Dynamic Wetting of Soft Materials and Applications of Dynamic Tensiometry

by

Justin Alan Kleingartner

B.S. Chemical Engineering
Iowa State University, 2010

M.S. Chemical Engineering Practice
Massachusetts Institute of Technology, 2013

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Signature redacted

Author: ...............................................

Department of Chemical Engineering
August 14, 2015

Signature redacted

Certified by: ...........................

Robert E. Cohen
St. Laurent Professor of Chemical Engineering
Thesis Supervisor

Signature redacted

Certified by: ...........................

Gareth McKinley
School of Engineering Professor of Teaching Innovation
Thesis Supervisor

Signature redacted

Accepted by: ...........................

Richard D. Braatz
Edwin R. Gilliland Professor of Chemical Engineering
Chairman, Committee for Graduate Students
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Abstract

Surfaces and interfaces pervade our world and understanding the phenomena that occur at them is imperative for a wide range of commercial and industrial applications. This thesis focuses on investigating the influence of physical and chemical parameters on surface wettability and characterizing interfacial phenomena in a range of solid-liquid systems. In particular, a surface characterization technique (dynamic tensiometry) has been extended to provide further insight into the wetting properties of liquid-repellent surfaces, and the efficacy of engineered surfaces for applications in drag reduction, oleophobic fabric design and fog harvesting is detailed.

Goniometric techniques traditionally quantify two parameters, the advancing and receding contact angles, that are useful for characterizing the wetting properties of a solid surface; however, dynamic tensiometry can provide further insight into the wetting properties of a surface. A framework for analyzing tensiometric results will be detailed that allows for the determination of wetting hysteresis, wetting state transitions, and characteristic topographical length scales on textured, nonwetting surfaces, in addition to the more traditional measurement of apparent advancing and receding contact angles.

Switchable polymer multilayer coatings were prepared that reversibly and repeatedly rearrange from hydrophobic to hydrophilic (or vice versa) when contacted with water (or air). By examining the time evolution of the water contact angle at various temperatures, the apparent activation energy for the forward surface rearrangement ($E_{a,f}$) can be determined. Further insight can be gained into the kinetics of this surface reconstruction process by utilizing dynamic tensiometry to measure the evolution in the contact angle of a liquid meniscus at several rates and temperatures as it advances or recedes over the multilayer films.

Next, the efficacy of engineered surfaces for three applications is explored. First, the ability of a superhydrophobic surface to reduce skin friction in turbulent Taylor-Couette flow is investigated. A reduction in the wall shear stress measured at the rotating inner cylinder is demonstrated by depositing sprayable superhydrophobic microstructures on the inner rotor surface. The magnitude of skin friction reduction
becomes progressively larger as $Re$ increases with a decrease of 22% observed at $Re = 80,000$.

I next detail a framework for designing robust hierarchically textured oleophobic fabrics. The liquid repellency of woven and nano-textured oleophobic fabrics is analyzed using a nested model with $n$ levels of hierarchy that is constructed from modular units of cylindrical and spherical building blocks. For a plain-woven mesh comprised of chemically treated fiber bundles ($n = 2$), the tight packing of individual fibers in each bundle imposes a geometric constraint on the maximum oleophobicity that can be achieved solely by modifying the surface energy of the coating. I demonstrate how the introduction of an additional higher order micro/nano-texture on the fibers ($n = 3$) is necessary to overcome this limit and create more robustly non-wetting fabrics.

Finally, previous work on fog harvesting is expanded at both the lab and pilot scales. The methodology for coating lab scale meshes is scaled up, allowing standard fog collectors (SFCs) to be coated, which are currently being deployed in the field for real world testing. Furthermore, a lab scale fog harvesting apparatus is used to investigate how mesh wire geometry affects the prevalence of mesh clogging and observe that thin rectangular wires show promise in reducing the effect of clogging for a given fog mesh spacing.

Thesis Supervisor: Robert E. Cohen
Title: St. Laurent Professor of Chemical Engineering

Thesis Supervisor: Gareth H. McKinley
Title: School of Engineering Professor of Teaching Innovation
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Chapter 1

Introduction

1.1 Wetting: Surface Chemistry and Roughness

The wettability of a solid surface by a probe liquid is driven by two factors: the surface energy and the surface roughness.\(^1\)\(^-\)\(^9\) For flat, chemically homogeneous surfaces, such as the surface depicted in Fig. 1-1, the equilibrium contact angle (\(\theta\)) has been determined by Young using a force balance:\(^10\)

\[
\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}
\]

where \(\gamma_{sv}\), \(\gamma_{sl}\), and \(\gamma_{lv}\) are the interfacial tensions of the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively. However, in practical applications surfaces are generally neither flat nor chemically homogeneous. Physical roughness and chemical heterogeneities give rise to contact angle hysteresis and several observed wetting

![Figure 1-1: Schematic of a partially wetting liquid drop (with surface tension \(\gamma_{lv}\)) on a flat chemically homogeneous surface (with surface energy \(\gamma_{sv}\)) exhibiting an equilibrium contact angle of \(\theta_E\). The solid-liquid interfacial energy is \(\gamma_{sl}\).](image-url)
regimes. Contact angle hysteresis manifests itself when the three-phase contact line becomes pinned on a physically or chemically heterogeneous surface. For a pinned contact line, a range of contact angles, including the equilibrium contact angle, will be observed before the contact line de-pins and advances or recedes.

Two models predict how surface roughness alters the observed apparent contact angle ($\theta^*$) from the equilibrium value ($\theta$) predicted by Young for a flat surface. For strongly nonwetting, rough (or textured) surfaces, a probe liquid will not penetrate the texture asperities. Instead, the liquid will rest on a composite solid-air interface, which is referred to as the Cassie-Baxter state, which is shown schematically in Fig. 1-2a.

The apparent contact angle for a liquid resting on this composite interface is given by the Cassie-Baxter relation:

$$\cos \theta^* = r \phi_s \cos \theta - 1 + \phi_s \quad (1.2)$$
where \( r_s \phi_s \) is the total area of the solid-liquid interface divided by the projected area and \( \phi_s \) is the wetted solid fraction. Extreme nonwetting (or super-repellency) can be obtained from surfaces with small solid fractions \( (\phi_s << 1) \), even for surfaces with hydrophilic equilibrium contact angles \( (\theta < 90^\circ) \). If the liquid penetrates the surface asperities, then it assumes the Wenzel state shown in Fig. 1-2b. The apparent contact angle for an imbibed liquid is given by the Wenzel relation:

\[
\cos \theta^* = r_w \cos \theta
\]  

(1.3)

where \( r_w \) is the ratio between the total solid-liquid area and the projected area. The actual solid-liquid area will always be greater than or equal to the projected area, and therefore \( r \geq 1 \). As a result, Wenzel drops will have their current wetting state enhanced (i.e., hydrophilic drops will become more hydrophilic and hydrophobic drops will become more hydrophobic). Probe liquids in the Wenzel state are found to pin more readily than those in the Cassie-Baxter state, and as a result are found to have increased surface adhesion.

1.2 Stability of Wetting States

The stability of the two aforementioned wetting states can be investigated by performing a free energy analysis of a liquid drop on a surface. The Wenzel relation (given in Eq. 1.2) becomes unphysical \( (\cos \theta^* < -1) \) for extremely rough (large \( r \)) or extremely hydrophobic (large \( \theta \)) surfaces. Therefore, as the equilibrium contact angle \( (\theta) \) increases the thermodynamically stable wetting state will be the Cassie-Baxter regime. The critical contact angle \( (\theta_c) \) between these two wetting regimes can be found by equating eq 1.2 and 1.3:

\[
\cos \theta_c = \frac{\phi_s - 1}{r_w - r_s \phi_s}
\]  

(1.4)

For contact angles, \( \theta \), greater (less) than the critical value, \( \theta_c \), an interfacial free energy analysis shows the Cassie-Baxter (Wenzel) regime is the thermodynamically...
stable state. However, meta-stable Cassie-Baxter drops can be observed for contact angles less than the critical value. Additionally, for low surface tension liquids, reentrant surface texture (e.g., the textural features seen in Fig. 1-2) is required to obtain robust meta-stable Cassie-Baxter states (thermodynamically stable Cassie-Baxter states are not attainable for low surface tension liquids because \( \theta < 90^\circ \) for all known surfaces).

Perturbations to meta-stable Cassie-Baxter state drops, such as an applied pressure differential across the interface, can force a transition to the Wenzel regime. A dimensionless parameter \( A^* \) has been developed to predict the robustness of meta-stable Cassie-Baxter interfaces. The dimensionless robustness parameter \( A^* \) is the ratio of the breakthrough pressure (the pressure required to disrupt the Cassie-Baxter interface and cause imbibition of the probe liquid into the surface texture) and a characteristic reference pressure, defined as \( P_{\text{ref}} = 2\gamma_{lv}/\ell_{\text{cap}} = 2\sqrt{\rho_l g/\gamma_{lv}} \), where \( \rho_l \) is the probe liquid density and \( g \) is the gravitational acceleration. For periodic surface texture of horizontally aligned cylinders the robustness parameter is given as:

\[
A^* = \frac{P_{\text{breakthrough}}}{P_{\text{ref}}} = \frac{\ell_{\text{cap}}}{R(D^* - 1)} \left[ \frac{1 - \cos \theta}{D^* - 1 + 2 \sin \theta} \right] \tag{1.5}
\]

where \( D^* = (R + D)/R \) is the dimensionless spacing ratio, \( R \) is the radius of the cylindrical features, \( D \) is half the gap between the surface features and \( \ell_{\text{cap}} = \sqrt{\gamma_{lv}/\rho_l g} \). Large values of \( A^* \) correlate to robust Cassie-Baxter interfaces, but as the value of the robustness parameter passes through unity a breakdown of the composite interface is predicted. The robustness parameter \( A^* \) allows for the rational design of robust nonwetting surfaces.

1.3 Thesis Outline

My thesis focuses on investigating the influence of physical and chemical parameters on surface wettability and characterizing interfacial phenomena in a range of solid-liquid systems. First, I demonstrate how a technique for characterizing interfacial phenomena (dynamic tensiometry) can be extended to provide enhanced insight into
the wetting properties of liquid-repellent surfaces. Traditionally, surfaces are interro-
gated by placing probe liquids of interest on the surface and measuring the resulting
advancing and receding contact angle via goniometric techniques. I detail a frame-
work for analyzing tensiometric results that allows for the determination of wetting
hysteresis, wetting state transitions, and characteristic topographical length scales on
textured, nonwetting surfaces, in addition to the more traditional measurement of
apparent advancing and receding contact angles.

Some surfaces have the ability to alter their surface chemistry in response to
environmental stimuli.\textsuperscript{24-27} I investigate one type of these surfaces, switchable polymer
multilayer coatings, that reversibly and repeatedly rearrange from hydrophobic to
hydrophilic (or \textit{vice versa}) when contacted with water (or air). Dynamic tensiometry
is again used to provide further insight into the kinetics of this surface reconstruction
process by quantifying the evolution in the contact angle of a liquid meniscus at
several rates and temperatures as it advances or recedes over the multilayer films. A
simple first-order thermally-activated rate process is employed to describe the forward
and reverse surface reconstruction and enables the shape of the measured tensiometric
force curves during repeated immersion and emersion to be predicted quantitatively.

Next, I turn to three application-oriented projects that benefit from the design
and utilization of properly engineered coatings (with uniquely tuned surface chemistry
and roughness): utilizing superhydrophobic surfaces to obtain skin friction reduction
in turbulent flows, designing robust oleophobic fabrics, and scaling up lab-based fog
harvesting meshes for real world testing. In the first project, the air trapped at the in-
terface (know as a plastron), which is characteristic of all superhydrophobic surfaces,
allows for slip at the interface leading to a reduction in the measured skin friction. In
the next project, the inherent hierarchical nature of commercially available woven fab-
rics allows for a plastron to be maintained even in the presence of low surface tension
liquids. Previous work by other researchers\textsuperscript{28,29} is extended to develop a framework
that allows for the rational design of robustly nonwetting oleophobic fabrics. Finally,
past work on designing fog harvesting meshes with enhanced efficiency is extended
and scaled-up for field testing.
Chapter 2

Utilizing dynamic tensiometry to quantify contact angle hysteresis and wetting state transitions on nonwetting surfaces


Goniometric techniques traditionally quantify two parameters, the advancing and receding contact angles, that are useful for characterizing the wetting properties of a solid surface; however, dynamic tensiometry, which measures changes in the net force on a surface during the repeated immersion and emersion of a solid into a probe liquid, can provide further insight into the wetting properties of a surface. We detail a framework for analyzing tensiometric results that allows for the determination of wetting hysteresis, wetting state transitions, and characteristic topographical length scales on textured, nonwetting surfaces, in addition to the more traditional mea-
surement of apparent advancing and receding contact angles. Fluorodecyl POSS, a low-surface-energy material, was blended with commercially available poly(methyl methacrylate) (PMMA) and then dip- or spray-coated onto glass substrates. These surfaces were probed with a variety of liquids to illustrate the effects of probe liquid surface tension, solid surface chemistry, and surface texture on the apparent contact angles and wetting hysteresis of nonwetting surfaces. Woven meshes were then used as model structured substrates to add a second, larger length scale for the surface texture. When immersed into a probe liquid, these spray-coated mesh surfaces can form a metastable, solid-liquid-air interface on the largest length scale of surface texture. The increasing hydrostatic pressure associated with progressively greater immersion depths disrupts this metastable, composite interface and forces penetration of the probe liquid into the mesh structure. This transition is marked by a sudden change in the wetting hysteresis, which can be systematically probed using spray-coated, woven meshes of varying wire radius and spacing. We also show that dynamic tensiometry can accurately and quantitatively characterize topographical length scales that are present on microtextured surfaces.

2.1 Introduction

Extremely nonwetting surfaces have attracted great interest for their potential in many commercial and industrial applications, such as self-cleaning,4,5,30,31 drag reduction,32–35 and oil-water separation.19,36,37 To facilitate the design of nonwetting surfaces, which have apparent advancing contact angles $\theta^* > 90^\circ$, accurate and reliable methods for the characterization of both static and dynamic surface wetting properties are necessary. Goniometric techniques are most frequently used to characterize surface wetting properties, but they suffer from significant measurement variability when quantifying high apparent contact angles ($\theta^* > 160^\circ$) as a result of gravity-induced sagging that leads to challenges in imaging the meniscus as $\theta^* \rightarrow 180^\circ$.38–40 Several studies have been carried out to compare the accuracy and precision of various tensiometric and goniometric methods,41,42 but no universally accepted best method.
has emerged for measuring liquid contact angles.\textsuperscript{43-48} In this work, we explore a framework for analyzing tensiometric results and investigate the utility of dynamic tensiometry as a means to probe wetting state transitions, wetting hysteresis and the role of different topographical length scales on nonwetting surfaces.

Typically a range of contact angle values is observed for a given probe liquid on a smooth solid surface, bounded by the advancing ($\theta_{adv}$) and receding ($\theta_{rec}$) contact angles.\textsuperscript{42,49,50} The difference between these bounds is the contact angle hysteresis ($CAH = \cos \theta_{rec} - \cos \theta_{adv}$). For the case of a textured solid surface, the wetting behavior of a selected probe liquid depends on both the solid surface energy and the surface roughness.\textsuperscript{1-6,8,9,51,52} When the solid surface energy is low and the surface exhibits re-entrant topography, extremely nonwetting surfaces with very high apparent contact angles ($\theta_{adv} > 150^\circ$) and low contact angle hysteresis ($\theta_{adv} - \theta_{rec} < 10^\circ$) can be obtained for a wide range of liquid surface tensions.\textsuperscript{11,19,53} In general, a probe liquid can interact with surface texture (altering the apparent contact angle from the flat surface equilibrium value, $\theta_{eq}$, predicted by Young\textsuperscript{10}) in one of two ways:\textsuperscript{5} imbibition of the probe liquid into the texture (the Wenzel\textsuperscript{2} state) or formation of a composite, solid-liquid-air interface on the texture (the Cassie-Baxter\textsuperscript{3} state). The Cassie-Baxter state can often be visually observed through the reflective nature of the trapped air layer or ‘plastron’ on a textured surface.\textsuperscript{54} Droplets of probe liquid that sit on the surface in the Wenzel state pin more readily than those in the Cassie-Baxter state, resulting in increased surface adhesion and consequently increased contact angle hysteresis.\textsuperscript{4}

The conditions controlling the transition between the Cassie-Baxter and Wenzel states depend on both the surface chemistry and the length scale of the surface texture.\textsuperscript{5,30} It is now widely recognized\textsuperscript{55,56} that properly applying a smaller length scale of texture on top of a larger textural structure (creating hierarchical textural elements)\textsuperscript{29} leads to the formation of more robust nonwetting states. This is illustrated in Figure 2-1 with a steel mesh that has been spray-coated with a low surface energy coating\textsuperscript{57} to create a two-length scale structure, which has then been immersed in water. The plastron is clearly visible as a silvery film. The increase in hydrostatic
Figure 2-1: (A) Scanning electron microscopy image of a spray-coated stainless steel mesh \( (R = 127 \, \mu m \text{ and } D = 330 \, \mu m) \) which forms a surface with hierarchical texture (scale bar = 200 \( \mu m \)). The sprayed corpuscles have a droplet diameter \( d \approx 20 \, \mu m \).\(^{57}\) (B) Spray-coated mesh undergoing a transition from the Cassie-Baxter to the Wenzel regime on the largest textural length scale. A “macroplastron” is observable until the hydrostatic pressure forces a wetting state transition on the largest (mesh) scale. A “microplastron” (indicating a Cassie-Baxter state on the smaller textural length scale) is still observable on the individual, spray-coated wires of the mesh.

