\text{Pin}}/F_{\text{Buoy}} \approx 10^4$, based on the advancing and receding contact angles of water, $\theta_a = 60^\circ$ and $\theta_r = 0^\circ$ (Table S1, Supporting Information). As a result, the air remained trapped inside the cavities. The drop-wise condensation eventually led to the formation of a film inside the cavity, which rose upward to merge with the primary meniscus stabilized at the doubly reentrant edge. This capillary condensation of water also displaced the air inside the cavity, because of the low solubility of the air in water under our experimental conditions\(\text{[52]}\) (Figure S5, Supporting Information). We explain the pressurization of the air using the ideal gas theory\(\text{[53]}\) that can be used to describe air under normal pressure and temperature (NTP = 1 atm, 295 K) conditions. The enhanced pressure was estimated to be $P_2 = P_1 V_1/V_2$, where $P_1 = 1$ atm, $V_1$ was the cavity volume, and $V_2$ was the cavity volume after capillary condensation; since $V_2 < V_1$, $P_2 > P_1$. To mitigate the pressure difference, the primary meniscus on top bulges upward (Figure S5, Supporting Information) and the dissolution of the trapped air into water accelerates. The Cassie-to-Wenzel transition took place in 9 days ($\approx 8 \times 10^5$ s) (Figure 4).

In contrast to DRCs, SCs with hydrophilic make-up failed to prevent water from filling them up instantaneously, following the same mechanism as explained in Figure 3I–P. In some cases, however, a tiny fraction of air was trapped underwater, such that the water meniscus penetrated to a depth of $\approx 15 \mu$m. In this case, Cassie-to-Wenzel transitions took place within 2 days (Figure S6, Supporting Information). These findings underscore the significance of the profile—DRC versus SC—on Cassie-to-Wenzel transitions.

2.3. Wetting Transitions in DRCs and SCs with Hydrophobic Surface Make-Up ($\theta_o \approx 112^\circ$)

DRCs and SCs with hydrophobic make-up stabilized the water column of height $z \approx 5$ mm above ($P = 49$ Pa) and robustly entrapped air inside them. Due to the small size of the microcavities, relative humidity increased dramatically inside them leading to the condensation of discrete water drops (Figures S7, Supporting Information and Figure 2C,F). As a result, and due to the low solubility of air in water, an equal amount of air got displaced, pushing the air–water interface upward (Figures 5 and 6). This excess air pressure curbs capillary condensation, but it is gradually relieved via the diffusion of air into the water, leading to a flat air–water meniscus. At this point, capillary condensation kicks in and the process repeats, thus, driving the wetting transition. Since the diffusion is a slow process, it took nearly 222 days to completely fill the DRCs and nearly half of that for the SCs. This difference is attributed to the robust pinning of water at the DR edge, whereas in the SCs, the meniscus advances along the walls inside the cavity and merges with the condensed water drops on the cavity walls. Thus, for the SCs, we observed asymmetric filling/intrusion inside the cavity due to the stochastic merger of the condensed water drops with the primary meniscus (Figure S8, Supporting Information).

We also exploited confocal laser scanning microscopy (CLSM) to track the air–water interface in the DRCs. Figure 6A–D presents the isometric and cross-sectional views of the hydrophobized DRCs filling sequence ($H = 53 \mu$m) on immersion in water. During CLSM, the Cassie-to-Wenzel transition in DRCs occurred within 4 h, whereas when probed via upright optical microscopy, it took months (Figure 5). This is due to the heating of water by the CLSM laser. Thus, this technique provides only qualitative insights into wetting transitions, for example, tracking the capillary condensation of water and droplet coalescence (Figure 6E–G).

To summarize, by modifying the surface chemistry of silica, such that the actual (or intrinsic) contact angle for water drops, $\theta_o$, varied from $0^\circ$, $40^\circ$, and $112^\circ$, the duration of wetting transition in the DRCs varied dramatically—from 1 s to 9 days ($\approx 8 \times 10^5$ s) to 222 days ($\approx 1.9 \times 10^7$ s), respectively (Figures 3–5). Similarly, for the SCs, the durations pertaining to $0^\circ$–$112^\circ$ ranged from $\approx 50$ ms to 88 days ($\approx 7.6 \times 10^6$ s). Thus, surface chemistry and profile can lead to over a billion-fold retardation in Cassie-to-Wenzel wetting transitions. Next, we investigated wetting transitions under significantly higher hydrostatic pressures for DRCs and SCs with hydrophobic make-up.

