Droplet Levitation and Underwater Plastron Restoration using Aerophilic Surface Textures

by

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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

This thesis explores the use of active components in liquids and responsive surfaces to resist the wetting of water on solid surface textures. When a superhydrophobic surface comes into contact with water, it traps a thin layer of air (plastron) within its surface texture. This entrapped air is advantageous for reducing the contact line pinning of water droplets on the surface and lowering the skin friction drag experienced by the surface underwater. However, these aerophilic textures are prone to impregnation by water due to turbulent pressure fluctuations from external flows and dissolution of the trapped gas into the water. It is therefore desirable to develop strategies to restore the plastron underwater.

A common method used to reduce the contact line pinning of water droplets on surfaces is the Leidenfrost effect, wherein the droplets are levitated on a cushion of vapor over the surface. But this typically requires the substrate to withstand high temperatures and also results in the loss of the droplet volume due to thermal evaporation. In this work, we explore new methodologies for locally generating gas near superhydrophobic surfaces to achieve room temperature droplet levitation and recover submerged superhydrophobic surfaces from wetting failure.

In the first part of this thesis, we explore a novel chemical method to replenish the plastron in situ on superhydrophobic textures which have undergone a Cassie-to-Wenzel transition underwater. We use the decomposition reaction of hydrogen peroxide on superhydrophobic surfaces prepared with a catalytic coating to generate oxygen gas for plastron recovery. We also provide a thermodynamic framework for designing superhydrophobic surfaces with optimal texture and chemistry for underwater plastron regeneration. We finally demonstrate the practical utility of this method by fabricating periodic microtextures on aluminum surfaces that incorporate a cheap catalyst, manganese dioxide. We perform drag reduction experiments under turbulent flow conditions in a Taylor-Couette cell which show that more than half of the drag increase ensuing from plastron collapse can be recovered spontaneously using this method.

In the second part of this thesis, we demonstrate room-temperature Leidenfrost
effect by using carbonated water droplets on superhydrophobic surfaces. We observe the levitation-to-wetting transition of these degassing droplets using light interferometry on transparent superhydrophobic substrates. We characterize the timescales of wetting transitions with respect to the concentration of dissolved carbon dioxide, and show that a critical dissolved CO$_2$ concentration of at least 10 mM is required for achieving droplet levitation. We also derive a model based on lubrication theory combined with a lumped capacitance approach to predict the levitation time of degassing droplets. We finally display the practical utility of this phenomena for reducing friction between droplets and surfaces, droplet sorting, droplet self-propulsion, and triggering on-demand droplet levitation using chemical reactions.

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Chapter 1

Introduction

Superhydrophobic surfaces are of interest in industrial applications where it is important to control the wettability of water or the adherence of water vapor to the surface. These include stain-proof fabrics [132, 69], self-cleaning [116, 34], fog collection [113], anti-icing [72, 10], underwater drag reduction [121], anti-corrosion [90, 147], and anti-biofouling [6] applications. Synthetic superhydrophobic surfaces are often inspired from naturally occurring water repellent surfaces such as the leaves of a lotus plant, the feet of a water strider, the wings of a butterfly or a housefly, the back of a backswimmer etc. These naturally occurring surfaces have a hierarchical texture with micro- and nanoscale features, coupled with a hydrophobic chemical coating which collectively impart the property of super-repellency towards water [117]. Figure 1-1 shows examples of naturally occurring superhydrophobic surfaces and the SEM micrographs of the respective microscale or nanoscale texture.

Currently, most superhydrophobic textures are made of passive coatings and materials, which do not provide any extra functionality to the surface. This thesis explores active methods to sustain and expand the functionalities of superhydrophobic surfaces for applications in air and under water.
Figure 1-1: Examples of superhydrophobicity found in nature. (a) Leaf of a Lotus plant, photograph by Shijan Kaakkara and SEM by Barthlott et al. [8]; (b) Foot of a Water strider, photograph by Rasto Belan and SEM from Gao et al. [44]; (c) Eye of a Common housefly, photograph by Miroslaw Świętek and SEM from Cook et al. [27]; (d) Feather of a Common shelduck, photograph by Dick Daniels and SEM from Srinivasan et al. [134]; (e) Upper side of the wing of a Morpho butterfly, photograph by Rudy Tiben and SEM from Vukusic et al. [151]; (f) Upper side of the elytra of a Backswimmer, photograph and SEM from Ditsche-Kuru et al. [33]
1.1 Aerophilicity of Superhydrophobic Surfaces

When a superhydrophobic surface is submerged underwater, a thin layer of air is trapped within its microtexture corresponding to the three phase configuration known as the Cassie state [22] (described in Section 1.1.1). Hence, these textures are also known as underwater *superaerophilic* surfaces [139, 47]. The air entrapped within the texture is termed a *plastron* in the biological community and this phenomena is observed in nature among many insects and plants which have evolved the ability to breathe underwater [138, 41, 9]. Figure 1-1f shows a picture of a backswimmer which is covered by a shiny plastron when swimming on its back. In addition to preventing water from wetting the underlying substrate, the plastron acts as a barrier towards corrosion on metal surfaces [152]. The surface air layer reduces the skin friction drag experienced by superhydrophobic surfaces underwater both in the laminar [121] and turbulent regimes [161, 28, 135]. This is due to the no slip condition at the interface being replaced by a surface with some effective slip (due to the air pockets). Figure 1-2 illustrates how the air in a superhydrophobic texture introduces a non-zero slip at the solid-liquid contact. This is useful in marine applications like ships, tanks and submarines where greater than 50% of the energy consumption is due to the skin friction on the hull [97].

1.1.1 Wetting Properties

The wettability of water on a flat solid surface is characterized by using the Young’s contact angle of a sessile water droplet. Young’s contact angle (or simply contact
Figure 1-3: Illustrations of the Young contact, the advancing, and the receding contact angles of a water drop on a flat surface.

angle), $\theta^\gamma_w$, is defined as the internal angle made by the liquid-air interface of a sessile droplet on a flat solid surface at the three phase contact line [159]. It is depicted by the angle $\theta^\gamma_w$ in Figure 1-3a. Its relation to the interfacial energies in the 3 phase system described is by the Young equation.

$$\cos \theta^\gamma_w = \frac{\gamma_{s,a} - \gamma_{s,l}}{\gamma_{l,a}} \quad (1.1)$$

where $\gamma_{s,a}$, $\gamma_{s,l}$, and $\gamma_{l,a}$ are the solid-air, solid-liquid, and the liquid-air interfacial energies. The Young’s contact angle is $< 90^\circ$ for hydrophilic surfaces, and $> 90^\circ$ for hydrophobic surfaces. However, Young’s contact angle is a thermodynamic property which is difficult to measure experimentally unless the surface is extremely smooth and defect free. Therefore, wetting characteristics are instead reported in terms of the advancing contact angle, $\theta^{adv}_w$ and the receding contact angle, $\theta^{rec}_w$. The advancing contact angle is the angle made by the liquid-air interface with the solid surface when the contact line is advancing slowly on the surface. Similarly receding contact angle in the angle made by the liquid-air interface with the solid surface when the contact line is retracting slowly. These are schematically depicted in Figure 1-3b-c. The stickiness of a liquid to a surface is described by the contact angle hysteresis, given by $\Delta \theta = \theta^{adv}_w - \theta^{rec}_w$.

When a surface is textured, the wetting characteristics are described by an apparent contact angle, $\theta^*_w$, made by the liquid-air interface with the solid texture. The value of this angle depends on the state of wetting of the liquid on the texture. When the liquid is partially wetting the surface but impregnated into the texture as shown
in Figure 1-4a, it is known as the Wenzel state [157]. It is related to the Young contact angle by the following relation.

\[ \cos \theta^* = r \cos \theta_w^{0*} \] (1.2)

where \( r \) is the Wenzel roughness of the surface. Wenzel roughness is defined as the total surface area divided by the projected surface area of the texture. When the liquid droplet is sitting on top of the texture without impaling the texture, it is known as the Cassie state [22] (See Figure 1-4b). It is given by the relation -

\[ \cos \theta^* = \phi_s \cos \theta_w^{0*} + (\phi_s - 1) \] (1.3)

where \( \phi_s \) is the wetted solid fraction. Wetted solid fraction is defined as the surface area of the wetted texture (tips of the texture) divided by the projected surface area of the texture. Finally, if the liquid is favorably wicked into the texture, then the droplet is a Hemiwicking state (Figure 1-4c), described by -

\[ \cos \theta^* = \phi_s \cos \theta_w^{0*} + (1 - \phi_s) \] (1.4)

Superhydrophobic surfaces are defined as surfaces with apparent contact angle \( \theta_w^{0*} > 150^\circ \), and a contact angle hysteresis \( < 5 - 10^\circ \) [34, 19].

### 1.2 Underwater Plastron Recovery

Continued stability of the Cassie state is essential for exploiting the desirable properties of underwater superaerophilic surfaces. But the air in this three-phase state is easily displaced by water under pressure fluctuations, shear flow, and low dissolved gas concentrations [14, 124, 15, 53, 95] causing them to transition into the Wenzel or fully-wetted state [157]. They can be recovered with minimum energy input by drying the surfaces in air and re-immersing them but, fabricating coatings with a simple plastron recovery mechanism would be useful in applications where air drying
Figure 1-4: Illustrations of the Wenzel, Cassie, and Hemiwicking states on a textured solid surface. Photographs in (a) and (b) have been taken from Callies and Quéré [21], and the photograph in (c) has been taken from Ishino et al. [62]

would not be possible such as ship hulls, submarines (which can use superhydrophobic coatings for drag reduction) etc. Thus in order for such a surface to recover its drag-reducing and anti-corrosion properties, it is necessary to induce a Wenzel-to-Cassie state transition on the textured surface while it remains submerged in the liquid phase. Wenzel-to-Cassie state transitions on textured surfaces have been achieved for sessile water droplets in air using electrowetting [149, 96], boiling [71], modulation of the Laplace pressure [82], and vibration [16]. However, these methods (except boiling) cannot easily be applied when the surface is submerged underwater because there is no source of air available in the surroundings to displace the water in the texture. Therefore in order to actively regenerate a plastron by restoring the Cassie state, there is a clear need to implement a gas or vapor source underwater.

1.2.1 Limitation of Current Methods

Methods that have been developed to address this need can be broadly classified into three categories: (i) gas/vapor generation; (ii) gas injection; (iii) increasing concentration of dissolved gas in the contacting liquid. Figure 1-5 shows examples from each of
these categories. The first approach uses \textit{in-situ generation of gas/vapor} to replenish the gaseous/vapor phase that initially formed the lost plastron. These regenerative techniques include electrolysis [76, 91], photoelectrocatalytic water splitting [78], and film boiling [127]. Lee et al. demonstrated \textit{in-situ} plastron recovery using electrolysis on Pt/Au coated silicon pillars [76]. Although this method has the advantage of being self-limiting, it is expensive to perform water-splitting using noble metals. On the other hand, film boiling has no material limitations but is energy intensive to perform on a large scale [58]. The second method, \textit{gas injection}, relies on providing a continuous supply of gas/air to the plastron. This can be achieved using a \textit{connected plastron} (plastron connected to an air reservoir through a porous microstructure[88], a large bubble [148], or a region of compressed gas [42]), or by injecting gas bubbles directly into the boundary layer of the flow [35]. Connecting a plastron to an external reservoir does not require any expensive materials or energy input, but needs precise control of pressure in the reservoir to favor plastron spreading. Also, bubbles injected into the boundary layer do not adhere to the surface immediately due to the lubrication pressure exerted on the bubble by the draining liquid film [31]. These methods are typically not self-limiting and are susceptible to the formation of large bubbles that reside on the texture instead of forming a thin plastron layer within the texture [35]. These macroscopic bubbles increase the form drag by disrupting the boundary layer, even though the skin friction drag contribution is lower [30]. The final approach is to saturate the water with dissolved air/gas to achieve plastron recovery by diffusion through the liquid and mass transfer at the interface [87, 142]. This technique requires the gas concentration to be controlled locally near the surface by increasing the temperature or decreasing the pressure of the water \textit{in situ}.

1.3 Droplet Levitation

When a drop of water contacts a hot surface, it disappears quickly by boiling. However if the temperature of surface is high enough, the drops sustains 100 times longer over the surface [119]. This is because a thin cushion of vapor forms between the drop
Figure 1-5: Methods used in literature to generate vapor/gas on surfaces underwater. (a) Electrolysis to generate H₂ and O₂ gas [76]; (b) Boiling to generate vapor [127]; (c) Air injection through a porous substrate [88]; (d) Decreasing the pressure of the water to induce Wenzel-to-Cassie transition [42]; (e) Supersaturating the water with gas by increasing the temperature [142]; (f) Supersaturating the water with gas by increasing decreasing the pressure [87].
and the surface above a critical temperature (Leidenfrost temperature), insulating it from the heat of the surface [52]. This effect is eponymously named after the German doctor Johann Gottlob Leidenfrost, who first described it in his work, *A Tract About Some Qualities of Common Water*, in 1756 (translated by Carolyn Wares in 1966 [79]). In the Leidenfrost state, the weight of the droplet is counteracted by the lift force created by the outflow of water vapor underneath the droplet and enables the droplet to stay afloat until it evaporates completely.

The lift force needed to levitate a droplet can be achieved by various other techniques including air entrainment by moving surfaces [133, 80], thermo-capillary flows [107, 48], and blowing air through a porous-substrate [50]. A common aspect of all of these methods of droplet levitation is that the lift force is created by hydrodynamic lubrication effect of the gas/vapor flow under the drop. For example, Goldshtik et al. [50] demonstrated levitation of water droplets on air cushions created by blowing air through porous substrates. A similar air cushion can be created by moving the substrate at high speed to allow surrounding air to be entrained between the droplet and surface [80, 46]. This effect can also be observed when droplet coalescence is prevented or delayed due to Marangoni flows or forced fluid flows. For example, Sreenivas et al. showed that drops deposited at the edge of a circular hydraulic jump display non-coalescence due to air entrainment by the flow below the drop [133]. Similarly, cold drops are observed to briefly levitate on hot baths before coalescence due to Marangoni stresses inducing thermocapillary flows in the drop and the bath [107, 48]. Other studies which use thin film lubrication effect to support droplets or small solids in levitation state include sublimating dry ice [156, 74] and evaporating liquid nitrogen [23, 131, 1].

Previous studies have studied various aspects of the Leidenfrost effect such as - effect of wettability on critical Leidenfrost temperature [145], effect of solid roughness on Leidenfrost temperature [73, 11, 67], vapor film thickness under the drop [12], vapor film shape under the drop [130], and droplet bouncing [140]. Biance et. al. showed that the scaling law for the thickness of vapor layer ($h_g$) under Leidenfrost droplets depends on the droplet size i.e. on whether the system is gravity dominated
Figure 1-6: Methods used in literature to levitate droplets over a solid or liquid surface. (a) Evaporation of water [119]; (b) Evaporation of liquid nitrogen [23]; (c) Water levitated using an air cushion created by blowing air through a porous substrate [50]; (d) Water drop over a hydraulic jump [133] (e) Silicone oil drop over a moving surface [80] (f) Non-coalescence of a cold drop of silicone oil with a hot bath of silicone oil [48]
or surface tension dominated.

\[ h_g \sim \left( \frac{\kappa_v \Delta T \eta_v \rho_l g}{\mathcal{L} \rho_v \gamma_{lv}^{2}} \right)^{1/3} R^{4/3} \quad \forall \quad R < l_{cap} \]

\[ h_g \sim \left( \frac{3 \kappa_v \Delta T \eta_v}{4 \mathcal{L} \rho_v \rho_l g l_{cap}} \right)^{1/4} R^{1/2} \quad \forall \quad R > l_{cap} \]

where \( \Delta T \) is the substrate superheat temperature, \( R \) is the equatorial radius of the drop, \( l_{cap} \) is the capillary length, \( \mathcal{L} \) is the latent heat of evaporation, \( \kappa_v, \eta_v \) and \( \rho_v \) are the thermal conductivity, viscosity and density of the vapor phase, \( \rho_l \) is the density of the liquid, and \( \gamma_{lv} \) is the surface tension of the liquid.

The Leidenfrost effect has been utilized for self-propelling droplets on ratchet-like textures [89, 74], measuring viscosity of liquids [112], achieving drag reduction underwater [144, 127], and nanopatterning [39]. It has also been reported that droplet levitation has potential applications in preventing contact of corrosive substances, and contamination (or defects) in pure materials [57, 37].

### 1.3.1 Limitation of Current Methods

In the classical Leidenfrost effect, the hydrophilic substrates must be typically heated to about 150-400°C to achieve levitation with water droplets [11]. This restricts the applications of this effect to only materials which can withstand high temperatures. Superhydrophobic substrates on the other hand stabilize the vapor layer at lower temperatures and hence show Leidenfrost effect at lower temperatures [145]. But it is still required to heat the water to tens of degrees above the boiling point of water to achieve a stable levitation film [127]. Apart from the material limitations in this method, it has been reported that the heat energy input for achieving the vapor film outweighs the energy saved by frictional drag reduction in underwater applications [58]. Thus any method that lowers the Leidenfrost temperature would be advantageous in terms of the extending the range of materials that can be used and the energy consumption.

Although heating is not required for the case where an air cushion is generated by
blowing air through the substrate, it requires a porous substrate and an air pumping system for the functioning of the substrate. In the case where the substrate is translated to entrained air under the droplet, the applications are limited to those where the substrate can be in continuous motion.

1.4 Outline of Thesis

All of the aforementioned methods use either thermal, electrical or mechanical energy to perform work (re-inflating the plastron or lifting the droplet). A source of energy that has been untapped so far is chemical potential energy of dissolved species. In this thesis, we demonstrate that chemical energy stored inside the liquid in the form of dissolved gas or unstable compounds can be used to perform mechanical work.

This thesis addresses the challenges in superhydrophobic surfaces in three parts. Chapter 2 describes a new chemical method to replenish plastron underwater using the decomposition reaction of hydrogen peroxide on superhydrophobic surfaces fabricated with a catalyst coating. Here we probe the effect of roughness on plastron recovery and methodologies to make the method cheap and scalable. Chapter 3 describes a new method to achieve room temperature Leidenfrost effect using carbonated water droplets on superhydrophobic surfaces. Here we investigate the effect of concentration of CO₂ on the levitation period and determine the parameters important for achieving droplet levitation. Chapter 4 discusses the advantages of having levitation in carbonated water droplets on superhydrophobic surfaces, and alternate ways to achieve the same effect. Appendix A explores the advantages and limitations of using side-light emitting optical fibers for delivering light in photocatalysis applications (a side project independent of the main thesis topic). Supplementary figures, tables and derivations have been provided in Appendices B, C, and D respectively.
Chapter 2

Underwater Plastron Recovery using Catalytic Gas Generation

Author note: The Taylor-Couette Cell in Section 2.3.3 was designed and fabricated by Anoop Rajappan. The drag reduction experiments in Section 2.5.2 were performed jointly with Anoop Rajappan.

2.1 Concept

In this chapter, we demonstrate a novel chemical method to replenish air loss from an established plastron by using catalytic decomposition of hydrogen peroxide. Figure 2-1 depicts the stages of plastron failure-recovery cycle using the chemical gas generation concept. In the first stage, the superhydrophobic surface ‘fails’ or transitions from Cassie to Wenzel state upon impregnation by water e.g. due to large external pressure fluctuations from turbulent flow. At this point, dilute concentrations of hydrogen peroxide added to the bulk liquid can react with the catalyst deposited at the bottom of the wetted microtexture and generates gas which spreads through the textured surface laterally, until ultimately the plastron has been fully restored. Because the reaction only occurs where the catalyst is in direct contact with the H₂O₂ solution (i.e. in regions where the plastron has collapsed), it is self-limiting. Furthermore, it requires only dilute concentrations (3-4%) of the reactant, hydrogen peroxide, to
observe plastron recovery. It also does not require electrical power input and can
be performed using cheaper catalysts than those typically used in electrolytic water-
splitting. This cycle can be repeated multiple times until the reactant is depleted or
the catalyst is degraded.

Plastron recovery occurs only when the conditions are optimal for lateral gas
spreading. Lee et al. [76] derived a criterion for plastron recovery by stipulating
that the lateral breakthrough pressure must be lower than the vertical breakthrough
pressure. Forsberg et al. [42] obtained another condition on the premise that the
lateral front of the plastron must touch the successive pillar before the vertical front
reaches the top of the microtexture. Lee et al. [76] and Verho et al. [148] found
that a superimposed nanotexture is a necessary condition for plastron recovery; by
contrast, Forsberg et al. obtained plastron recovery on pillared microtextures with
smooth walls. One of the reasons for the inconsistency in these observations is that the
corresponding theories were derived based on geometric principles and the inherent
thermodynamic stability of the plastron in the texture was ignored. Jones et al. [64]
and Marmur et al. [98] show that the stability of the Cassie state is the primary
condition for underwater stability of the plastron. We explore the importance of this

Figure 2-1: Schematic of an active superhydrophobic microtexture which generates
gas on-demand upon addition of the reactant, hydrogen peroxide.
condition for the lateral spreading of the plastron in an underwater superhydrophobic texture.

We fabricate micropillars interspersed with platinum catalyst on silicon wafers, hydrophobize them with a Teflon layer, and demonstrate plastron recovery underwater when dilute concentrations of hydrogen peroxide are introduced. We propose a thermodynamic model based on energetics of gas hemiwicking underwater, and derive a criterion for plastron recovery. We explore this criterion using platinum-coated micropillar arrays of varying height and pitch. Finally, we also demonstrate practical plastron recovery during measurements of frictional drag on an inexpensive and scalable aluminum surface with manganese dioxide catalyst using a Taylor-Couette cell [54].

2.2 Gas Generation using Chemical Decomposition of Hydrogen Peroxide

Hydrogen peroxide is an unstable compound which slowly decomposes into water and oxygen (Equation 2.1) even at room temperature and pressure.

\[
2H_2O_2 \xrightarrow{\text{catalyst/heat}} 2H_2O + O_2 \tag{2.1}
\]

This reaction is slow under room temperature conditions (with a decomposition half-life of \( t_{1/2} \sim 3 \) years [84]) but can be accelerated by increasing the temperature or using a suitable catalyst. There are a range of possible catalysts including the enzyme catalase [101], platinum and its alloys [103], iodide [83] and metal oxides [122] (see Table C.1). This reaction has been previously recently exploited in studies of active matter which use gas generation to propel nanorods and microtubes underwater [125, 155]. In this work, we use the overpressure of the oxygen gas generated by the decomposition reaction to dewet the microtexture and drive a wetting state transition from the Wenzel state back to the Cassie state.