Pressure with immersion depth causes a wetting transition on the larger length scale of the mesh, while a finer scale “microplastron” remains on the individual wires of the mesh and is stabilized by contact line pinning on the finer-scale sprayed structure. Similar transitions between micro- and nano-Cassie-Baxter states have been documented on other hierarchically textured surfaces.\(^{58}\) Probing and quantifying such transitions through a single measurement of an integrated quantity, such as an apparent contact angle \( (\theta^*) \), is clearly insufficient. In the present work we develop a quantitative analysis of the net tensile force exerted by a liquid on a plate, mesh, or other object during an immersion and emersion cycle, and we explain the sequence of observed force transitions expected as the plastron (characterizing the Cassie-Baxter state) is progressively displaced with increasing immersion depth.

### 2.1.1 Stability of wetting states

A free energy analysis of a liquid drop on a solid surface shows that there is a critical equilibrium contact angle for a given solid-liquid system below (above) which liq-
uid drops are in a thermodynamically stable Wenzel (Cassie-Baxter) state.\textsuperscript{4,12,17,19,22} However, metastable Cassie-Baxter drops can also be observed for contact angles less than the critical value.\textsuperscript{4,8,9} Perturbations to metastable Cassie-Baxter interfaces, such as externally imposed vibrations or pressure perturbations, can force an irreversible transition to the Wenzel regime.\textsuperscript{4,59} A dimensionless parameter $A^*$ has been developed to quantify the resistance of a textured surface to this transition.\textsuperscript{11,22,23} The magnitude of $A^*$ is a direct measure of the robustness of the metastable Cassie-Baxter interface to a Wenzel transition. This dimensionless robustness parameter is the ratio of the "breakthrough pressure" $\Delta p_b$ (i.e., the external pressure difference required to disrupt the Cassie-Baxter interface and cause imbibition of the probe liquid into the surface texture) and a characteristic reference pressure $p_{\text{ref}} = 2\gamma_{lv}/\ell_{\text{cap}}$, where $\ell_{\text{cap}} = (\gamma_{lv}/\rho_l g)^{1/2}$ is the capillary length of the liquid, $\gamma_{lv}$ is the liquid-vapor surface tension, $\rho_l$ is the probe liquid density, and $g$ is the gravitational acceleration. For the simplest case of a periodic, cylindrical surface texture with a single characteristic length scale ($2R$ in Figure 2-1a) the robustness parameter is given by the following expression:\textsuperscript{22}

$$A^* = \frac{\Delta p_b}{p_{\text{ref}}} = \frac{\ell_{\text{cap}}}{R(D^* - 1)} \left[ \frac{1 - \cos \theta}{D^* - 1 + 2 \sin \theta} \right]$$

(2.1)

where $R$ is the radius of the cylindrical features, $D$ is half the intercylinder spacing, is the three-phase contact angle, and $D^* = (R + D)/R$ is the dimensionless spacing ratio of the texture.

Large values of $A^*$ correlate to highly robust Cassie-Baxter interfaces with large breakthrough pressures (or, equivalently, large breakthrough depths $x_b = \Delta p_b/\rho_l g$ when immersed in a vessel of liquid with density $\rho_l$). As the value of the robustness parameter passes through unity, the composite interface is disrupted and spontaneous imbibition of the probe liquid into the texture is expected. The simple 1-D cylindrical model for $A^*$ given above in eq 2.1 has been shown to be effective in understanding the pressure difference required to disrupt a metastable Cassie-Baxter interface on woven wire meshes,\textsuperscript{23} and these structures are used in the present work as a canonical
example of a hierarchical, textured surface being immersed in a liquid.

Solution spraying\textsuperscript{57} of woven, wire meshes produces extremely nonwetting surfaces with two well-defined and distinct textural length scales. The hierarchical texture allows structured surfaces to exhibit liquid repellency even when moderately wettable surface chemistries are employed.\textsuperscript{29,53,60,61} We use such surfaces to enable systematic investigation of wetting transitions on multiple length scales. Previously, wetting state transitions have been studied on dip-coated, woven meshes using goniometric techniques by systematically varying the mesh spacing and the probe liquid surface tension;\textsuperscript{22,23,36,62} however, dynamic tensiometry permits the controlled imposition of a wetting state transition for a given mesh/liquid combination through an immersion and subsequent emersion cycle.

2.1.2 Dynamic tensiometry of nonwetting surfaces

In a Wilhelmy plate tensiometer, a solid sample is suspended from a sensitive microbalance and a container of probe liquid is raised and lowered at a constant velocity around the sample while the axial force, $F(t)$, acting on the sample and the sample position, $x(t)$, relative to the free surface datum are measured. A comprehensive analysis for the full immersion and emersion of a nonwetting and wetting plate in a low viscosity fluid is given by Chappuis and Georges.\textsuperscript{63} A schematic representing a partially immersed plate with a nonwetting surface is shown in Figure 2-2.

In general, three forces are at play in the tensiometer system: interfacial, viscous, and buoyant. For small values of the capillary number ($Ca = \mu U/\gamma_{lv} \ll 1$, where $U = \dot{x}$ is the immersion velocity and $\mu$ is the liquid viscosity), the effect of viscous shear stress exerted by the fluid on the surface of the wetted solid can be neglected.\textsuperscript{64} As a result, the net force on a sample in the tensiometer system is $F = P\gamma_{lv}\cos\theta^* - \rho g Ax$, where $P = 2(t + w)$ is the length of the solid-liquid-air contact line, $A = tw$ is the cross-sectional area of the solid plate, and $x$ is the immersed depth of the solid. Although interpretation of wetting hysteresis data is clearest when the planar test substrates being immersed are textured or chemically treated on both sides, in principle, the sensitivity of the force transducer makes it possible to probe changes in
the contact angle hysteresis for surfaces that are patterned on a single side only. In this case, two separate measurements need to be made: one for the untextured test substrate followed by an identical immersion/emersion cycle on the substrate after patterning/surface treatment. The difference between the two signals is a measure of the changes in the wetting characteristics that are induced by the surface treatment.

To enable comparison of different surfaces and liquids, the resultant tensiometric force can be scaled by $P_{\gamma lv}$, which is the magnitude of the maximum interfacial force in the vertical direction (occurring when $\theta^* = 0^\circ$ or $180^\circ$). Likewise, it is appropriate to scale the immersion depth $x$ by $\sqrt{2} \ell_{cap}$, the maximum height of the meniscus, which occurs when $\theta^* = 0^\circ$ or $180^\circ$. This scaling yields the dimensionless force balance

\[
\hat{F} = \cos \theta^* - B \hat{x}
\]

where $\hat{F} = F/P_{\gamma lv}$ is the nondimensionalized force, $\hat{x} = x/\sqrt{2} \ell_{cap}$ is the nondimensionalized immersion depth, and $B = \sqrt{2}A/P\ell_{cap}$ is a dimensionless group characterizing the magnitude of the buoyant force in the system. For $B \ll 1$ (e.g., thin fibers or very thin sheets for which $A \ll P\ell_{cap}$) the buoyant force can be neglected.\(^{66}\)
but this is not the case in the present work.

A force trace, \( \hat{F}(\hat{x}) \), for an immersion/emersion cycle with a model nonwetting surface is shown in Figure 2-3. We first seek to describe the separate physical processes that govern the shape of this curve and the locus of points \( \text{ABCDEA} \). When a nonwetting surface first contacts the probe fluid in the tensiometer, the liquid pins on the advancing edge of the solid and the meniscus bends as indicated in Figure 2-2. Because the surface is nonwetting, we expect \( \theta^* > 90^\circ \) and the initial tensile force from eq 2.2 is thus negative, \( \hat{F} < 0 \). The resultant force during initial development of the meniscus is \( \hat{F} = \cos \theta^*(\hat{x}) - B\hat{x} \), which is shown as segment AB in Figure 2-3. The instantaneous contact angle, \( \theta^*(\hat{x}) \), can be determined from the shape of the meniscus in contact with the vertically aligned solid. The Young-Laplace equation for the profile of a meniscus on a vertical plate can be written in Cartesian coordinates in the form: \(^{67}\)

\[
2\hat{x} = \frac{d^2\hat{x}/d\hat{y}^2}{[1 + (d\hat{x}/d\hat{y})^2]^{3/2}} \quad (2.3)
\]

where \( \hat{x} \) is the dimensionless vertical displacement of the meniscus from the flat probe liquid surface, and \( \hat{y} = y/\sqrt{2\ell_{\text{cap}}} \) provides the horizontal position of the meniscus from the sample surface (as indicated in Fig 2-2). This result can be integrated with the boundary condition \( d\hat{x}/d\hat{y} = \hat{x} = 0 \) when \( \hat{y} \to \infty \), which yields an equation for the slope of the liquid meniscus:

\[
\frac{d\hat{x}}{d\hat{y}} = \sqrt{\left(\frac{1}{1 - \hat{x}^2}\right)^2 - 1} \quad (2.4)
\]

For \( Ca \ll 1 \), the curvature of the meniscus will only depend on the contact angle at the solid surface. \(^{67,68}\) Therefore, the slope of the meniscus profile at the solid surface, \( \frac{d\hat{x}}{d\hat{y}}|_{\hat{y}=0} \), will be effectively at equilibrium during slow immersion/emersion and eq 2.4 can be directly related to the instantaneous contact angle, denoted \( \theta(\hat{x}) \), during the development of the pseudo-steady meniscus shape (see Fig 2-2):

\[
\frac{d\hat{x}}{d\hat{y}}|_{\hat{y}=0} = -\cot \theta \quad (2.5)
\]
Figure 2-3: Model of the dimensionless force trace for an ideal solid sample with advancing and receding water contact angles of $130^\circ$ and $110^\circ$, respectively, and $B = 0.25$. Line segment AB corresponds to the formation of the nonwetting meniscus with the contact line pinned at the leading edge of the immersing sample. At B, the contact angle reaches the advancing value and the contact line depins. The sample immerses into the probe liquid from B to C with an apparent contact angle $\theta^*_\text{adv}$. The direction is reversed at C, and the contact line pins while the contact angle decreases to the receding value, $\theta^*_\text{rec}$, which is achieved at point D. Line segment DE represents the equilibrium emersion of the sample from the liquid with $\theta^* = \theta^*_\text{rec}$. The contact line pins on the leading edge of the solid sample at E and the contact angle decreases below the receding angle until the sample emerges beyond the surface of the probe liquid. The shaded region denotes the wetting hysteresis, $\mathcal{H}$.

Substituting eq 2.5 into eq 2.4 thus yields an explicit relationship for the instantaneous contact angle as a function of the vertical displacement of the meniscus, $\dot{x}$:

$$\theta^*(\dot{x}) = 180^\circ - \arcsin[1 - \dot{x}^2] \quad (2.6)$$

The meniscus curvature increases until the instantaneous contact angle, $\theta^*(\dot{x})$, increases to the value of the advancing contact angle, $\theta^*_\text{adv}$, at which point the interface depins from the advancing edge, and a steady advancing state is subsequently observed with a constant value of meniscus deflection, $x_{\text{adv}}$ (Figure 2-2). The sub-
merged depth at which the contact line depins and begins to advance is given by rearrangement of eq 2.6:

$$\hat{x}_{adv} = \sqrt{1 - \sin\theta_{adv}^*}$$  \hspace{1cm} (2.7)

The slope of the tensiometric force trace at this point is obtained by evaluating the derivative of the force, given in eq 2.2 at $x = \hat{x}_{adv}$ (where $\theta^*(\hat{x}) = \theta_{adv}^*$):

$$\left.\frac{d\hat{F}}{d\hat{x}}\right|_{\theta^* = \theta_{adv}^*} = \frac{-2\sin\theta_{adv}^*}{\sqrt{1 + \sin\theta_{adv}^*}} - B$$  \hspace{1cm} (2.8)

Therefore, for a surface with $\theta^* > 90^\circ$, the maximum (least negative) slope of the force trace occurs at the moment of depinning and can be no greater than $-B$, which is the value of $d\hat{F}/d\hat{x}$ when $\theta_{adv}^* = 180^\circ$.

Once the contact line depins, a linear relationship for the force $\hat{F}_{adv} = \cos\theta_{adv}^* - B\hat{x}$ (segment BC in Figure 2-3) is obtained. Upon switching from immersion to emersion (point C in Figure 2-3), the contact line again becomes pinned resulting in a transient period during which the contact angle decreases from the advancing value to the receding value (segment CD in Figure 2-3). Once the contact angle reaches the receding angle, $\theta^*(\hat{x}) \to \theta_{rec}^*$, the contact line again depins and the resulting force varies linearly during the emersion phase $\hat{F}_{rec} = \cos\theta_{rec}^* - B\hat{x}$ (segment DE in Figure 2-3).

The advancing and receding contact angles for a flat, nonwetting substrate can thus be extracted by fitting the steady advancing and receding force balances to the linear portions of the immersion (segment BC) and emersion (segment DE) force traces, respectively. However, for textured surfaces where the wetted perimeter is not known, eq 2.7 can be used to determine the apparent advancing contact angle and concomitantly provide an estimate of the wetted perimeter (i.e., the length of the three-phase contact line) upon rescaling of the linear advancing force data. Dynamic tensiometry also allows for the clear visualization of wetting hysteresis (shaded region in Figure 2-3). This quantity can be defined as the area enclosed by the tensiometry curves and evaluated as follows:
\[ H \equiv \frac{\sqrt{2\ell_{cap}}}{L} \int F \, d\hat{x} \]

\[ = \frac{1}{(\hat{x}_2 - \hat{x}_1)} \left[ \int_{\hat{x}_1}^{\hat{x}_2} F_{em}(\hat{x}) \, d\hat{x} - \int_{\hat{x}_1}^{\hat{x}_2} F_{im}(\hat{x}) \, d\hat{x} \right] \quad (2.9) \]

where \( \hat{F}_{em}(\hat{x}) \) and \( \hat{F}_{im}(\hat{x}) \) are the experimental force traces measured during emersion and immersion, respectively, and \( L = x_2 - x_1 \) is the distance over which the hysteresis is computed (typically, but not always, corresponding to the maximum immersion depth). For an ideal tensiometric system, such as that shown in Figure 2-3 with linear segments BC and DE, eq 5.6 can be reduced to the familiar definition of contact angle hysteresis \( H = \cos \theta_{rec} - \cos \theta_{adv} \). However, eq 5.6 can be applied much more generally; specifically, if wetting/dewetting transitions take place at different immersion depths, this will result in measurable changes to the slope of the force-displacement curves as well as changes in the hysteresis of the dynamic wetting process. Tensiometry thus provides a powerful way of probing Cassie-Baxter to Wenzel transitions on textured and patterned surfaces.