2.4. Breakthrough Pressures for DRCs and SCs Immersed in Water

For applications that require submergence of surfaces in liquids, such as drag reduction in pipes and packaging of wet foods and beverages,\(\text{[54]}\) it is crucial to investigate wetting transitions under pressure. We characterized breakthrough (or liquid entry) pressures, $P_B$, defined as the pressure at which the probe liquid penetrates the cavity and touches its floor. Using a home-built experimental setup (Figure S9, Supporting Information). However, unlike the superhydrophilic DRCs, the entrapped air in the hydrophilic case did not escape as bubbles. We estimated the ratio between the pinning force and buoyancy to be, $F_{\text{Pin}}/F_{\text{Buoy}} \approx 10^4$, based on the advancing and receding contact angles of water, $\theta_a = 60^\circ$ and $\theta_r = 0^\circ$ (Table S1, Supporting Information). As a result, the air remained trapped inside the cavities. The drop-wise condensation eventually led to the formation of a film inside the cavity, which rose upward to merge with the primary meniscus stabilized at the doubly reentrant edge. This capillary condensation of water also displaced the air inside the cavity, because of the low solubility of the air in water under our experimental conditions\(\text{[52]}\) (Figure S5, Supporting Information). We explain the pressurization of the air using the ideal gas theory\(\text{[53]}\) that can be used to describe air under normal pressure and temperature (NTP = 1 atm, 295 K) conditions. The enhanced pressure was estimated to be $P_2 = P_1 V_1/V_2$, where $P_1 = 1$ atm, $V_1$ was the cavity volume, and $V_2$ was the cavity volume after capillary condensation; since $V_2 < V_1$, $P_2 > P_1$. To mitigate the pressure difference, the primary meniscus on top bulges upward (Figure S5, Supporting Information) and the dissolution of the trapped air into water accelerates. The Cassie-to-Wenzel transition took place in 9 days ($\approx 8 \times 10^5$ s) (Figure 4).

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Information), we investigated pressure-induced wetting transitions on surfaces (cavities of diameter, $D = 200 \mu m$ with depths of, $H \approx 30, 53, \text{ and } 90 \mu m$) with hydrophobic make-up (Table 1; Figures 2 and 5). In a typical experiment, a sample was immersed under a 10 mm column of water and the air in the headspace was pressurized at the rate of $\approx 1.3 \text{ kPa s}^{-1}$. We have previously reported that DRCs with $D = 200 \mu m$ and $H \approx 53 \mu m$ with $\theta_o = 40^\circ$ for water demonstrate dramatically higher breakthrough pressures than simple cavities. Curiously, the trend reverses for the hydrophobic surface make-up, that is, $\theta_o = 112^\circ$: the breakthrough pressures for the DRCs ($P_B = 103 \pm 2 \text{ kPa}$) were $\approx 57\%$ lower than those of the commensurate SCs ($P_B = 169 \pm 1 \text{ kPa}$) (Figure 7A1–D1,E1–H1; Figure S10 and Movies S3 and S4, Supporting Information). To explain this unexpected result, we utilized confocal laser scanning microscopy that we describe next.

Complementary to optical imaging, we utilized CLSM and a custom-built pressure device to visualize the water–vapor interface during wetting transitions as a function of external pressure. For cavities with $H < 0.5 \times D$, we observed that as water penetrates inside the DRCs, the liquid meniscus gets pinned at the DR edge (Figure 7A2–D3). Subsequently, as the pressure is increased, the curvature of the spheroid-shaped water–vapor interface keeps increasing until the water touches the