Table C.1 shows that catalase has the lowest activation energy for the reaction
and hence is the most efficient catalyst for the $\text{H}_2\text{O}_2$ decomposition reaction. We fabricated substrates with a conformal coating of catalase using the layer-by-layer self-assembly technique and observed their catalytic activity in dilute concentrations of $\text{H}_2\text{O}_2$ (See Figure B-1). It can be observed that bubbles are generated on the surface but do not spread on it because the surface is intrinsically hydrophilic. As we show later in this work, we require the catalyst to be functionalized with hydrophobic groups to promote plastron recovery. It was difficult to hydrophobize the enzyme and retain its catalytic activity after any chemical treatment. Therefore, we chose platinum and manganese dioxide as catalysts for this work due to their ease of deposition, durability, and chemical modifiability. In addition to the aforementioned advantages, manganese dioxide is about 100 times cheaper than platinum (See Table: catalyst). Hence, it was used to demonstrate the scalability of this method in large scale applications such as marine vessels.

2.3 Experimental Methods

2.3.1 Fabrication of Catalyst Impregnated Microtextures

Silicon Micro-textures

We fabricated microtextures with selective catalyst coverage on silicon wafers using image reversal photolithography, reactive ion etching (RIE), e-beam evaporation of catalyst onto the pillars, and subsequent lift-off of the catalyst from the tops of the micropillars. 6" Silicon wafers (University wafers) were first coated with the image reversal photoresist, AZ5214, and an array of circular pillars of photoresist was created on the wafer by using image reversal photolithography. RIE (STS Pegasus) was then used to etch the exposed Si in the photoresist mask to create micropillars in the silicon. The depth of the pillars was controlled by adjusting the RIE process time. Platinum was then uniformly deposited onto the pillars using e-beam evaporation. The catalyst on the tops of the micropillars was subsequently removed using a lift-off procedure. These pillars were then spin-coated with Teflon AF solution (1 wt.%,
Figure 2-2: Micrographs of (a) Silicon texture with platinum coating on the sides and bottom of the texture, and teflon coating on the entire texture; (b) Silicon microposts with platinum catalyst on top of the pillars (H = 150 \( \mu \text{m} \), L = 100 \( \mu \text{m} \), 2R = 50 \( \mu \text{m} \)). (c) Smooth-walled micropillar arrays fabricated using SU8 photoresist.; (d) Laser textured aluminum pillars coated with MnO\(_2\) and Teflon, the tops are shaved to remove catalyst; (e) Laser textured aluminum pillars coated with MnO\(_2\) and a fluorinated silane; (f) Square pillars machined on an aluminum rotor (width 100 \( \mu \text{m} \), height 200 \( \mu \text{m} \), and spacing 100 \( \mu \text{m} \)) and coated with MnO\(_2\) and a fluorinated silane. All Scale bars = 50 \( \mu \text{m} \).
Chemours) at 3000 rpm to render the surface chemistry of the microtexture array hydrophobic. Figure 2-2a shows a micrograph of a Si-Pt-Teflon texture with 150 μm depth, and Pt-less tops. The thickness of the Teflon layer was measured to be 80 ± 5 nm using contact profilometry on a flat silicon wafer coated with Teflon at the same conditions (The measurement was made over a scratch in the coating on the surface). The thickness of Teflon could be higher on the textured substrates due to the confinement of the polymer in the interstices of the pillars while spin-coating. The lift-off step was omitted for testing the samples in which the catalyst was retained on the tops of the pillars and these are shown in Figure 2-2b. The dimensions of these pillars are given in Table C.3. Smooth-walled micropillar arrays were fabricated using photolithography with SU8 photoresist on Pt-coated Si wafers and a micrograph of this texture is shown in Figure 2-2c.

**Aluminum Micro-textures**

We fabricated catalyst-impregnated superhydrophobic aluminium microtextures by using laser texturing, electroplating and silanization. An egg-crate microtexture \((r = 5.1)\) was patterned onto flat sheets of Aluminum (Al 6106) by scribing equally spaced lines \((\text{pitch} = 75 \, \mu\text{m})\) in the horizontal and vertical directions using a laser scriber (Electrox Scriba E-Box, 200 mm/s, 20 repetitions). This surface was then dipped into 5 wt% sodium hydroxide for 45 s to remove any organic contaminants. The substrate was then electroplated with manganese dioxide by using anodic electrolytic deposition [7]. The substrate and counter electrode (a flat Al plate cleaned using the sodium hydroxide protocol described earlier) were dipped into 100 ml of 0.05 M Manganese acetate solution with a gap of 20 mm between them. The solution was maintained at 60 °C and stirred using a stir bar at 60 rpm. Electrolytic deposition was performed at 5 mA/cm² for 5 min, and then the electrodes were immediately removed from the solution and dried at 100 °C in air. Fresh solutions of Mn(CH₃COO)₂ were used for every new deposition. Figure B-3 shows MnO₂ electrodeposited on a flat Al substrate under similar deposition conditions. The electroplated substrates were then cleaned using a plasma cleaner (Harrick) for 5 mins and placed into a glass beaker
for silane chemical vapor deposition. An open vial with 3 ml of a fluorinated silane (Trichloro(1H,1H,2H,2H-perfluorooctyl)silane) was placed into the glass beaker along with the other substrates. The beaker was then covered with an aluminum foil and placed on a hotplate at 120 °C for 3 hours. The substrates were then rinsed with isopropanol to remove excess silane and dried in air, to obtain a superhydrophobic texture with \(\theta_{\text{adv}} = 162^\circ \pm 3^\circ, \theta_{\text{rec}} = 148^\circ \pm 4^\circ\). A micrograph of this texture is shown in Figure 2-2e. Aluminium microtextures with selective catalyst coverage were fabricated by adding an abrasion step after the above procedure. The abraded texture does not have platinum on the top of the texture but has the catalyst in the interstices of the texture (See Figure 2-2d).

**2.3.2 Imaging of Plastron Recovery**

The substrates were immersed into a quartz cell (2"L x 1"W x 2"H, ramé-hart) containing 30 ml of de-ionized (DI) water and supported at approximately 45° to the horizontal plane. A microscope (Zeiss) was used to observe the plastron at high magnification. A spot light source (Dolan-Jenner MI-150) was used to illuminate the plastron at an angle greater than the critical angle for total internal reflection \(\theta_c = 48.75^\circ\) to visualize the air-water interface as shown in Figure 2-3. The plastron that is initially present on the substrate after immersion into DI water was removed
from the substrates by applying suction/pressure at the surface using a pipette. To
trigger plastron recovery, 1-3 ml of 30 wt.% hydrogen peroxide (inhibited hydrogen
peroxide, Sigma Aldrich) was gently added to the water and allowed to diffuse to the
surface. Videos were then recorded using a CCD camera at 24 fps.

2.3.3 Drag Reduction Experiments

Drag reduction experiments were performed on a controlled stress rheometer (TA
Instruments AR-G2) using a bespoke Taylor-Couette cell with rotor radius 14 mm, cell
gap 20 mm and rotor length 42 mm [135], and a fluid inlet port to inject hydrogen
peroxide into the cell during the experiment as shown in Figure 2-4. In this Taylor-
Couette cell, transition to fully turbulent flow occurs at Re > 10,000. Microgrooves
were machined onto the rotor (Al 6061-T6) using a CNC lathe (Burlington Machine,
Wilmington, MA). The rotor was then electroplated in manganese acetate solution
(0.05 M, 60 °C, stirring at 60 rpm) with a cylindrical counter electrode at a current
density of 5 mA/cm² for 5 min as shown in Figure 2-5a. It was then dried and
plasma cleaned in air for 5 min before depositing silane using the same procedure as
the flat aluminum plates. A photograph of the machined and coated rotor is shown
in Figure 2-5b. The microgrooves on the surface of the rotor are 100 μm in width as can be seen in Figure 2-2f.

2.4 Thermodynamic States of Gas Bubbles on Aerophilic Textures

Bubbles interact with textured solid surfaces in different ways depending on the roughness and chemistry of the surface [129]. We classify the states of wetting of a gas bubble generated on a textured solid surface immersed underwater based on their thermodynamic stability. Comparison with the corresponding system in which a drop of liquid wets a textured solid surface in air enables the identification of four distinct regimes, and the stability of each of these gas bubble-in-water states depends on both the surface chemistry and roughness of the texture. Figure 2-6a shows a schematic illustrating the four regimes on a microtextured solid surface - bubble, blister, hemiwicking blister, and plastron. *Bubble* identifies the state in which the gas does not want to wet the solid surface and is pinned to the surface with minimal solid-air contact area. *Blisters* are bubbles that partially spread on the solid surface
Figure 2-6: (a) Schematic of the thermodynamic states of gas bubbles spreading on textured surfaces. The stability of the states is dictated by both the microtexture and surface chemistry. The scale bar represents 0.5 mm; (b) Plot of the apparent contact angle of water ($\theta^*_w$) on a textured surface (Wenzel roughness $r = 2$, solid fraction $\phi_s = 0.4$) versus Young's contact angle of water on a flat surface ($\theta_w$). The theoretically predicted regime of stable underwater gas wetting or aerophilicity is also indicated by the shading in the plot. Plastron recovery is favored only in the region shaded in green.
until they establish an equilibrium pressure and apparent contact angle. They do not imbibe spontaneously into the texture. The Plastron is the state in which the gas is completely imbibed in the texture and only the top of the surface texture contacts the liquid phase. Finally, the intermediate state identified as Hemiwicking Blisters are blisters that spread on top of a microtexture imbibed with air i.e. plastron. The distinction between a blister and a hemiwicking blister is that the fluid phase preferentially imbibed in the texture surrounding the gas blister is different. We define this state using a nomenclature derived from the work of Bico et al. who considered corresponding states for liquid droplets wetting microtextured dry substrates in air [13]. It can be seen from detailed examination of Figure 2-6a (i)-(iv) that the pillars are visible for the bubble and blister states while the pillars are hidden inside the gas layer for the hemiwicking blister and plastron states. When gas is produced in the texture through the decomposition of hydrogen peroxide, it may leave the surface through buoyancy effects as a macroscopic bubble, or spread through the microscopic texture in one of the other states depending on the texture chemistry and roughness, and the rate of generation compared to the rate of spreading.

In this work, we follow Quéré’s hemiwicking model for hydrophilic textures [13] to obtain an equivalent hemiwicking model for superhydrophobic textures underwater. In ideal plastron recovery, the gas would spread along the surface microtexture without displacing the water on top of the texture as depicted in Figure 2-1. This process involves the creation of new solid-air and water-air interfaces while replacing the water-solid interfaces during de-wetting. The change in energy of the system when the gas front displaces water from a small area $dx$ is given by the following equation.

$$dE = \gamma_{w,g}(1 - \phi_s)dx + \gamma_{s,g}(r - \phi_s)dx - \gamma_{s,w}(r - \phi_s)dx$$

(2.2)

where $\gamma_{w,g}$, $\gamma_{s,g}$ and $\gamma_{s,w}$ represent the respective interfacial energies between the three phases, $r$ and $\phi_s$ denote the Wenzel roughness and the projected solid fraction respectively, and $l$ is the length into the plane of Figure 2-1. The Wenzel roughness $r$
is defined as the total surface area per unit projected area of solid surface, and solid
fraction $\phi_s$ is defined as the area wetted by the liquid in the Cassie state per unit
projected surface area of solid. For example on a microtexture with circular pillars,
$r$ and $\phi_s$ are calculated by using the following equations.

$$r = 1 + \frac{2\pi RH}{L^2}$$  \hspace{1cm} (2.3)

$$\phi_s = \frac{\pi R^2}{L^2}$$  \hspace{1cm} (2.4)

The change in energy $dE$ of the system must be negative in order for the gas to
preferentially wick into the texture. Hence by setting $dE < 0$ and simplifying the
expression using the expression for Young’s three phase contact angle equation [159],
we obtain the thermodynamic condition for spontaneous plastron recovery.

$$\cos \theta_w < \frac{1 - \phi_s}{r - \phi_s}$$  \hspace{1cm} (2.5)

Equation 2.5 implies that plastron recovery is only possible for textures with hydrophobic chemistries ($\theta_w > 90^\circ$) since the expression on the right is always negative.

The favorable regimes of underwater gas wetting can be represented on the plot
illustrating the relationship between the cosine of the apparent contact angle of a
water droplet on a textured solid in air, $\cos \theta_w^*$ and the cosine of the Young’s contact
angle of a water droplet on a flat surface in air, $\cos \theta_w$, as shown in Figure 2-6b. Here
it can be seen that plastron and hemi-wicking blisters are favorable in the textures
which are Cassie-stable towards sessile water droplets in air, blisters are favorable in
the textures which are Wenzel-stable towards sessile water droplets in air, and bubbles
are favored in the textures which are hemiwicking towards sessile water droplets in
air. Since gas displaces water in the texture during plastron spreading, it is most
appropriate in Equation 2.5 to use the receding contact angle of a sessile water droplet
on a smooth surface with the same chemistry. Rearranging Equation 2.5 using the
receding water contact angle gives us the condition that needs to be satisfied for
textural design parameters such as the solid area fraction $\phi_s$ and the solid roughness $r$. 

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This also matches with the monostable Cassie state condition derived by Li et al. for the Wenzel-to-Cassie transition of liquid droplets on microtextures [82]. For plastron recovery to be favorable over blister formation, we therefore require microtextures with roughness exceeding a critical value.

\[
 r > 1 - \left( \frac{1}{\cos \theta_{\text{mc}}^{\text{ec}}} + 1 \right) (1 - \phi_s) \quad \forall \theta_{\text{mc}}^{\text{ec}} > 90^\circ 
\]  

(2.6)

2.5 Results and Discussion

2.5.1 Plastron Recovery on Microtextured Surfaces

In this work, we use two types of textured surfaces for testing plastron recovery - lithographically patterned silicon and laser-textured aluminum (See Figure 2-2a-e). In order to systematically study the effect of surface roughness on plastron recovery, micro-pillar arrays with varying pillar heights and spacing were fabricated on silicon wafers using photolithography. Platinum, a well-known catalyst for the hydrogen peroxide decomposition reaction, was selectively deposited on the bottom and the sides of the micro-pillars using lift-off photolithography (see the experimental methods section for more details), to ensure that the plastron re-inflation process is self-limiting. The textures were then spin-coated with a 1 wt.% Teflon solution and cured to render them hydrophobic.

Figure 2-2a shows an example of an Si-Pt-Teflon texture in which the plastron regeneration mechanism is self-limiting. The textures were immersed in deionized water and imaged at an angle of 45° with yellow light reflecting off the air-water interface as shown in Figure 2-3. For example, the first frame in Figure 2-7a shows an image of an immersed silicon microtexture (150 μm depth, 50 μm pillar width, 100 μm pitch corresponding to \( \phi_s = 0.196, r = 3.356 \)) which has been partially impregnated by water. The plastron filled region reflects yellow light via total internal reflection at the air-water interface and appears golden in color, while the other wetted regions appear dark due to the absence of air within the texture. The subsequent frames in Figure 2-
Figure 2-7: (a) Plastron recovery on silicon texture underwater at 4.5 wt.% H$_2$O$_2$; (b) Plastron recovery underwater at 1.5 wt.% H$_2$O$_2$
7a show plastron recovery after addition of a few drops of 30 wt.% hydrogen peroxide to the solution (Final H$_2$O$_2$ concentration in solution = 4.5% wt.). Defects in the hydrophobic coating allow the dissolved hydrogen peroxide to come in contact with the Pt catalyst in between the pillars of the texture and the resulting decomposition reaction causes oxygen gas to nucleate within the microtexture. Figure 2-7a shows the time evolution of a Si-Pt-Teflon surface transitioning from a partially-wetted state to a fully-recovered plastron state. Experiments were also performed on silicon micropillars whose tops were not stripped of platinum catalyst (See Figure 2-2b) and it was found that plastron recovery is possible in these cases too. We believe that this is possible because the nucleation of gas is favored at the sharp corners at the bottom of the texture, even though there is catalyst at the top (See Figure 2-8a). We also note that Si micropillars fabricated using the Bosch RIE process also have a nanoscale texture which can promote plastron recovery. Hence, further tests were conducted using smooth-walled micropillars made of SU8 photoresist (See Figure 2-2c). It was observed that smooth-walled micropillar textures also show plastron recovery similar to the dry-etched Si micropillars, further supporting our observation that nanoscale roughness is not necessary for plastron recovery.

Figure 2-9 shows a regime map classifying the silicon micro-pillar experiments into two categories based on whether plastron spreading or blister formation was favored based on the texture parameters characterizing each surface. The receding contact angle of a water droplet on a Teflon coated smooth silicon wafer was measured to be $\theta_{rec}^{w} = 111^\circ \pm 2^\circ$ and this value has been used to plot the recovery condition given by Equation 2.6. The shaded region around the theoretical prediction line indicates the sensitivity of Equation 2.6 to a receding contact angle variation of $\pm 2^\circ$. It can be seen from both the theory and the experiments that textures with larger roughness and higher solid fraction favor plastron recovery, while those with lower roughness and smaller solid fraction promote blister formation. We also see that the textures which have catalyst on top of the pillars favor plastron recovery as well. Although it has been reported in previous studies that the presence of a nano-Cassie state is necessary for plastron recovery [76, 148], we observe that satisfying the thermody-
Figure 2-8:  (a) Sequence of images showing gas nucleating at the bottom of the pillar texture after the addition of $\text{H}_2\text{O}_2$, and merging with gas nuclei at the adjacent pillars.; (b) Sequence of images showing the pressure buildup in the plastron leading to the de-pinning of the contact line and merging of plastron between adjacent regions. The transition occurs between images 1-2 and images 3-4.
dynamic condition for plastron gas spreading alone is sufficient to allow for plastron recovery on microtextures even without a nanoscale texture to hold a stable plastron. Figure B-2 shows a plot of the $H/L$ and $\phi_s$ of smooth-walled micropillar textures used in previous plastron studies [76, 148, 42]. Here we notice that the textures follow our thermodynamic prediction for plastron recovery (assuming a fluorinated chemistry i.e. $\theta_w^{rec} = 110^\circ$). Plastron recovery was not observed for textures which fall below the theoretical line because it was not thermodynamically favorable, while textures above the line show recovery like those in Forsberg's work.

It was observed in our work that a few textures show recovery even though they
lie below the theoretical condition for plastron recovery. This can be explained by the fact that these textures can transition from a metastable Wenzel state to a stable Cassie state if they satisfy Equation 2.6 with $\theta_w^{rec} = \theta_w^{young}$, the Young contact angle for Teflon. This curve would lie in between the theoretical curves for $\theta_w^{adv}$ and $\theta_w^{rec}$ shown in Figure 2-9, and define the bi-stable region where the Wenzel state is metastable [82]. In underwater Wenzel-to-Cassie transitions, the energy barrier between the Cassie and Wenzel states in the bistable region can be overcome by the gas over-pressure in the plastron due to continuous generation of gas. We believe that this thermodynamic condition derived assuming a simple patterned texture is a necessary but not a sufficient condition for plastron recovery. While this condition is an important global factor, there are various other local factors which can also influence the dynamics of plastron spreading such as the pillar breakthrough pressure [76], contact of gas meniscus with pillars in the direction of spreading [42], contact line pinning, and texture re-entrance [141]. Figure 2-8b shows the contact line depinning of the plastron front in the texture caused by pressure build-up in the gas. The plastron spreads through the texture via a sequence of pinning-pressurizing-depinning-depressuring cycles.

In order to make this method scalable for large scale drag reduction applications, catalytically active textures were fabricated on textured aluminum using an inexpensive catalyst, manganese dioxide. Flat polished aluminum plates were laser textured, electroplated with manganese dioxide, and conformally coated with a fluorinated silane to obtain catalytically active superhydrophobic textures. Figure 2-2d shows a micrograph of a so-called egg-crate [68] aluminum microtexture coated with MnO$_2$ and silane. The Wenzel roughness of this texture was calculated from the surface area measured using an optical profilometer and corresponds to $r = 5.1$. The electroplated MnO$_2$ deposit has both microscale and nanoscale features as can be seen in Supplementary Figure B-3. Since the texture has a dual scale roughness, it is expected that the nano-Cassie state can be supported in the nanofeatures of the texture even after impregnation at the micro-scale [148]. In order to ensure maximum water impregnation in the texture, the samples were immersed into boiled deionised water under
vacuum for 12 hours before the introduction of hydrogen peroxide. Figure 2-7b shows the process of plastron recovery on such a texture at a hydrogen peroxide concentration of 1.5 wt.%. Note that the MnO$_2$ coating was not removed from the tops of the aluminum pyramids in this experiment; however, plastron recovery was still favored over blister formation. This is in agreement with our previous observation on silicon pillars with platinum-coated tops.

In all of the experiments for which plastron recovery was observed, the gas spreads laterally along the texture until the contact line becomes sufficiently pinned to prevent further advancement. When the contact line is unable to de-pin further, the gas breaks through the top of the pillars and forms a hemiwicking blister. At this point the gas generated within the texture is preferentially channeled into the hemiwicking blister which has a low Laplace pressure due to the large radius of curvature of the blister. This stops the connected plastron from spreading further into other wetted parts of the texture. Hence, it is important to fabricate surface textures with high plastron connectivity and low pinning defects for complete plastron recovery.

2.5.2 Slip Recovery in Frictional Drag Tests

To measure the drag reduction performance and slip recovery capabilities of these plastron promoting textures, aluminum rotors with catalytically active textures were tested in a Taylor-Couette cell under turbulent flow conditions [135]. Cylindrical rotors ($R_{rotor} = 14$ mm) were textured by machining microgrooves onto the surface in both the circumferential and longitudinal directions to obtain a regular array of square micropillars of width 100 $\mu$m, height 200 $\mu$m, and spacing 100 $\mu$m ($r = 2$, $\phi_s = 0.25$). The rotor was then electroplated with MnO$_2$ and hydrophobized using a fluorinated silane in a similar manner to the flat laser-textured aluminum samples. Figure ???f shows a micrograph of this texture; where the micro-deposits on the pillars correspond to MnO$_2$ electroplated on the texture, while Figure 2-5b shows a droplet of water sitting on the superhydrophobic surface of the textured aluminum rotor. All drag reduction experiments were performed under fully turbulent flow conditions in a custom-fabricated Taylor-Couette Cell (shown in Figure 2-4) at $Re = 47,000$, where
the Reynolds number is calculated as \( \text{Re} = \frac{R_i \Omega \Delta R}{\nu} \). Here \( R_i \) is the rotor radius, \( \Delta R \) is the cell gap, \( \Omega \) is the angular velocity of the rotor (\( R_{\text{rotor}} \)), and \( \nu \) is the kinematic viscosity of the working fluid. The mean value of the frictional wall shear stress (\( \tau_w \)) on the rotor is defined as \( \tau_w = \frac{T}{2\pi R_i^2 L} \) where \( T \) and \( L \) are the averaged torque experienced by the rotor and the length of the rotor respectively. The percentage drag reduction is defined as \( DR = 100 \times \frac{(\tau_{\text{Smooth}} - \tau_{\text{Cassie}})}{\tau_{\text{Smooth}}} \), where \( \tau_{\text{Smooth}} \) is the shear stress on an untextured cylindrical rotor and \( \tau_{\text{Cassie}} \) is the shear stress on the patterned rotor with a fully inflated plastron. Note that the solid fraction \( \phi_s \) of the grooved rotor is high (\( \phi_s = 0.25 \)) to promote plastron regeneration (See Figure 2-9), but the experimentally measured turbulent drag reduction is only about 3\% compared to a smooth untextured hydrophilic rotor at the same Reynolds number of \( \text{Re} = 47,000 \). However, this rotor can still be used to evaluate the effectiveness of the plastron recovery method by comparing the torques on the rotor in its original plastron inflated state (Cassie), its wetted state (Wenzel) and its final recovered state.