### 2.2 Materials and Methods

#### 2.2.1 Materials

The probe liquids used for the wetting/dewetting studies were glycerol (≥ 99%, Sigma-Aldrich), hexadecane (99%, Sigma-Aldrich), and heptane (99%, Sigma-Aldrich), which were used as received. Deionized water (18.2 MΩ·cm) was purified using a Millipore Milli-Q Academic A10 purification system. Poly(methyl) methacrylate (PMMA, Scientific Polymer Products, \( M_w = 102 \) kg mol\(^{-1} \) and \( M_w = 540 \) kg mol\(^{-1} \)) was used as received and 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsesquioxane (fluorodecyl POSS, \( \gamma_{sv} \approx 10 \) mJ m\(^{-2} \)) was synthesized using previously reported protocols. The hydrochlorofluorocarbon solvent Asahiklin AK-225 (Asahi Glass Company) was used to prepare solutions of PMMA and fluorodecyl POSS for dip- and spray-coating applications. Standard (soda lime) glass microscope
slides (VWR, 75 mm × 25 mm × 1 mm) and commercially available stainless steel woven meshes (McMaster-Carr) were used as substrates for the dip and spray-coating processes. The glass microscope slides were cleaned by successive sonication in a 4% (v/v) solution of Micro-90 (International Products Co.), 1 N sodium hydroxide (BDH), and deionized water for 15 min prior to coating. The stainless steel woven meshes were coated as received.

2.2.2 Sample preparation

Cleaned glass microscope slides and stainless steel woven meshes were used as substrates for the spray- and dip-coating processes. To produce the dip-coated samples, the substrates were immersed for 60 min in an Asahiklin AK-225 solution of POSS/PMMA followed by 30 min of air drying, a second 60 min immersion, and a final 30 min drying. The solution contained 20 mg/mL of dissolved solids at a 50/50 POSS/PMMA ($M_w = 540$ kg mol$^{-1}$) weight ratio. The spray coated samples were prepared using a previously reported solution-spraying technique. The spraying solution contained 50/50 (by weight) POSS/PMMA ($M_w = 102$ kg mol$^{-1}$) dissolved in Asahiklin AK-225 with 50 mg/mL total dissolved solids.

2.2.3 Surface characterization

Static contact angle measurements were performed using a Ramé-Hart model 590 goniometer. Advancing and receding contact angles were measured optically using the circular-segment-fitting technique with drop volumes of $V \approx 10$ μL. The reported contact angle values represent averages over four or more measurements taken at different locations on the sample with the reported uncertainties representing standard deviations of the measurements. Tensiometric force measurements were made using a DCAT 11 (DataPhysics Instruments) dynamic tensiometer. The glass slide and woven mesh samples were probed at a velocity of $U = 0.1$ mm/s and $U = 0.2$ mm/s, and a sampling frequency of 50 and 5 Hz, respectively. All probe liquids were held at $20.0 \pm 0.2^\circ$ C, except for heptane which was held at $2.0 \pm 0.2^\circ$ C to prevent
significant evaporation during the time scale of the experiment. The hysteresis \( \mathcal{H} \), defined in eq 5.6, was computed by trapezoidal numerical integration of the experimental tensiometric data. The surface topography of the spray-coated samples was investigated using a JSM-6060 scanning electron microscope (JEOL) operated at an accelerating voltage of 5 kV. The specimens were sputter coated with \( \sim 10 \) nm of gold before imaging. Atomic force microscopy measurements were made in tapping mode with a Dimension 3100 instrument (Veeco Metrology Group).

2.3 Results and Discussion

2.3.1 Effects of chemistry and roughness on hysteresis

Surface chemistry and texture play critical and complementary roles in designing robustly nonwetting surfaces. To demonstrate this, we use dip- and spray-coating techniques to systematically control how we impart a low solid-phase surface energy and surface texture to standard glass microscope slides. Two flat surfaces with differing surface chemistries and two chemically equivalent surfaces (one with a controlled surface texture and one nominally flat surface) were fabricated.

To examine the effects of texture, solutions of 50/50 (by weight) PMMA/POSS solution were either dip- or spray-coated onto glass slide substrates to produce flat and textured surfaces, respectively, with the same low-energy surface chemistry. The tensiometric force traces are compared in Figure 2-4. The differing slopes of the immersion and emersion lines in Figure 2-4A and the area enclosed by the curves (shaded region) show that this flat nonwetting surface exhibits noticeable hysteresis \( \theta_{\text{adv}} = 129^\circ \) and \( \theta_{\text{rec}} = 110^\circ \) even with the extremely low surface energy molecule fluorodecyl POSS coating. However, the addition of microtexture by applying the PMMA/POSS solution as a spray-on coating promotes the establishment of a stable composite Cassie-L"{A}Baxter interface which increases the observed advancing and receding contact angle significantly (i.e., the value of the measured force \( \hat{F} \) becomes increasingly negative). When the force curve is linearly extrapolated back to the
ordinate axis \( \hat{x} = 0 \), the value of the intercept, denoted \( \hat{F}_0 \), is directly related to the apparent contact angle. The contact angle hysteresis on this spray-coated surface also becomes immeasurably small resulting in a super nonwetting surface (Figure 2-4B).

Using the force balance given in eq 2.2 and the known surface tension of water \( \gamma_{lv} = 72 \text{ mN/m} \) (with the measured macroscopic perimeter of the glass slide \( P_{macro} = 52 \text{ mm} \)), both the immersion and emersion data shown in Figure 2-4B lead to an intercept at \( \hat{x} = 0 \) of \( \hat{F} = -1.02 \), which is unphysical because it corresponds to \( \cos \theta < -1 \). This result suggests that the true value of the wetted perimeter is larger than the nominal macroscopic value; a situation that arises because the three-phase contact line conforms on microscopic length scales to the tortuous corpuscular texture produced by solution spraying (inset Figure 2-4B). To determine the true wetted perimeter, the advancing contact angle can, in principle, be calculated from the position at which the contact line depins (point B in Figure 2-3). For the experimental force trace shown in Figure 2-4B identifying a single point at which the contact line depins is unclear, because the depinning is a distributed event in real systems. However, the average position at which the contact line depins can be unambiguously defined as the point of intersection between the force trace during the initial meniscus formation (segment AB in Figure 2-2) and the straight line that describes the steady advancing portion of the force trace (segment BC). Equation 2.7 can then be used to determine the apparent advancing contact angle. For the spray-coated slide in Figure 2-4B this analysis yields an advancing water contact angle of \( \theta_{adv}^* = 154^\circ \) (by contrast, \( \theta_{adv}^* = 160^\circ \) when determined goniometrically) and thus leads to calculation of the true value of the wetted perimeter, \( P_{micro} = 59.3 \text{ mm} \), which corresponds to a 14% increase over the nominal value obtained from macroscopic measurement of the specimen width and thickness. Dynamic tensiometry can thus be used to measure effective contact angles for extremely nonwetting surfaces where the wetted perimeter is unknown, and this provides insight into the topography traversed by the moving contact line (i.e., the effective tortuosity of the textured coating).

The effects of surface chemistry in the absence of texture were also investigated and are shown in Figure 2-5 (traces I and II). Two glass slides, one uncoated and the other
Figure 2-4: Measured force traces plotted against dimensionless immersion depth for 50/50 (by weight) PMMA/POSS (A) dip-coated and (B) spray-coated glass slides being immersed in water, $l_{cap} = 2.73$ mm. The dip-coated surface in (A) was relatively smooth with a root-mean-square roughness of $R_q = 19.5$ nm measured by atomic force microscopy. Inset in (B) is a micrograph of the textured surfaces prepared by spray-coating (scale bar = 100 $\mu$m).\textsuperscript{57}
Figure 2-5: Measured tensile force plotted against immersed depth for a bare glass slide (red, I), a 50/50 (by weight) PMMA/POSS dip-coated glass slide (green, II), and a 50/50 (by weight) PMMA/POSS spraycoated glass slide (blue, III) immersed in water and the same spraycoated slide immersed in hexadecane (orange, IV).

dip-coated in a 50/50 (by weight) solution of PMMA/POSS present very different surface chemistries. The high surface energy, uncoated glass slide had advancing and receding water contact angles of $\theta_{\text{adv}} = \theta_{\text{rec}} = 0^\circ$ and the tensile force acting on the slide is thus positive (trace I). The low surface energy, dip-coated glass slide has large apparent advancing and receding water contact angles of $\theta_{\text{adv}} = 129^\circ$ and $\theta_{\text{rec}} = 110^\circ$, respectively, and substantial contact angle hysteresis (trace II).

The additional force traces III and IV presented in Figure 2-5 for the low-energy, spray-coated surfaces highlight the effects of liquid surface tension on surface wettability and hysteresis. The increase in contact angle hysteresis (summarized in Table 2.1) of the textured surface when probed with hexadecane (trace IV) compared to water (trace III) is primarily driven by the lower robustness ($A^*$) of the surface to the lower surface tension probe liquid ($\gamma_{\text{hexadecane}} = 27.5$ mN/m compared to $\gamma_{\text{water}} = 72.8$ mN/m). Less robust Cassie-Baxter interfaces are pushed more deeply into the re-entrant micro-texture causing them to pin more readily on physical surface heterogeneities and consequently produce greater contact angle hysteresis on emersion. The
lower robustness of the Cassie-Baxter state for a hexadecane interface is also most apparent in the nonlinear form of the receding force trace (IV), which results from progressive imbibition of the probe liquid into the surface texture with increasing depth. Near the point of maximum immersion depth ($\hat{x} \approx 3.5$) the instantaneous wetting hysteresis associated with the difference in the dimensionless advancing and receding force is $(\hat{F}_{\text{rec}} - \hat{F}_{\text{adv}})|_{\hat{x}=3.5} = 0.056$. At this instant, the meniscus is located at a surface position (relative to the leading edge) of $x = 13.5$ mm and is receding over textured surface that has not been immersed deeply into the hexadecane. By contrast, at the point $\hat{x} = 1.0$ corresponding to a depth near the point at which the advancing interface first depins, the instantaneous wetting hysteresis is increased 5-fold to $(\hat{F}_{\text{rec}} - \hat{F}_{\text{adv}})|_{\hat{x}=1.0} = 0.27$. At this instant, the meniscus is located at a position relative to the leading edge of $x = 3.9$ mm but is now receding over a textured surface that has already been immersed deeply into the fluid.

Table 2.1: Goniometric advancing ($\theta^*_{\text{adv}}$) and receding ($\theta^*_{\text{rec}}$) contact angles, contact angle hysteresis ($CAH = \cos \theta^*_{\text{rec}} - \cos \theta^*_{\text{adv}}$), and wetting hysteresis ($\mathcal{H}$) for six solid/liquid systems. The tensiometric force traces for systems I - IV are presented in Figure 2-5.

<table>
<thead>
<tr>
<th>System</th>
<th>Surface</th>
<th>Liquid</th>
<th>$\theta^*_{\text{adv}}$ (degrees)</th>
<th>$\theta^*_{\text{rec}}$ (degrees)</th>
<th>$CAH \times 10^{-2}$</th>
<th>$\mathcal{H} \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Bare Glass Water</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>II</td>
<td>POSS/PMMA Dip-coated Water</td>
<td>124</td>
<td>118</td>
<td>8.8</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>POSS/PMMA Spray-coated Water</td>
<td>159</td>
<td>157</td>
<td>1.3</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>POSS/PMMA Spray-coated Hexadecane</td>
<td>150</td>
<td>125</td>
<td>29.2</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>POSS/PMMA Dip-coated Hexadecane</td>
<td>79</td>
<td>73</td>
<td>10.7</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>POSS/PMMA Dip-coated Heptane</td>
<td>63</td>
<td>19</td>
<td>49.2</td>
<td>36.0</td>
<td></td>
</tr>
</tbody>
</table>

The integrated effect of these immersion/emersion cycles can be represented by calculating the hysteresis ($\mathcal{H}$) for these surfaces using eq 5.6. Both the superhydrophilic, bare glass (with extremely low water contact angle) and the extremely nonwetting, highly textured surface exhibit essentially no hysteresis in water (systems I and III in Table 2.1 and Figure 2-5). By contrast, when liquids with intermediate values of surface tension are used to probe the solid surfaces, significant hysteresis is apparent. For textured surfaces, imbibition of the probe liquid (e.g., in system IV) can lead to a dependence of the instantaneous wetting hysteresis on immersion depth.
2.3.2 Effects of multiple textural length scales

To demonstrate the changes in wetting hysteresis that can be induced by adding an additional textural length, we use a commercially available stainless steel mesh (wire radius $R = 254 \, \mu m$, weave half-spacing $D = 457 \, \mu m$) as the substrate for the spray-coating process. We use the resulting two-length scale structure to investigate the stability of the Cassie-Baxter state and the collapse of the macro-plastron film shown in Figure 2-1. The Cassie-Baxter regime established when the meniscus advances over the surface is often metastable and as a result can be forced to transition irreversibly to the Wenzel regime under an external pressure perturbation. Dynamic tensiometry allows for the systematic investigation of this transition, since the hydrostatic pressure in the system increases with the immersion depth. However, the challenge faced in deconvoluting the information contained in the measured force trace is that it contains two distinct contributions: a buoyancy term that depends on the volume of liquid that is displaced by the immersed sample, and a capillary force associated with the present location of the contact line as it advances over a dry nonwetted surface, or recedes over a surface that has been previously immersed to a user-specified, maximum depth. Prior to reaching the breakthrough depth ($\hat{x}_b$), the observed tensiometric force is described by eq 2.2: $F = \cos \theta^*_\text{adv} - B_c \hat{x}$, where $B_c = \sqrt{2} A_c / P_c \ell_{\text{cap}}$ is a dimensionless measure of the buoyant force, $A_c$ is the effective displaced cross-sectional area in the Cassie-Baxter state, and $P_c$ is the length of the contact line in the Cassie-Baxter state. After breakthrough and collapse of the macroplastron, the length of the wetted perimeter and the effective cross-sectional area of the immersed sample (that displaces fluid and gives rise to the buoyant force) both change. For the specific case of the periodic mesh, the analysis is somewhat simplified because the mesh interstices are filled with air when it is in the Cassie-Baxter regime (Figure 2-1) and a fluid volume equivalent to the entire macroscopic volume of the mesh (consisting of both air and wire) is displaced upon immersion. Therefore, both $A_c$ and $P_c$ can be calculated using the macroscopic dimensions of the rectangular mesh sample. After breakthrough of the composite interface ($\hat{x} > \hat{x}_b$) and collapse of the macroscopic plastron, there is
a decrease in the effective displaced volume; the effective cross-sectional area of the sample decreases as a result of the probe liquid penetration into the woven mesh structure. This yields a resultant immersion force after breakthrough given by

\[ \hat{F} = \cos \theta - B_c \hat{x}_b - B_w(\hat{x} - \hat{x}_b) \quad \text{for} \quad \hat{x} > \hat{x}_b \]  

where \( B_w = \sqrt{2}A_w/P_c \ell_{cap} \) and \( A_w \) is the effective cross-sectional area of the sample in the Wenzel regime. We note here that we retain our initial scaling of \( \hat{F} \) with the wetted perimeter in the Cassie-Baxter state \( (P_c) \) to avoid introducing a discontinuity in the dimensionless force, which would result from the jump in the wetted perimeter at the breakthrough event. The cross-sectional area of the sample in the Wenzel regime, \( A_w \), is computed by averaging the cross-sectional area of the mesh over the immersion depth. Comparing the expected force before and after breakthrough, it is evident that there should be a change in the slope of the immersion force curve at \( x = x_b \) of magnitude \( (B_c - B_w) \) due to the change in the effective displaced cross-sectional area \( (A_c > A_w) \) between the two wetting regimes.

Tensiometry measurements for spray- and dip-coated meshes are shown in Figure 2-6. The predicted slopes of the force traces (Figure 2-6A) determined from a priori knowledge of the mesh geometry are \( B_c = 0.25 \) and \( B_w = 0.11 \) in the Cassie-Baxter and Wenzel regimes, respectively. As a result, the wetting transition is predicted to show only a subtle change in slope for the spray-coated mesh. The values for the experimentally measured buoyancy slopes were \( B_c = 0.16 \) and \( B_w = 0.12 \) in the Cassie-Baxter and Wenzel regimes, respectively, which are consistent with the expected trend. The lower than expected value of the dimensionless buoyancy \( B_c \) in the Cassie-Baxter state results from the assumption that the effective cross-sectional area \( (A_c) \) of the coated mesh can be computed from its macroscopic cross-sectional area. Due to the woven nature of the mesh and sagging of the liquid-air interface into the mesh interstices, the calculated value of \( A_c \) actually serves as an upper bound on the value of \( B_c \).