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**Figure 5.** Optical micrographs (top-view) of silica surfaces with arrays of doubly reentrant and simple cavities with hydrophobic make-up on immersion in water. The cavities got filled, A–J) 222 days for DRCs and K–O) 82 days for simple, mainly due to the diffusion of trapped air and the merging of the condensed water and the primary meniscus on top. Filled cavities are marked with a “star” symbol. (Scale bar: the diameter of all the cavities in this figure is 200 $\mu m$).
cavity floor (Figure 7A2–D3). In stark contrast, in the SCs the water meniscus is never pinned and it keeps advancing along the cavity walls. Thus, the advancing water–vapor interface is significantly flatter as it progresses toward the cavity floor, so much more air has to be displaced/compressed during the forced imbibition (Figure 7E2–H3). The upshot of pinning in the DRCs and lack thereof in the SCs is that for cavities with \( H < 0.5 \times D \), the liquid touches the cavity floor at lower pressure in the DRCs than in the SCs (and breakthrough happens). This trend was observed for DRCs and SCs with \( D = 200 \mu m \) and \( H \approx 30, 53, \) and \( 90 \mu m \) (Figure 8). We explain the growing differences in the breakthrough pressures of SCs and DRCs with the cavity depth based on the increasing volumes of the entrapped air that must be compressed in the SCs as water invades inside (Figure 8). However, these \( (H < 0.5 \times D) \) geometries did not allow us to investigate what might happen when the water-meniscus does not touch the cavity floor at the time of achieving its maximum curvature \((D/2)\).

To incorporate samples with \( H > 0.5 \times D \), while overcoming the limitations posed by our microfabrication protocol (Section S2, Supporting Information), we made DRCs and SCs of diameter, \( D = 50 \mu m \) and depth, \( H \approx 53 \mu m \). Now, for the DRCs, with the increase in the pressure to the 50–70 kPa range, the primary meniscus reached its maximum curvature (or the lowest radius of curvature equal to \( D/2 \)). Subsequently, the meniscus depinned from DR edge onto the walls of the cavity. Thereafter, the advantages of DR features were lost and DRCs behaved as SCs. (Figures S11 and S12, Supporting Information). Such a transition has not been reported thus far in the literature to the best of our knowledge.

2.5. Underwater Wetting Transitions in DRCs and SCs with Hydrophobic Make-Up Under External Pressure

Here, we investigate underwater wetting transitions in DRCs and SCs with hydrophobic make-up at significantly higher hydrostatic pressures \((P_h)\)—50, 60, 70, 80, and 90 kPa—than those we have described above, but below the breakthrough pressures (Figures 4 and 5; Table 1). While it is common knowledge to not operate at the breakthrough pressure \((P_b)\), yet some applications might take place at, say, 10% of that value, hence these results should have practical relevance. We chose cavities with dimensions \( D = 200 \mu m \) and \( H \approx 53 \mu m \) for these experiments (Figure 1). Right after the immersion of the samples in water, the pressure was ramped to the desired magnitude and held constant thereafter (Figure S13, Supporting Information). Due to the elevated pressure, the entrapped air dissolved quickly in water, and the primary meniscus approached toward the cavity floor. Here, we define the “failing-time” as the duration in which the liquid meniscus touches the cavity floor after the application of the external pressure (Figure 9). We found that the failing-times in the DRCs were significantly shorter than those in the SCs (Figure 9A). The reasoning is similar to that for the breakthrough pressures: in the DRCs, water meniscus remains pinned at the DR edges (Figure 9B1–3), whereas in the SCs the meniscus keeps advancing along the cavity walls. Thus, the key factors were: i) the higher liquid–vapor interfacial area in the DRCs compared to the SCs, facilitating the diffusion of air, and ii) the amount of air that needs to be removed from the cavity for the liquid to touch the cavity floor is lesser in the DRCs than that in the SCs due to the latter’s flatter curvature (compare schematics in Figure 9B1–3,C1–3). To pinpoint the role of the external pressure on the failing-times in DRCs and SCs, we developed a theoretical model.

2.6. Analytical Modeling of Pressure-Induced Wetting Transitions

Building upon previous reports on the diffusion of the air entrapped inside cavities submerged in liquids,[9,55–57] we developed a 1-D model to gain insights into our experimental results. Previous reports, however, did not consider the effects of the pressure during the ramp-up phase. In contrast, here, we consider the effects of the ramping of the external pressure—from
zero to the required value—on the movement of the liquid meniscus by incorporating it as small steps of pressure increment with time, following our experiments. The pressure ramping is assumed to be a quasi-equilibrium process with the following balance of forces satisfied at all times (Figure 10A),