The plastron recovery tests were performed in three stages as shown in Figure 2-10. The plastron is initially tested for its stability by running a long test (4 hours) under air-saturated water conditions. There is minimal change in the shear stress, \( \tau_{\text{Cassie}} \), as the plastron is stable during this time period. A wetting transition was then artificially induced by flushing de-aerated water through the system until the shear stress rises and reaches a new steady state value corresponding to a fully wetted Wenzel state, \( \tau_{\text{Wenzel}} \). Visual inspection of the textured rotor in the cell also showed almost complete loss of the silvery plastron film. The rotor was maintained in this state for a few minutes before introducing hydrogen peroxide into the system. 1 ml of 7.5 wt\% hydrogen peroxide was introduced into the cell over a period of 5 mins to increase the \( \text{H}_2\text{O}_2 \) bulk concentration up to \( 1.3 \times 10^{-5} \text{ mol ml}^{-1} \). The average shear stress exerted on the inner rotor is observed to decrease slowly and reaches a steady state value, \( \tau_{\text{Recovered}} \), over a period of 20 min after which any additional oxygen produced only contributed to blister formation on the rotor. The plastron recovery is observed to be patchy in most parts due to pinning defects as can be seen in Figure 2-11a. Figure 2-11b shows "unwrapped" views of the rotor in its
Figure 2-10: (e) Plot of the average wall shear stress, \( \tau_w \), experienced by the rotor in the Taylor-Couette cell at \( Re = 47,000 \) during the initial period of drag reduction (Cassie state), plastron failure (Wenzel state) and plastron recovery (partial Cassie) stages.

Cassie state, Wenzel state and after partial recovery (reconstructed from a sequence of images). Although the plastron recovery is imperfect, the presence of the air layer contributes to improving the average level of wall slip induced on the rotor surface. The percentage slip recovery is calculated as \( SR = 100 \times (\tau_{\text{Wenzel}} - \tau_{\text{Cassie}}) / \tau_{\text{Recovered}} \), where \( \tau_{\text{Wenzel}} \) is the torque on the completely wetted rotor and \( \tau_{\text{Recovered}} \) is the torque on the rotor after plastron recovery. The average slip recovery percentage over four repeated experiments was found to be \( 51 \pm 14 \% \). Figure B-4 shows the data obtained in the four experiments.

It can be estimated from the rotor texture parameters that \( 6.1 \times 10^{-7} \) mol of oxygen is required for every square centimeter of rotor surface for plastron recovery to occur over the complete surface area of the rotor assuming near atmospheric pressure conditions and a texture depth of \( H = 200 \mu m \). However, since all the hydrogen peroxide injected does not come into contact with the catalyst surface and thus does not contribute to plastron recovery, it is necessary to inject an amount of hydrogen peroxide, \( n_{H_2O_2}^{\text{injected}} \), higher than the required stoichiometric quantity, \( n_{H_2O_2}^{\text{utilized}} \), in order to
achieve a significant rate of plastron recovery. The maximum efficiency of chemical re-
geneneration of plastron can be calculated as $\eta_{\text{max}} = \frac{n_{\text{utilized}}^{\text{H}_2\text{O}_2}}{n_{\text{injected}}^{\text{H}_2\text{O}_2}}$, and it was found to be 1.1% in the current configuration. Since the plastron recovery is partial, this efficiency must also be multiplied by the percentage area recovered to get the effective efficiency. For example, in Figure 2-11b, the percentage of the wetted area over which plastron recovery is observed is only estimated to be 58%, and hence the efficiency $\eta = 0.58\eta_{\text{max}} = 0.6\%$. The plastron recovery coverage could be increased by incorporating a dual-scaled texture like that in the laser textured aluminum substrates, which allows for the gas to spread more easily through the nanotexture without pinning, thus reducing contact angle hysteresis. The mass transfer efficiency could be also potentially improved by injecting the hydrogen peroxide directly into the boundary layer from within a porous surface.

![Image of rotor recovery](image)

Figure 2-11: (a) Picture of the rotor after partial recovery; (b) Unwrapped views of the cylindrical surface of the rotor before plastron failure, after plastron failure, and after partial plastron recovery. This image was produced by imaging the rotating rotor at constant speed, and stitching together vertical sections of the rotor captured across one entire rotation.
2.6 Summary

In this chapter, we show a novel method to regenerate plastron underwater by using the catalytic decomposition reaction of hydrogen peroxide on superhydrophobic textures coated with a catalyst. We achieve superhydrophobic microtextures with catalytic activity by using lift-off photolithography with a platinum deposition step, and a subsequent coating step with Teflon. We also fabricate low-cost and scalable catalytically active superhydrophobic textures by laser texturing aluminum, electroplating of manganese dioxide catalyst, and vapor-depositing a fluoroalkyl silane. We visualize the generation and spreading of gas in the microtextures using total internal reflection of light on the gas-liquid interface and demonstrate plastron recovery on the silicon microtextures using hydrogen peroxide solutions with less than 5 wt.% concentration. We also provide a thermodynamic framework for designing textures for plastron recovery using the energetics of gas spreading on a solid texture underwater. We show that microtextures without a dual scale texture promote plastron recovery provided they satisfy the thermodynamic conditions for recovery. We finally demonstrate plastron recovery under turbulent flow conditions using a micro-grooved (machined) rotor in a Taylor-Coutte cell. By comparing the shear stress exerted on the rotor in the Cassie, Wenzel and plastron-recovered states, we show that 51 \( \pm \) 14\% of the slip lost due the impregnation of the texture can be recovered by using this method of replenishment. We anticipate that introducing an hierarchical roughness such as those on the laser textured aluminum surfaces will help in reducing pinning defects and promoting enhanced slip recovery in the drag reduction experiments.
Chapter 3

Levitation of Carbonated Water Drops

Author note: Data reported in Figure 3-4 were obtained jointly with A. Chotrat-tanapituk. Figure 3-8 and Figure 3-11a were obtained jointly with P. Bourrianne.

3.1 Concept

In this chapter, we explore a novel chemical method to levitate water droplets over a superhydrophobic surface by supersaturating water with a dissolved gas. The difference in chemical potential of dissolved gas in the drop and the gas in the environment drives the gas out of the water into the environment. The expressions for the chemical potential of carbon dioxide in the liquid ($\psi_{\text{CO}_2}^l$) and the vapor ($\psi_{\text{CO}_2}^v$) phases are given below [36].

\begin{align}
\psi_{\text{CO}_2}^l(T,P,C) &= \psi_{\text{CO}_2}^{(0)}(T,P) + RT \ln C_{\text{CO}_2} + RT \ln \gamma_{\text{CO}_2}(T,P,C) \\
\psi_{\text{CO}_2}^v(T,P,x) &= \psi_{\text{CO}_2}^{(0)}(T) + RT \ln x_{\text{CO}_2}P + RT \ln \phi_{\text{CO}_2}(T,P,x)
\end{align}

where $P$ is the vapor phase pressure, $C_{\text{CO}_2}$ is the molality of CO$_2$ in liquid phase, $x_{\text{CO}_2}$ is the mole concentration of CO$_2$ in the vapor phase, $\gamma_{\text{CO}_2}$ and $\phi_{\text{CO}_2}$ are the
activity and fugacity coefficients respectively, $\psi_{\text{CO}_2}^{l(0)}$ is the chemical potential in an ideal solution of unit molality, and $\psi_{\text{CO}_2}^{v(0)}$ is the ideal gas chemical potential of $\text{CO}_2$ when the pressure is equal to 1 bar. When water is pressurized with $\text{CO}_2$ gas and held at equilibrium, the chemical potentials of $\text{CO}_2$ in both the phases are equal to each other i.e., $\psi_{\text{CO}_2}^{l} = \psi_{\text{CO}_2}^{v}$. When the pressure of this system is released suddenly, $\psi_{\text{CO}_2}^{v}$ drops immediately due to the decrease in $P$, whereas the $\psi_{\text{CO}_2}^{l}$ remains high due to the dissolved gas content in the water i.e., the water is supersaturated with gas. This chemical potential difference leads to the spontaneous desorption of gas from the liquid until the system reaches a new equilibrium. The process of degassing produces a gas flow close to the surface of the liquid which can be used to perform mechanical work; for example, it can be used to levitate a droplet of water. In this work, we exploit the gas flow emanating from degassing water droplets to achieve room-temperature Leidenfrost effect. We use the carbon dioxide-water system as a model gas-liquid system to study this phenomena due to the high solubility of $\text{CO}_2$ in water (See Table C.2 for the values of the Henry’s law solubility constants of common gases in water) and the practical utility of this system in many industrial applications [40]. Although sulphur dioxide and ammonia are 50 and 1000 times more soluble than $\text{CO}_2$ in water respectively (see Table C.2), they were not used due to the handling hazards involved. Previous studies have reported levitation of solid objects using carbon dioxide in the form of dry ice [156]. However, this is the first study to report levitation of liquid water droplets using dissolved carbon dioxide.

This method has additional advantages compared to the Leidenfrost effect because it can be used on substrates or coatings which cannot withstand high temperatures such as plastics, biological materials, and organic surface treatments. It also preserves the volume of the liquid droplet since there is no thermal evaporation. This effect can be triggered by any method that induces gas supersaturation in the liquid. For example, the solubility of a gas in the liquid can be changed by varying either the pressure or the temperature, i.e. Henry’s law. Alternatively, dissolved gas can be produced in solution using a chemical reaction, for example, the reaction of an acid with a bicarbonate salt produces carbon dioxide gas. This effect does not rely on
the volatility of the liquid but instead, it depends on the solubility of the gas in the liquid, which can be chosen appropriately based on the liquid composition.

3.2 Chemical Equilibrium Species in Carbonated Water

Carbon dioxide dissolves in water to form a weakly dissociating acid, carbonic acid. Carbonic acid is a diprotic acid with two dissociation constants. The equations describing the chemical equilibrium established between the dissolved CO$_2$, carbonic acid, and its dissociated species are given below.

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]  
\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]  
\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]

where $K_h$ is the hydration constant for carbon dioxide, and $K_{a1}$ and $K_{a2}$ are the first and second acid dissociation constants for carbonic acid respectively. The values of these dissociation constants and other physical properties of CO$_2$ are provided in Table 3.1. Typically, Equations 3.3 and 3.4 are combined and reported with an apparent dissociation constant, $K_{a1}^*$.

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons K_{a1}^* \text{H}^+ + \text{HCO}_3^- \]  

The relative equilibrium concentrations of the dissolved CO$_2$, hydrogen ions, carbonate ions, and bicarbonate ions in a closed system can be determined by considering the two dissociation reactions of carbonic acid, the self-ionization of water $K_w=[\text{H}^+][\text{OH}^-]$, and the charge neutrality condition $[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$. The absolute concentrations of the species can be obtained by solving a cubic equation and knowing the concentration of one of the species in the system (or the total
Table 3.1: Physical and chemical properties of carbon dioxide at $T = 23^\circ C$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>$\rho_g$</td>
<td>1.796 kg m$^{-3}$</td>
<td>[150]</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$\mu_g$</td>
<td>$1.484 \times 10^{-5}$ Pa s</td>
<td>[150]</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>$k_H$</td>
<td>2755 Pa m$^3$ mol$^{-1}$</td>
<td>[126]</td>
</tr>
<tr>
<td>Hydration constant</td>
<td>$K_h$</td>
<td>$1.5 \times 10^{-3}$</td>
<td>[154]</td>
</tr>
<tr>
<td>Apparent first dissociation con-</td>
<td>$K_{a1}^*$</td>
<td>$4.33 \times 10^{-7}$</td>
<td>[104]</td>
</tr>
<tr>
<td>stant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular diffusivity in air</td>
<td>$D_g$</td>
<td>$1.6 \times 10^{-5}$ m$^2$ s$^{-1}$</td>
<td>[99]</td>
</tr>
<tr>
<td>Molecular diffusivity in water</td>
<td>$D_l$</td>
<td>$1.97 \times 10^{-9}$ m$^2$ s$^{-1}$</td>
<td>[49]</td>
</tr>
</tbody>
</table>

Dissolved inorganic carbon (DIC). In this work, the concentration of dissolved carbon dioxide in the solution is set by overhead gas pressure and the Henry’s law constant $k_H$ (in Pa m$^3$ mol$^{-1}$).

$$[\text{CO}_2\text{(aq)}] = \frac{P_{\text{CO}_2}^{\text{app}}}{k_H}$$  \hspace{1cm} (3.7)

For $\text{pH} < pK_{a1}^*$, the majority of the dissolved inorganic carbon content exists in the form of dissolved CO$_2$ and bicarbonate ions (This can be inferred from a Bjerrum plot of a closed carbonate system [56]). In this region, the aqueous concentration of CO$_2$ can be analytically calculated in terms of the hydrogen ion species by neglecting the concentration of bicarbonate ions in the cubic equation, which leads to the following expression.

$$[\text{CO}_2\text{(aq)}] = \frac{[\text{H}^+]^2}{K_{a1}^*}$$ \hspace{1cm} (3.8)

$$\implies \text{pH} = -\log_{10}\sqrt{K_{a1}^*[\text{CO}_2\text{(aq)}]}$$ \hspace{1cm} (3.9)
Thus by measuring the pH of the carbonated water, we can estimate the concentration of dissolved carbon dioxide in the system using equation 3.9.

3.3 Experimental Methods

3.3.1 Controlling Concentration of Dissolved CO₂

Carbonated water was prepared by pressurizing gaseous carbon dioxide into deionized water at constant temperature and pressure. Deionized water is filled into a commercially available PET bottle (Poland Spring Sparkling water, Original, 500 ml) up to a volume of 450 ml. The bottle is then closed with a carbonation cap (Ferroday, Stainless Carbonation Cap Counter Pressure Bottle Filling With 5/16" Barb, Item No. COMINHKPR121135) and connected to a gas line (CMB, 5/16" Gas Line Assembly with Ball Lock, Part No: RKTCH-PN-29574256) which delivers carbon dioxide from a CO₂ tank (Airgas carbon dioxide Bone Dry 200). Figure 3-1a shows a photograph of the bottle with the carbonation cap. The bottle is vigorously shaken by hand under constant CO₂ pressure delivered by a CO₂ pressure regulator (Airgas Part No.: Y12215A320-AG for 0 psi < $P^{app}_{CO₂}$ < 25 psi, and Harris Model No: 425-125-320 for 25 psi < $P^{app}_{CO₂}$ < 120 psi). It is shaken until the inlet pressure gauge reading does not change anymore (when the cylinder valve is closed), indicating that gas-liquid equilibrium has been achieved. The carbonation cap allows to maintain the pressure within the bottle after the gas line is disconnected from it. All of the carbonation steps were performed at ambient temperature conditions $T_{amb} = 23 \pm 1 \degree C$. Note that the partial pressure of CO₂ applied, $P^{app}_{CO₂}$, is equal to the gauge pressure reading on the CO₂ pressure dial (Proof provided in Section D.1).

The initial concentration of dissolved carbon dioxide, $[CO₂(aq)]$, was determined by measuring the pH of the solution immediately after opening the bottle. Figure 3-1b shows the pH readings obtained after the immersion of a micro pH electrode (Thermo Scientific Orion, Cat. No.: 9810BN) into carbonated water prepared at various partial pressures of CO₂ where $t_{dg}$ refers to the time elapsed since the pressure in the
bottle is released. The ‘initial’ pH reading (representing the initial dissolved CO₂ concentration) is taken to be the quasi-steady value reached after a few seconds of inserting the electrode. The initial readings are fluctuating because it takes approximately 5 seconds to insert the probe into the bottle and another 5 seconds for the probe to respond to the environmental change. Although the pH rises steadily over a longer period of time due to degassing of the solution (see Figure B-5a), the change is less than 1% for \( t_{dg} < 60 \) s as can be seen in Figure 3-1b. Thus, drops sampled from the bottle within this time period can be assumed to have approximately the same concentration of CO₂.

Similar pH measurements were performed on drops of carbonated water sampled from freshly prepared solutions of carbonated water. A drop of carbonated water \( (V_{drop} = 40 \mu L) \) is sampled using a micropipette and is placed contact with a micro-pH electrode suspended over a superhydrophobic surface as shown in Figure 3-2a (Details of droplet deposition are given in Section 3.3.2). The pH probe takes about 3-4 seconds to respond in the drop environment. Figure 3-2b shows the evolution of pH in the drop with respect to time (Note that a superhydrophobic ring was used to hold the drop in place during these measurements, although not shown in Figure 3-2a.)
Figure 3-2: (a) pH measurement in a carbonated water droplet ($V_{\text{drop}} = 40 \, \mu\text{L}$) using a micro-pH electrode; (b) Evolution in pH of carbonated water droplets ($V_{\text{drop}} = 40 \, \mu\text{L}$) sampled from solutions prepared at various partial pressures of CO$_2$.

This is to simulate conditions similar to the drop levitation experiments described in Section 3.3.4).

Figure 3-3a shows a plot of the ‘initial’ pH, $pH_{t=0}$, as a function of the partial pressure of CO$_2$ applied, $P_{\text{CO}_2}^{\text{app}}$, for the pH measurements both in the bulk and in the drop. The theoretical pH prediction was obtained by combining equations 3.7 and 3.9 to give the pH as a function of $P_{\text{CO}_2}^{\text{app}}$.

$$\text{pH} = -\log_{10} \sqrt{\frac{K_{a1}^*}{k_H} P_{\text{CO}_2}^{\text{app}}} \quad (3.10)$$

The values of the apparent acid dissociation constant and the Henry’s law constant at $T = 23^\circ C$ were taken to be $K_{a1}^* = 4.33 \times 10^{-7}$ [104] and $k_H = 27.55$ atm kg mol$^{-1}$ [126] for the calculations. Note that the solubility of CO$_2$ does not deviate from Henry’s law for $P_{\text{CO}_2}^{\text{app}} < 10$ atm at $T = 296$ K [36].

Figure 3-3b shows the initial concentration of dissolved CO$_2$, $C_{\text{CO}_2}^{(i)}$, calculated from the pH measurements (both in the bulk liquid and the drop) using equation 3.9 as a function of the applied partial pressure of CO$_2$. It is observed that the concentration measurements in the bulk are in agreement with Henry’s law for partial pressures of
Figure 3-3: (a) pH measurement in carbonated water prepared at various partial pressures of CO₂. (b) CO₂ concentration versus partial pressure of CO₂. The theoretical line is calculated using Henry’s law at T_{amb} = 23 °C.

CO₂ lower than 3 atm, while they deviate from the theoretical prediction at higher pressures. This is because some of the gas is lost due rapid degassing at the time of opening the bottle. The concentration of CO₂ measured in the drops is even lower due to further nucleation of gas in the pipette during the transfer of the drops before deposition. However, the drop measurements only provide a lower bound for C^{(i)}_{CO₂} as the time scale of response of the pH probe is about 5-10 s which is slower than the rate of degassing in the drop (See Figure 3-2b). Also, the precision rating of the pH microprobe is ΔpH = ±0.02. Hence the error in the measurement of C^{(i)}_{CO₂} was calculated as follows-

\[ ΔC_{CO₂,i} = 2(ln 10)C_{CO₂,i}ΔpH \quad (3.11) \]

Note that it is important to use a micro pH electrode even for measurements in the bulk liquid as it reduces the systematic error introduced by gas nucleation on a large probe. Comparison between Figure 3-3a and Figure B-5b shows that the pH readings obtained using the micro pH electrode are lower than those obtained by a regular pH probe (VWR Symphony pH electrode, Cat. No.: 89231-600). Therefore, the micro pH electrode was chosen over the regular electrode to measure the concentration of
the prepared carbonated water solutions for the drop levitation experiments.

### 3.3.2 Controlling the Drop Volume

Drop volume is another important parameter that affects the levitation time of the drops as it indirectly influences the total exposed surface area to volume ratio of the droplet, the total CO₂ content in the drop, and the drop basal contact area. Drop volumes were varied from 15 µL - 80 µL for the purpose of this study.

There are many ways to dispense drops with volumes in the microliter range, the most common among them being micro-pipettes and metallic needles. Although metallic syringe needle tips are typically more precise for droplet volume control, gas nucleation at the needle walls leads to plug flow bubbles which disrupt the smooth dispensing of carbonated water drops. Hence plastic micro-pipette tips (20 - 200 µL) were chosen for dispensing carbonated water drops as they have lower surface area-to-volume ratio for gas nucleation. The micro-pipette tips were truncated to a tip diameter of approximately 1.8 mm, to further reduce the surface area of contact inside the pipette tip and increase the pinch-off volume of the drops. The volume of the dispensed drops were then characterized systematically by measuring the mass of each dispensed drop individually using a mass micro-balance (Mettler Toledo SX64). The blue triangular symbols in Figure 3-4a show the average and standard deviation of the drop volumes measured at various partial pressures of CO₂ when the pipette set volume is 80 µL. It can be observed that the volume of carbonated water drops dispensed is smaller than the actual volume set on the pipette (V\text{drop} = 80 \mu\text{L}). This is due to the nucleation of gas in the pipette tip (shown in the inset within Figure 3-4a). However, target droplet volumes can be achieved by increasing the volume set on the pipette proportionally for all partial pressures of CO₂. The red circular symbols in Figure 3-4a show the droplet volumes achieved after over-compensation in the pipette set volume. It can also be seen that the standard deviation in the drop volumes increases with increasing partial pressure of CO₂ because the nucleation of gas on the walls of the pipette is not well controlled at high P^{\text{app}}_{\text{CO₂}}. Figure 3-4b shows a plot of the droplet volume characterization at constant partial pressure of CO₂ (P^{\text{app}}_{\text{CO₂}})
Figure 3-4: (a) Volume of carbonated drops dispensed at various partial pressures of CO$_2$ for a pipette set volume of 80 $\mu$L. The inset shows the nucleation of gas in the pipette leading to the loss of liquid volume. The two data sets indicate the difference in measurements before compensation and after compensation for water volume lost due to gas nucleation in the micro-pipette tip (pipette set volume is increased proportionally); (b) Volume of carbonated water drops dispensed versus pipette set volume at constant partial pressure of CO$_2$ ($P_{\text{CO}_2}^{\text{app}} = 4.08$ atm).