While only a subtle change in the slope of the force trace is expected (and observed)
Figure 2-6: Measured force as a function of immersed depth for (A) a spray-coated and (B) a dip-coated stainless steel mesh ($D = 457 \, \mu m$, $R = 254 \, \mu m$) immersed in 50/50 (by volume) glycerol/water. Solid red and dashed green lines correspond to first and second tensiometric cycles, respectively. The breakthrough depth corresponds to the large jump in the hysteresis of the immersion/emersion force trace. A capillary length of $\ell_{cap} = 2.47$ mm and a maximum interfacial force of $P_{\gamma_{lv}} = 2.12$ mN were used to scale the measured displacement and tensile force, respectively.
at \( x_b \), there is a very distinct change in the wetting hysteresis at the transition. The part of the mesh that persists in the Cassie-Baxter regime shows noticeably less hysteresis than the portion associated with the Wenzel regime. This is a result of the differences in the wetting dynamics between the composite, solid-liquid-air interface as compared to the solid-liquid Wenzel interface. While receding in the Cassie-Baxter state, the three-phase contact line is only weakly pinned, because the wetted area fraction of the solid is small. Therefore, the meshes initially recede with low hysteresis as the Cassie-Baxter portion emerges from the probe liquid. However, after receding for a distance greater than the breakthrough depth, \( x_b \), the portion of the mesh that is in the Wenzel regime emerges from the liquid reservoir with dramatically increased hysteresis. The experimentally observed breakthrough depths for spray- and dip-coated meshes (with \( D = 452 \, \mu m, R = 254 \, \mu m \)) were \( x_b^{\text{spray}} \approx 9.9 \, mm \) and \( x_b^{\text{dip}} \approx 6.0 \, mm \), corresponding to breakthrough pressures of \( \Delta p_b^{\text{spray}} = 97 \, Pa \) and \( \Delta p_b^{\text{dip}} = 59 \, Pa \), respectively.

The spray- and dip-coated stainless steel woven meshes were used to investigate the wetting transition for two different values of the robustness parameter (defined in eq 2.1), while maintaining the same overall geometry. The goniometric advancing contact angles for the spray- and dip-coatings on a flat substrate were \( \theta_{\text{spray}}^{*} = 160^\circ \) and \( \theta_{\text{dip}}^{*} = 124^\circ \), which yield robustness factors for the macroscopic mesh texture of \( A_{\text{spray}}^{*} = 4.7 \) and \( A_{\text{dip}}^{*} = 2.7 \), and water breakthrough depths (of the macroplastron) of \( x_b^{\text{spray}} = 25.5 \, mm \) and \( x_b^{\text{dip}} = 14.5 \, mm \), respectively. While the absolute values of the breakthrough predictions (corresponding to the condition at which the hydrostatic pressure \( \rho_l g x_b \) exceeds the pressure \( \Delta p_b \) from eq 2.1) deviate slightly from the experimental results, the robustness framework performs well in predicting changes in relative breakthrough depth, which is approximately 1.75 times larger for the spray-coated mesh. This result supports the findings of past work that investigated the qualitative and quantitative predictive power of the robustness parameter \( A^{*} \).\(^{23}\)
Figure 2-7: Measured force as a function of immersion depth for six spray-coated meshes (summarized in Table 2.2) immersed in 50/50 (by volume) glycerol/water. Panels A-C and D-F show the effect of increasing the mesh spacing for fixed wire diameters of $R = 127 \mu m$ and $R = 254 \mu m$, respectively. Solid red and dashed green lines correspond to first and second tensiometric cycles, respectively. Through repeated cycling no changes were observed in the measured force traces.

### 2.3.3 Hysteresis in the Cassie-Baxter and Wenzel regimes

Six spray-coated woven meshes (with geometric properties summarized in Table 2.2) were used to investigate the effect of mesh spacing on the hysteresis and breakthrough depth of a two-length scale textured surface. As the spacing of the mesh increases, the robustness ($A^*$) of the composite liquid interface on the mesh decreases (eq 2.1). The consequences of this decrease in robustness have been observed previously using sessile drops of various liquids placed on wire meshes and fabrics.$^{11,23}$ This same trend (Table 2.2) is observed using a single probe liquid in our dynamic tensiometry experiments presented in Figure 2-7. The breakthrough event is triggered by steadily increasing the applied pressure difference $\Delta p$ (or, equivalently, the immersion depth $x = \Delta p/\rho g$) acting on the plastron as opposed to progressively reducing the liquid surface tension of different sessile drops that are sequentially placed on the textured surface.

The tensiometric results show that breakthrough occurs at lower pressures as the
Table 2.2: Mesh number (number of openings per inch), wire radius (R), weave half-spacing (D), dimensionless spacing ratio (D*), predicted robustness factor (A*), experimental breakthrough depth (x_b), and Cassie-Baxter (H_c) and Wenzel (H_w) state hysteresis for spray-coated woven meshes immersed in 50/50 (by volume) glycerol/water. The predicted breakthrough pressure can be determined from the dimensionless robustness A* as Δp_b = p_{ref}A* (eq 2.1), where the reference pressure is p_{ref} = 55 Pa for this system.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>R (μm)</th>
<th>D (μm)</th>
<th>D*</th>
<th>A*</th>
<th>x_b (mm)</th>
<th>H_c (x10^-2)</th>
<th>H_w (x10^-2)</th>
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<td>191</td>
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</tbody>
</table>

dimensionless mesh wire spacing D* increases, or as R increases at constant D*. For the finest mesh (Mesh 40; R = 127 μm), no breakthrough is observed; the plastron remains intact up to the maximum immersion depth and the surface remains in the Cassie-Baxter state throughout the entire immersion/emersion cycle. The pressure-induced transition from the Cassie-Baxter to Wenzel states is most readily observed in tensiometry as a sudden increase in the hysteresis of the tensiometric force trace. The hysteresis in the Cassie-Baxter regime (H_c) and in the Wenzel regime (H_w) can be computed by integration of eq 5.6 over the portion of the force trace corresponding to each regime of interest. The results are shown graphically in Figure 2-8 and are tabulated in Table 2.2.

The data clearly reveal the increase in hysteresis that accompanies the transition from the Cassie-Baxter to the Wenzel state (H_c < H_w). This increase in hysteresis is in good agreement with previous results reported for metastable Cassie-Baxter interfaces exposed to externally applied pressures. As D* increases for a given mesh wire radius, the wetted area fraction of solid in the Cassie-Baxter state and the value of H_c also decreases. By contrast, the value of the hysteresis associated with the Wenzel state increases. For the hierarchically textured surface (spray-coated mesh), the increase in hysteresis results from an increase in meniscus pinning upon transition.
Figure 2-8: Cassie-Baxter ($H_c$) and Wenzel ($H_w$) state hysteresis for spray-coated woven meshes immersed in 50/50 (by volume) glycerol/water. The Wenzel hysteresis for the mesh with $D^* = 2.5$ could not be measured, because the breakthrough depth ($x_b = 43$ mm) was greater than the maximum immersion depth ($x_{max} \approx 30$ mm) attainable with the tensiometer.
from the Cassie-Baxter state to the Wenzel state, and a concomitant increase in the amplitude of the oscillations in the receding force traces after transition.

2.3.4 Quantifying topographical length scales with tensiometry

The stainless steel woven meshes also offer a model periodic texture for investigating characteristic geometric length scales by tensiometry. The force data shown in Figure 2-7 exhibit regular periodicity in both the immersion and emersion force traces as a result of the liquid meniscus traversing the individual horizontal wires of the spray-coated mesh. To quantify the frequency of these oscillations the measured force data was first detrended (i.e., the effective slope resulting from the buoyancy term in eq 2.2 was first removed from the data) and a discrete Fourier transform was then used to evaluate the corresponding power spectrum of the fluctuating force signal. The frequency distribution, in conjunction with the experimentally imposed velocity \( U = 0.2 \text{ mm/s} \), enables the calculation of the texture periodicity from the primary harmonic of the spectrum. Advancing and receding power spectra gave virtually identical values for the period of the mesh texture (Figure 2-9) and agreed well with the manufacturer-specified periodicity for the meshes. The high reproducibility of the measurements (shown in Figure 2-8) across immersion and emersion force traces, and in repeated cycling demonstrates the ability of dynamic wetting measurements to quantify the characteristic geometric length scales of periodic textures without the need for potentially destructive microscopic techniques. The resolution of the surface features that can be investigated is limited primarily by the spatial resolution of the displacement stage of the tensiometer, which is less than 1 \( \mu \text{m} \) for modern systems.

2.4 Conclusions

In this work we have demonstrated the utility of dynamic tensiometry for determining wetting state transitions and topographical length scales on textured nonwetting
Figure 2.9: Fourier transform power spectrum of the detrended (A) immersion and (B) emersion (in the Wenzel regime) force data from a spray-coated mesh (Mesh 18; $R = 254 \, \mu m$; $D = 457 \, \mu m$). The primary harmonic (1456 $\mu m$) is in strong agreement with the actual periodicity ($2R + 2D = 1422 \, \mu m$) of the mesh for both sets of data. The receding spectrum also shows higher order harmonics.

surfaces, as well as for the more traditional measurement of apparent advancing and receding contact angles. We have shown how dynamic tensiometry can be used to analyze surface topography and obtain an effective wetted perimeter on textured substrates that properly reflects the tortuosity of the advancing or receding three-phase contact line. The wetting hysteresis ($H$) of a textured surface was defined in terms of the enclosed area between the advancing and receding force traces, which provides additional insight for chemically or physically heterogeneous surfaces beyond the traditional single-point definition of contact angle hysteresis, $CAH = \cos \theta_{rec} - \cos \theta_{adv}$.

With respect to the determination of the transition from the metastable Cassie-Baxter regime to the Wenzel regime, only small changes in the overall slope of the advancing force trace are observed, whereas the transition between the wetting states can be detected very clearly in an immersion/emersion cycle by a sudden and pronounced change in the hysteresis. This allows for the ready determination of the breakthrough depth ($x_b$) from a single tensiometric experiment. The wetting hysteresis, defined by eq 5.6, is always smaller in the Cassie-Baxter regime than in the Wenzel regime ($H_c < H_w$) for hierarchically textured systems that show a pressure-induced transition between the two regimes. It was also demonstrated that dynamic tensiometric
characterization of surface wettability can accurately and reliably probe the characteristic length scales that are present on microtextured surfaces, and which control the macroscopically observed hysteresis. Dynamic tensiometry thus provides a rapid and reliable test protocol for more completely characterizing the wetting properties of textured and patterned surfaces.
Chapter 3

Exploring the kinetics of switchable polymer surfaces with dynamic tensiometry


Switchable polymer multilayer coatings consisting of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) were prepared via Layer-by-Layer (LbL) assembly and post-functionalized with poly(ethylene glycol methyl ether) (PEG). This resulted in a soft polar coating that reversibly and repeatedly rearranges from hydrophobic to hydrophilic (or vice versa) when contacted with water (or air). Goniometry is used to quantify the forward surface rearrangement in the form of transient measurements of the water contact angle. By examining the time evolution of the water contact angle at various temperatures, the apparent activation energy for the forward surface rearrangement ($E_{a,f}$) can be determined. Further insight can be gained into the kinetics of this surface reconstruction process by utilizing dynamic tensiometry to measure the evolution in the contact angle of a liquid meniscus at several rates and temperatures as it advances or recedes over the multilayer films. A simple first-order
thermally-activated rate process is shown to describe the forward and reverse surface reconstruction and enables the shape of the measured tensiometric force curves during repeated immersion and emersion to be predicted quantitatively. Using this model we show that the character of this switchable surface coating can appear to be hydrophobic or hydrophilic depending on a single dimensionless parameter which incorporates the characteristic time-scale for temperature-dependent surface rearrangement, the speed of immersion and the capillary length of the liquid meniscus.

### 3.1 Introduction

Switchable polymer surfaces have the ability to rearrange on a molecular level in response to changes in their surrounding environments. A number of research groups have developed surfaces that can switch their surface wetting in response to environmental stimuli.\textsuperscript{24-26,71-82} Many experimental tools have been employed to investigate surface reconstruction phenomenon, including electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS),\textsuperscript{25,26,83,84} sum-frequency generation microscopy (SFM),\textsuperscript{74} surface acidity titration,\textsuperscript{26} and contact angle goniometry.\textsuperscript{24-26,71-81} Although each technique has specific advantages depending on the intended probing depth and sensitivity, contact angle measurements generally offer a very simple, convenient method of characterizing solid-liquid interfaces that are undergoing surface reconstruction. Contact angle measurements probe the top molecular layer of a surface (typically less than 1 nm deep),\textsuperscript{85} making them appropriate for elucidating the details of surface phenomena, which are primarily governed by local molecular motions and short-range interactions. Advancing and receding contact angles of a probe liquid are used to provide an upper and lower bound on the thermodynamic equilibrium contact angle.\textsuperscript{86} In the measurement of an advancing water contact angle ($\theta_{\text{adv}}$), the advancing three-phase contact line of the expanding liquid drop always sees the solid-air interface where primarily low surface energy moieties are present; whereas, the receding three-phase contact line of a contracting liquid drop moves across a solid-liquid interface that has been enriched with higher
surface energy moieties due to local molecular reorientation that provides preferential interactions with the wetting liquids.\textsuperscript{27} This procedure provides measurements of two distinct interfacial states that bracket the equilibrium behavior of the three phase system.

Previous work has primarily focused on measuring contact angle hysteresis ($CAH = \theta_{\text{adv}} - \theta_{\text{rec}}$) to quantify surface reconstruction phenomena.\textsuperscript{24,27} Although large contact angle hysteresis has been associated with significant surface reconstruction,\textsuperscript{24,76} surface roughness\textsuperscript{7} and chemical heterogeneity\textsuperscript{51,87} also result in hysteresis even in the absence of surface reconstruction. A more insightful characterization of surface reconstruction can be accomplished through quantitative investigation into the kinetics of surface rearrangement. Recently, time dependent measurements of contact angles on various reconfigurable surfaces have been used to probe the rate of the surface rearrangement of biopolymer coatings,\textsuperscript{72} poly(methyl methacrylate) (PMMA),\textsuperscript{74} and siloxane-based polymeric surfaces.\textsuperscript{73}

Morra \textit{et al.} have previously used dynamic tensiometry to investigate rearranging hydrogel surfaces.\textsuperscript{81} In the present work, we show that rate and temperature dependent tensiometry measurements provide a powerful framework for completely characterizing the forward (hydrophobic to hydrophilic) and reverse (hydrophilic to hydrophobic) reconstruction phenomena, as well as the temperature dependencies of these thermally-activated kinetic processes. In a dynamic tensiometer, force and relative position data are collected while a container of probe liquid is raised and lowered at a constant velocity such that the liquid contact line advances (or recedes) across the solid surface at a programmed speed. In the quasi-static limit, when viscous forces are negligible, the net force acting on the sample results from a combination of interfacial and buoyant forces and is given by $F = P\gamma_{lv} \cos \theta - \rho_l g A x$, where $P$ is the total perimeter of the solid-liquid-air contact line, $\gamma_{lv}$ is the probe liquid surface tension, $\rho_l$ is the liquid density, $g$ is the gravitational acceleration, $A$ is the cross-sectional area of the immersed solid, and $x$ is the immersed depth of the solid.\textsuperscript{63,64} This force balance can be conveniently nondimensionalized, scaling the resultant tensiometric force by $P\gamma_{lv}$ (the maximum possible interfacial force in the vertical direction) and the im-
mersed depth by $\sqrt{2}\ell_{\text{cap}}$ (the maximum height associated with capillary rise of a liquid meniscus on the solid in the limit of perfect wetting $\theta \to 0$), where $\ell_{\text{cap}} = \sqrt{\gamma_{lv}/\rho g}$. This scaling allows for a more insightful analysis of the shape of tensiometric force traces and results in the compact expression

$$\hat{F} = \cos \theta - B \hat{x}$$

(3.1)

where $\hat{F} = F/P\gamma_{lv}$ is the scaled force, $\hat{x} = x/\sqrt{2}\ell_{\text{cap}}$ is the scaled immersion depth, and $B = \sqrt{2}A/P\ell_{\text{cap}}$ is a dimensionless group quantifying the buoyant force acting on the immersed solid. By measuring the transient force $F(t)$ in the system as the liquid contact line advances or recedes across the surface (at a specified rate $\dot{x} = \pm V$) dynamic changes in the advancing or receding contact angle (denoted as $\theta(t)$) can be calculated.