$$P_h + P_{\text{cap}} = P_c + P_V$$  \hspace{1cm} (1)

where $P_h$ is hydrostatic pressure, $P_{\text{cap}}$ is capillary pressure due to the meniscus curvature, $P_c$ is the pressure of entrapped air (excluding water vapor) within the cavities and $P_V$ is the vapor pressure of water. In this model, we considered $P_V$ to be constant as it depends only on temperature, and our experiments take place under isothermal conditions. The capillary pressure of the water meniscus over a circular cavity with axial symmetry is evaluated utilizing the Laplace equation:

$$P_{\text{cap}} = \frac{2 \gamma_{LV} \cos\theta}{r}$$  \hspace{1cm} (2)

where $\gamma_{LV}$ is the surface tension of water, $\theta$ is the angle between the water–vapor interface and the wall and $r$ is the radius of the cavity (Figure 10B).

Considering the entrapped air to be an ideal gas, which for our experimental conditions is a reasonable assumption, the following relationship holds as the external pressure is applied:

$$P_{c,2} V_2 = P_{c,1} V_1$$  \hspace{1cm} (3)

where $V$ is the volume of entrapped air, states 1 and 2 represents before and after compression. Also, with the increase in the pressure, the solubility of the air in water increases, and
accordingly the increased equilibrium concentration of the air at the interface, \(c_0\), is obtained from the Henry’s law as,

\[
H^{\text{eq}}_c = \frac{c_0}{P_c}
\] (4)

For simplicity, we assume the entrapped air to be a binary mixture of nitrogen and oxygen. Thus, the Henry’s constant, \(H^{\text{eq}}_c\), is evaluated as the molar average of Henry’s coefficients for nitrogen and oxygen (Section S3, Supporting Information). The difference in the concentration of the air at the water–vapor interface, \(c_0\), and bulk water, \(c_\infty\), drives the diffusion (Figure 10C). Assuming that the air diffuses along the \(y\)-axis only, its concentration over time follows the Fick’s second law of diffusion,

\[
\frac{\partial c}{\partial t} = D_c \frac{\partial^2 c}{\partial y^2}
\] (5)

where, \(D_c\) is the diffusion coefficient of the air in water (details in the Section S3, Supporting Information), \(t\) is the time and \(y\) is the distance from the interface. The rate of transport through the interface governs the change in the entrapped air volume over time, according to the relation,

\[
A_{\text{int}} D_c \frac{\partial c}{\partial y} \bigg|_{y = -y_\text{eq}} = \frac{d}{dt} \left( \frac{P_c V}{RT} \right)
\] (6)

where, \(A_{\text{int}}\) is the area of the water-vapor interface, \(R\) is the universal gas constant and \(T\) is temperature. The governing differential equations were numerically integrated using the Runge–Kutta method of fourth-order to predict wetting transitions in DRCs and SCs with \(D = 200 \mu m, H = 53 \mu m\), hydrophobic make-up, and subjected to a hydrostatic pressure of 80 kPa ramped at 1.3 kPa s\(^{-1}\). Specifically, we tracked the apparent angle, \(\theta\), the depinning length, \(h\), and the sagging depth of the meniscus, \(l\) during wetting transitions (Figure 10B,D,G).

The dotted lines in Figure 10D,G, labeled as 1, 2, 3, and 4, correspond to some key events during the wetting transitions in the DRCs and SCs, respectively. State 1: before ramping up the pressure, the apparent angle, \(\theta = 90^\circ\) and the liquid meniscus is flat such that \(h = 0\). State 2: as the hydrostatic pressure is ramped up, the water meniscus starts curving but it does not advance until the apparent angle reaches a particular transition angle (\(\theta_{\text{tr}}\)). State 3: when the transition angle (\(\theta_{\text{tr}}\)) is reached, the liquid advances into the cavity, and this continues based on the relative magnitudes of the hydrostatic pressure, the compressibility of the entrapped air, and the diffusion rate. State 4 (only applicable to DRCs with \(H < 0.5 \times D\)): the sharp discontinuity of the DR edge renders \(\theta < \theta_{\text{tr}}\), which pins the liquid meniscus and prevents its contact with the cavity walls. The predicated failing times for the DRCs and SCs at various elevated pressures were in excellent agreement with our experimental results (Figure 10F,I). Amidst states 1 and 2, for DRCs and SCs, \(\theta\) increases, \(h\) remains at zero, and \(l\) increases following a simple geometrical relationship (SI Equation 5). Between states 2 and 3, \(\theta = \theta_{\text{tr}}\) remains constant, while \(h\) and