The partial pressure of CO$_2$ was varied between $0 < P_{\text{CO}_2}^{\text{app}} < 5.5$ atm for the drop levitation experiments as it was difficult to control the concentration of dissolved CO$_2$ and the drop volumes for $P_{\text{CO}_2}^{\text{app}} > 5.5$ atm.

### 3.3.3 Preparation of Transparent Superhydrophobic Substrates

Superhydrophobic coatings were prepared on transparent substrates to observe the interaction of water droplets with the superhydrophobic surface from below. Microscope glass slides were sonicated in 5 %wt. sodium hydroxide solution (5 min), rinsed with DI water and plasma treated in oxygen plasma for 5 min to remove any contaminants on the surface. The cleaned glass substrates were dip-coated in a colloidal dispersion of hydrophobic silica nanoparticles in isopropanol (Glaco Mirror Coat Zero, SOFT99 Corporation) and heat treated at 250°C on a hotplate for 15 min. The dip-coating and heat treatment procedures were repeated twice more (three times in total) to obtain uniform coatings. The resulting superhydrophobic substrates...
are transparent, and display advancing and receding contact angles of $169^\circ \pm 2^\circ$ and $165^\circ \pm 2^\circ$ respectively for sessile water droplets. Figure 3-5a shows a photograph of two deionised water drops (dyed blue) resting on a Glaco-coated glass slide, illustrating the transparency and superhydrophobicity of the coating. A high resolution SEM image of the surface (Figure 3-5b) shows the uniformity of the coating and nanoscale roughness of the texture. Figure 3-5c shows the roughness profile of a Glaco-coated Si wafer obtained using an AFM measurement. The average rms roughness over three measurements ($10\mu m \times 10\mu m$) was calculated to be $R_{rms} = 60.3 \pm 8.7$ nm.

### 3.3.4 Visualization of Drop Levitation

The height profile of the gas film under levitating droplets was observed using monochromatic light interferometry which uses the interference between light reflected from the substrate and the bottom of the droplet to detect the thickness of the gas layer entrained between the substrate and the carbonated water droplet. Fully levitating droplets display circular interference fringes due to radial symmetry of the height profile under the drop [18]. Figure 3-6a shows a schematic of the setup in which carbonated water droplets are imaged through transparent superhydrophobic substrates in an inverted microscope. An inbuilt fluorescence imaging system in the microscope
Figure 3-6: (a) Schematic of setup used to visualize drop levitation using light interferometry; (b) Photograph of a single drop levitation experiment using green light interferometry (scale bar = 2 mm); (c) Interference patterns observed at the bottom of a levitating droplet (scale bar = 0.5 mm).
is used to deliver monochromatic light for interferometry. The incoming light is filtered using a bandpass filter to deliver green light of center wavelength 542 nm and bandwidth 20 nm (TRITC filter). The reflected light is recorded by a camera at 30 fps.

In order to perform drop levitation experiments, the superhydrophobic substrates are first heated to 45 °C on a hot plate to remove any residual moisture in the texture. The samples are then placed in the field of view of the microscope and a small ring (Metallic plain washer with inner diameter 4 mm and height 0.93 mm) is placed over the substrate to hold the carbonated water droplets ($V_{\text{drop}} = 40 \mu$L) in place. Note that the ring radius is varied according to the droplet volume used to ensure sufficient basal contact area with the substrate. The samples are at approximately 2 °C above room temperature during the deposition of the droplet to avoid condensation of water vapor from the droplet onto the sample [106]. A drop of carbonated water is then sampled from a freshly pressurized bottle using a micro-pipette and dispensed onto the substrate to observe the levitation dynamics. A photograph of the setup is shown in Figure 3-6b and an image of a typical interference pattern observed in carbonated water droplets is shown in Figure 3-6c. The height difference corresponding to the distance between a bright and a dark fringe is $\lambda/4$, where $\lambda$ is the wavelength of light used. Hence, the height resolution of this method is $\lambda/4$. Also, since the resolution of the image is 208 px/mm and the height difference between two bright fringes is $\lambda/2$ (271 nm), the maximum slope that can be detected is around $2.8 \times 10^{-2}$. Beyond this slope, the fringes are too close to resolve using the pixel intensities.

Note that the drop is dispensed onto the substrate within 15 seconds of opening the bottle. A minimum of 3 experiments was performed for every partial pressure of CO$_2$ and drop volume. The value of $C^{(i)}_{\text{CO}_2}$ was obtained from bulk pH measurements in Figure 3-3b for $P_{\text{CO}_2}^{\text{app}} > 2$ atm as the measurement is time sensitive due to intense degassing. While for $P_{\text{CO}_2}^{\text{app}} < 2$ atm, the bulk pH was recorded for every experiment individually since the measurements are very sensitive to the pressure-equilibration time at low concentrations of CO$_2$. 

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Figure 3-7: Extracting the radius of curvature \( R_{\text{curv}} \) of the water-air interface under a carbonated water drop deposited on a superhydrophobic surface: (a) Height profile of the blister interface found by counting the fringes from the edge; (b) Evolution of the shape (height profile) of the blister with respect to time elapsed since drop deposition.

### 3.3.5 Analysis of Interferometry Videos

The dynamics of the interferometric fringe patterns were analyzed by using kymographs of the droplet base diameter. Kymographs were constructed from the horizontal and vertical base diameters of the droplet using ImageJ or Python. The spatial and temporal variation of the thickness of the gas film under the drop, \( h_g(r, t) \), was extracted from the kymograph by counting the fringes from the edge of the drop base and taking the height difference between two dark fringes to be \( \lambda/2 \) (illustrated in Figure 3-7a and b).

\[
h_g(r, t) = n_{\text{dark}} \frac{\lambda}{2}
\]

(3.12)

where \( n_{\text{dark}} \) is the number of dark fringes. Note that the height information is relative to the edge and not the absolute gap height of the film. In order to get the absolute height of the gap, it is necessary to use multichromatic interferometry. The instantaneous radius of curvature of the gas film, \( R_{\text{curv}}(t) \), was calculated using a spherical cap fit on \( h_g(r) \).
3.4 Results and Discussion

J. G. Leidenfrost proved the existence of a vapor film under water droplets on superheated surfaces by placing a candle behind the levitating drop and observing the contact region of the heated drop from the side. Inspired by this technique, we imaged the CO₂ gas film under carbonated water drops on superhydrophobic surfaces using a bright light source and a high speed camera. Glaco-coated silicon wafers were placed on a leveling stage and adjusted for horizontality using a precise spirit level ($\Delta \theta = \pm 0.1^\circ$). The drops were then dispensed from a freshly opened bottle of carbonated water and suspended over the superhydrophobic surface using a metallic needle (1 mm in diameter). Videos were recorded at 2000 fps. Figure 3-8 shows the back-lit photographs of a deionized water drop and a carbonated water drop imaged at similar conditions on a superhydrophobic substrate. The inset images were obtained using a high-magnification lens (Navitar). While the DI water droplet does not allow any light to pass through its contact region, the carbonated water drop displays a thin gap of $\sim 10\mu$m between the drop and its reflection on the substrate. This proves that the drop is levitating over a film of CO₂ gas (thickness $\sim 5\mu$m) which is emanating from the liquid droplet. This gap can be observed for a few seconds until the light stops penetrating the gap. At this point, it is unclear if the drop has completely touched the surface or if the gap thickness is below the resolution of the imaging technique. Therefore, it is necessary to observe the drop from below to get a more clear picture of the wetting transition. This was realized through interferometric imaging described in the next section.

3.4.1 Regimes of Degassing Under the Drop

Light interferometry is a technique that has been used for determining thickness of thin fluid films such as oil film over water, soap bubbles, etc. Here we use it to determine the thickness profile of the CO₂ gas film under the droplet by interfering light reflected from the drop base and the glass substrate. It was determined in the Leidenfrost effect that the vapor film thickness below the evaporating drop is of the
atm 2mm

Figure 3-8: Photographs of (a) a deionized water drop sitting on Glaco-coated silicon wafer; (b) a carbonated water drop sitting on Glaco-coated silicon wafer. The insets show the respective contact line regions, and prove the existence of a gap between the carbonated drop and the substrate. The gap height measured from the inset image is \( \sim 5 \mu m \).

Figure 3-9 shows the bottom views of a DI water drop and a carbonated water drop \( \left( P_{\text{CO}_2}^{\text{app}} = 2.72 \text{ atm} \right) \) after deposition on a glaco-coated substrate. There is a stark difference between the DI water droplet and the carbonated water droplet because the DI water is contact with the superhydrophobic surface while the carbonated water droplet is levitating over the surface. The DI water droplet displays a random microscopic pattern because the drop is sitting on the superhydrophobic texture in the Cassie state i.e. the drop is wetting only the tops of the nanotextured surface and the interstices of the texture is filled with air. On the other hand, the carbonated water drop displays Newton’s rings which are representative of a drop base with positive Gaussian curvature [18]. Note that the drop edge displays fringes in the azimuthal direction because it experiences fluctuations due to the \( \text{CO}_2 \) gas flow under the neck. This proves that the carbonated water drops are indeed in levitation when placed on

order of 10-100 \( \mu m \) using laser diffraction method [12]. In this work, monochromatic light of wavelength 542 nm \( (\Delta \lambda = \pm 10 \text{ nm}) \) was used for interference imaging of the gas film under the carbonated water droplets.
a nano-textured superhydrophobic surface. Figure B-6 shows the equivalent images obtained using multichromatic light interferometry (obtained without using the filter).

An approximate estimate of the solid contact area, \( \phi_s \), was determined by calculating the fraction of the dark pixels in the drop base (The thresholding value was set at 130 for binarizing the 8-bit greyscale image). The solid fraction was found to be \( \phi_s = 0.37 \pm 0.09 \), and assuming a contact angle of \( \theta_w = 110^\circ \) for the hydrophobic coating, we can estimate the apparent contact angle in the Cassie state using Equation 1.3. The apparent contact angle was calculated to be \( \theta^*_w = 140^\circ \pm 6^\circ \), which is significantly lower than the experimentally measured value (165° ± 2°). This is because the water is not entirely contacting the surface in the dark regions. Destructive interference at the air-water interface would also make the region appear dark, and hence this method overestimates the solid fraction.

Since the carbonated water drop is losing CO\(_2\) gas continuously, it is expected that the drop will reach the state of deionized water (Cassie state) after it has degassed sufficiently. And it is indeed observed that the drop touches the surface after about 20 - 30 seconds of levitation (at \( P_{CO_2}^{app} = 2.72 \) atm). Figure 3-10a shows the evolution of the wetting state of a carbonated water droplet (\( P_{CO_2}^{app} = 2.72 \) atm) on a superhydrophobic surface. It is evident from these sequence of images that the drop undergoes a number of distinct regimes of degassing and wetting before reach-
Figure 3-10: (a) Time sequence images of the drop basal area after placement of a carbonated water drop (P_{CO_2}^{opp} = 2.72 atm) on the superhydrophobic surface; i. Fully levitating state just after the placement of the drop; ii. Fully levitating state when the drop is very close to the surface; iii. Edge pinning of drop with gas trapped in the center; iv. Collapse of the central blister, v. Cassie state. (Scale bar = 0.5 mm); (b) Pixel intensity values of the horizontal diameter of the drop base plotted as a function of time.
ing the Cassie state. The dynamics of this process can be captured effectively by using a space-time diagram known as kymograph. Kymographs are a simple way to represent the dynamics of moving structures in a 2-D image [128]. Since the drop degassing dynamics are axisymmetric about the center of the drop, most of the information about the drop's wetting state can be obtained by viewing just one radial slice of the drop with respect to time. Figure 3-10b shows a kymograph constructed for the levitating drop shown in Figure 3-10a. The x axis corresponds to the time elapsed since the deposition of the drop, while the y axis is a plot of the intensity values of a diametrical slice of the drop at every instant. It is interesting to note that the various regimes of wetting and the transitions between them are clearly distinguishable in this plot. We classify the drop degassing dynamics into three regimes and two corresponding transitions, which have been described in detail below.

1. **State: Levitation**

A uniform CO₂ gas film is formed underneath the droplet almost immediately after the deposition of a drop of carbonated water on a superhydrophobic surface. This appears as a sharp change in brightness on the kymograph at \( t = 0 \) s (labeled as \( t_{dep} \)). This is the 'levitation' regime when the droplet is not contacting the surface at any region as shown in Figure 3-10a-i. High speed imaging during the deposition period confirms that there is no surface contact during the placement of the drop (See Figure 3-11a), although the drop may undergo 1-2 small bounces on the gas layer before stabilizing its height (all of this happens within \( 0 < t < 0.5 \) s). The interference fringes at the drop base are initially unclear since the height of the gas film and curvature of the drop base are higher than the respective resolution capabilities of the setup (See Section 3.3.4). However as the time passes by, the fringes become clearer and they move apart from each other as can be seen between \( 5s < t < 10s \) in the kymograph. From Equation 3.12, we can say infer that the gas film is reducing in thickness and the drop base is lowering in curvature as the drop is degassing. At this stage, the drop sees any nanoparticle agglomerates on the surface which subsequently act as the first pinning points. Between \( 10s < t < 20s \), the drop is levitating
very close to the surface ($\sim 3.25\mu m$) and the drop is pinned at two points as can be seen in Figure 3-10a-ii (one at the edge and one near the center).

2. **Transition: Edge Pinning**

At $t \simeq 20$ s ($t_{pin}$), the edge of the drop base abruptly touches the surface causing part of the drop edge to pin to the surface. The pinning starts at one side of the base and spreads around the rim until almost the entire edge is pinned at around $t = 36$ s (See Figure 3-10a-iii). Another significant observation is that the fringe patterns intensify almost instantaneously around $t_{pin}$ in the kymograph. This indicates that $CO_2$ gas starts to accumulate at the base of the drop around the time it starts to pin at the edge. This is an important parameter which will be used to define the time of levitation in the next section. Since the gas bubble pinned underneath the drop has the shape of a shallow spherical cap, this bubble will be henceforth be referred to as a *gas blister*.

3. **State: Gas Blister**

After the edge pinning of the drop base at $t_{pin}$, the gas blister grows and reaches its highest volume within approximately 1-2 seconds. This volume remains constant with minor fluctuations (indicated by the fringe fluctuations around the center of the base) between $20s < t < 50s$. This implies that the rate of gas incoming into the blister from the drop is equal to the rate of gas outgoing from the blister underneath the drop through any un-pinned regions. Also, the un-pinned regions at the edge are progressively and gradually closed during this period.

4. **Transition: Collapse of the Blister**

At about $t = 55$ s, the fringes begin to thin down and the contact line advances inwards slowly, indicating the collapse of the blister. Figure 3-10a-iv shows an instant during the collapse of the blister. The volume of the blister reduces with time until it collapses completely and the drop reaches the Cassie state at a time we denote as $t_{CB}$ (Here $t_{CB} \simeq 96$ s).
5. **State: Cassie State**

After the collapse of the blister, the entire base of the drop contacts the tops of the surface texture for the first time after deposition. This state is similar to that observed when a deionized water drop is placed on the surface (Figure 3-9a). Note that new lines emerge on the kymograph even after $t_{CB}$. This is because the large blister collapses to form smaller blisters on the surface initially. These mini-blisters collapse and increase the wetted solid fraction ($\phi_s$) gradually. Every new contact region is manifested as a dark straight line parallel to the $x$ axis in the kymograph.

In order to test the effect of hydrophobicity of the substrate, similar experiments were performed on a flat substrate coated with Teflon ($\theta_{adv}^{\omega} = 120^\circ \pm 1^\circ$, $\theta_{rec}^{\omega} = 111^\circ \pm 2^\circ$). Figure 3-11b shows a sequence of images taken after the deposition of a carbonated water drop ($P_{CO_2}^{app} = 2.72$ atm) on the flat hydrophobic substrate. It is observed that the drop contacts and spreads on the surface immediately after deposition, and CO$_2$ blisters (spreading bubbles) nucleate at the surface within 30 ms (As observed in the first frame in Figure 3-11b). The base of the drop is large in diameter compared to the superhydrophobic case because of the lower contact angle of the water droplet on the flat substrate which leads to a higher basal contact area. The blisters grow and merge with nearby blisters on the substrate until $t = 7.5$ s (fourth frame in Figure 3-11b). After this point, the blisters start to decrease in size slowly. This could be due to the diffusion of the gas back into the droplet or due to the gas finding a pathway to leave the drop through the edge/surface of the drop.

### 3.4.2 Critical Timescales

There are two time scales of interest in this system, namely, the duration of levitation ($t_L$) and the duration of the blister ($t_b$). As described in the previous section, the carbonated water droplet undergoes transition from a completely levitating state to the blister state through a series of pinning events at the edge. It is observed that the fringes intensify around the time of edge of edge pinning, indicating that the gas
Figure 3-11: (a) Bottom view of a carbonated water drop ($P_{CO_2}^{app} = 2.72$ atm) imaged at high speed during its deposition on a superhydrophobic surface (Glaco-coated glass slide). (b) Bottom view of a carbonated water drop ($P_{CO_2}^{app} = 2.72$ atm) imaged after its deposition on a flat hydrophobic surface (Teflon-coated glass slide). (Scale bar = 0.5 mm).

is starting to accumulate under the drop due to the closing of the gap at the edge. This can be quantitatively analyzed by tracking the radius of curvature of the water-air interface ($R_{curv}$) with time. The plot in Figure 3-12 shows that $R_{curv}$ increases initially to reach a maximum value of 115 mm and then starts dropping suddenly at $t = 23$ s, to reach a value of 40 mm (Note that this kymograph was obtained for a droplet of carbonated water pressurized at $P_{CO_2}^{app} = 4.1$ atm, which is different from the one in Figure 3-10). This non-monotonic trend is due to the onset of edge-pinning which restricts the gas flow under the drop. In this work, we define the time of levitation, $t_L$, as the time elapsed between drop deposition and the edge-pinning events i.e., $t_L = t_{pin} - t_{dep}$. This timescale is labeled in Figure 3-10b and Figure 3-12. The intensification of fringes at the onset of edge-pinning was observed across all experiments, and hence it was a well-defined event which could be used to quantify the levitation time.

Note that the edge is only partially pinned at $t_{pin}$ and the closing of the entire
Figure 3-12: Evolution of the radius of curvature of the blister with time plotted along with the kymograph for a carbonated water drop deposited on a superhydrophobic surface ($P_{CO_2}^{app} = 4.1$ atm).

Figure 3-13: Kymograph of the edge of the base of a carbonated water drop deposited on a superhydrophobic surface: (a) $P_{CO_2}^{app} = 2.72$ atm; (b) $P_{CO_2}^{app} = 4.1$ atm.
levitating gap takes place over 10s of seconds. A kymograph of the circular edge illustrates this process clearly (shown in Figure 3-13). The horizontal lines indicate the regions where the edge is permanently pinned to the surface and hence is unchanging in time. Here, we notice that the edge pinning event can be sudden as seen in Figure 3-13a (this edge-kymograph corresponds to the experiment shown in Figure 3-10) or gradual as seen in Figure 3-13b (this edge-kymograph corresponds to the experiment shown in Figure 3-12), depending on the local conditions at the contact line during the experiment. Hence, $t_{pin}$ corresponds to the onset of edge-pinning, and not complete edge-pinning. After the onset of edge-pinning, the central blister grows and collapses at $t_{CB}$ due to progressive degassing. We define the blister time as $t_b = t_{CB} - t_{pin}$. This includes the time when the blister is degassing through un-pinned gaps at the edge, and the time when the blister shrinks radially and collapses completely to reach the Cassie state.

Figure 3-14 shows a plot the levitation time, $t_L$, and the blister time, $t_b$, as a function of the initial concentration of CO$_2$ in the drop, $C_{CO_2}^{(i)}$ (The raw data is provided in Figure B-7). The plot is divided into three regimes based on whether levitation or blister is observed in each of the regions - levitation (red); blister only (blue); no levitation or blister (colorless). The first observation is that there is a critical concentration of dissolved CO$_2$, $C_{CO_2}^{crit} \sim 10$ mM, below which there is no droplet levitation. This is analogous to the Leidenfrost effect where there is a critical temperature below there is no levitation. Secondly, we observe that $t_L$ increases non-linearly with $C_{CO_2}^{(i)}$ and reaches a magnitude of 34 s at a concentration of 170 mM ($P_{CO_2}^{app} = 5.4$ atm). The standard deviation of the measurements increase with $C_{CO_2}^{(i)}$ because of the variability in the concentration and droplet volume at high applied partial pressure of CO$_2$ (See Figure 3-3b and Figure 3-4a). On the other hand, it is observed that the blister time does not show any dependency on $C_{CO_2}^{(i)}$ above the critical concentration $C_{CO_2}^{crit}$. The average blister time in this regime is equal to $83 \pm 25$ s. We believe that the high statistical variation of $t_b$ is due to the fact that it depends on the nature and rate of edge-pinning for each experiment. The pinning depends on the texture roughness and the relative amount of condensation of water vapor in the nanopores during the
Figure 3-14: Plot of the levitation time $t_L$ and blister time $t_b$ as a function of the initial concentration of CO$_2$ in the drop, $C_{CO_2}^{(i)}$. The plot is divided into three regimes: levitation (red); blister only (blue); no levitation or blister (colorless). $C_{crit}^{L}$ and $C_{crit}^{b}$ are the respective threshold concentrations of CO$_2$ for the levitation and blister regimes.
Figure 3-15: Kymograph of a carbonated droplet with concentration of dissolved CO\textsubscript{2}, \(C_{\text{CO}_2}^{(i)} = 0.9\) mM, deposited on a superhydrophobic substrate.

experiment (which would block the pores and resist CO\textsubscript{2} flow). Below \(C_{\text{crit}}^{\text{inj}}\), it is observed that degassing leads to the formation of multiple blisters on the surface although there is no levitation. For instance, Figure 3-15 shows a kymograph of a droplet with \(C_{\text{CO}_2}^{(i)} = 0.9\) mM deposited on the superhydrophobic surface. The drop is in the Cassie state initially after deposition, but two blisters simultaneously nucleate, grow and collapse on the texture due to the degassing of the drop. The blister time \(t_b\) is defined as \(t_b = t_{CB} - t_{dep}\) in this regime, and it is observed to increase from zero at \(C_{\text{CO}_2}^{(i)} \sim 0.3\) mM to \(C_{\text{CO}_2}^{(i)} = 10\) mM. The final observation is that there is a critical concentration, \(C_{\text{crit}}^{b} \sim 0.3 - 0.9\) mM, below which there is no blister formation and the carbonated droplet behaves identical to a deionized water droplet.