In the search for a mechanically robust antifrost, and antifogging coating, we have recently developed a new multilayer system. This system exhibited two interesting characteristics: One is zwitter-wettable behavior whereby the multilayer film exhibits a facile, rapid absorption of water into a film from the gas phase while simultaneously exhibiting very high contact angles for drops of liquid water placed on the surface of the same film, and the other is transient water contact angle behavior. The former feature has been discussed in detail previously. In the present study, we investigate the time-dependent wetting behavior of these coatings, which results from the transient surface rearrangement of hydrophilic functional groups towards the surface in response to exposure to a liquid water environment.

### 3.2 Experimental

#### 3.2.1 Materials

Poly(vinyl alcohol) (PVA, $M_w = 131$ kDa, PDI = 1.50, 87-89% hydrolyzed, Sigma-Aldrich), poly(acrylic acid) (PAA, $M_w = 225$ kDa, 20% aqueous solution, Sigma-Aldrich), glutaraldehyde solution (Grade II, 25% in $H_2O$, Sigma-Aldrich), 2-butanol
(MEK, 99+ % A.C.S. reagent, Sigma-Aldrich), diiodomethane (Sigma-Aldrich), hexadecane (Sigma-Aldrich), poly(glycidyl methacrylate) (PGMA, $M_w = 25$ kDa, 10% solution in MEK, Polysciences), and poly(ethylene glycol methyl ether) (PEG, $M_w = 5$ kDa, Sigma-Aldrich) were used as received. Standard soda-lime glass microscope slides and phosphate buffered saline (PBS) were obtained from VWR. Deionized water (DI, 18.2 MΩ cm, MilliQ) was used in all aqueous polymer solutions and rinsing procedures.

### 3.2.2 Fabrication of PEG-functionalized PVA/PAA multilayer film

The glass substrates were first degreased by sonication in a 4% (v/v) solution of Micro-90 (International Products Co.) for 15 min, subsequently sonicated twice in DI water for 15 min, and then dried with compressed air. They were treated with oxygen plasma (PDC-32G, Harrick Scientific Products, Inc.) for 2 min at 150 mTorr and then PGMA anchoring chemistry was applied using previously described protocols to covalently bond the first layer of PVA to the substrate. Hydrogen bonded PVA/PAA films were produced via Layer-by-Layer (LbL) assembly using a Stratosequence VI spin dipper (Nanostrata Inc.) controlled using StratoSmart v6.2 software. The LbL assembly process employed dipping times of 10 min for each polymer solution, followed by three rinses of 2, 1, and 1 min. The concentration of the PVA and PAA solutions was 1 mg mL$^{-1}$ and the pH of these solutions and the rinse water were adjusted to pH 2.0 with 0.1M HCl. The as-assembled PVA/PAA multilayer films (consisting of 30 bilayers) were then thermally cross-linked at 140 °C for 5 min in vacuum to impart pH-stability, and these stabilized films were subsequently immersed in 10 mg mL$^{-1}$ PEG solution (pH 2.0) for 20 min. The PEG-functionalized PVA/PAA multilayer films were prepared by soaking in 0.13% (w/w) glutaraldehyde in PBS at 30 °C for 10 min, rinsing with DI water, and drying with compressed air.
3.2.3 Film characterization

Transient goniometric water contact angle measurements were performed using a ramé-hart model 590 goniometer after vertically dispensing sessile droplets of deionized water ($\gamma_{lv} = 72.8$ mN m$^{-1}$) on various coatings. Advancing water contact angles were measured as deionized water was supplied via a syringe. Transient water contact angle measurement commenced immediately after the water drop was advanced to a volume of approximately 10 mL. Measurements were taken over three or more different locations on each LbL film, and the reported uncertainties are standard deviations associated with the measurement of these contact angle values. The reversibility of surface rearrangement was demonstrated by immersing the initially dry sample into deionized water for 10 min, and then measuring advancing water contact angles on the hydrated film (immediately after the sample was removed from the water) as well as in a dry state (after drying in ambient lab conditions, $22 \pm 1^\circ$C and $40 \pm 10\%$ RH, for 15 min). The temperature-dependence of the transient water contact angles was quantified using an environmental chamber (ramé-hart, P/N 100-07) with water circulation. Water drops were placed on the surface after the sample had been pre-equilibrated in the environmental chamber at the specified test temperature for at least 10 min. Contact angle measurements with other probe fluids (specifically the nonpolar liquids diiodomethane and hexadecane) were performed in the same manner. Tensiometric force measurements were made using a DCAT 11 (DataPhysics Instruments) tensiometer. The samples were probed at velocities ranging from $0.01 < V < 1$ mm s$^{-1}$ and temperatures ranging from 10-40 $^\circ$C with a sampling frequency of 50 Hz and total immersion depths of $x \leq 25$ mm.

3.3 Results and Discussion

Thin multilayer coatings consisting of PVA and PAA were produced via LbL assembly at low pH conditions (pH= 2.0), stabilized for use at higher pH by post-assembly thermal or chemical treatments, and then further functionalized with poly(ethylene glycol methyl ether) (PEG) using glutaraldehyde chemistry. A graphic representa-
tion of this process is shown in Fig. 3-1. This procedure results in a dry coating that rearranges on a molecular scale with time when contacted with liquid water.

The dynamics of this molecular-scale, surface rearrangement were first investigated through the measurement of changes in the surface wetting properties of the coatings. Goniometric measurements of the time-dependent contact angle with water were conducted for PEG-functionalized PVA/PAA multilayer films and fluorosilane-treated glass slides as shown in Fig. 3-2a. The surfaces of all of these coatings exhibited initial advancing water contact angles greater than 100°. In the case of the fluorosilane-treated glass (initial advancing contact angle of 112 ± 1°), the water contact angle decreased by less than 10° over the period of 20 min, which can be attributed to evaporation of fluid from the static drop over the elapsed time of the experiment. For the PEG-functionalized PVA/PAA multilayer film, the initial water contact angle (θi = 117 ± 1°) decreased monotonically dropping to approximately 40° after 20 min. After the initial stage of rapid decay, the water contact angle decreased linearly with time in a similar fashion to the fluorosilane-treated glass slide. The
linear decrease in contact angle at long times is expected as a result of evaporation and has been reported by others.\textsuperscript{72,74}

The PEG-functionalized PVA/PAA multilayer films possess two particularly striking features: they have an unusually high initial water contact angle for a coating that is produced entirely from water-soluble polymers, as well as a very strong transient water contact angle behavior (exhibiting a large decay in contact angle upon exposure to a liquid water drop). The former feature has been discussed in detail previously\textsuperscript{88} and results from the combined effects of an initial surface enrichment of hydrophobic acetate moieties and the softness of the multilayer film. The latter feature can be rationalized in the context of surface reconstruction, specifically the time-dependent spatial orientation of hydrophobic and hydrophilic functional groups at the liquid water-solid polymer interface.\textsuperscript{71-75,79} To test the latter hypothesis, contact angle measurements were performed on the same samples using two nonpolar
liquids, diiodomethane (DM) and hexadecane (HD), with surface tension values of $\gamma_{lv}^{DM} = 50.8$ mN m$^{-1}$ and $\gamma_{lv}^{HD} = 27.5$ mN m$^{-1}$, respectively. These results are shown in Fig. 3-3. Both liquids exhibited low contact angle hysteresis ($CAH \approx 15^\circ$) on the LbL films and only a weak linear time dependence in their contact angles, which can again be attributed to evaporation. There was no evidence of the strong exponential transient response in the contact angle measured with liquid droplets of DM or HD. This suggests that the hydrophilic groups buried just beneath the surface of the initially-dry films are not driven to the solid-liquid interface when nonpolar liquids are used to probe the surface.

The reversibility of the surface reconstruction, shown in Fig. 3-2b, was investigated by measuring the initial advancing water contact angle while alternating the environment between hydrated and dry states. The PEG-functionalized PVA/PAA multilayer film, which exhibits an initially hydrophobic contact angle, was repeatedly placed in hydrated conditions (submerged in water) and then dried in ambient lab conditions ($22 \pm 1$ °C, $40 \pm 10\%$ RH) for 15 min. In the hydrated state the film exhibited an advancing water contact angle near zero, which is likely due to a thin residual layer of adsorbed water covering the surface. As the surface is gradually dried
under ambient conditions, the initial advancing water contact angle increased from $0^\circ$ to more than $100^\circ$ indicating that the surface of the multilayer film reconfigures as water molecules are removed to enrich the concentration of lower energy hydrophobic acetate moieties to the hydrophobic state. After five cycles the film still displayed complete reversibility (Fig. 3-2b).

The initial rapid response of the surface reconfiguration can be characterized by an exponential of the form $\sim \exp(-t/\tau_f)$ where $\tau_f$ is a material-dependent time constant. Furthermore, if this surface reconstruction is viewed as a thermally-activated process, the characteristic time scale ($\tau_f$) of the mechanism should depend on temperature according to an Arrhenius or similar formalism. This aspect of the film behavior was explored goniometrically by performing time dependent measurements of the water contact angle at $T = 10$, $20$, $30$, and $40$ °C The results of these experiments are shown in Fig. 3-4a. The initial exponential decay of the water contact angle clearly proceeds more rapidly at higher temperatures. The forward surface rearrangement occurs within the first half of the experiment and the subsequent linear decrease in the measured contact angle was used to estimate the evaporation rate. The time constant for the forward surface rearrangement ($\tau_f$) was then determined after removing the effects of evaporation. The surface rearrangement was modeled as a first-order process:

$$\frac{\cos \theta(t) - \cos \theta_{phil}}{\cos \theta_{phob} - \cos \theta_{phil}} = \exp(-t/\tau_f)$$

(3.2)

where $\theta_{phil}$ indicates the equilibrium value of the advancing contact angle in the low-contact-angle hydrophilic state and $\theta_{phob}$ indicates the equilibrium value of the advancing contact angle in the high-contact-angle hydrophobic state, respectively.

Table 3.1 shows clearly that the time constant characterizing surface reconstruction in the PEG-functionalized PVA/PAA multilayer films decreases with increasing temperature, while $\theta_{phob}$ and $\theta_{phil}$ remain nearly constant. The temperature dependence of the surface rearrangement rate was assumed to follow an Arrhenius form:
Figure 3-4: (a) Time dependence of the water contact angle $\theta$ for the PEG-functionalized PVA/PAA multilayer film at $T = 10, 20, 30, 40 ^{\circ}C$. The individual data points represent the average value of three separate measurements over 10 s intervals; (b) a plot of $\ln \tau_f$ versus $T^{-1}$ where $\tau_f$ is obtained from fits of the transient data in (a) after correcting for evaporation.

\[
\tau_f^{-1} = A_f \exp(-E_{a,f}/RT)
\]  

(3.3)

where $A_f$ is the Arrhenius pre-exponential factor, $E_{a,f}$ is the activation energy associated with the forward rearrangement mechanism, $R$ is the ideal gas constant, and $T$ is the absolute temperature. A semi-logarithmic plot of the time constant versus reciprocal temperature is presented in Fig. 3-4b, and shows good agreement with eq 3.3 over the range of temperatures studied here. An Arrhenius activation energy of $E_{a,f} = 40.5$ kJ mol$^{-1}$ was obtained from the best fit slope of the plot which is similar to the value (39.0 kJ mol$^{-1}$) reported for transient contact angle data obtained on a poly(methyl methacrylate) film. The relatively low value of the activation energy results from the enhanced segmental motion that is possible at the interface as well as the effects of water plasticizing the film. These activation energies are consistent with segmental motion of polymer chains in environments with large free volumes, such as the high temperature asymptotic limit of the Williams-Landel-Ferry formalism(17.2 kJ mol$^{-1}$), and with the values associated with $\beta$-relaxation processes in bulk polymers ($\sim$59 to 66 kJ mol$^{-1}$ for PVA).
Table 3.1: $\theta_{\text{phob}}$, $\theta_{\text{phil}}$, and $\tau_f$ for the forward surface rearrangement calculated from fitting the time-dependent goniometric contact angle data at various temperatures using eq 3.2. The averaged set of individual data with the effects of evaporation removed and the corresponding fitted results can be found in Fig. 3-5.

<table>
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<th>$\theta_{\text{phil}}$ (deg)</th>
<th>$\tau_f$ (s)</th>
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</tbody>
</table>

Figure 3-5: Time dependence of the contact angle with water $\theta$ for PEG-functionalized PVA/PAA multilayer film at (a) $T = 10$ °C, (b) $T = 20$ °C, (c) $T = 30$ °C, (d) $T = 40$ °C with the effects of evaporation removed. Open boxes, circles, and triangles represent individual data points averaged every 10 sec while the bold line represents the model fit.
3.3.1 Modeling the kinetics of surface rearrangement in dynamic tensiometry

Dynamic tensiometry allows for a more complete characterization of the wetting behavior of switchable surfaces, including the investigation of both the forward and reverse rearrangement. The first immersion into water of the PEG-functionalized PVA/PAA surface in a dynamic tensiometer probes the forward surface rearrangement through the measurement of an apparent velocity-dependence in the advancing contact angle of the air-equilibrated surface, as shown schematically in Fig. 3-6a. During emersion (i.e., as the sample is removed from the liquid) the receding contact angle of water on the reconfigured surface is measured. As the sample is re-exposed to air the surface rearranges back towards the original dry state. Upon the second and all subsequent immersions, the rate of this reverse rearrangement will be probed, because the contact line is now moving over locations on the surface that are in various degrees of rearrangement back to the original state.

The extent of surface rearrangement in the PEG-functionalized PVA/PAA multilayer film is manifest in the advancing water contact angle of the surface. In a goniometric system the time evolution of the advancing water contact angle on the surface is observed; in the case of tensiometry, a single velocity-dependent advancing water contact angle is observed where the deflection of the liquid meniscus (i.e., the contact angle) reaches a steady state configuration as the three-phase contact line advances across the surface. If the selected rate of immersion, \( V \), is much faster than the rearrangement kinetics, then the high advancing water contact angle associated with the initial hydrophobic state is expected to dominate the tensiometric measurements. Conversely, very slow immersion will produce tensiometric data that approach the asymptotic hydrophilic behavior that was observed in goniometric experiments at long times.

To quantify the qualitative descriptions of "slow" and "fast," first observed by Morra et al.,\(^{81}\) we compare the time scale associated with molecular rearrangement \( \tau_f \) with the characteristic time scale at which the liquid meniscus advances across
Figure 3-6: (a) Schematic of the PEG-functionalized PVA/PAA multilayer film undergoing surface reconstruction during the first tensiometric immersion in water. Hydrophobic moieties are represented by acetate groups and hydrophilic groups, such as PEG and carboxylic acid groups, are represented by hydroxyl groups; (b) force trace for the first immersion of the PEG-functionalized PVA/PAA multilayer film into water at 30 °C occurring at three different rates. Solid red, dashed green, and dotted blue lines correspond to instrument speeds of 1.0 mm s⁻¹, 0.1 mm s⁻¹, and 0.01 mm s⁻¹, respectively; (c) force trace for first immersion of the same surface into water at 10 °C. Colored lines correspond to the same rates as in (b). The values of $\alpha_f$ are 186, 18.6, and 1.86 for the three instrument speeds of 1.0 mm s⁻¹, 0.1 mm s⁻¹, and 0.01 mm s⁻¹, respectively.
the surface during the immersion process \( \tau_c = \ell_{cap}/V \), where \( \ell_{cap} \) is the capillary length of the liquid. The resulting dimensionless ratio of time scales for the forward rearrangement is given by

\[
\alpha_f = \frac{\tau_f}{\ell_{cap}/V} = \frac{\tau_f V}{\ell_{cap}}
\]  

(3.4)

In the limit \( \alpha_f \ll 1 \) we expect surface rearrangement to be fast so that the advancing contact angle is small and the surface appears hydrophilic. If \( \alpha_f \gg 1 \) the meniscus advances very rapidly compared to the rearrangement rate and the surface will appear hydrophobic. Eq 3.2 models the advancing contact angle of the reconfiguring surface as a function of elapsed rearrangement time. If we evaluate this equation after a characteristic elapsed time of \( t_c = \ell_{cap}/V \) we obtain the following expression:

\[
\frac{\cos \theta(t_c) - \cos \theta_{phil}}{\cos \theta_{phob} - \cos \theta_{phil}} = \exp \left( -\frac{\ell_{cap}/V}{\tau_f} \right) = \exp(-1/\alpha_f)
\]  

(3.5)

A transition from a high contact angle regime (\( \theta \approx \theta_{phob} \)) to a rearrangement-dominated, low contact angle regime (\( \theta \approx \theta_{phil} \)) is expected as the magnitude of the dimensionless group \( \alpha_f \) passes through unity.