Figure 8. Breakthrough pressures of DRCs and SCs with hydrophobic make-up as a function of cavity dimensions. For \(H < 0.5 \times D\), breakthrough pressure increases with the cavity depth as shown for cavities with a diameter of 200 \(\mu m\) and depth equal to 30, 53, and 90 \(\mu m\). Overall, breakthrough pressures of SCs are higher than those of commensurate DRCs. It is because, in the SCs, the increments in the pressure lead to the advancement of the solid–liquid–vapor interface along the cavity wall, whereas in the DRCs, the liquid meniscus remains pinned at the inlet. As a result, the liquid–vapor interface penetrating inside the SCs is significantly flatter than that in the DRCs, which leads to a significantly higher compression of air, leading to higher breakthrough pressure.

Figure 9. Effects of external pressure on underwater wetting transitions in DRCs and SCs with hydrophobic make-up. A) Failing times for DRCs and SCs with respect to the applied hydrostatic pressure. B,C) Schematics of wetting transitions in B1–B3) DRCs and C1-C3) SCs based on the CLSM data presented in Figures 7 and S12.
l increase. Crucially, for DRCs, \( h \) is limited to the length of the vertical overhang, which was 4 µm in our samples, whereas there is no such limit for SCs (Figure 10E,H). In DRCs, beyond state 3, the value of \( h \) remained fixed at 4 µm, and \( \theta \) keeps on increasing until \( l \) becomes equal to \( H \).

We determined \( \theta_{tr} \approx 135^\circ \) based on our confocal microscopy data (Figure 7H3). This is a counterintuitively high value, but it should be noted that this wetting dynamics manifest inside a confined/closed cavity under hydrostatic pressure and on a solid surface with micro/nano scale roughness. Thus, significant deviation from the common advancing/receding behavior of water on a smooth FDTS-coated surface is expected. [9] Lastly, there was a significant deviation in our predictions and the experimental observations for the experiments conducted at lower hydrostatic pressures, namely, 50–60 kPa (Figure 10F,I). This was due to the fact that our model does not include the effects of capillary condensation, which plays a major role at lower pressures. This feature will be incorporated in the model in the future.

3. Conclusion

To investigate the strengths and weaknesses of bio-inspired DRCs over simple cylindrical cavities (SCs) toward achieving long-term entrapment of air underwater, we tracked pressure-induced wetting transitions of water in them as a function of the cavities’ chemical make-up (\( \theta_o \approx 0^\circ \), 40°, 112°), size, and aspect ratio. For the superhydrophilic make-up (\( \theta_o \approx 0^\circ \)) and at a nominal hydrostatic pressure of \( \approx 50 \) Pa, DRCs and SCs got filled within \( \approx 10 \) s and \( < 0.050 \) s, respectively. Here, DRCs entrapped air on submersion, which got released as bubbles, while the SCs did not entrap air at all. For the hydrophilic and hydrophobic make-ups (\( \theta_i \approx 40^\circ \) and 112°), DRCs underwent Cassie-to-Wenzel transitions in \( \approx 9 \) days (\( \approx 8 \times 10^5 \) s) and \( \approx 222 \) days (\( \approx 1.9 \times 10^7 \) s), respectively, whereas the SCs for the hydrophilic case got filled right away and the hydrophobic ones took about 88 days (\( \approx 76 \times 10^6 \) s). Thus, it is clear that surface chemistry and cavity profile can lead to over a billion-fold retardation (\( 10^{-2} – 10^7 \) s) in Cassie-to-Wenzel wetting transitions.