Figure 3-16 shows the evolution of the blister properties (maximum height, radius of curvature, and volume) from the onset of edge-pinning to the end of blister collapse for various partial pressures of carbon dioxide, \(P_{\text{CO}_2}^{\text{app}}\) (each curve represents a single experiment). Note that the x-axis is the time after onset of edge-pinning, \(t_{bc} = t - t_{pin}\). The volume of the blister is calculated using the following expression (assuming a spherical cap geometry).

\[
V_{\text{blister}} = \frac{\pi h_g^2}{3}(3R_{\text{curve}} - h_g)
\]

(3.13)

As discussed earlier, the volume of the blister increases rapidly after the onset of edge
Figure 3-16: (a) Schematic of a blister under a degassing droplet; Evolution of blister properties with respect to the time elapsed since edge pinning ($t_{bc} = t - t_{pin}$) - (b) maximum height of the blister ($h_g$), (c) radius of curvature ($R_{curv}$), and (d) volume of the blister ($V_{blister}$)
pinning and reaches a maximum value of \( V_{\text{blister}} = 10.5 \times 10^{-3} \pm 1.5 \times 10^{-3} \mu L \) (Figure 3-16d). The central height of the blister reaches its maximum value \( h_{g,\text{max}} = 9 \pm 2 \mu m \) (Figure 3-16b) and the radius of curvature reaches its minimum value \( R_{\text{curv}} = 45 \pm 5 \) mm (Figure 3-16c) at the same time. An interesting observation is that these values are independent of the partial pressure applied. In Figure 3-16d, we observe that blister remains at its maximum volume for a brief duration before starting to collapse. This duration is highly variable but it not a function of \( P_{\text{CO}_2}^{\text{app}} \). We believe that this variability is due to the the uncertainty involved in the closing of the edge gap and is the reason for the high variability of the blister time, \( t_b \). Secondly, the rate of collapse of the blister is approximately constant for all the experiments (\( \approx 2.5 \times 10^{-4} \mu L/s \)). A possible explanation for this could be that the collapse starts to happen at a certain critical concentration of \( \text{CO}_2 \) in the drop and the dynamics are governed by Darcy’s law under the drop as the drop is transitioning to the Cassie state. This analysis provides a qualitative picture of the blister dynamics but a more detailed analysis is required for quantitative modeling of this phenomena.

We also varied the droplet size at a constant partial pressure of \( \text{CO}_2 (P_{\text{CO}_2}^{\text{app}} = 4.1 \text{ atm}) \) to understand the effect of droplet radius on the critical timescales. Figure 3-17 shows the dependence of levitation time and the blister time on droplet size. Both the levitation and blister times were observed to increase with droplet volume. Note that it is difficult to dispense droplets below \( V_{\text{Drop}} < 12 \mu L \) due to pinning of the water drops to the plastic pipette tip and the drop base becomes non-circular for \( V_{\text{Drop}} > 50 \mu L \). More experiments are needed to quantify the timescales of levitation and blister collapse due to the high statistical uncertainty in this phenomena (The data presented is an average over 3 experiments for every droplet volume).

In order to determine if there is any effect of the ring on the levitation time, we performed levitation tests with alternate setups. Figure 3-18a shows the various setups used. We first tried different rings of same inner hole diameter \( D_{\text{hole}} = 4 \text{ mm} \) to check the variation between them. We then checked if the ring confines the gas flow near the drop by using setups which expose the contact region of the drop. In the first case, a shallow plano-convex lens (Diameter = 25 mm, Radius of curvature
Figure 3-17: Effect of droplet volume on the (a) levitation time, and (b) blister time at constant partial pressure of CO₂ ($P_{CO₂}^{app} = 4.1$ atm)

A larger ring was used for this case as the radius of the drop is larger than the radius of the base. Figure 3-18b shows the levitation time achieved for the various cases (at $P_{CO₂}^{app} = 2.72$ atm). We observed that the levitation time did not depend strongly on the conditions except for the ‘Probe only’ case. The ‘Probe only’ and ‘Lens’ cases differ from the other cases in that the drop is free to move laterally during levitation. This allows the drop to de-pin at pinning sites on the Glaco-coated surface using lateral movement (Any asymmetry in the degassing under the drop causes the drop to be gently propelled sideways), thus increasing the levitation time. However, the curved nature of the substrate in the ‘lens’ case introduces other issues like pinning at the center, which overcomes the aforementioned advantage. Hence, we can say that the ‘Ring’ method imitates the conditions of a carbonated water droplet resting without constraints on a superhydrophobic surface, enough to cause the the same time of levitation. Note that the ring diameter $D_{hole} = 4$ mm, was chosen in such a way that the water droplet would fit snugly at the center. This reduced the drop’s base
radius by approximately 20% from the case where it is sitting on a superhydrophobic surface without any physical constraint.

### 3.4.3 Modeling

We model the gas flow under the drop using thin film lubrication theory, which is similar to the approach used in Leidenfrost literature [119]. Here we obtain the height of the gap in terms of the mass flux of CO₂ out of the drop. We then estimate the mass flux of CO₂ from the drop, using the lumped capacitance approach wherein we consider an effective mass transfer coefficient, $k_{\text{eff}}$, to model the resistance of the liquid and gas phases to the mass transfer of CO₂ from the well-mixed drop at concentration $C_l$ to the environment at concentration $C_e$. We then use this estimated mass flux to obtain the height of the gap as a function of time. Finally, we postulate that there exists a critical height at which touch-down occurs, which then allows us to estimate the timescale for levitation. Figure 3-19 shows a schematic of a levitating drop labelled with the important variables used in this model.

Thin film lubrication theory can be applied to model the gas flow underneath the droplet during levitation. Here we start with the Navier-Stokes equation in cylindrical coordinates and compare the relative magnitudes of the terms by using the characteristic length scales and time scales in the system. Assuming a quasi-steady flow in
Figure 3-19: Schematic of a degassing water drop supersaturated with dissolved CO₂ levitating over a textured superhydrophobic surface. The instantaneous concentrations of CO₂ in the interior of the drop, at the surface of the drop (liquid side), and in the surrounding air environment are \( c_i(t) \), \( c_s(t) \), and \( c_e \) respectively. The mass flux of CO₂, \( \dot{m}_g(t) \), from the drop is denoted by the green arrows. The other labeled variables include the droplet radius \( R \), base radius \( R_b \), height of the lubricating gas film \( H_g(t) \), liquid and air mass transfer coefficients \( k_l \) and \( k_a \), pressure at the base of the drop (liquid side) \( P_D \), and the local pressure in the gas film \( P_g(r,t) \).

The gas layer and taking that \( \frac{H_g}{R} \ll 1 \), we get the following partial differential system for the system (See Section D.2 for the detailed derivation).

\[
\frac{\partial P}{\partial r} = -\mu_g \frac{\partial^2 u_r}{\partial z^2} \tag{3.14}
\]

where \( u_r(r, z, t) \) is the dominant radial velocity component in the gas film.

We can solve Equation 3.14 assuming Poiseuille flow conditions in the gap i.e., that the no-slip boundary condition is satisfied at both the drop interface and the solid surface i.e. \( u_r|_{z=0} = u_r|_{z=H_g} = 0 \) (similar to the assumption in Leidenfrost literature). Although this is not exact since the liquid in reality has a small but finite velocity at the liquid-air interface (See Section D.2.1), this assumption allows us to
get a first order estimate of the radial velocity in the gap. Also, we assume that the droplet has a flat base i.e., $H(r) \sim H_g$ for simplifying the calculations.

$$u_r(r, z, t) = \frac{1}{2\mu_g} \frac{\partial P}{\partial r} (z^2 - H_g z)$$  \hspace{1cm} (3.15)$$

We can obtain the mass flow rate at any radial position under the drop by integrating Equation 3.15 through the height of the gap.

$$\dot{m}_r = -\rho g \int_0^{H_g} 2\pi r u_r dz$$

$$\Rightarrow \dot{m}_r = -\frac{\pi r \rho g H_g^2(t) \frac{\partial P}{\partial r}}{6\mu_g}$$  \hspace{1cm} (3.16)$$

Equating the incoming mass flow rate of CO$_2$ gas from the drop base, $\dot{m}_g'' \pi r^2$, to the outgoing radial mass flow rate in the gap and integrating in the radial direction, we obtain the pressure profile $P(r, t)$ in the gap. We use the boundary condition that the pressure is atmospheric at the edge of the gap i.e., $P|_{r=R_b} = P_a$.

$$\dot{m}_r = \dot{m}_g'' \pi r^2$$

$$\Rightarrow -\frac{\pi r \rho g H_g^2 \frac{\partial P}{\partial r}}{6\mu_g} = \dot{m}_g'' \pi r^2$$

$$\Rightarrow -\int_{P_c}^{P} dp = \frac{6\dot{m}_g'' \mu_g}{\rho_g H_g^3} \int_0^r r dr$$

$$\Rightarrow P - P_a = \frac{3\dot{m}_g'' \mu_g}{\rho_g H_g^3} (R_b^2 - r^2)$$  \hspace{1cm} (3.17)$$

The drop is sustained in a levitating state because the weight of the droplet is counteracted by the pressure field in the thin lubricating gas layer under the drop. In very small drops ($V_{drop} < 10 \mu L$), the Laplace pressure in the drop is counteracted by the lubricating gas pressure. For droplet volumes considered in our study ($V_{drop} = 40 \mu L$), both the gravitational body force and the surface tension forces are equally important as the Bond number, $Bo = \rho g R^2/\sigma \sim 0.6$. Balancing the gravitational and
Laplace pressure inside the drop against the lubrication pressure below the drop, we derive the expression for the height of the gap in terms of the CO₂ mass flux and the other parameters in the system.

We first couple the gravitational and Laplace pressure at the base of the drop to get a new variable, $P_D$, given below.

$$P_D = \rho_w g(2R) + \frac{2\gamma}{R}$$  \hspace{1cm} (3.18)

where $R$ and $\sigma$ are the radius and surface tension of the drop respectively. Then, we perform a force balance on the droplet interface at the base as shown below.

$$P_D \pi R_b^2 = \int (P - P_a) dA$$

$$= \int_0^{R_b} \frac{3 \dot{m}_g \mu_g}{\rho_g H_g^3} (R_b^2 - r^2)(2\pi r) dr$$

$$= \frac{3\pi \dot{m}_g \mu_g}{2 \rho_g H_g^3} R_b^4$$

$$\Rightarrow P_D = \frac{3\dot{m}_g \mu_g R_b^2}{2\rho_g H_g^3}$$

$$\Rightarrow H_g = \left( \frac{3\dot{m}_g \mu_g R_b^2}{2\rho_g P_D} \right)^{1/3}$$  \hspace{1cm} (3.19)

Thus we have an expression for the gap height in terms of the CO₂ mass flux from the drop. Since the CO₂ mass flux is varying with respect to time due to degassing in carbonated water drops, the height of the gap also varies until it touches the surface. In the following section, we model the mass-flux of CO₂ from the drop using the lumped capacitance method, and obtain $\dot{m}_g'$ as a function of time.

In order to determine the mass flux of CO₂ from the drop, it is necessary to determine if the mass transfer in the system is convection or diffusion dominated. Forced convection takes place inside the drop due to the viscous drag forces exerted by the gas flow under the drop, while the gas flow outside the drop is assumed to be driven by natural convection as carbon dioxide is $\sim 1.5$ times heavier than air.
The approximate flow profiles inside the liquid drop and in the surrounding air are illustrated in Figure 3-19. The Peclet number of the flow inside the drop can be calculated by using the following equation -

$$\text{Pe}_D = \frac{u_l(2R)}{D_l}$$  \hspace{1cm} (3.20)

where $u_l$ and $D_l$ are the characteristic velocity in the liquid and the mass diffusivity of CO$_2$ in the liquid phase respectively. Taking that $u_l \sim u_i \sim 0.9u_g$ where $u_i$ is the interfacial velocity (See Section D.2.1 for the derivation), and that $u_g \sim 0.1$ m/s (from Leidenfrost literature [119]), we obtain $\text{Pe}_D \sim 10^6$ ($D_l = 1.97 \times 10^{-9}$ m$^2$/s [49], and $R = 2.12 \times 10^{-3}$ m). Since $\text{Pe}_D \gg 1$, the mass transfer inside the drop is convection dominated. Similarly we can calculate the Rayleigh number, $\text{Ra}_D$, for the flow outside the drop using the Grashof number ($\text{Gr}_D$) and Schmidt Number ($\text{Sc}$) of the system.

$$\text{Gr}_D = \frac{g(\rho_g - \rho_{air})\rho_g(2R)^3}{\mu_g^2}$$

$$\text{Sc} = \frac{\mu_g}{\rho_g D_g}$$

$$\text{Ra}_D = \text{Gr}_D \text{Sc}$$

where $\rho_g$ and $\rho_{air}$ are the densities of CO$_2$ gas and air respectively, and $\mu_g$ is the viscosity of CO$_2$ gas. Substituting the respective values from Table 3.1, we obtain $\text{Gr}_c \sim 2 \times 10^3$ and $\text{Sc} \sim 0.6$, implying that $\text{Ra}_D \sim 10^3$. Since $\text{Ra}_D \gg 1$, the mass transfer outside the drop is also dominated by convection.

The convective mass transfer of CO$_2$ from the well-mixed interior of the drop to the surroundings is given by the following equation.

$$\dot{m}_g(t) = -k_{\text{eff}}A_d(c_l - c_e)$$  \hspace{1cm} (3.21)

where $m_g(t)$ is the mass of CO$_2$ in the drop at any instant, $k_{\text{eff}}$ is the effective phase mass transfer coefficient, $A_d$ is the surface area of the drop, and $c_e$ and $c_l$ represent the
environmental concentration of CO\textsubscript{2} and the dissolved concentration of CO\textsubscript{2} in the well-mixed interior of the drop respectively. The effective mass transfer coefficient is modeled using two mass transfer resistances, \( k_a \) (air-side resistance) and \( k_l \) (liquid-side resistance) in series and is given by the following equation (derived in Section D.3).

\[
\frac{1}{k_{\text{eff}}} = \frac{1}{k_l} + \frac{1}{k_a k^*_H}
\]

where

\[
k^*_H = \frac{k_H M_{\text{CO}_2}}{R_{\text{gas}} T}
\]

Here \( k^*_H \) is the non-dimensional Henry’s law constant, \( M_{\text{CO}_2} \) is the molecular mass of CO\textsubscript{2}, and \( R_{\text{gas}} \) is the universal gas constant. The non-dimensional Henry’s law constant is calculated to be \( k^*_H = 2152 \) for the CO\textsubscript{2}-water system. The gas phase mass transfer coefficient, \( k_a \), is estimated using the Sherwood number correlation for natural convection around a sphere (Churchill 1983 [26]).

\[
\text{Sh}_D = \frac{k_a (2R)}{\varphi_g} = 2 + \frac{0.589 R_{\text{ad}}^{1/4}}{1 + \left(\frac{0.469}{\text{Sc}}\right)^{9/16}}^{4/9}
\]

The Sherwood number is estimated to be \( \text{Sh}_D \simeq 4.7 \) from Equation 3.23 (using \( R = 2.12 \) mm and \( \varphi_g = 1.6 \times 10^{-5} \) m\(^2\) s\(^{-1}\)), implying that \( k_a \simeq 2 \times 10^{-2} \) m/s.

The liquid mass transfer coefficient, \( k_l \), is estimated using an empirical model for the absorption and desorption mass transfer coefficients of gases in falling drops. Falling drops experience internal flows similar to levitating droplets as both of them are driven by the gas flow outside the drop. Gas absorption/desorption kinetics in falling drops are well studied for the CO\textsubscript{2}-water and SO\textsubscript{2}-water systems due to the their environmental importance (acid rain) [123, 55, 2, 4]. This is the closest model system for which experimental and empirical mass transfer coefficients are available in literature. Angelo et al. [5] proposed a surface stretch model for the liquid mass transfer coefficient which postulated that fresh surface area formed by drop oscillations (in drops larger than 1 mm diameter) promote the exchange of gas between the bulk and the surface. Hsu et al. [60] report a semi-empirical correlation for liquid-phase mass transfer coefficient in falling drops by performing a best fit of the surface-stretch model on experimental data reported by previous works which
study the absorption of gases like CO$_2$ and SO$_2$ into falling droplets [2, 45, 66]. Their
correlation gives

$$k_l = (0.78 \pm 0.21) \frac{4}{\pi} \left( \frac{\gamma}{\rho_l} \right)^{1/4} \mathcal{D}_l^{1/2} (2R)^{-3/4}$$  \hspace{1cm} (3.24)

where $\gamma$ is the surface tension of the liquid. The surface tension of carbonated water
is taken to be $\gamma = 72$ mN/m (although this can be as low as 61 mN/m for
carbonated water pressurized at 6 atm [94]). Equation 3.24 gives an estimate of
$k_l = (2.37 \pm 0.6) \times 10^{-4}$ m/s. Note that this only provides an upper limit for the
liquid mass transfer coefficient as the carbonated water drops on superhydrophobic
surfaces do not undergo oscillations similar to falling drops.

From Equation 3.22, it can be concluded that the overall mass transfer in the
system is limited on the liquid side since $k_l \ll k_H^* k_a$. Hence, the concentration of CO$_2$
at the surface of the drop (inside the liquid) can be calculated by using the Henry’s
solubility constant assuming that the surface is at equilibrium with atmospheric CO$_2$
i.e., $c_s \simeq k_H^* c_e$. Taking the partial pressure of CO$_2$ in the environment to be $P_{env}^\text{CO}_2 = 4 \times 10^{-4}$ atm, we obtain $c_s = 1.4 \times 10^{-2}$ mM. Since $c_s \ll C^{(s)}_{\text{CO}_2}$ in this work, we can
neglect $c_e (=c_s)$ in Equation 3.21. Hence, the model can be approximated to the
following expression:

$$\dot{m}_g(t) \simeq -k_l A_d c_l$$  \hspace{1cm} (3.25)

Assuming that the bulk of the interior of the drop is well mixed and has an average
concentration of dissolved CO$_2$, $c_l(t)$, equation 3.25 can be written as-

$$V_d \frac{dc_l(t)}{dt} = -k_l A_d c_l$$  \hspace{1cm} (3.26)

where $V_d$ is the volume of the drop. Rearranging and solving the equation using the
initial condition $c_l = c_0$, we can obtain the concentration of CO$_2$ in the drop as a
function of time.
\[
\frac{dc_l}{dt} = -\frac{k_l A_d}{V_d} c_l
\]

\[
\Rightarrow \int_{c_0}^{c_l} \frac{dc_l}{c_l} = -\int_0^t \frac{k_l A_d}{V_d} dt
\]

\[
\Rightarrow \frac{c_l}{c_0} = \exp\left\{-\frac{k_l A_d}{V_d} t\right\}
\]

\[
\Rightarrow \frac{c_l}{c_0} = \exp\left\{-\frac{t}{\tau_m}\right\}
\]  \hspace{1cm} (3.27)

where \(\tau_m = V_d/k_l A_d\) is the characteristic time constant of mass transfer in the system.

(Note that for a spherical drop, \(\tau_m = R/3k_l\)). Therefore the instantaneous mass flux of CO\(_2\) from the drop as a function of time is given by -

\[
m''_g = -k_l c_l
\]

\[
\Rightarrow m''_g = -k_l c_0 \exp\left\{-\frac{t}{\tau_m}\right\}
\]  \hspace{1cm} (3.28)

Substituting Equation 3.28 into Equation 3.19, we obtain an expression for the height of the gap as a function of time.

\[
H_g(t) = \exp\left\{\frac{3\mu_g k_l R_b^2}{2\rho_g P_D} \frac{1}{c^0} \frac{1}{3!} \exp\left\{-\frac{t}{3\tau_m}\right\}\right\}
\]  \hspace{1cm} (3.29)

Let us consider that the drop touches the surface when the height of the gap reaches a critical height close to the surface, \(H_{\text{crit}}\). We postulate that the critical height is set by the scale of roughness of the texture \(R_{\text{rms}}\). This can then be used to determine the levitation time of the droplet by setting \(H_g(t_L) = H_{\text{crit}}\).
Substituting \( c_0 = C_{\text{CO}_2}^{(i)} \),

\[
\begin{align*}
\frac{t_L}{\tau_m} = \ln \left( \frac{C_{\text{CO}_2}^{(i)}}{c_{\text{crit}}} \right) & \quad : \text{where} \quad c_{\text{crit}} = \frac{2 \rho_g P_D H_{\text{crit}}^3}{3 \mu_g k_l R_b^2}, \tau_m = \frac{V_d}{k_l A_d} \\
\end{align*}
\]

Note that all of the variables in this model are experimentally known except for
\( k_l \) (which sets the values of \( \tau_m \) and \( c_{\text{crit}} \)) and \( H_{\text{crit}} \) (which sets the value of \( c_{\text{crit}} \)). The values of the other variables are \( \rho_g = 1.77 \text{ kg/m}^{-3} \), \( R = 2.12 \text{ mm} \), \( \gamma = 72 \text{ mN/m} \)
(although this can be as low as 61 mN/m for carbonated water pressurized at 6 atm [94]), \( \mu_g = 1.47 \times 10^{-5} \text{ Pa.s} \), and \( R_b = 0.95 \pm 0.03 \text{ mm} \) (from experiments). The pressure at the base of the drop is calculated to be \( P_D \approx 110 \text{ Pa} \) using Equation 3.18.

We fit our model (Equation 3.31) to the experimental data in Figure 3-14 to extract the unknown parameters \( c_{\text{crit}} \) and \( \tau_m \). Figure 3-20 shows the best fit with the extracted parameters \( \tau_m^{\text{fit}} = 12.0 \pm 1.5 \text{ s} \) and \( c_{\text{crit}}^{\text{fit}} = 10.7 \pm 2.3 \text{ mM} \) (0.47 kg/m\(^3\)), which are within 95% confidence bounds. These values are used to extract the mass transfer coefficient and critical height which were found to be \( k_l^{\text{fit}} = (5.88 \pm 0.70) \times 10^{-5} \text{ m/s} \) and \( \tau_{\text{crit}} = 1.48 \pm 0.11 \mu\text{m} \). Note that the value of \( k_l^{\text{fit}} \) is found to be lower than, but of the same order of magnitude, as the correlation estimate \( k_l^{\text{cor}} = (2.37 \pm 0.60) \times 10^{-4} \text{ m/s} \) (i.e., \( \tau_{\text{crit}}^{\text{cor}} = 3.0 \text{s} \)) calculated using Equation 3.24 given by Hsu et al.