Similarly, the reverse rearrangement can also be modeled as a first-order thermally-activated rate process with the additional consideration of the evaporation of bulk water from the surface of the previously immersed and swollen multilayer film. For simplicity, we assume that the reverse rearrangement does not begin until the excess water evaporates from the surface of the film (i.e., after a delay time \( t_d \)). Therefore, the following first-order model with time delay is used to describe the reverse surface rearrangement:

\[
\frac{\cos \theta(t) - \cos \theta_{af}}{\cos \theta_{rec} - \cos \theta_{af}} = H(t - t_d) \exp(-(t - t_d)/\tau_r)
\]  

(3.6)

where \( \theta_{rec} \) is the receding water contact angle, \( \theta_{af} \) is the advancing water contact angle observed in the tensiometric system during the forward rearrangement (i.e., eq 3.5 evaluated at \( t_c \) or \( \alpha_f = \tau_f/t_c \)), \( H \) is the Heaviside unit step function, and
\( \tau_r \) is the characteristic time constant of the reverse rearrangement. The elapsed time that the surface material at a given position on the sample is out of the probe liquid and exposed to air can be expressed in terms of instrument parameters as
\[
t = \frac{2x}{V} + 2s \approx \frac{2x}{V},
\]
where \( x \) is the immersion depth (starting at \( x = 0 \)) and the additional 2 seconds results from the instrument idle time between emersion and immersion.

### 3.3.2 Effects of rate and temperature

As mentioned above, probing the surface of the PEG-functionalized PVA/PAA multilayer film over increasingly greater velocities at a given temperature should result in higher measured advancing water contact angles during the first immersion of the sample, because the material near the meniscus will have had less time to rearrange relative to the time scale \( \ell_{cap}/V \) of contact line advancement. This behavior, increasing \( \theta_{adv} \) with increasing \( \alpha_f \), was observed clearly in our experiments, shown in Fig. 3-6b. The contact angle is extracted from the force measurements by fitting eq 3.1 to the data. As a result, \( \cos \theta \) is directly related to the value of the measured force \( F_0 \) when the fit over the linear portion of the data is extrapolated to \( x = 0 \). Positive values of \( F_0 \) correspond to wetting contact angles (\( \theta < 90^\circ \)) and negative values to nonwetting contact angles (\( \theta > 90^\circ \)). \( \alpha_f \) was determined by fitting all of the measured force data with eq 3.1 using eq 3.3, 3.5, and 3.6 to determine the time-varying value of the contact angle.

In addition to varying the rate of immersion/emersion, \( V/\ell_{cap} \), the temperature of the fluid was also varied in the tensiometry experiments to further characterize the kinetics of the surface rearrangement phenomena. Experiments were carried out at four temperatures (40 \(^\circ\)C, 30 \(^\circ\)C, 20 \(^\circ\)C, and 10 \(^\circ\)C) and three speeds (1.0 mm s\(^{-1}\), 0.1 mm s\(^{-1}\), and 0.01 mm s\(^{-1}\)). The force traces for the first immersion at 10 \(^\circ\)C at the three experimental speeds are shown in Fig. 3-6c. Unlike the results seen in the 30 \(^\circ\)C data of Fig. 3-6b, at 10 \(^\circ\)C the results of the three experiments nearly coincide and the advancing contact angle of \( 120 \pm 7^\circ \) that is extracted from the data is close to the initial hydrophobic state value of \( 111 \pm 4^\circ \) obtained via goniometry. Thus at
10 °C the rate of the forward rearrangement is significantly slower than the rate of contact line advancement \(i.e., \alpha_f > 1\), even at the lowest experimental velocity of \(10^{-2} \text{ mm s}^{-1}\).

The full set of rate- and temperature-dependent immersion and emersion tensiometry data is shown in Fig. 3-7. As expected, upon immersing at the highest speed (right most column of plots in Fig. 3-7) the initial advancement into water yields a high initial contact angle \(F_0 < 0\) throughout the first immersion. After exposure to water, the contact line recedes with a low receding contact angle \(F_0 > 0\) over the rearranged surface. Subsequent immersion/emersion cycles show only the low contact angle, rearrangement-dominated regime, because the surface does not have time to revert back to the hydrophobic state at the high immersion/emersion speed \(i.e., the analogous dimensionless parameter for the reverse surface rearrangement is \alpha_r > 1\). Experiments carried out at a speed that is an order of magnitude lower (middle column of plots in Fig. 3-7) show that the initial advancement of the meniscus still proceeds with a high advancing contact angle and after exposure to water the contact line recedes with a low receding contact angle. However, upon a second advancement into water, the advancing contact angle exhibits transient behavior as the surface rearranges back to its initial hydrophobic state. At this instrument speed the sample is exposed to air for a sufficient period of time that the reverse surface rearrangement (from the hydrophilic to the hydrophobic state) occurs within the time scale of the experiment \(i.e., \alpha_r \sim 1\). This behavior is repeated in subsequent cycles, which highlights the complete reversibility of this surface switching phenomena. Finally, immersing at the slowest speed \(V = 0.01 \text{ mm s}^{-1}\), the advancing force traces indicate that the surface is hydrophilic \(F_0 > 0\) for temperatures \(T \geq 20 \degree\)C. The rate of surface reconfiguration is fast \(\alpha_f < 1\) compared to the translation rate of the meniscus. Subsequent immersions again show recovery towards \(\theta \rightarrow \theta_{a,f}\) introduced in eq 3.6 since the surface has sufficient time out of the water to undergo the reverse rearrangement.

The effect of temperature on the surface rearrangement can be clearly seen in the lowest immersion/emersion speed \(0.01 \text{ mm s}^{-1}\) data taken at \(10 \degree\)C and \(20 \degree\)C. At 20
Figure 3-7: Dynamic tensiometry measurements for switchable PEG-functionalized PVA/PAA multilayer films probed with water. Three rates and four water temperatures were examined. Solid red, dashed green, and dotted blue lines correspond to first, second, and third tensiometric cycles, respectively. The values of the dimensionless parameter $\alpha_f$ (defined in eq 3.4) are given for each condition with the (temperature-dependent) values of $\tau_f$ evaluated from the Arrhenius fit described in the text. The delay time for drying $t_d$ mentioned in the text is evident for the re-immersion traces at the lower temperatures and two lower speeds.
°C the surface appears hydrophilic even during the first immersion with a low contact angle and positive force intercept, \( F_0 \); however, at 10 °C the surface rearrangement has slowed enough (\( \tau_{10\,°C} > \tau_{20\,°C} \)) that the initial immersion now occurs faster than the time scale of rearrangement (i.e., \( \alpha_f > 1 \)) and the surface appears hydrophobic with a high advancing contact angle. Likewise, the effect of temperature on the reverse rearrangement (from the hydrophilic to the hydrophobic regime) can be observed in the intermediate rate (0.1 mm s\(^{-1}\)) results. The recovery to the hydrophobic state (observed during the second immersion) occurs more rapidly at 40 °C than at 10 °C. The higher temperature increases the rate of surface rearrangement and allows for faster restoration of the hydrophobic state.

### 3.3.3 Model and kinetic parameters for surface rearrangement

The measured force data was fitted with eq 3.1 using eq 3.3, 3.5, and 3.6 to calculate the time-varying value of the contact angle \( \theta(t) \). When the tensiometer changes directions there is a small transition region where the contact line pins as the contact angle moves from the advancing value to the receding value or *vice versa*. The contact angle in this region was modeled by solving the Young-Laplace equation for our system’s geometry.\(^{63,67}\) The resulting model for the tensiometric force data contains eight parameters, for which the fitted values are summarized with their goniometric equivalents in Table 3.2.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Goniometry</th>
<th>Tensiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_{phob} )</td>
<td>degrees</td>
<td>109</td>
<td>125</td>
</tr>
<tr>
<td>( \theta_{phil} )</td>
<td>degrees</td>
<td>66</td>
<td>53</td>
</tr>
<tr>
<td>( \log_{10} A_f )</td>
<td>—</td>
<td>5.5</td>
<td>4.7</td>
</tr>
<tr>
<td>( E_{a,f} )</td>
<td>kJ mol(^{-1})</td>
<td>40.5</td>
<td>40.1</td>
</tr>
<tr>
<td>( \theta_{rec} )</td>
<td>degrees</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>( t_d )</td>
<td>seconds</td>
<td>—</td>
<td>151</td>
</tr>
<tr>
<td>( \log_{10} A_r )</td>
<td>—</td>
<td>—</td>
<td>1.2</td>
</tr>
<tr>
<td>( E_{a,r} )</td>
<td>kJ mol(^{-1})</td>
<td>—</td>
<td>18.5</td>
</tr>
</tbody>
</table>
Table 3.2 shows that good agreement between the Arrhenius parameters can be obtained from the two experimental methods (goniometry and tensiometry) for the forward surface rearrangement. The activation energy of this process arises from the segmental motion of hydrophobic and hydrophilic moieties at the interface between the PEG-functionalized PVA/PAA multilayer film and liquid water.

The value for the advancing water contact angle in the hydrophobic regime \( \theta_{\text{phob}} \) obtained from tensiometry is slightly higher than the value obtained from goniometry, which is due to the inherent experimental difficulties in obtaining this value with a goniometer. The surface immediately begins to rearrange when contacted with water and as a result several seconds elapse between placing the drop, the decay of all internal motion, and starting the contact angle measurement in a goniometric system. Tensiometry avoids this issue by immersing the sample into a reservoir of the probe liquid at a slow fixed speed and the tensile force on the surface is measured in real time. The advancing water contact angle is then obtained from regression of eq 3.1 to the linear portion of the immersion force traces.

The force traces produced from the dynamic model with the fitted parameters from Table 3.2 are shown with the corresponding experimental data in Fig. 3-8 and 3-9 for selected temperatures and rates. The complete set of model results plotted in a form analogous to Fig. 3-7 can be found in Fig. 3-10 with their corresponding \( \alpha_f \) values.

In general, good agreement is observed between the model and the data. In Fig. 3-8 the initial advancing contact angle is in agreement with the data, and the fitted activation energy of 40.1 kJ mol\(^{-1}\) captures the temperature dependence of the rearrangement process. The effect of immersion speed is clearly illustrated by Fig. 3-9. At low wetting speeds \( \alpha_f \lesssim O(1) \) the surface rearranges as it is exposed to water and the surface appears hydrophilic \( (i.e., F_0 > 0) \). However, at high immersion speeds \( \alpha_f \gg 1 \) the surface appears strongly hydrophobic. The onset and duration of the reverse rearrangement is also well predicted by the model for both varying rate and temperature; however, the shape of the force trace during the reverse rearrangement associated with the second and third immersion cycles does not fully
Figure 3-8: Comparison of the predicted values and measurements for the tensiometric force of PEG-functionalized PVA/PAA multilayer films probed with water at 0.01 mm s\(^{-1}\) during immersion and emersion. Solid red, dashed green, and dotted blue lines correspond to first, second, and third tensiometric cycles, respectively. The values of \(\alpha_f\) for each condition are shown in the figure.
Figure 3-9: Comparison of the predicted values and measurements for the tensiometric force of PEG-functionalized PVA/PAA multilayer films probed with water at 20 °C. Solid red, dashed green, and dotted blue lines correspond to first, second, and third tensiometric cycles, respectively. The values of $\alpha_f$ for each condition are shown in the figure.
Figure 3-10: Complete set of model results plotted analogous to Fig. 3-7.
Figure 3-11: IR thermal imaging of the films during the tensiometer experiment. 

agree with the experimental data. The small deviations are most likely a result of some surface rearrangement taking place as the excess water dries from the exposed sample surface, which the model does not account for. The parameter values for the model characterizing the reverse rearrangement are also expected to be less accurate than the corresponding forward rearrangement parameters, because the air temperature and humidity (i.e., the ambient environment in which the reverse rearrangement occurred) was not rigorously controlled. As a result, the surface temperature of the multilayer film during the reverse rearrangement is not necessarily the same as the temperature of the probe liquid. IR thermal imaging of the films during the tensiometer experiment (Fig. 3-11), show that at low temperatures (10 °C) the multilayer film is at the liquid temperature during the reverse rearrangement; however, at higher temperatures (40 °C) the multilayer film rapidly cools as a result of evaporation of the water during rearrangement with most of the process occurring at ambient temperatures (≈ 22 °C).

3.4 Conclusions

PEG-functionalized PVA/PAA multilayer films exhibit a transient and reversible contact angle behavior as a result of thermally-activated surface reconstruction. Contact angle goniometry was used to measure and analyze the time evolution of water con-
tact angles over a range of temperatures and a temperature-dependent characteristic
time constant ($\tau_f$) for the forward surface reconstruction (from hydrophobic to hy-
drophilic) was subsequently extracted. Furthermore, an Arrhenius relationship was
used to determine the activation energy ($E_{a,f} = 40.5$ kJ mol$^{-1}$) of the surface re-
construction process from the goniometric data. Utilizing dynamic tensiometry the
kinetics of the surface rearrangement could be probed in more detail by immersing
(and subsequently withdrawing) glass substrates coated with the multilayer film into
(and out of) a reservoir of water at various speeds ranging from 0.01 mm s$^{-1}$ to 1 mm
s$^{-1}$ and over a range of temperatures from 10 °C to 40 °C. Modeling the forward and
reverse surface reconstruction with a first-order rate equation, the activation energies
for both of these processes can be determined. The value obtained for the forward
surface rearrangement ($E_{a,f} = 40.1$ kJ mol$^{-1}$) agrees well with the goniometric re-
sults. The dynamics of this reversible surface switching process could be understood
in terms of a single dimensionless grouping $\alpha_f = \tau_f V/\ell_{cap}$ that represents a ratio of
the time scale for molecular rearrangement ($\tau_f$) to a characteristic tensiometric time
scale for the advancement of the solid-liquid-air interface ($\ell_{cap}/V$). The experimental
measurements and first order model both show that the wettability characteristics of
this switchable surface transition from strongly hydrophobic (with a high advancing
contact angle at high speeds or low temperatures) to strongly hydrophilic (dominated
by surface rearrangements and low contact angles at low speeds or high temperatures)
as this dimensionless group is reduced below $\alpha_f \sim O(1)$. This dimensionless group
thus plays the same role in dynamic tensiometry as the Deborah number in rheo-
logical problems$^{93,94}$ and characterizes the interplay between the rate of the surface rearrangement process and the observation period. It will be interesting to see how
well this idea can be used to understand, quantify and compare the dynamical re-
sponses of the wide range of other switchable and reconfigurable surfaces that are
currently being developed.
Chapter 4

Sustainable drag reduction in turbulent Taylor-Couette flows by depositing sprayable superhydrophobic surfaces


We demonstrate a reduction in the measured inner wall shear stress in moderately turbulent Taylor-Couette flows by depositing sprayable superhydrophobic microstructures on the inner rotor surface. The magnitude of reduction becomes progressively larger as the Reynolds number increases up to a value of 22% at $Re = 8.0 \times 10^4$. We show that the mean skin friction coefficient $C_f$ in the presence of the superhydrophobic coating can be fitted to a modified Prandtl-von Kármán-type relationship of the form $(C_f/2)^{-1/2} = M \ln(Re(C_f/2)^{1/2}) + N + (b/\Delta r)Re(C_f/2)^{1/2}$ from which we
extract an effective slip length of \( b \approx 19 \mu m \). The dimensionless effective slip length \( b^+ = b/\delta_\nu \), where \( \delta_\nu \) is the viscous length scale, is the key parameter that governs the drag reduction and is shown to scale as \( b^+ \sim Re^{1/2} \) in the limit of high \( Re \).