Figure 10. Analytical modeling of wetting transitions in DRCs and SCs with hydrophobic make-up as a function of the applied hydrostatic pressure. A) Force body diagram in DRCs with contributions from hydrostatic pressure, capillary pressure, and the pressurization of the entrapped air. These forces along with the contact angle hysteresis data dictate the shape and the position of the liquid–vapor interface over time as the entrapped air starts diffusing. B) Schematic depicting the advancement of liquid into a DRC submerged in water and under a hydrostatic pressure. The liquid meniscus makes an apparent angle equal to \( \theta \) with the cavity wall. C) The diffusion of the air entrapped inside the cavity into water takes place because the concentration of the dissolved air in water at the interface, \( c_0 \) is higher than that in the bulk water, \( c_\infty \). D) In DRCs, the primary meniscus is pinned at the DR edge, but as the diffusion of the air continues, the liquid–vapor interface keeps sagging inward (stages 1–3), eventually touching the cavity floor (stage 4). E) Analytical predictions for DRCs with \( D = 200 \mu m, \ H = 53 \mu m \), hydrophobic make-up, and subjected to a hydrostatic pressure of 80 kPa ramped at 1.3 kPa s\(^{-1}\). F) Predicted failing time with experimentally observed value for DRCs at different hydrostatic pressures for \( H = 54 \) µm. G) Schematic of progression of interface inside the simple cavity (SC) with hydrophobic make-up. The interface advances along the wall after reaching transition angle. H) Analytical predictions for SCs with \( D = 200 \mu m, \ H = 53 \mu m \), hydrophobic make-up, and subjected to a hydrostatic pressure of 80 kPa ramped at 1.3 kPa s\(^{-1}\). I) Predicted failing time with experimentally observed value for SCs at different hydrostatic pressures.
For the hydrophilic case, the capillary condensation of water inside the cavities compressed the entrapped air, leading to its dissolution in water followed by diffusion to the atmosphere. For the hydrophobic make-up, however, the capillary condensation was significantly slower, which slowed down the wetting transitions. Interestingly, DRCs with the hydrophobic make-up took nearly 250% longer time for Cassie-to-Wenzel transitions in comparison to the commensurate SCs. This was due to the fact that in the SCs, the primary liquid meniscus advanced along the cavity walls, where it merged with the capillary condensed water drops and aggravating the curvature pressure. On the other hand, in the DRCs, the primary remained pinned at the cavity mouth and only sagged downward, which precluded its merger with the capillary condensed drops on the walls. For the hydrophobic make-up, we found that wetting transitions at elevated pressures were significantly faster in the DRCs than in SCs; the breakthrough pressures for the DRCs were also significantly lower than those for the SCs. Our high-resolution experiments with CLSM revealed that as the liquid penetrates inside the DRCs, the primary meniscus remains pinned at the DR edge; as the pressure increases, the curvature of the spherical-shaped water–air interface keeps increasing until the water touches the cavity floor. In stark contrast, in the SCs, the water meniscus is never pinned and it keeps on advancing along the cavity walls with the increasing hydrostatic pressure. As a result, the advancing water–air interface in the SCs at elevated pressures was significantly flatter as it progressed toward the cavity floor. Thus, much more air had to be displaced/compressed to reach the cavity floor. Additionally, in this scenario, the air-water interfacial area available for the diffusion of the entrapped air was smaller than in the case of DRCs. Thus, the breakthrough pressures were higher for the SCs in comparison with the DRCs. While investigating pressure-induced wetting transitions, we found that for DRCs with the cavity depth, \( H > D/2 \), as the liquid curvature reached the value of \( D/2 \), the primary meniscus depinned from the doubly reentrant edge and landed onto the cavity wall. Thereafter, the advantages of DR features were lost and DRCs behaved as SCs. This is the first-ever report of this transition to the best of our knowledge. To gain mechanistic insights into the pressure-induced wetting transitions, we developed an analytical 1-D model based on the Fick’s laws of diffusion. With a special emphasis on the effects of pressure ramping from zero to the desired value and the apparent advancing contact angles of water inside confined cavities, the predictions were in excellent agreement with the experimental results. Taken together, these findings provide a comprehensive framework for rationally engineering surfaces for robustly entrapping air underwater by exploiting microtexture and chemistry. For example, at low hydrostatic pressures, DRCs demonstrate dramatically longer entrapment of air underwater in comparison to the SCs, and methods for restoring the diffused air inside the cavity should be explored along with the subtle effects of surface make-up. In contrast, SCs with hydrophobic make-up outperform commensurate DRCs under gradually-ramped elevated hydrostatic pressures. Thus, the pressure range must be carefully considered while choosing DRCs or SCs for practical applications. In the future, it would be interesting to explore the effects of intermittent or oscillating hydrostatic pressure on these wetting transitions.