We also measure \( k_l \) experimentally by tracking the instantaneous concentration of \( \text{CO}_2 \) in the drop using a micro pH-electrode (See Section 3.3.1). Figure 3-21a shows a plot of the concentration of \( \text{CO}_2 \) in the drop versus time for various partial pressures
of CO\textsubscript{2} obtained from the data in Figure 3-2 using Equation 3.9. We then extract the characteristic timescale of mass transfer in the system, $\tau_m$, by fitting Equation 3.27 to each curve, and plot $\tau_m$ as a function of $P_{\text{CO}_2}^{\text{app}}$ in Figure 3-21b. We observe that there is no dependence of $P_{\text{CO}_2}^{\text{app}}$ on the mass transfer coefficient. Hence, $\tau_m$ is averaged over all the experiments to obtain $\tau_m^\text{exp} = 47.6 \pm 14.6$ s i.e., the experimentally measured liquid phase mass transfer coefficient, $k_l^\text{exp} = (1.5 \pm 0.5) \times 10^{-5}$ m/s.

Figure 3-22 shows a comparison of experimental data with respect to the model using the $k_l$ values estimated experimentally ($k_l^\text{exp}$) and using literature correlation ($k_l^\text{cor}$). Note that the critical concentration was held at $c_{\text{crit}} = 10.7$ mM across all the curves. This plot indicates that the pH measurements underestimate the effective mass transfer coefficient (i.e., overestimates the characteristic time $\tau_m$), and the literature correlation over-estimates the mass transfer coefficient (i.e., underestimates the characteristic time $\tau_m$). This is because the pH measurements were made with a probe whose rated response time ($\sim 5$ seconds) is of the same order as the time scale of the phenomena, and thus the time-resolved measurements may be convolved with
Figure 3-21: (a) Evolution of concentration of CO$_2$ in the drop with respect to time; (b) Characteristic timescale of mass transfer, $\tau_m$ versus applied partial pressure of CO$_2$.

the response function of the probe. On the other hand, the literature correlation was developed for millimetric droplets free falling in air with velocities of the order of 0.1 m/s which would have higher mass transfer coefficients compared to the carbonated water levitation experiments where the drops are essentially quiescent (except for the radial flow across the bottom of the drop). The values of $k_l$ reported in studies which characterize the absorption/stripping of CO$_2$ in water using bubble columns, packed columns, static mixers, plate columns, membrane contractors etc. range between $(0.04 < k_l < 20) \times 10^{-4}$ m/s [40]. The critical height for touchdown, $H_{crit}$, varies with the mass transfer coefficient $k_l$ for a fixed $c_{crit}$ (See Equation 3.31). The critical height is estimated to be $H_{crit}^{exp} = 970$ nm using $k_l^{exp}$ from the pH measurements and $H_{crit}^{cor} = 2.36 \mu$m using $k_l^{cor}$ from the literature correlation ($c_{crit} = 10.7$ mM). We believe that the critical height is higher than the roughness of the texture ($R_{rms} \simeq 60$ nm obtained from AFM measurements; see Section 3.3.3) because the drop oscillation under the drop can lead to earlier pinning than predicted. Also the drop could be pinning at defect sites which are higher than the scale of roughness measured.

In order to have a more accurate model, it is necessary to measure the mass flux of CO$_2$ from the drop experimentally with methods more precise than the pH measurement.
Figure 3-22: Comparison of the model calculated using the value of $\tau_m$ from the experimental best fit, literature correlation, and experimental pH measurements.

... probe measurements. Secondly, it is important to consider that the mass transfer from the drop is asymmetric about the z-axis since the gas flow is confined at the bottom of the drop. Time-resolved numerical simulations coupled with mass transfer are required to obtain the actual CO$_2$ flow field inside and outside the drop. Finally, more experiments are required to understand the dependence of levitation time on the radius of the drop which is an important parameter in the model.

3.5 Summary

In this chapter, we demonstrate a novel method to levitate droplets at room temperature by using degassing carbonated water droplets on superhydrophobic substrates. We observe the levitation and wetting dynamics of carbonated water droplets using monochromatic light interferometry on transparent superhydrophobic surfaces. We characterize the levitation time $t_L$ as a function of the dissolved gas concentration and show that a minimum concentration of $c_{crit} \approx 10$ mM is required to achieve droplet levitation using the carbonated water system. Above the critical concentration, $t_L$...
increases logarithmically with the dissolved gas concentration. We also show that the drop first pins at the edge of the base at the end of the levitation regime and traps a gas bubble defined as a blister, which then degasses through unpinned gaps at the edge and collapses finally to reach the Cassie state. We find that the blister time $t_b$ is equal to zero for $0 < C^{(i)}_{CO_2} < 0.3$ mM, increases with the concentration of dissolved CO$_2$ for $0.3 < C^{(i)}_{CO_2} < 10$ mM, and is approximately constant at $83 \pm 25$ s for $C^{(i)}_{CO_2} > 10$ mM.

We also derive a model to estimate the levitation time of the degassing droplets using lubrication theory and the lumped capacitance mass transfer model, which predicts that the time of levitation is a logarithmic function of the initial concentration of CO$_2$ in the drop. We show that the experimental data agrees well with the logarithmic model, and estimate the effective liquid mass transfer coefficient in the drop to be $k_l = 5.8 \pm 0.7 \times 10^{-5}$ m/s along with the critical gap height for the onset of edge-pinning, $H_{crit} = 1.5 \pm 0.1$ μm. In the next chapter, we explore the potential applications of this work and possible future directions.
Chapter 4

Degassing on Superhydrophobic Surfaces: Applications

Author note: Data reported in Figure 4-1, Figure 4-2, Figure 4-4c, and Figure 4-8 were obtained jointly with Philippe Nicoller.

In the previous chapter, we characterized the levitation time of carbonated water droplets on nanotextured superhydrophobic surfaces and analyzed the critical parameters influencing the phenomena. In this chapter, we explore the various advantages of this effect and discuss their potential applications.

4.1 Reduction of contact line pinning in mobile droplets

We investigate the reduction in contact line pinning force on moving carbonated water droplets by observing the attenuation rate of a drop oscillating in a U-shaped groove. A toroidal groove of longitudinal radius of curvature $R_{gr} = 635$ mm and axial radial of curvature $R_{a} = 8.3$ mm was machined into a flat block of aluminum using a CNC lathe (MIT Central Machine Shop). The part diagram of the groove is provided in Figure B-8. The groove was then treated with Glaco Mirror Coat Zero (SOFT99) with the same procedure as described in Section 3.3.3). A drop of deionized water or carbonated water of volume 80 $\mu$L is released at the top the
Figure 4-1: Drop oscillation experiments on a superhydrophobic groove of $R_{gr} = 635$ mm and $L_{gr} = 65$ mm. (a) Schematic of the groove experiment; (b) A carbonated water droplet ($P_{CO_2}^{app} = 5.44$ atm, $V_{drop} = 80\mu$L) released at the edge of the groove oscillates multiple cycles (bottom), while a deionized water drop oscillates for hardly two periods before pinning at the center (top). The snapshots are taken every 20 ms. Scale bar = 20 mm; (c) Plot of the magnitude of $\theta(t)$ versus time for the deionized and carbonated water droplets.
superhydrophobic groove, and allowed to oscillate until it comes to rest at the center of the groove as shown in Figure 4-1a. The substrate was maintained at a temperature of 5° above the carbonated water temperature to avoid condensation of water vapor in the nanotexture. The lateral position of the droplet in the groove was imaged from above using a high speed camera at 100 fps. Figure 4-1b shows a comparison between the oscillation dynamics of a deionised water drop and a carbonated water drop (P_{\text{CO}_2}^{\text{app}} = 5.44 \text{ atm}). The period of oscillation matches with the theoretical time period,
\[ T = 2\pi \sqrt{R_{gr}/g} = 1.6s, \]
where \( g \) is the acceleration due to gravity. While the deionized water drop comes to a complete stop after 2 cycles, the carbonated water drop continues to oscillate further for multiple cycles (The complete experiment is shown in Figure B-9). Figure 4-1c shows the plot of the magnitude of the angle made by the drop with respect to the center of curvature of the groove, \(|\theta|\), versus time for both the drops and it is observed that the carbonated water drop oscillates for atleast for about 7 cycles before the amplitude becomes diminished. Although the aerodynamic drag contribution is the same for both the drops since they have the same volume, the DI water drop comes to rest much faster due to the friction exerted by pinning forces at the bottom of the drop. The carbonated drop on the other hand experiences no surface pinning forces as it is in a state of levitation, and hence oscillates for a longer period of time. Another distinction between the two cases is that the DI water drop comes rest after a sudden pinning event while the carbonated water droplet comes to rests very gradually. This distinct behavior between carbonated and uncarbonated water drops can be exploited in the beverage industry for sorting out beverages which are undercarbonated.

### 4.2 Self-propulsion on ratchet-like textured superhydrophobic surfaces

Previous studies have shown that Leidenfrost droplets can self-propel themselves on ratchet-shaped textures using viscous drag exerted by the directional vapor flow under
Figure 4-2: (a) Image of a droplet of 300 μL self-propelling on a ratchet-like texture. Inset shows the dimensions of the texture. The dimension are in mm. This diagram has been produced by Andrew Gallant (MIT Central Machine Shop); (b) Snapshots of a carbonated water droplet ($P_{\text{CO}_2}^{\text{app}} = 5.44$ atm) of volume, $V_{\text{drop}} = 300$ μL, released on the a ratchet-like textured superhydrophobic surface in the direction opposite to the propelling force. The droplet reverses its direction, accelerates and attains terminal velocity in the direction of viscous propelling force due to the ratchet texture (to the right). The frames were taken at an interval of 1 s (Scale bar = 1 cm).
the drop [89, 38]. We perform similar experiments using carbonated water drops on a ratchet-like texture machined on an aluminum plate (texture depth = 0.26 mm, spacing = 1.5 mm) and coated with Glaco Mirror Coat Zero (SOFT99), as shown in Figure 4-2a. The ratchet surface was maintained at a temperature of 35° (room temperature = 23°) during the experiments to avoid any pinning due to condensation of water vapor in the nanotexture. Figure 4-2b shows a carbonated droplet (P_{CO_2}^{app} = 5.44 atm) of size 300 µL released with an initial velocity v_i ≈ 1 cm/s towards the left on the superhydrophobic ratchet surface. The droplet decelerates initially, then stops, and accelerates to the right, eventually attaining terminal velocity. This is because the surface’s asymmetric teeth exert a viscous driving force towards the right on the drop. The terminal velocities attained using this method is about 10 times smaller than that achieved using heat in Leidenfrost droplets (≈10 cm/s [38]). This can be explained by the fact that the height of the levitation gap under the carbonated drop (≈ 5 µm, shown in Figure 3-8) is an order of magnitude smaller than that in Leidenfrost literature (≈ 100 µm for superheat temperature of 200°C [12]). Since the terminal velocity is proportional to the temperature of the substrate in evaporating droplets [38], the terminal velocity of carbonated water droplets (P_{CO_2}^{app} < 5.5 atm) is comparable to the that of droplets self-propelling on a low-temperature (compared to leidenfrost temperature) ratchet texture (≈ 2 cm/s for 100°C) [38].

4.3 On-Demand Levitation of Sessile Water Droplets

In Chapter 3 and in the previous sections, carbonated water droplets were sampled from a freshly opened bottle of carbonated water and deposited on a superhydrophobic surface to observe levitation. Since the drop is already degassing when it nears the surface, it starts levitating spontaneously. However, more utility can be realized if sessile droplets sitting on a superhydrophobic surface in the Cassie state could be made to levitate on-demand. In this case, since the droplet is in contact with the surface initially, it is necessary to overcome the contact line pinning forces to achieve droplet levitation. In this section, we infuse or produce gas inside the droplet in situ.
Figure 4-3: (a) Schematic of the pressure cell used for on-demand droplet levitation; (b) Image of the pressure cell with a transparent polycarbonate window for imaging to achieve droplet levitation on-demand.

4.3.1 In-Situ Pressure Modulation

In this experiment, a drop of deionized water sitting on a nanotextured superhydrophobic substrate is infused with CO₂ by increasing the pressure of CO₂ in the environment using a pressure cell and is levitated on-demand by releasing the pressure in the cell rapidly to create a large chemical potential difference between the drop and the environment. A cylindrical pressure cell (Diameter =3", Height =2") was built for this purpose using commercially available sanitary fittings (Best Value Vacs) - a spool, a lid with two openings, two gaskets, a sight glass made of polycarbonate, and two tri-clamps. The transparent polycarbonate window allows for the visualization of the bottom of the drop using light interferometry. Figure 4-3a and b shows a schematic of the experiment and the photograph of the pressure cell. The gas inlet and outlet valves on the lid are connected to the gas tank and to the atmosphere respectively.

A transparent superhydrophobic substrate (Glaco-coated glass slide) is placed on the polycarbonate window after removing moisture using a heating step described in Section 3.3.4). A drop of deionized water (20 μL) is placed on the substrate with a superhydrophobic ring in a similar manner to the experiments conducted
Figure 4-4: On-demand droplet levitation experiments on a transparent nanotextured superhydrophobic substrate. (a) In-situ de-pressurization of a water droplet of volume, $V_{\text{drop}} = 20 \mu\text{L}$, equilibrated at $P_{\text{app}}^{\text{CO}_2} = 6.8$ atm; (b) In-situ generation of CO$_2$ gas by addition of a droplet of sodium bicarbonate (20 $\mu$L, 0.5 M) to a droplet of hydrochloric acid (20 $\mu$L, 5 M) resting on the surface; (c) In-situ generation of O$_2$ gas by addition of a droplet of hydrogen peroxide (10 $\mu$L, 30 wt.%) to a droplet of potassium iodide (10 $\mu$L, 3 wt.%) resting on the surface (All scale bars = 0.5 mm).
in Chapter 3. The cell is then sealed and pressurized to 6.8 atm with CO\textsubscript{2} gas. The drop is equilibrated at this pressure for 15 mins. The pressure is released back to atmospheric pressure to observe levitation on-demand. Figure 4-4a shows the sequence of images of the drop after the onset of de-pressurization (t = 0). Note that it takes \(~15\) s to reach atmospheric pressure inside the cell. The first few frames are out of focus due to the deformation of the polycarbonate window under pressure. At t = 8 s, multiple blisters are observed to nucleate at the droplet-substrate interface. These blisters grow in size as the pressure is released and finally de-pin the contact line to set the droplet into levitation. We also notice that the droplet is propelled off the surface during the final-depinning event before levitation. Note that it takes about 9 s to achieve complete de-pinning after the end of de-pressurization.

4.3.2 In-Situ Generation of Gas using Chemical Reaction

CO\textsubscript{2} gas can also be produced in the droplet in-situ by decreasing the pH of a carbonate/bicarbonate solution. For example, sodium bicarbonate reacts with hydrochloric acid to give carbon dioxide gas.

\[
\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2(\text{g})
\]

We use this reaction to generate CO\textsubscript{2} gas in the droplet and achieve droplet levitation. A droplet of 5 M HCl of volume 20 \(\mu\text{L}\) is placed on a superhydrophobic substrate (any moisture content in the substrate is removed using the heating step described in Section 3.3.4) and a droplet of 0.5 M NaHCO\textsubscript{3} of volume 20 \(\mu\text{L}\) is gently added to the HCl drop to trigger the reaction. Figure 4-4b shows the rapid depinning of the contact line within 0.2 s after the addition of the NaHCO\textsubscript{3} droplet. After a brief period of wetting-dewetting cycles, the droplet jumps off the surface completely at \(t = 1.67\) s. Fringes can be observed clearly in the last frame when the drop is back in the focal plane.

Droplet levitation through degassing is not specific to carbon dioxide gas. In Chapter 2, we use the catalytic decomposition of hydrogen peroxide to generate oxy-
gen gas for underwater plastron restoration (See Section 2.2 for more details on this reaction). In this work, we use the same reaction with an aqueous phase catalyst (iodide ion) to generate oxygen gas for droplet levitation.

A droplet of 3 wt.% KI of volume 10 μL is placed on a superhydrophobic substrate (after removal of moisture in the texture using a heating step described in Section 3.3.4) and a droplet of 30 wt.% H₂O₂of volume 10 μL is gently added to the KI droplet to trigger the reaction. Figure 4-4c shows the blistering of gas bubbles on the surface after the mixing of the droplets. The blisters depin the contact line slowly using multiple droplet jumping events (An high speed image sequence of a jumping event is shown in Figure 4-5a). It takes about 180 s to achieve complete de-pinning of the edge (See last frame in Figure 4-4c). This reaction is observed to be different from the other cases both in terms of the timescale of de-wetting as well as the growth of gas bubbles in the drop. Gas bubbles were observed to accumulate and grow at the top surface of the drop (like a soap foam) and the droplet slowly turns yellow during this time (as shown in Figure 4-5b). The yellow color is due to the formation of I₂ as an intermediate during the catalytic reaction [83] and the liquid film drainage of the bubble at the top could be delayed by Marangoni flows induced by concentration gradients of the ionic species in the drop. Further experiments are required to confirm this hypothesis. Droplet levitation using hydrogen peroxide decomposition reaction was also attempted using manganese dioxide catalyst. Here, manganese dioxide was electrodeposited on a flat aluminum substrate and a laser textured aluminum substrate and coated with a fluorinated silane to render it superhydrophobic (same as the procedure described in Section 2.3.1). SEM images of the catalyst-coated flat and laser-textured aluminum surfaces are shown in Figure B-3 and Figure 2-2e respectively. A drop of 30 wt.% H₂O₂of volume ~40 μL is placed on each of the substrates to observe levitation (droplet would be mobile if there is levitation). However, it is observed that the gas generation rate is too low to levitate the droplets. Figure 4-6a shows that there are a few bubbles generated at the MnO₂-coated flat surface but the gas leaves the drop as bubbles instead of depinning the contact line. On the other hand, there is no visual evidence of gas generation in the case of the laser textured
Figure 4-5: (a) Vigorous production of bubbles when a droplet of KI (10 wt %, 10 µL) is added to a droplet of H$_2$O$_2$ (30 wt %, 10 µL) sitting on a superhydrophobic nanotextured substrate (Si nanograss coated with Teflon); (b) Jumping of the KI-H$_2$O$_2$ droplet upon coalescence of a large bubble at the top of the droplet with a blister at the bottom of the droplet.

Figure 4-6: (a) H$_2$O$_2$ drop (30 wt.%) on a flat Al substrate coated with an MnO$_2$ catalyst; (b) H$_2$O$_2$ drop (30 wt.%) on a laser textured Al substrate coated with an MnO$_2$ catalyst.
surface (See Figure 4-6b). This is probably due the fact that the gas has a low resistance path in the microtexture and hence it can escape without disturbing the drop. Thus it is difficult to obtain droplet levitation on superhydrophobic catalytic textures due to low contact area between the reactant and the catalyst resulting in a low rate of gas generation.

4.4 Bubble-Free Surfaces

It is common experience that when a freshly-opened carbonated beverage is poured into a glass cup, bubbles nucleate rapidly on the walls of the container and vitiate the clarity of the glass surface. While this is not a problem for drinking beverages, this can be an issue in applications where optical transparency may be important. For example, bubble formation or adherence to sight glasses in chemical reactors can impair the visibility of chemical processes. Visualization can be a challenge in lab studies which use supersaturated gas solutions due to the nucleation of bubbles at the viewing window. We address this challenge by taking inspiration from anti-fogging surfaces [77, 75]. It has been shown that superhydrophilic surfaces have anti-fogging properties due the the ability of the water to spread as a thin film on the hydrophilic texture (θw ≈ 0°) instead of nucleating as droplets with finite contact angle on the surface. This reduces the scattering of light passing through the system because of the relatively flat air-water interface. In this work, we show that the same is possible with the phases inverted.

In order to make transparent superhydrophobic containers, we treated a 150 ml glass beaker (VWR 10754-950) with Glaco superhydrophobic coating using the procedure described in Section 3.3.3. Another beaker was cleaned with isopropanol to be used as a reference. Carbonated water was pressurized at P_{\text{CO}_2}^{\text{app}} 5.44 atm and poured into the untreated and superhydrophobic containers for observation. Figure 4-7 shows an image of the nature of degassing on the untreated and treated beakers. It can be observed that while the gas prefers to nucleate as bubbles on the glass wall in the untreated beaker, there are no bubbles visible on the superhydrophobic beaker. The
Figure 4-7: Carbonated water ($P_{\text{CO}_2}^{\text{app}} = 5.44 \text{ atm}$) in a clean untreated glass beaker (left), and a glaco-treated glass beaker (right).

Figure 4-8: Comparison of the gas desorption kinetics in 300 ml of carbonated water ($P_{\text{CO}_2}^{\text{app}} = 5.44 \text{ atm}$) in an untreated beaker and a beaker with superhydrophobic walls.

gas instead diffuses into the plastron at the wall and flows out of the system through the porous superhydrophobic texture. During the initial stages of degassing, pulsing columns of gas were observed on walls of the beaker like the one shown in the inset in Figure 4-7. Vakarelski et al. showed that superhydrophobic textures transition to the Leidenfrost boiling regime without going through the phase of nucleate boiling [145, 118]. We observe the same phenomena with supersaturated gas solutions i.e., there is no gas bubble nucleation on superhydrophobic substrates.

We measured the mass transfer kinetics of the systems with and without bubble nucleation by measuring the concentration of dissolved carbon dioxide using the pro-
procedure described in Section 3.3.1. A 400 ml glass beaker (VWR 10754-954: Inner diameter = 73.3 mm) was coated with Glaco Mirror Coat to render it superhydrophobic (using the procedure described in Section 3.3.3). Freshly prepared carbonated water ($P^\text{app}_{\text{CO}_2} = 5.44$ atm) was poured into the beaker upto the 300 ml marking, and a micro pH electrode was inserted immediately after into the solution. Figure 4-8 shows the evolution of $c_{\text{CO}_2}$ in the untreated and superhydrophobic beakers as a function of time. This shows that the carbonated water de-gasses faster in the superhydrophobic beaker compared to the smooth-walled hydrophilic beaker. This is possibly due to the higher surface area to volume ratio of the superhydrophobic beaker for mass transfer as the plastron behaves as both an interface for gas diffusion and an effective pathway for gas transport. Thus, we believe that this could be an effective way to increase the surface area for mass transport in gas stripping applications.