### 4.1 Introduction

It is well known that superhydrophobic (SH) surfaces can reduce drag in laminar flows by presenting an effective wall slip boundary condition due to stable pockets of vapor within the asperities of the textured substrate.\(^4\)\(^9\)\(^5\) The trapped vapor layer adjacent to the solid wall lubricates the fluid flow by introducing an effective slip boundary condition along portions of the wall, and consequently reduces the overall drag.\(^9\)\(^6\) The magnitude of the effective slip length \( b \) in viscous laminar flows is governed by the surface feature length scale and the wetted solid fraction.\(^9\)\(^7\)\(^-\)\(^9\)\(^9\) Measurements in various microchannel flows\(^1\)\(^0\)\(^0\)\(^-\)\(^1\)\(^0\)\(^4\) yield values of \( b \) that are typically in the range of \( 10 \sim 30 \mu m \).

There is less consensus on the extent to which microscopic effective slip can influence macroscopic skin friction in turbulent flows.\(^1\)\(^0\)\(^5\)\(^,\)\(^1\)\(^0\)\(^6\) Numerical simulations of turbulent channel flows indicate that the shear-free liquid-vapor interface can reduce skin friction by introducing an effective slip velocity in the viscous sublayer,\(^1\)\(^0\)\(^7\)\(^,\)\(^1\)\(^0\)\(^8\) and by the suppression of turbulent flow structures in the near-wall region.\(^1\)\(^0\)\(^9\) While recent experimental studies report varying amounts of drag reduction in turbulent flows using SH surfaces,\(^1\)\(^1\)\(^0\)\(^-\)\(^1\)\(^1\)\(^2\) there are inconsistencies in the magnitude of observed drag reduction across studies, and its dependence on the slip length, surface characteristics, and Reynolds number in turbulent flow remain unclear.

In this chapter, we demonstrate sustained reduction in frictional drag in turbulent Taylor-Couette (TC) flows by applying a polymeric SH coating to the inner rotor. The extent of drag reduction \( DR = 100 \times (T^{flat} - T^{SH})/T^{flat} \) based on the inner rotor torque \( T \), steadily increases with \( Re \) up to 22% at \( Re = 80,000 \). The reduction in friction arises from finite slip effects at the moving rotor. The two key results we describe in our Letter are (i) the magnitude of drag reduction is directly related to
a dimensionless slip length \( b^+ \equiv b/\delta_v \), which couples the effective slip length \( b \) to the viscous length scale \( \delta_v = \nu/u_r = \nu \sqrt{\rho/\tau_i} \) of the turbulent flow (where \( \nu \) is the kinematic viscosity, \( \rho \) is the liquid density, \( \tau_i \) is the wall shear stress measured at the inner rotor and \( u_r = \sqrt{\tau_i/\rho} \) is the friction velocity), and (ii) the proposal of a modified skin friction law from which a single value of \( b \) is obtained that accounts for the entire range of measured drag reduction for various \( Re \).

4.2 Materials and Methods

The large gap TC apparatus, shown schematically in Fig. 4-1(a), has a rotating recessed end inner cylinder of radius \( r_i = 14 \pm 0.01 \text{ mm} \) and stationary outer cylinder of radius \( r_o = 34.3 \pm 0.1 \text{ mm} \) (so that \( r_i = r_i = 0.41; \Delta r = r_o r_i = 20.3 \text{ mm} \)). The recessed end traps a pocket of air inside the cavity, shown in Fig. 4-1(a), to avoid end effects in torque measurements. The height of the inner rotor was \( L = 42.0 \pm 0.1 \text{ mm} \), having an aspect ratio of \( \zeta = L/(r_o r_i) = 2.1 \). The gap between the cylinders is filled with deionized water at 25 °C. The maximum rotation rate of the inner rotor was \( \Omega_{\text{max}} = 250 \text{ rad/s} \), which represents a maximum attainable Reynolds number of \( Re_{\text{max}} \equiv r_i \Omega_{\text{max}} \Delta r/\nu = 8 \times 10^4 \). This allows us to generate shear driven turbulent TC flows (past the Taylor vortex regime) [20,21], the onset of which occurs at a transition Reynolds number of \( Re_c \approx 1 \times 10^4 \) for our system (for details, see the Supplemental Material [22]). We fabricated our SH surface on the inner rotor by spray coating a 50/50 (by weight) solution of poly (methyl methacrylate) (PMMA)/fluorodecyl polyhedral oligomeric silsesquioxane (FPOSS) at a concentration of \( c = 50 \text{ mg/ml} \), as described previously. The coating was separately applied to produce either an unconnected configuration [Fig. 4-1(b)] where the trapped air (or “plastron”) is isolated, or a connected configuration [Fig. 4-1(c)] in which the air layer is in continuous contact with an external air reservoir.
4.3 Results and Discussion

4.3.1 Quantifying the surface morphology

To quantify the initial wetted solid fraction, we extend the approach of Papadopoulos et al.\textsuperscript{113} to enable \textit{in situ} imaging of the plastron on a random textured SH surface using confocal microscopy. In Fig. 4-2(a), we show the reconstructed 3D isosurface of the composite solid-liquid-air interface when a water drop (fluorescently labeled green), was deposited onto the SH coating (fluorescently labeled red). As expected, we observed that the liquid meniscus wets only on a fraction of the PMMA/FPOSS structures. The cut-away region reveals the unwetted (dry) PMMA/FPOSS structures beneath the liquid. Figure 4-2(b) shows an orthoslice of the spray coated texture and the liquid meniscus resting in the nonwetting state\textsuperscript{3} along the $AA'$ direction in Fig. 4-2(a). We determined the local height profile $h(x, y)$ of the PMMA/FPOSS and the vertical position of the liquid meniscus $z_0(x, y)$ from a series of these slices. Computing the averaged height-height correlation function\textsuperscript{114} $H(r) = \langle (h(x' + r) - h(x'))^2 \rangle_{x,y}$ allows us to estimate a lateral correlation length, which corresponds to the size of the sprayed features, as $\xi = 15 \text{ $\mu$m}$ and a root-mean-square roughness $\omega = 8.5 \text{ $\mu$m}$. 
Figure 4-2: (a) Reconstructed 3D isosurface from confocal microscopy of water (green) resting on PMMA/FPOSS structures (red) in the nonwetting state. (b) Superimposed fluorescence images of the PMMA/FPOSS structures (red) and the liquid meniscus (green) along the $AA'$ slice plane.
4.3.2 Experimental and theoretical results for Taylor-Couette flow

In order to investigate the influence of the SH coating in turbulent TC flows, we systematically varied rotation rates to measure the global torque $T$ on coated and uncoated rotors for $N = 17$ values of $Re \in [1600, 80000]$. A single run consisted of either a ramp up in discrete steps from a minimum rate of $\Omega = 5$ rad/s ($Re = 1600$) or a ramp down from the maximum $\Omega = 250$ rad/s ($Re = 80,000$). The torque $T$ is measured over a period of 600 s at each $Re$. Viscous heating effects are negligible over this short time period. At least four replicates were performed for both the connected and unconnected state [see Fig. 4-1(b)]; the torque was averaged across all runs for each $Re$. In Fig. 4-3, we plot the averaged dimensionless torque $G = T/(\rho \nu^2 L)$ for the various $Re$. For the uncoated inner rotor, where the relative standard deviation in the measured torque is $\sigma_r = 0.01$, we fit the measured torque to the predicted scaling $G \sim g(\eta) Re^{5/3}$ for a turbulent TC flow in the wide-gap limit, as indicated by the dotted line in Fig. 4-3. While our best fit is in good agreement with the predicted exponent of $5/3$, the value of $g(\eta) = 0.3$ that we obtained is smaller than the predicted value of $g(\eta) = [(1 + \eta)/2]/[\eta^{1/3}(1 - \eta)^2]$ from Eckhardt et al., suggesting that a very large gap width ($\eta < 0.5$) and small aspect ratio ($\zeta = 2.1$) influences the prefactor but not the torque scaling.

Upon applying our PMMA/FPOSS coating onto the inner rotor, we consistently obtained a significant reduction in the measured torque for $Re > Re_c$. Remarkably, we found that the averaged drag reduction steadily increases with $Re$ (see Fig. 4-3), from 6% at $Re = 19,000$ to a maximum of 15% at $Re_{max}$ for the unconnected configuration with an isolated plastron, and up to 22% at $Re_{max}$ in the case of the connected plastron. In the inset of Fig. 4-3, we plot the average inner wall shear stress $\tau_i = T/(2\pi r_i^2 L)$ measured over a period of 600 s for a single measurement at $Re_{max}$. Initially, the rotor is at rest and is then accelerated to $\Omega = 250$ rad/s at $t = 0$. The measured torque reductions due to the superhydrophobic coating are 2 orders of magnitude larger than the $\sim 0.02$ Pa resolution limit of the sensor. The
unconnected superhydrophobic coating shows a steady reduction of $\Delta \tau_i = 3.2$ Pa over the entire duration of the measurement. The connected configuration exhibits an additional decay in the measured torque with time, caused by the augmentation of air to the connected plastron at high rotor velocities, resulting in a final reduction in torque of $\Delta \tau_i = 8.0$ Pa in this configuration. Upon time averaging across multiple runs, we found larger relative deviations in the measured torque ($\sigma_T = 0.08$ at $Re_{max}$) for the SH coated rotor (see error bars in Fig. 4-3). In contrast, the PMMA-only coating does not support a plastron and drops of water deposited on the surface wet in the Wenzel state. Consequently, this surface shows a drag increase ($\Delta \tau_i = 0.7$ Pa) as a result of the increased wetted surface area that interacts with the turbulent flow. For a roughness amplitude of $k = 35 \mu m$ [see Fig. 4-2(b)], the drag increase in the Wenzel state at the largest Re corresponds to a surface with dimensionless roughness $k^+ = k/\delta_v = 6.6$. In order to relate our measured drag reduction to effective slip phenomena, we apply a boundary layer theory to relate the global shear-stress measurements to Re. The dimensionless wall shear stress is typically expressed using a skin friction coefficient $C_f = \tau_i / (1/2 \rho V_i^2) = 2(u_T/V_i)^2$. Here, $u_T = (\tau_i/\rho)^{1/2}$ is the friction velocity and $V_i = r_i \Omega$ is the inner rotor velocity for our TC system.
In most shear driven turbulent flows, $C_f$ is described either by a power law\textsuperscript{115} or a semiempirical logarithmic law\textsuperscript{116,117} expressed in Prandtl-von Kármán coordinates as

$$\sqrt{\frac{2}{C_f}} = M \ln \left( Re \sqrt{\frac{2}{C_f}} \right) + N \quad (4.1)$$

where $M$ and $N$ are geometry-dependent constants that are analogous to the “universal” von Kármán constant $\kappa$ and the additive constant $B$ obtained for a perfect flat plate boundary layer.\textsuperscript{117} The product $Re(C_f/2)^{1/2}$ is identical to the friction Reynolds number $Re_r \equiv u_r \Delta r / \nu$ which varies from $Re_r \sim 480 - 3810$ in our system. Although the relative validity of the power-law theory compared to the logarithmic theory is still under dispute, empirical fits to the two forms are often indistinguishable.\textsuperscript{118} In Fig. 4-4, we plot the measured skin friction coefficients for the flat, uncoated inner rotor as filled circles in Prandtl-von Kármán coordinates.\textsuperscript{119} The solid line represents a linear regression of eq 4.1 applied to data points in the shear driven turbulent flow regime, (i.e., $Re > Re_c$), yielding values of $M = 3.9$ and $N = 11.7$. Deviations to the logarithmic skin friction law given by eq 4.1 are observable only when $Re < Re_c$ and the flow is still dominated by Taylor vortices.\textsuperscript{116,117} To determine how Navier wall slip alters the skin-friction law given by eq 4.1 in our wall-bounded turbulent TC flow with a SH surface, we apply the angular momentum defect theory of Panton\textsuperscript{120} and incorporate finite wall slip at the inner surface. Direct measurements of angular momentum profiles\textsuperscript{121,122} as well as direct numerical simulations of turbulent TC flows\textsuperscript{123} verify the existence of a core region with a weakly varying angular momentum dependence, as well as thin wall layers near the inner and outer cylinders that are characterized by a sharp decay in the angular momentum. Panton\textsuperscript{120,124} asymptotically matches the expressions for the mean azimuthal momentum in the core region and the inner wall region to derive a logarithmic skin friction law of the form expressed in eq 4.1.

We modify this theory by introducing a finite averaged slip velocity $\langle V_{\text{slip}} \rangle$ that we relate to the local viscous stress at the inner rotor by the Navier slip hypothesis as $\langle V_{\text{slip}} \rangle = b(d(V_0)/dy)_{y=0}$, where $b$ is the effective slip length due to the superhy-
drophobic coating and $(d(V_/\theta)/dy)_{y=0}$ is the time-averaged velocity gradient at the wall. In the immediate vicinity of the inner rotor, the slip velocities and angular momentum can be rescaled using inner variables defined in terms of the friction velocity $u_*/\Delta r/\nu$ and viscous length scale $\delta_\nu$. The distance away from the inner rotor expressed in wall units is $y^+ = (r - r_i)/\delta_\nu$. If the velocity in the viscous sublayer close to the inner wall is shifted by a constant value according to Min and Kim, so that $\langle V_\theta^+ \rangle = y^+ + b^+$ and $d(V_/\theta^+)/dy^+ = 1$, the Navier-slip hypothesis upon scaling reduces to $V_+/\text{slip} = b^+$, where $V_+/\text{slip} = V_\text{slip}/u_*$ and $b^+ = b/\delta_\nu$. Following Panton, we derive a skin-friction law that incorporates wall slip:

$$\frac{V_i}{u_*} = M \ln \text{Re}_r + N + b^+$$

where $M$ and $N$ are the same geometry-dependent constants as in eq 4.1. An additional simplification is introduced by assuming that the dimensional effective slip length $b$ of the textured superhydrophobic surface is independent of the Reynolds number, so that, upon scaling
With this assumption of a constant physical slip length $b$ in eq 4.2, and introducing $C_f$ and $Re$ in place of $u_r$ and $Re_r$, we obtain a modified skin-friction law for turbulent flow that accounts for wall slip at a superhydrophobic surface and is of the form

$$b^+ = \left( \frac{b}{\Delta r} \right) Re \sqrt{\frac{C_f}{2}}$$

(4.3)

$$\sqrt{\frac{C_f}{2}} = M \ln \left( \sqrt{\frac{C_f}{2}} \right) + N + \left( \frac{b}{\Delta r} \right) \sqrt{\frac{C_f}{2}}$$

(4.4)

In Fig. 4-4 the measured values of $C_f$ for the unconnected and connected SH surfaces are plotted in the Prandtl-von Kármán coordinates. The deviation of the SH data from the linear fit [eq 4.1 for the case of no slip] in Fig. 4-4 arises solely from the final term in eq 4.4. As the values of $M$ and $N$ were previously determined from the uncoated rotor, a nonlinear regression for the SH data using eq 4.4 results in values of $b = 12 \, \mu m$ and $b = 19 \, \mu m$ for the effective slip lengths of the unconnected and connected FPOSS coatings respectively. Therefore, a single value of the dimensional effective slip length is able to account for the entire range of drag reduction observed experimentally. The increasing values of $b^+$ and the larger values of drag reduction at higher $Re$ are therefore a direct consequence of the smaller viscous length scale $\delta_v$ in the flow. In the limit of $Re \to \infty$ we expect the logarithmic term in eq 4.4 to become much smaller than the final term for $b^+$ which varies linearly with $Re(C_f/2)^{1/2}$. Matching the left-hand side of eq 4.4 with this last term results in a predicted scaling of $C_f \sim 1/Re$, which in conjunction with eq 4.4 implies that $b^+ \sim Re^{1/2}$ at large $Re$. To verify this scaling, we compute the value of $b^+$ at each $Re$ using the best-fit value of $b$ (see Fig. 4-4) and the measured value of $\delta_v = \nu(\rho/\tau_i)^{-1/2}$. From Fig. 4-5, it is evident that $b^+$ indeed scales as $Re^{1/2}$ at large $Re$, for both the connected and unconnected SH surfaces. A similar scaling is expected for superhydrophobic drag reduction in turbulent boundary layer flows.
Figure 4-5: Scaling of the dimensionless slip length $b^+ = b/\delta_v$ that is obtained using a fixed value of $b$ from the nonlinear regression of eq 4.4 and with $\delta_v$ determined from measurements of the torque $T$ at various Re. The dashed line is a fit to the scaling $b^+ \sim \sqrt{Re}$ for the last six data points.