4. Experimental Section

Microfabrication: The surfaces adorned with arrays of microscale cavities—simple cylindrical and doubly reentrant—achieved through multi-step photolithography and dry etching processes on a silicon wafer with a 2 μm thick silica layer on top. The microfabrication procedure was adopted from our previous work. Plasma Treatment: The plasma treatment was carried out using a Diener Electronics platform (Atto model) at the power of 200 W for 10 min, using ultrapure (99.999%) \( \text{O}_2 \) gas supply at a flow rate of 16.5 sccm. FDTS Deposition: FDTS was chemically grafted onto the silica surfaces using the ASMT molecular vapor deposition (MVD) 100E system. Prior to the FDTS deposition, the surfaces were cleaned by exposing them to a 200 W oxygen plasma for 2 min, which oxidized organic contaminants and hydroxylated silica surfaces. Subsequently, those surfaces were placed in the MVD to expose them to gas-phase FDTS molecules for silanation reactions. Contact Angle Measurement: Apparent contact angles of water drops on the samples were measured using the Kruss Drop Shape Analyzer (DSA100E). Liquid was advanced/receded at the rate of 0.2 μL s\(^{-1}\). All the data were analyzed using the Advance software. The reported data points were an average of at least three measurements.

High-Speed Imaging: Phantom v1212 from Vision Research was used for high-speed imaging (more details please refer Figure S4, Supporting Information).

Immersion Experiments: A monochrome USB camera (Edmund optics, EO-S310) along with a microscopic lens with coaxial white light illumination was used to observe the long-term wetting transition in cavities on immersion in water. The silica surfaces were fixed with cavities into the petri dish using double-sided tape and introduced water on top till it submerges the samples and recorded at a different time interval. For all the immersion experiments DI water saturated with atmospheric air was used.

Scanning Electron Microscopy: Nova Nano 630 was used for scanning electron microscopy (SEM). Prior to SEM samples were coated with 3 nm of platinum using a sputter coater (Quorum Q150T S) to eliminate charging effects.

Environmental SEM: The Quanta 600 SEM tool was used to study the condensation pattern. The sample was glued to SEM stub using double-sided copper tape and sample temperature was lowered and held at \( \sim 293 \text{ K} \). By varying the chamber pressure (750–800 Pa) the relative humidity was increased to 100%. The images were taken using a gaseous secondary electron detector at 10 kV accelerating voltage, beam current 0.42 nA and working distance 4–5 mm.

Confocal Microscopy: A Zeiss LSM710 upright laser confocal microscope was used to visualize the meniscus morphology under low and high hydrostatic pressures. A custom-built chamber was fabricated using a 3D printer (BCN3D SIGMA R19) to fit with the confocal lens (Zeiss 20×—W Plan—Apochromat). Rhodamine B (Acros) used as a fluorescent dye for water. After fixing the sample containing the petri dish at the bottom of the chamber, the fluorescent solution was gently poured manually using a syringe till submerges the sample. After properly sealing all the open ends, the required pressure was applied using a portable pump via a pressure regulator. Sequential images (1024 px × 1024 px) were taken using 20× immersion objective in the Z-stack mode, in which several confocal images were taken from the bottom of the cavities up to 50 microns above the top surface. The intensity of the laser was kept as low as possible; this was 0.2 mW for Rhodamine/water solution. Subsequently, using the Imaris v.8.1 software, by Bitplane, it was able to make 3D rendered surfaces and several cross-sections to help visualize the meniscus shape inside the cavity.

Breakthrough Pressure Experiments: A custom-built pressure cell along with an SMC (AW20-N02CH-CZ) pressure regulator and a Keller (LEO3 digital manometer) pressure gauge and compressed air were utilized to apply the external pressure. Cavities were observed from the top using a microscope (Figure S9, Supporting Information). The sample was fixed into the petri dish and kept inside the cell and water was added using a...
syringe to submerge the sample prior to the application of the external pressure.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
breakthrough pressure, capillary condensation, diffusion, doubly reentrant cavities, hydrostatic pressure, simple cavities, underwater, wetting transitions

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