4.5 Summary

In this chapter, we demonstrate the utility of the room-temperature Leidenfrost effect in both droplet systems and bulk systems. We designed a simple harmonic drop oscillator which was used to quantify the mobility of drops on surfaces by measuring the attenuation of oscillating drops. We show that droplets of carbonated water experience lesser friction compared non-carbonated water droplets, and propose a method to sort droplets based on their carbonation content. Carbonated water droplets also exhibit other characteristics of Leidenfrost droplets such as self-propulsion on superhydrophobic surfaces with asymmetric teeth (ratchet-like textures). We also show that sessile droplets can be depinned from the Cassie state into levitation when gas producing reactions are triggered in the droplet. We observe a film boiling-like regime when carbonated water contacts a superhydrophobic surface i.e., a thin film of gas envelopes the surface of superhydrophobic solids immersed in bulk carbonated water. We expect that this will have drag reduction and heat transfer properties similar to Leidenfrost films due to the slip-inducing and insulating properties of gases [144, 143]. All of the aforementioned properties are substrate material independent and can be
obtained on any material including plastics and biological materials which cannot withstand high temperatures.
Chapter 5

Conclusion and Outlook

This thesis explores novel strategies to control the interaction between liquids and solid surfaces using an active component in the liquid. We tap the chemical potential energy stored in dissolved gases and peroxides to perform mechanical work in applications where liquid-solid contact needs to be prevented or reduced.

In Chapter 2, we demonstrated a novel chemical method to replenish a surface air layer or plastron in-situ on superhydrophobic textures that are fully immersed underwater using catalytic decomposition of hydrogen peroxide. We also showed that plastron spreading is possible on microtextures without a nano-Cassie state by performing experiments on silicon microtextures with platinum catalyst without a second level of nano-texture. Although we show that defects are need in the hydrophobic coating to have catalytic activity, future studies are needed to quantify the number and size of defects for the achieving optimal catalytic activity while retaining hydrophobicity. Our thermodynamic framework for predicting recovery on hydrophobic textures can be used to design textures with optimal roughness and surface chemistry functionalization for plastron recovery but it also important to investigate the other parameters which promote recovery such as re-entrant textures, pinning sites, lateral breakthrough pressure, etc. We demonstrate the scalability of this method by fabricating a suitable 'egg crate' structure on laser-textured aluminum surfaces with an inexpensive manganese dioxide catalyst and demonstrating plastron recovery on this surface. Finally we have performed fluid frictional drag measurements
on a microtextured aluminum rotor loaded with MnO₂ catalyst. Skin friction measurements in a turbulent Taylor-Couette flow showed that it is possible to obtain an average slip recovery of 51 ± 14% from the texture's fully wetted state when hydrogen peroxide was added to the system. Future work is needed to understand the effect of the Reynolds number on slip recovery. All the textures used in the study are connected-porous textures. It would be very useful to device strategies to achieve plastron recovery on unconnected textures as well. We anticipate that these catalytically-active drag-reducing surface microtextures can be scaled-up further and implemented in the marine environment to extend the stable lifetimes of frictional drag reduction and anti-corrosion.

In Chapter 3, we use the gradient in chemical potential of dissolved carbon dioxide and ambient carbon dioxide to achieve levitation of droplets. We show that degassing of carbonated water droplets can be used to sustain the droplets in levitation over superhydrophobic surfaces for a period up to 35 s depending on the concentration of dissolved gas. We also show that a minimum concentration of 10 mM is required to achieve droplet levitation, and a minimum of 0.3-0.9 mM is required to have any nucleation and growth of blisters at the liquid-solid contact interface. Although we have characterized only the carbonated water system, the outlined methodology can be used to characterize any gas-liquid-solid system. In our work, we derive a model to estimate the levitation time of the degassing droplets which predicts that the time of levitation is a logarithmic function of the initial concentration of CO₂ in the drop. The model also identifies two important parameters, the liquid mass transfer coefficient and the critical height of touch-down, which set the timescales in the problem. We show that the experimental data agrees well with the logarithmic model, and estimate the liquid mass transfer coefficient in the drop to be \((5.8 \pm 0.7) \times 10^{-5} \text{ m/s}\) along with the critical gap height for the onset of edge-pinning, \(H_{\text{crit}} = 1.5 \pm 0.1 \mu\text{m}\). Future studies are needed to understand the effect of the droplet size and gas-liquid composition. Currently, a large amount of CO₂ gas is lost through the top surface of the drop. Finding methods to reduce the mass transfer at the top surface of the drop could enhance the effect by an order of magnitude.
In Chapter 4, we discuss that the utility of the room-temperature Leidenfrost effect observed in carbonated water droplets. We show that carbonated water droplets also exhibit many features of Leidenfrost droplets such as enhanced mobility and self-propulsion on superhydrophobic surfaces with asymmetric teeth (ratchet-like textures). Just like a thin film of vapor is observed on hot solids in water in the film boiling regime, we observe that a thin film of gas envelopes the surface of superhydrophobic solids in bulk carbonated water. Future studies could focus on studying the heat transfer and drag reduction properties of these gas films, which could be used in low-temperature applications with continuous pumping of aerated water. We exploit the advantage that the gas film forms at room temperature, to obtain these properties on organic substrates. We also demonstrate the versatility of this effect by showing that droplet levitation can be achieved using methods other than pressurizing the liquid with gas. We show that sessile droplets can be de-pinned from the Cassie state and set into levitation when gas is produced in situ in the drop by using a chemical reaction. Future studies are needed to characterize the optimal reacting species concentrations for achieving droplet levitation. We anticipate that this method could be extended to other commonly used liquids like alcohols and oils by appropriately tuning the surface treatment.

We envision that this work will open up new pathways to achieve ‘active interfaces’ using a combination of active fluids and active surfaces. Utilizing dissolved species as a source of energy could change the way energy is delivered in many applications and also extend the range of materials that can be used to make the surfaces. We also believe that further research on other liquid-gas pairs could lead to implementation in a wider number of interfacial engineering applications.
Appendix A

Light Delivery for Photocatalytic Reactions

A.1 Introduction

A.1.1 Photocatalysis

Photocatalysis is an advanced oxidation process that was discovered by Fujishima and Honda in the 1970s [43]. It is used to degrade organic pollutants in air or water medium using ultraviolet light or sunlight. The method is attractive because it can be done at ambient pressure and temperature and is a non-contact method of cleaning contaminated surfaces. When light of the appropriate wavelength is irradiated on a photocatalytic material (which is usually a semiconductor), the valence band electrons are excited to the conduction band, leading to the creation of electron-hole pairs in the material. The electron-hole pairs aid the formation of free radicals in the presence of moisture which then attack organic molecules in contact with the catalyst. Long chain organic molecules are broken down into shorter chains, and small molecules are oxidized into carbon dioxide. The most commonly used photocatalyst is Titanium dioxide (TiO₂) which has a band gap of 3.2 eV which corresponds to an excitation wavelength in the UV region. It is commercially attractive because it is relatively cheap and non-toxic. Titanium dioxide has been investigated extensively
for wastewater purification in the past four decades as it can break down organic pollutants that come in contact with it into less harmful products when activated using UV light. Visible light photocatalysts can also be synthesized by doping TiO$_2$ with N$_2$ or other materials to reduce its band gap. But this is still in the research phase and large scale manufacturing techniques for such catalysts are not yet available.

A.1.2 Limitations of Photocatalytic Reactors

Although photocatalysis is a promising technology for water and air purification, it is currently being limited by scalability issues. Photocatalysis can be broadly classified into two types - homogeneous catalysis (catalyst is suspended as particles in the reactant medium) and heterogeneous catalysis (catalyst is immobilized on a support structure). Homogenenous photocatalysis involves an energy intensive catalyst separation step post-reaction which limits its application and scalability. On the other hand, heterogeneous catalysis suffers two major types of limitations - photon transfer limitations (low illumination efficiency) and mass transfer limitations (limited contact between the reactants and activated catalyst). Conventionally, heterogeneous photocatalytic reactions are carried out using annular flow reactors where the catalyst is coated on the tube wall and the light is delivered externally at the tube walls or at the tube center. The light has to travel through the reactant medium before reaching the catalyst and hence it suffers from high losses due to attenuation in the reactant medium. The reactants have to diffuse from the bulk of the reactor to reach the catalyst surface for the reaction to take place. For the case when the catalyst is coated on a UV lamp, the mass transfer limitations still persist. Some of the other types of reactor configurations that have been studied in literature are - fixed bed, fluidized bed, rotating disc, monolith, corrugated plate, falling film, Taylor vortex reactor, optical fiber, microreactors and swirl flow reactors [146, 102]. Each one of them has its own advantages and drawbacks and hence, the choice of reactor design is generally application driven depending on whether the mass transfer or the illumination needs to be optimized the most. Hence there is a need for holistically designing more efficient reactors.
A.1.3 Fiber Optic Photocatalytic Reactors

In order to reduce the illumination losses in the system, it is necessary to deliver the light as close as possible to the catalyst. It is also important that maximum catalyst area is illuminated, including the particles located farther away from the light source. One of the ways in which this can be achieved by using optical fibers to distribute the light to the catalyst. The structure of a simple step-index optical fiber includes a core fiber made of a highly transparent material and a symmetrical coating called cladding, which has a lower refractive index than the core. Light is transmitted along the core of the fiber through total internal reflections. Figure A-1a shows how an optical fiber can be modified to promote photocatalysis. When the optical fiber is stripped off its cladding or if defects are introduced randomly into the fiber cladding, it allows the light transmitted in the core to be partially refracted out of the fiber. This light escaping from the sides of the fiber makes it appear glowing. This type of fibers are known as side-light emitting optical fibers. This technique is being used by the interior design and fashion industry to create woven light emitting displays, glowing clothes and other innovative products [70, 114]. If the core is coated with a photocatalyst after the fiber is stripped off its cladding, it becomes a photoactive fiber. The light escaping the core excites the catalyst to produce holes and electrons which catalyse the reaction. This has been studied using
single fibers or fiber bundles by many groups. Figure A-2a-c show optical fibers that have been stripped off their cladding and coated with titanium dioxide. Figure A-2d-i show photocatalytic reactors systems using optical fiber bundles for light delivery.

While designing fiber optic reactor systems, it is possible to align the fibers in various configurations. Three configurations of fiber reactors have been studied widely - parallel fiber reactor, monolith reactor and woven fiber reactor. The parallel fiber reactor has catalyst-coated fibers oriented in parallel along or perpendicular to the flow as shown in Figure A-2h. In the monolith reactor, while the optical fiber is used to deliver light on its sides, the catalyst is coated on a channel surrounding the fiber to avoid backlighting problems as shown in Figure A-2i. In the woven fiber type of reactor, we see that the fiber is woven along with other non-active fibers for achieving a tight knit structure (Figure A-2d). This type of reactor is interesting for two reasons. Each of the pores can act like a micro-channel for the reactant phase where illumination distance is small and catalyst surface area is high. Secondly, the woven structure can be used as a separator/filter and hence multi-functional membranes can be created. In the field of wastewater treatment, it is required that the water be treated for both suspended and dissolved contaminants. Therefore, a design configuration where the optical fiber guides will be arranged in the form of a mesh structure to obtain a multifunctional membrane with both filtration and catalytic properties will be a novel contribution to this field. It is ideal if the entire weave structure could be made up of optical fibers without introducing other kinds of reinforcement. This would ensure that the entire structure can act as a self-cleaning membrane with every fiber being able to clean itself using photocatalysis. However, one of the major limitations with creating such a structure is that the recommended radius of curvature of an optical fiber is very large compared to the needed radius of curvature for woven meshes. Although there are problems that need to be overcome to make woven fibers successful, they can still have an high impact as their configuration would be similar to microreactors[100]. It is estimated that microreactors can have greater than 10,000 m² of illuminated catalyst area per unit m³ of reactor. Thus, in a woven optical fiber reactor, we can have high illumination efficiency combined with
A.1.4 Chapter Objectives

In this work, we use a novel side-light emitting optical fiber, Corning® Fibrance® (commercially known as light diffusing fiber), which does not require the cladding to be removed for side radial emissivity. This optical fiber was developed by Corning Inc. and is currently distributed by Versalume™ LLC[20, 92]. Fibrance has a fused silica core of diameter 170 μm with a helical coil (Diameter ~ 4 μm) of nano-sized voids at the center of the core. Figure A-3 shows a schematic of the structure of a Fibrance fiber. The nano-voids scatter light passing through the core, eliminating the need to introduce defects in the cladding for deflecting light. Although it is commercially sold for aesthetic applications only, it has been reported that this fiber can be used to promote light-driven reactions as well[32]. This fiber is advantageous compared to side-light emitting optical fibers used in previous studies because the cladding is intact. The cladding retains the flexibility of the quartz core fiber, making it possible to implement these fibers in woven reactors (previous woven reactors use plastic fibers). It also helps in preventing degradation of the silica core in underwater applications. Also, since the fiber core is made of fused silica, it can be used to distribute visible light as well as UV light for photocatalytic applications[93].

In this chapter, we explore the pollutant degradation and self-cleaning properties
of three types of optical fiber reactor systems.

1. **Self-cleaning of parallel fiber reactor membrane using UV-light in an oil-water environment**

   Fouling by oil is a major problem in membranes used for oil-water separation in various industries [3, 65, 110]. Previous work shows that it is possible to remove oil fouling from photocatalyst-coated membranes underwater using UV light [108, 160, 111]. These studies use a UV lamp to deliver light to the membrane, and this entails losses described in Section A.1.2. Hence, we build a parallel-fiber membrane reactor and test its ability to remove oil-fouling underwater.

2. **Pollutant degradation in a photocatalytic glass-wool reactor utilizing UV-light**

   It is well known that photocatalytic activity is proportional to the surface area of illuminated catalyst [146]. Hence it is important to have both high surface area of catalyst as well as sufficient illumination for triggering the reaction. Glass wool photocatalytic reactors achieve both of these conditions by having a high surface area of catalyst per unit volume of reactor due to the use of thin fibers (\(\sim 10 \mu m\) diameter; Thinner fibers have higher surface area to volume ratio) and increased depth of light penetration due to the light-transmitting material of the fibers [85, 109, 120]. However, the intensity of light at larger depths is significantly affected due to the absorption of light in the top parts of the glass wool. We use the side-light optical fibers to illuminate the interior of a commercially procured photocatalytic glass wool sheet and test its ability to degrade an organic dye flowing through the system in the presence of UV-light.

3. **Pollutant degradation in a single-fiber photocatalytic reactor using visible light**

   In has been reported that titanium dioxide can degrade organic contaminants under visible light using dye-sensitization[24] or in the presence of hydrogen peroxide[81]. We study the self degradation of Rhodamine 6G dye (absorbance
peak at 530 nm) in the presence of TiO$_2$ and H$_2$O$_2$ using a single-fiber photocatalytic reactor (coupled to a 532 nm source).

A.2 Experimental Procedure

A.2.1 Connectorizing fibers

Fibrance optical fiber was procured in bulk (Versalume, Bulk fiber, 100 m, Diffusion length 1m) and cut into smaller pieces of length 15 cm for connectorization. 16 fibers were connectorized together by using a FC optical fiber connector of bore diameter 1050 μm (Thorlabs Inc. 30126G2-1050: FC/PC Multimode Connector, ÁY1050 Âtm Bore, SS Ferrule). For connectorization, the fibers are first aligned together and slid into the FC connector bore. An epoxy glue (Thorlabs Inc. F112: Epoxy for Fiber Optic Connectors, Long Pot Life) is then injected gently injected into the bore using a syringe for setting the fibers together. After a setting time of about 12 hours, the excess length protruding out of the bore face are cut carefully using a fiber optic scribe (Thorlabs Inc. S90R: Ruby DualScribe Fiber Optic Scribe) at a distance of approximately 1 mm from the face. The rest of the fiber length is abraded and polished using a polishing disk (Thorlabs Inc. D50-FC: FC/PC and SC/PC Connector Polishing Disk) on 3 grades of lapping sheets (Thorlabs LF5P,LF3P,LF1P: 11" x 9" Silicon Carbide Lapping Sheets - 5 μm, 3 μm, 1 μm Grit). Lapping sheets are used in the order of decreasing grit size to get a smooth and defect free fiber face. An image of the polished faces of the fibers is shown in Figure A-4a. The inset shows the uniform distribution of light across all fibers when they are illuminated on the other end using a diffuse light source. The fibers were coupled to a UV light source (Omnicure S2000, $\lambda_{peak} = 365$ nm) using a factory-aligned fixed-focus collimation package (Thorlabs Inc. F671FC-405: 405 nm, f=4.02 mm, NA=0.60 FC/PC Fiber Collimation Pkg.) which contains an aspheric lens to focus the diffuse light on the fiber faces. The transmittance of the collimator at $\lambda = 365$ nm is 99.4%. Figure A-4b shows a picture of the connectorized fibers with the collimator. The liquid light guide
A.2.2 Photocatalytic Parallel Fiber Reactor

A parallel-fiber reactor was built by aligning the connectorized fibers in a single plane and sticking them on a tape to fix the alignment. The fibers were then spray coated with a dispersion of TiO$_2$ nanoparticles dispersed in ethanol (1 wt.%) using a procedure reported in Sadullah et al. [51]. An SEM micrograph of TiO$_2$ coating is shown in Figure A-4c. The coated fibers were then secured to a plastic surface and submerged underwater. Figure A-4d shows a picture of the fiber reactor illuminated with UV light submerged underwater.
Figure A-5: (a) SEM Micrograph of Quartzel fibers coated with TiO₂. The inset shows the morphology of the TiO₂ coating on a single fiber.; (b) Degradation of Methylene blue dye on a Quartzel sample under UV irradiation (240 mW/cm²). The illuminated region regains its original white color (circular white patch) while the rest of the sample remains unaffected.; (c) Glass wool photocatalytic reactor combined with side-light emitting optical fibers for dye degradation. The optical fiber array is arranged perpendicular to the pollutant flow direction.
A.2.3 Photocatalytic Glass Wool Reactor

A transparent chamber of dimensions W1" × L3" × H0.5" was built with an inlet and outlet port for flowing the pollutant solution. 16 connectorized Fibrance fibers were aligned perpendicular to the flow direction in the chamber by passing them through laser-cut holes of diameter 250 μm on the sides of the chamber. Photocatalytic glass wool was commercially procured (Quartzel® PCO, Saint-Gobain) and stuffed into the acrylic chamber before sealing the chamber. The glass wool consists of randomly oriented TiO₂-coated fibers of diameter 10 μm as shown in Figure A-5a. The photocatalytic activity of this wool was checked by dyeing a piece of the glass wool with methylene blue and illuminating it with UV light (240 mW/cm²) from a UV lamp (Omnicure S2000). Figure A-5b illustrates how the glass wool section illuminated with UV light is restored to its original white color while the rest of the glass wool remains blue. This is because the methylene blue is oxidized by the TiO₂ in the presence of UV light. It was observed that the dye was degraded through the entire cross-section (~ 1 cm) of the glass wool in the illuminated region, indicating that the UV light is able to sufficiently penetrate the glass wool to promote photocatalysis. The chamber was water-proofed using an epoxy glue at the edges and fiber holes. Methylene blue (Sigma-Aldrich) solution was used as a model pollutant to check the photocatalytic activity of the reactor.

A.2.4 Single Fiber Photocatalytic Reactor

A top-open acrylic cell of dimensions W1" × L2" × H0.5" was built by laser cutting an acrylic sheet (McMaster Carr, Thickness 1/8") to required dimensions and gluing the pieces together using an acrylic solvent cement (SCIGRIP 4). A hole of diameter 250 μm was incorporated into the opposite ends (using a laser cutter) of the cell to pass the optical fiber through the center of the chamber. A single Fibrance optical fiber was connectorized using an FC multimode connector (30240C1 FC/PC Multimode Connector, φ240 μm Bore, Ceramic Ferrule) and coupled to a laser source (Laserglow Technologies, 532 nm Green DPSS Laser System) using an
Figure A-6: (a) Power measured at the end of the fiber for various lengths of the fiber. The solid line is an exponential fit with two fitted parameters $P_{inlet}$ and $k$; (b) Calculated side-light intensity based on the power measurement in Part (a).

FC/PC fiber optic coupler (Laserglow Technologies, ACFVISHXX). The fiber was coated with TiO$_2$ nanoparticles by dip-coating it in an aqueous suspension of TiO$_2$ nanoparticles (5 wt%).

The side-light emission intensity was determined by measuring the power delivered at the end of the fiber for different lengths of the fiber. A power meter (Thorlabs Inc., PM16-401) was connected to the fiber end using an FC fiber adaptor (Thorlabs, S120-FC FC/PC Fiber Adapter Cap) to measure the power of light remaining in the core after undergoing scattering. Figure B-10 shows an image of the setup and Figure A-6a shows a plot of the power measured as a function of the length of the fiber for various source power settings. Assuming that the light scattering follows Beer-lambert law in the core of the fiber, we obtain a function for the power transmitted inside the core ($P$) as a function of the fiber length, $x$.

$$P(x) = P_{inlet}e^{-kx}$$  \hspace{1cm} (A.1)

where $k$ is the attenuation coefficient and $P_{inlet}$ is the power delivered at the entrance to the fiber. The power of light entering the fiber $P_{inlet}$ and the attenuation coefficient $k$ are estimated by fitting Equation A.1 to the data shown in Figure A-6a.
estimated inlet power is found to be approximately 12% of the source power, implying that the coupling efficiency of the system is 12%. The attenuation coefficient in the fiber core is estimated to be \( k = -0.036 \pm 0.001 \text{ cm}^{-1} \). The side light intensity at every position on the fiber is found by dividing the power emitted at every \( x \) by the circumferential area \( (\pi D_{fiber} \Delta x) \).

\[
I_s(x) = \frac{\Delta P}{\Delta x \pi D_{fiber}}
\]

\[
\Rightarrow I_s(x) = \frac{1}{\pi D_{fiber}} \frac{dP}{dx}
\]

\[
\Rightarrow I_s(x) = \frac{P_{inlet} e^{-kx}}{\pi D_{fiber}} \tag{A.2}
\]

Figure A-6b shows a plot of the sidelight intensity calculated using Equation A.2 using the data from Figure A-6a. It is observed that we obtain a side-light intensity between 5-30 mW/cm² for \( x < 20 \text{ cm} \) and \( 100 < P_{source} < 500 \text{ mW} \).

A.3 Results and Discussion

A.3.1 UV-Light Catalyzed Cleaning of Photocatalytic Membranes in Oil-Water Environments

In order to test the fouling removal ability of the optical fiber membrane, the TiO₂ coated fibers are contaminated with a model oil, dodecane [111] by using a few drops of dodecane to wet the fibers. The dodecane is dyed red (Oil Red O, Sigma Aldrich) to visualize changes in the system. The bath is then filled with deionized water to submerge the membrane to a depth of 1 cm. The fibers are coupled to a diffuse UV light source (side light intensity \( I_s \approx 1.1 \text{ mW cm}^{-2} \); this is estimated by measuring the power at the end of the fibers). The oil is expected to recede from the membrane upon photocatalytic degradation of oil [111]. However, no visible change is observed in the system even after 4 hours of illumination. This could be due to the fact that the side-light intensity is very low to activate the catalyst. Previous studies use UV light
intensities of $10 \text{ mW} < I < 250 \text{ mW}$ to catalyze the reaction with rate constants of the order of $k_p = 0.01 \text{ s}^{-1}$, i.e. the reaction is completed in a few minutes. Secondly, the fiber has a hydrophobic-oleophilic coating (contents are proprietary) which hinders the process of de-wetting of oil underwater. The dynamic contact angles of water on the surface of the fiber was measured using a tensiometer (DataPhysics DCAT11) by drawing a single fiber out of a bath of water and measuring the contact line force exerted on the fiber. The advancing and receding contact angles were found to be $\theta_w^{adv} = 96^\circ \pm 2^\circ$ and $\theta_w^{rec} = 54^\circ \pm 2^\circ$ respectively. Similar measurements were made using a dodecane bath and the contact angles were found to be $\theta_o^{adv} = 15^\circ \pm 2^\circ$ and $\theta_o^{rec} = 0^\circ \pm 2^\circ$. Since oil is more wetting towards the surface, it is not possible to remove the fouling from the surface underwater as the water does not spread on the oil wet regions. And lastly, it is difficult to distribute light uniformly among all of the connectorized fibers as can be noticed in Figure B-11. This would hamper the photocatalytic activity of all the fibers except for the 2-3 fibers which receive almost all of the light.

A.3.2 UV-Catalyzed Pollutant Degradation in a Photocatalytic Glass-Wool Reactor

In this experiment, we use the connectorized Fibrance fibers to illuminate a glass-wool reactor. An aqueous solution of methylene blue (concentration $\approx 0.02 \text{ mg/ml}$, total volume $60 \text{ ml}$) is circulated through the reactor at $10 \text{ ml/min}$ using a peristaltic pump (KrosFlo Research IIi TFF, Spectrum Labs). The direction of the flow is shown in Figure A-5c. The average side light UV intensity is estimated to be $0.6 \text{ mW cm}^2$. The methylene blue dye absorbs onto the glass wool at the start of the experiment and hence shows some decay in the methylene blue concentration at the start of the experiment, however, the dye concentration remains the same after this point (determined using UV-Vis absorbance measurements). This indicates that there is no photocatalytic degradation of the dye in the reactor. This is because the intensity of light delivered in the reactor is not sufficient for photocatalysis (within the timescale
Figure A-7: (a) Image of test tube reactor with methylene blue dye solution; (b) Single fiber reactor with Rhodamine 6G dye solution.; (c) Absorbance of the Rhodamine dye solution after storage in dark, exposure to visible light (100 mW/cm²) in the presence of H₂O₂, exposure to visible light (100 mW/cm²) in the presence of H₂O₂ and TiO₂, and exposure to green light (I_sine ~ 15-25 mW/cm²) in the optical fiber reactor in the presence of H₂O₂ and TiO₂. All of the tests were performed at c_{Rh6G} = 0.018 mg/ml and c_{H2O2} = 1.8 wt.% for t =12 hours.

### A.3.3 Visible Light Pollutant Degradation using Dye-Sensitization

In the previous section, we show that the delivery of UV light through these fibers is inefficient due to coupling inefficiency of a diffuse light source. However, the coupling efficiency can be drastically improved by using a collimated beam from a laser light source. In this section, we explore the possibility of performing dye-sensitized visible light reactions using Fibrance fibers.

We built a single-optical fiber photocatalytic reactor and coupled it to monochromatic laser source (532 nm). The optical fiber is coated with TiO₂ nanoparticles using a dip-coating procedure. The reactor is filled with an aqueous mixture of H₂O₂ and Rhodamine 6G (c_{H2O2} = 1.8 wt.%, c_{Rh6G} = 0.018 mg/ml). Figure A-7b shows a snapshot image of the experiment. Rhodamine has an absorbance maximum at around 532 nm (wavelength of the laser used) and is expected to promote self-degradation. H₂O₂ and TiO₂ were added to test if the reaction could be enhanced further. A baseline test was conducted using Rhodamine-H₂O₂-TiO₂ system in a test tube illuminated with visible light of intensity ~ 100 mW/cm² (An image of the setup is
shown in Figure A-7a. Note that the dye shown in the image is different from the Rhodamine dye used in this experiment. The image is for illustration purposes only. Figure A-7c shows the relative magnitude of degradation of Rhodamine dye (using absorbance values at 530 nm) for the test cases (in the test tube) and the optical fiber reactor. It can be observed that after a 12 hours of illumination, the maximum dye degradation is observed in the test-tube case with H₂O₂ and TiO₂ (about 80%). However, the optical fiber system using the same reactants showed only 20% dye degradation during this time. Further studies are needed to confirm the efficiency of this reaction using optical fiber illumination.

A.4 Conclusions

In this work, we performed experiments using three types of optical fiber illuminated reactors. Although these are only preliminary experiments, we recognize some limitations of the current configurations and recommend future directions.

- The major limitation of the current setup is that it is inefficient in coupling diffuse UV light into a bundle of Fibrance optical fibers. Less than 1 percent of the source power is coupled into the fibers. One of the reasons could be that the core diameter of the fiber, 170 μm, is too small for efficient butt coupling. Previous studies which report using optical fibers for UV photocatalysis typically have fiber core diameters larger than 400 μm (See Table C.4).

- The Fibrance fiber has a protective hydrophobic-oleophilic polymer cladding, which makes it unsuitable for oil-fouling remediation. However, it can still be used for degrading water-soluble pollutants.

- Visible light photocatalysis using Rhodamine-H₂O₂-TiO₂ in the laser-illuminated optical fiber system is a promising area to pursue, but systematic studies are needed to determine the efficiency of the system.
Appendix B

Supplementary Figures
Figure B-1: A glass slide coated with catalase using layer-by-layer self-assembly (10 bilayers) immersed in 3 wt.% H$_2$O$_2$.

Figure B-2: Plastron recovery observed by various studies [76, 42, 148] for microtextured surfaces without nanotexture. The theoretical curve is the same as Equation 2.6 but the roughness $r$ has been replaced using Equation 2.3 (similar to plot in Lee et al.[76]). It is evident that plastron recovery was not observed in the studies which did not have optimal texture parameters.
Figure B-3: Micrograph of MnO$_2$ electroplated on Aluminum flat plate

Figure B-4: Original data obtained in 4 experiments in the slip recovery tests using the TC cell.
Figure B-5: pH measurement in carbonated water (in bulk) prepared at various partial pressures of CO₂ using a regular pH probe (VWR Symphony) (a) pH vs. time of degassing, $t_{\text{degassing}}$ (time elapsed since the opening of the bottle); (b) pH verses partial pressure of CO₂. The theoretical line is calculated using Henry's law at $T_{\text{amb}} = 23 \, ^\circ\text{C}$

Figure B-6: Bottom view of a deionized water drop (left) and a carbonated water drop (right, $P_{\text{CO}_2}^{\text{app}} = 2.72 \, \text{atm}$) imaged immediately after their deposition on a glaco-coated glass slide. Images were obtained using multichromatic light interferometry. Note that the light used for these images was composed of unequal intensities of multiple wavelengths (i.e., not white light). (Scale bar = 0.5 mm).
Figure B-7: Compilation of all the data obtained in the drop levitation studies. The colored circles represent the data that obtained under the best controlled conditions, while the black circles represent all the other experiments. Chapter 3 reports the average of the colored points. (a) Levitation time (b) Blister time

Figure B-8: Part diagram of the grooves used for the drop oscillator experiments. The dimensions are in [mm] and inches. Experimental results have been reported for the groove in section D-D. This diagram has been produced by Andrew Gallant (MIT Central Machine Shop)
Figure B-9: Top view of drop oscillation experiments on a superhydrophobic groove of $R_{gr} = 635$ mm and $L_{gr} = 65$ mm: (a) A carbonated water droplet ($P_{CO_2}^{app} = 5.44$ atm, $V_{drop} = 80 \mu$L) released at the edge of the groove oscillates multiple cycles, and (b) a deionized water drop oscillates for two periods before pinning at the center. The snapshots are taken every 20 ms. Scale bar = 20 mm.

Figure B-10: Image of the setup used to characterize the attenuation of light through Fibrance optical fiber.

Figure B-11: A group of 16 connectorized Fibrance fibers to coupled with a diffuse UV light source. Note that the light is non-uniformly distributed between the fibers.
Appendix C

Supplementary Tables
Table C.1: Catalysts for decomposition of hydrogen peroxide

<table>
<thead>
<tr>
<th>Type</th>
<th>Catalyst</th>
<th>$E_0^*$</th>
<th>Cost**</th>
<th>Implementation Methods</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td>No Catalyst</td>
<td>75</td>
<td>0</td>
<td>N/A</td>
<td>Slow at room temperature</td>
</tr>
<tr>
<td>Enzyme</td>
<td>Catalase (liver)</td>
<td>23</td>
<td>0.10</td>
<td>LBL</td>
<td>Difficult to hydrophobize, sensitive to temperature and environment</td>
</tr>
<tr>
<td>Ion</td>
<td>Iodide ion</td>
<td>56</td>
<td>0.5</td>
<td>Solution</td>
<td>Needs to be added along with $\text{H}_2\text{O}_2$</td>
</tr>
<tr>
<td>Ion</td>
<td>Iron salts</td>
<td>-</td>
<td>0.02</td>
<td>Solution</td>
<td>Needs to be added along with $\text{H}_2\text{O}_2$</td>
</tr>
<tr>
<td>Colloidal Metal</td>
<td>Platinum</td>
<td>49</td>
<td>300</td>
<td>Self-assembly</td>
<td>Expensive, surface modification friendly</td>
</tr>
<tr>
<td>Metal thin film</td>
<td>Platinum</td>
<td>-</td>
<td>30</td>
<td>Sputtering, electroplating</td>
<td>Expensive, Conformal thin films, surface modification friendly</td>
</tr>
<tr>
<td>Oxides</td>
<td>MnO$_2$</td>
<td>58</td>
<td>10</td>
<td>Anodic deposition, spraying nanoparticles</td>
<td>Cheap, scalable, surface modification friendly</td>
</tr>
</tbody>
</table>

*Adapted from Moelwyn-Hughes 1947 [105] and Stark and Wallace 1975 [136]. Note that the rate of the reaction varies with the form of catalyst used (colloidal, film etc).

**Rough estimate from Sigma Aldrich. Note that the price varies with the purity, form (colloidal, film etc) and quantity of the catalyst.
Table C.2: Henry's law solubility constants of some common gases in water at $T = 23^\circ C$. [126]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Solubility (mol m(^{-3}) Pa(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$7.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$1.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$6.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$7.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Methane</td>
<td>$1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>$3.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>$2.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$5.9 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
Table C.3: Dimensions of Silicon pillars used in the experiments (2R = 50 μm had no catalyst on top of the pillars, 2R = 10 μm had catalyst on top of the pillars)

<table>
<thead>
<tr>
<th>Width 2R</th>
<th>Height H</th>
<th>Pitch L, and Micropost Shape*</th>
<th>(Solid fraction $\phi_s$, Wenzel roughness $r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>25</td>
<td>75C</td>
<td>(0.349, 1.698)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100C</td>
<td>(0.196, 1.393)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100S</td>
<td>(0.25, 1.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150C</td>
<td>(0.087, 1.175)</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>75C</td>
<td>(0.349, 2.396)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100C</td>
<td>(0.196, 1.785)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100S</td>
<td>(0.25, 2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150C</td>
<td>(0.087, 1.349)</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>75C</td>
<td>(0.349, 3.793)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100C</td>
<td>(0.196, 2.571)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100S</td>
<td>(0.25, 3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150C</td>
<td>(0.087, 1.698)</td>
</tr>
<tr>
<td>150</td>
<td>150</td>
<td>75C</td>
<td>(0.349, 5.189)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100C</td>
<td>(0.196, 3.356)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100S</td>
<td>(0.25, 4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150C</td>
<td>(0.087, 2.047)</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>15C</td>
<td>(0.349, 4.491)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20C</td>
<td>(0.196, 2.963)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35C</td>
<td>(0.064, 1.641)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60C</td>
<td>(0.022, 1.218)</td>
</tr>
</tbody>
</table>

*S = Square posts, C = Circular posts
Table C.4: Compilation of fiber diameters used and the intensities achieved in optical fiber reactor studies

<table>
<thead>
<tr>
<th>Study</th>
<th>Fiber Material* (Excitation Light)</th>
<th>Core Dia. (µm)</th>
<th>Max. Side light Intensity (µW/cm²)</th>
<th>Reactor Length (cm)</th>
<th>Medium</th>
<th>Pollutant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bourgeois (2012) [17]</td>
<td>P (UV)</td>
<td>480</td>
<td>112</td>
<td>20</td>
<td>air</td>
<td>formaldehyde</td>
</tr>
<tr>
<td>Choi (2001) [25]</td>
<td>Q (UV)</td>
<td>1000</td>
<td>7500</td>
<td>30</td>
<td>air</td>
<td>acetone</td>
</tr>
<tr>
<td>Danion (2004) [29]</td>
<td>Q (UV)</td>
<td>1000, 600</td>
<td>NA</td>
<td>13.5</td>
<td>water</td>
<td>hydroxy-butanedioic acid</td>
</tr>
<tr>
<td>Jinyu (2012) [63]</td>
<td>Q (Vis)</td>
<td>400</td>
<td>2580</td>
<td>30</td>
<td>water</td>
<td>Methylene blue</td>
</tr>
<tr>
<td>Peill (1995) [115]</td>
<td>Q (UV)</td>
<td>1000, 3000</td>
<td>7534</td>
<td>20</td>
<td>water</td>
<td>4-chlorophenol</td>
</tr>
<tr>
<td>Sun (2000) [137]</td>
<td>Q (UV)</td>
<td>125</td>
<td>99</td>
<td>10</td>
<td>gas</td>
<td>isopropanol</td>
</tr>
<tr>
<td>Xu (2008) [158]</td>
<td>Q (Vis)</td>
<td>NA</td>
<td>100</td>
<td>100</td>
<td>water</td>
<td>4-CP</td>
</tr>
</tbody>
</table>

*Q = Quartz fiber, P = Polymer fiber
Appendix D

Derivations

D.1 Calculating the Partial Pressure of CO₂

The headspace in the bottle in the pressurized state is composed of air (initially in the bottle), CO₂ gas, and water vapor. Hence the total pressure in the system can be written as follows.

\[ P = P_{CO₂} + P_{air} + P_v \] (D.1)

The total pressure can be calculated from the gauge pressure reading (\( P_{gauge} \)) on the pressure dial.

\[ P_T = P_{gauge} + P_{atm} \] (D.2)

\( P_{air} \) can be found from the initial conditions as the number of moles of air has not changed after pressurizing.

\[ P_{air} = \frac{n_aRT}{V_{headspace}} = P_{atm} \] (D.3)

The vapor pressure of water at \( T = 23 \, ^{°}C \) is known to be \( P_v = 0.027 \, atm \). \( P_v \) is negligible compared to the applied CO₂ pressure in most of the experiments. Hence neglecting \( P_v \) and solving the above equations, we obtain -
\[ P_{\text{CO}_2} = P_{\text{gauge}} \]  

\textbf{D.2 Lubrication Theory Approximation in Levitating Drops}

Here we start with the Navier-Stokes equation in cylindrical coordinates and compare the relative magnitudes of the terms by using the characteristic length scales and time scales in the system. Note that the \( \theta \) terms have been ignored due to the radial symmetry of the problem.

\[
\frac{\partial u_r}{\partial t} + u_r \frac{\partial u_r}{\partial r} + u_z \frac{\partial u_r}{\partial z} = -\frac{1}{\rho} \frac{\partial P}{\partial r} + \nu \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_r}{\partial r} \right) + \nu \frac{\partial^2 u_r}{\partial z^2} \]  

\[
\frac{U_R}{t_{\text{lev}}} \frac{U_R^2}{R} \frac{U_z}{H_g} \frac{P_c}{\rho R} \frac{\nu U_R}{R^2} \frac{\nu U_R}{H_g^2} \]

Here \( t_{\text{lev}} \sim 1 \text{s}, U_R \sim 1 \text{m/s}, R \sim 2 \text{mm}, H_g \sim 50 \mu\text{m} \). From scaling in the continuity equation, we obtain

\[ U_z \sim \frac{H_g^2}{R} U_R \implies U_z << U_R \]  

(D.6)

Using Equation D.6 in the third term of Equation D.5, and multiplying all the scaling terms by \( \rho H_g/\mu \) rearranging the terms we can obtain a scaling in terms of the Reynolds number in the flow gap, \( \text{Re}_H = U_R H_g/\nu \).

\[
\frac{\partial u_r}{\partial t} + u_r \frac{\partial u_r}{\partial r} + u_z \frac{\partial u_r}{\partial z} = -\frac{1}{\rho} \frac{\partial P}{\partial r} + \nu \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_r}{\partial r} \right) + \nu \frac{\partial^2 u_r}{\partial z^2} \]  

\[
\frac{\text{Re}_H}{t_{\text{lev}}} \frac{\text{Re}_H U_R}{R} \frac{\text{Re}_H U_R}{R} \frac{P_c H_g}{R \mu} \frac{U_R H_g}{R^2} \frac{\nu U_R}{H_g^2} \]

Comparing the magnitude of the different terms, we can eliminate terms I,II,III and V.
A similar scaling analysis in the $z$-direction shows that $\frac{\partial P}{\partial z} \sim \frac{H_a}{R} \frac{\partial P}{\partial r}$, implying that the flow in the $z$-direction can be neglected in comparison to the flow in the $r$-direction. Note that Equation D.8 implies that the flow is assumed to be quasi-steady in the gap (even though the height of the gap is changing with respect to time). Thus after eliminating the terms I-III & V, we finally obtain:

$$\frac{\partial P}{\partial r} \sim -\mu \frac{\partial^2 u_r}{\partial z^2}$$

(D.11)

### D.2.1 Estimating the Liquid Interfacial Velocity

At the liquid-air interface at the top of the gas film, the no-slip condition implies that the gas and the liquid have the same velocity at the interface. Let us denote this unknown interfacial velocity by $u_i$. The flow profile inside the liquid resembles a toroidal loop as shown in Figure 3-19 due to the drag of the outward radial flow of the gas under the drop. This implies the velocity inside the liquid drops to zero over a distance approximately equal to the radius of the drop. In addition to the no slip condition, we equate the shear stress in the liquid and gas phases to obtain an estimate for $u_i$. 

$$\frac{I}{VI} = \frac{H_a}{UR_t} \ll 1 \quad \text{(D.8)}$$

$$\frac{II}{VI} = \frac{II}{VI} = \frac{H_a}{R} \ll 1 \quad \text{(D.9)}$$

$$\frac{V}{VI} = \frac{H_a}{R^2} \ll 1 \quad \text{(D.10)}$$
\[
\begin{align*}
\tau_g &= \tau_l \\
\frac{du^{(g)}}{dz} &= \frac{du^{(l)}}{dz} \\
\mu_g \frac{u_g - u_i}{H_g} &\sim \frac{\mu_l u_i}{R} \\
\implies u_i &\sim \frac{u_g}{1 + \frac{H_g \mu_l}{R \mu_g}} \tag{D.12}
\end{align*}
\]

Taking \(H_g \sim 5 \mu m, R \sim 2.12 mm, \mu_g = 3.1 \times 10^{-5} \text{ Pa.s} \) and \(\mu_g = 8.9 \times 10^{-4} \text{ Pa.s} \), we obtain

\[
u_i \sim 0.9u_g \tag{D.13}
\]

### D.3 Effective Mass Transfer Resistance in a Degassing Drop

The mass transfer of CO\(_2\) in the drop and the surrounding environment are given by the following equations.

\[
\begin{align*}
\frac{dm}{dt} &= k_l A_d (c_l - c_s^l) \tag{D.14} \\
\frac{dm}{dt} &= k_a A_d (c_s^a - c_e^a) \tag{D.15}
\end{align*}
\]

where \(A_d\) is the total surface area of the drop, \(c_s^l\) is the liquid-side surface concentration of CO\(_2\), \(c_s^a\) is the air-side surface concentration of CO\(_2\) and \(c_e^a\) is the environmental concentration of CO\(_2\). Figure D-1 shows a schematic of the expected concentration profile of CO\(_2\) inside the drop and in the environment. The air-side concentrations of CO\(_2\) in Equation D.15 can be related to the liquid-side concentration of CO\(_2\) using the Henry’s law constant, \(k_H\).
Figure D-1: Schematic of the variation of CO$_2$ concentration inside and outside a carbonated water drop.

\[
\frac{dm}{dt} = k_a A_d (c_s^a - c_e^a) \\
= k_a A_d \left( \frac{P_{CO_2,s} M_{CO_2}}{R_{gas} T} - \frac{P_{CO_2,e} M_{CO_2}}{R_{gas} T} \right) \\
= k_a A_d \left( c_s^a \frac{k_H M_{CO_2}}{R_{gas} T} - c_e^a \frac{k_H M_{CO_2}}{R_{gas} T} \right) \\
= \left( k_a \frac{k_H M_{CO_2}}{R_{gas} T} \right) A_d (c_s^l - c_e^l) \\
= k_a k_H^* A_d (c_s^l - c_e^l) \\
\text{(D.16)}
\]

where $M_{CO_2}$ is the molecular mass of CO$_2$, $R_{gas}$ is the Universal Gas constant, $T$ is the absolute temperature of the air, $k_H^* = k_H M_{CO_2} / R_{gas} T$ is the non-dimensionalized Henry’s law constant, and $c_e^l$ is the dissolved concentration of CO$_2$ in the liquid when at equilibrium with the CO$_2$ concentration in the environment.

Thus the equivalent mass transfer resistance can be found by assuming that mass
transfer rate is constant from the drop interior to the environment.

\[
\frac{\text{dm}}{\text{dt}} \frac{1}{k_{\text{eff}}A_d} = \frac{\text{dm}}{\text{dt}} \frac{1}{k_l A_d} + \frac{\text{dm}}{\text{dt}} \frac{1}{k_a k_H^* A_d}
\]

\[
\Rightarrow \frac{1}{k_{\text{eff}}} = \frac{1}{k_l} + \frac{1}{k_a k_H^*}
\]

(D.17)
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