### 4.4 Conclusions

In summary, we have demonstrated a reduction in the measured inner wall skin friction in turbulent TC flows by applying a sprayable SH surface onto the inner rotor. We observed that the extent of drag reduction increases with Reynolds number from 6% at $Re \sim 2 \times 10^4$ to a maximum of 15% and 22% for the isolated and connected plastrons, respectively, at $Re \sim 8 \times 10^4$. By applying a boundary layer theory for turbulent TC flow, we developed a modified form of the Prandtl-von Kármán skin friction law from which we extracted an effective slip length $b$ that characterizes the connected and unconnected SH coatings and is consistent with earlier friction reduction measurements in viscous laminar flows. Our measurements demonstrate that the amount of drag reduction attainable in turbulent near-wall flows is directly related to the dimensionless effective slip length $b^+ = b/\delta_v$. As $b^+$ couples the effective slip length $b$ (a material parameter) to the viscous length scale $\delta_v$ of the turbulent flow, our results establish that superhydrophobic surfaces, despite typically exhibiting effective slip lengths of only tens of micrometers, can indeed reduce the skin friction in turbulent flows when the viscous sublayer is of comparable thickness, provided that the air plastron trapped in the SH surface can be stably maintained.
Chapter 5

Designing hierarchically textured oleophobic fabrics

Commercially available woven fabrics (e.g., nylon- or PET-based fabrics) possess inherently re-entrant textures in the form of cylindrical yarns and fibers. We analyze the liquid repellency of woven and nano-textured oleophobic fabrics using a nested model with \( n \) levels of hierarchy that is constructed from modular units of cylindrical and spherical building blocks. At each level of hierarchy, the density of the topographical features is captured using a dimensionless textural parameter \( D^*_n \). For a plain-woven mesh comprised of chemically treated fiber bundles \((n = 2)\), the tight packing of individual fibers in each bundle \((D^*_2 \approx 1)\) imposes a geometric constraint on the maximum oleophobicity that can be achieved solely by modifying the surface energy of the coating. For liquid droplets contacting such tightly bundled fabrics with modified surface energies, we show that this model predicts a lower bound on the equilibrium contact angle of \( \theta_E \approx 57^\circ \) below which the Cassie-Baxter to Wenzel wetting transition occurs spontaneously and this is validated experimentally. We demonstrate how the introduction of an additional higher order micro/nano-texture onto the fibers \((n = 3)\) is necessary to overcome this limit and create more robustly non-wetting fabrics. Finally, we show a simple experimental realization of the enhanced oleophobicity of fabrics by depositing spherical microbeads of poly(methyl methacrylate)/fluorodecyl polyhedral oligomeric silsesquioxane (fluorodecyl POSS)
onto the fibers of a commercial woven nylon fabric.

5.1 Introduction

The fabrication of non-wetting surfaces and coatings that repel low surface tension oils and organic liquids in the Cassie-Baxter state requires the presence of re-entrant topographies coupled with low surface energy coatings.\textsuperscript{19,125,126} Commercially available woven fabrics possess inherently re-entrant textures in the form of cylindrical yarns and fibers. Various coating techniques including dip-coating,\textsuperscript{22,127} chemical vapor deposition,\textsuperscript{128-130} and fluorosilane/acrylate chemistry\textsuperscript{131-134} have been used to chemically modify the surface energy of woven fabrics and impart an oleophobic character. This allows the treated fabric to support low surface tension drops (e.g., alkanes and organic liquids) in the non-wetting Cassie-Baxter state.\textsuperscript{135} However, despite exhibiting large values of the apparent contact angles, these liquid drops are inherently metastable,\textsuperscript{11,126} and irreversibly transition to a fully-wetted state if the liquid makes contact with a sufficiently large defect in the re-entrant topography, or a sufficiently large pressure differential is imposed across the composite Cassie-Baxter interface (e.g., an impacting drop, jet, spray, or submersion in a large reservoir of fluid).\textsuperscript{136} In order to enhance the robustness of the wetting transition on structured non-wetting surfaces (including woven fabrics), merely designing surfaces with large values of the macroscopic apparent contact angle is not sufficient. Instead, the relevant oleophobic character of these surfaces is governed by the degree to which they resist transition to a fully-wetted Wenzel state. In this context, designing fabrics that maximize oleophobicity involves understanding how the weave structure and chemical coating concomitantly influence the Cassie-Baxter to Wenzel wetting transition.\textsuperscript{135,137} The development of such a framework attains further significance in the context of designing fabrics that are resistant to wetting upon impact by chemical weapons/sprays consisting of low surface tension liquid droplets of small radii with correspondingly large internal Laplace pressures.\textsuperscript{138}

Multifilament woven fabrics can be modeled as hierarchically recursive microstruc-
tures. They consist of groups of adjacent cylindrical fibers that are wound together to form cylindrically bundled yarns, which are subsequently woven into fabrics. The design principles of hierarchical non-wetting structures were first investigated by Herminghaus, who established a recursive Cassie-Baxter expression for the value of the macroscopically observable contact angle (henceforth denoted $\theta^*$) on hierarchically textured surfaces and emphasized the possibility that for sufficiently high levels of structural recursion any non-zero value of the equilibrium contact angle (denoted $\theta_E$) is sufficient to engineer liquid and oil repellent hierarchical surfaces with large macroscopic contact angles. More recently, Paxson et al. investigated the self-similar depinning of the three-phase contact line at the edge of liquid drops sitting on various hierarchically structured non-wetting surfaces, and proposed design principles by which these recursive structures can be engineered to reduce pinning and increase the liquid repellency.

The seminal work of Cassie and Baxter, conducted in the 1940s, on understanding the water-repellency of porous substrates was initially formulated in the context of textile wettability using a canonical model consisting of arrays of parallel cylinders, and has since been extensively applied in the design of a diverse range of non-wetting textured surfaces including fabrics. Michielsen and Lee recognized the hierarchical nature of multifilament woven fabrics and recursively extended the Cassie-Baxter model to predict the apparent contact angle of a water drop on a superhydrophobic multifilament woven fabric. In their analysis, Michielsen and Lee introduce two generations of hierarchy. At the first level of hierarchy (which we denote $n = 1$), they consider the yarn as a series of large parallel cylinders of radius $R_1$ woven at a $30^\circ$ angle resulting in a half-spacing of $D_1 = R_1(\sqrt{3} - 1)$. The value of the apparent contact angle of the liquid drop on the yarn is then determined by a second level of hierarchy ($n = 2$); wherein the array of monofilament fibers are also modeled as closely spaced parallel cylinders with the mean half-spacing of the fibers $D_2$ assumed to be equal to the fiber radius $R_2$ (i.e., $D_2 \approx R_2$). Michielsen and Lee demonstrate that their recursive model can be used to characterize the water-repellency of multifilament woven fabrics. We extend this model to also consider higher levels of texture,
which might be generated, for example, by deposition of various structured nanoparticles. The addition of spherical\textsuperscript{128,143-146} and cylindrical\textsuperscript{147-149} nanoparticles has been shown to improve the non-wetting character of various fiber- and fabric-based materials. The model we propose can be applied to any such multi-level structure, composed of cylindrical or spherical units, and illustrates how an additional level of nanotexture can dramatically enhance the degree of liquid repellency.

In this work, we initially perform a series of contact angle measurements on a set of nine dip-coated oleophobic woven fabrics with varying yarn radius and half-spacing (see Table 5.1) using probe liquids of decreasing surface tensions (i.e., $\gamma_{lv} = 72.1$ mN/m to 25.3 mN/m). We observe that the trends of macroscopic apparent contact angles and the transition to the fully-wetted Wenzel state are analogous across all nine dip-coated woven fabrics despite the differences in construction. A modified version of the hierarchical model of Michielsen and Lee was fit to the measured contact angle data on each dip-coated fabric allowing for the determination of a single dimensionless geometrical parameter ($D^*_f$) that describes the observed wetting behavior on each woven fabric. The model further predicts the existence of a critical value of the equilibrium contact angle of $\theta_E^{(c)} \approx 57^\circ$, below which a liquid drop will spontaneously transition to the fully wetted Wenzel state via a wicking mechanism. The introduction of an additional higher order micro/nano-texture on the fibers ($n = 3$) is necessary to overcome this limit. Finally, we provide an experimental example of how introducing a spherical microtexture on the individual fibers can be used to overcome this limit and produce a strongly oleophobic fabric.

### 5.2 Materials and Methods

#### 5.2.1 Characterization of fabrics

A set of nine multifilament woven fabrics (four polyester and five nylon, International Textile Group) were investigated. Representative Scanning Electron Micrograph (SEM) images of each of the nine fabrics are provided in the Appendix B as
Fig. B-1–B-9. An image analysis program (ImageJ, NIH) was used to measure the mean radius and half-spacing of the fiber bundles in both the warp and weft directions. The four polyester-based fabrics are labeled A to D and the remaining Nylon-based fabrics are labeled E to I. In Table 5.1, we provide a summary of the fabric type, measured values of mean diameter of the yarn in the orthogonal warp ($2R_{\text{warp}}$) and weft ($2R_{\text{weft}}$) directions (warp and weft directions were defined arbitrarily), the mean spacing between warp yarns ($2D_{\text{warp}}$) and weft yarns ($2D_{\text{weft}}$).

Table 5.1: The base material used for fabric construction, values of the yarn half spacing in the warp ($D_{1,\text{warp}}$) and weft ($D_{1,\text{weft}}$) directions, and the yarn radius in the warp ($R_{1,\text{warp}}$) and weft ($R_{1,\text{weft}}$) directions for the fabrics used in this study. Corresponding images are provided in Appendix B as Fig. B-1–B-9.

<table>
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<th>Fabric</th>
<th>Material</th>
<th>$D_{1,\text{warp}}$ ($\mu$m)</th>
<th>$D_{1,\text{weft}}$ ($\mu$m)</th>
<th>$R_{1,\text{warp}}$ ($\mu$m)</th>
<th>$R_{1,\text{weft}}$ ($\mu$m)</th>
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<tr>
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5.2.2 Substrate coating

In order to confer liquid-repellent behavior to the woven fabrics, a dip-coating technique was used to deposit a low surface-energy coating to the fabrics. A 50/50 wt% solution of fluorodecyl polyhedral oligomeric silsesquioxane (fluorodecyl POSS; $\gamma_{sv} \approx 10$ mN/m)/Tecnoflon (BR9151; Solvay Solexis; $\gamma_{sv} \approx 12$ mN/m) with a total solids concentration of 20 mg/ml was prepared using the HCFC solvent Asahiklin (AK225, Asahi Glass Company). All fabrics were initially dipped in the fluorodecyl POSS/Tecnoflon solution for 2 minutes, and then allowed to dry in ambient atmospheric conditions for 5 minutes. The fluorodecyl POSS/Tecnoflon dip-coating treatment deposits a thin ($\sim 200$ nm) uniform conformal oleophobic coating onto
the individual fibers of the woven fabric, and thus allows us to control the wetting behavior across the various fabrics, without altering the underlying geometrical structure. The Tecnoflon is a fluoroethylene copolymer that acts as an elastomeric binder conferring flexibility and durability to the coating.\textsuperscript{151}

To impart random corpuscular microstructures ($D_{\text{mean}} \approx 5 \, \mu\text{m}$) on the fabrics a spray-coating technique previously developed in our laboratory was used.\textsuperscript{57} A 50/50 wt\% solution of fluorodecyl POSS/Poly(methyl methacrylate) (PMMA; $M_w = 102 \, \text{kg} \, \text{mol}^{-1}$) with a total solids concentration of 50 mg/ml was dissolved in Asahiklin and sprayed onto the fabrics from a distance of 20 cm.

### 5.2.3 Contact angle measurements

Contact Angle (CA) measurements were carried out using a ramé-hart goniometer after vertically depositing a drop of $V \approx 5 \, \mu\text{L}$ on each fabric sample. The probe liquids used in this study were reagent grade deionized (DI) water, dimethyl sulfoxide (DMSO), methylene iodide, ethylene glycol, rapeseed oil, dimethyl methylphosphonate (DMMP), hexadecane, decane, tributyl phosphate, methanol, 2-propanol, and heptane. The reported contact angle values represent averages over four or more measurements taken at different locations on the sample.

### 5.3 Theoretical Framework

Flat substrates with low surface energies on the order $\gamma_{sv} \sim 10 \, \text{mN/m}$ exhibit equilibrium Young’s contact angles with water drops ($\gamma_{lw} = 72.1\text{mN/m}$) that are larger than $90^\circ$.\textsuperscript{5,142} However, drops of various oils and low surface tension liquids (e.g., hexadecane; $\gamma_{lw} = 27.5 \, \text{mN/m}$) deposited on the same low energy surface result in Young’s contact angles that are much smaller (i.e., $\theta_E < 90^\circ$).\textsuperscript{151} Therefore, chemically treated flat surfaces with very low surface energies are typically still oleophilic to liquids with surface tensions $\gamma_{lw} \lesssim 30 \, \text{mN/m}$. The introduction of textured, re-entrant surface topographies (e.g., nanonails, hoodoos, or the cylindrical fibers and yarns of woven fabrics) is necessary to enable the low surface tension liquid drop to
rest in a metastable non-wetting Cassie-Baxter state.\textsuperscript{11,19}

Cassie and Baxter\textsuperscript{3} modeled the behavior of liquid drops on monofilament textiles as an array of parallel cylinders supporting a composite solid-liquid-air interface to obtain their well-known equation, which can be expressed in the following form:\textsuperscript{11}

\[
\cos \theta^* = -1 + \frac{1}{D^*} \left[ (\pi - \theta_E) \cos \theta_E + \sin \theta_E \right]
\]

Here, $\theta^*$ is the macroscopic apparent contact angle exhibited by the liquid drop deposited on the array of cylinders, $\theta_E$ is the corresponding Young's contact angle on a flat surface exhibiting an identical surface chemistry to that of the cylinder, and $D^* = (R + D)/R$ is a dimensionless geometric parameter defined in terms of the half-spacing between the cylinders $D$ and the radius of the cylinder $R$. This simple one-dimensional cylindrical model is widely used to model the wetting of monofilament textiles.

However, Michielsen and Lee\textsuperscript{28} draw attention to the hierarchical nature of multifilament woven fabrics, for which equation 5.1 cannot directly be applied and needs to be recursively modified. We illustrate the hierarchical structure of a typical fabric in Figure 5-1, where we show a series of Scanning Electron Micrographs (SEMs) on a multifilament woven fabric that demonstrates two levels of hierarchy corresponding to the bundled yarn and individual fibers. Figure 5-1a is an SEM of a woven nylon-based fabric (Fabric G) consisting of a uniform weave structure. The fabric has been dipcoated in a solution of 50 wt\% fluorodecyl POSS/Tecnoflon to deposit a conformal low-surface-energy coating. The uniform and regular weave that we observe in Fabric G is contrasted to a more loosely-woven polyester-based fabric (Fabric B) that is marked by the presence of weave openings between the warp and weft directions. The presence of these weave openings is captured by changes to the half spacing and radius of the bundled yarns. Therefore, at a macroscopic or 'coarse-grained' level, we expect the geometry of the bundled yarn to influence the wetting behavior of liquid drops on the woven fabric. In Figures 5-1c and 5-1d, we show micrographs at two different magnifications of a cured drop of a silicone elastomer (Sylgard 184, Dow
Figure 5-1: (a) Scanning Electron Micrograph (SEM) of a plain-woven Nylon fabric (Fabric G) which has undergone a hydrophobic treatment by dipcoating in a 50/50 fluorodecyl POSS/Tecnoflon solution. The inset shows a drop of water ($\gamma_{lv} = 72.1$ mN/m) vertically deposited onto the fabric exhibiting a high apparent contact angle of $\theta_1 = 146^\circ$; (b) SEM of a Polyester fabric (Fabric B) exhibiting randomly located weave openings in the woven structure; (c,d) SEM micrographs of the contact line structure of a cured PDMS ($\gamma_{lv} \approx 25$ mN/m) drop resting on Fabric G at different magnifications corresponding to different textural length scales in the fabric. (c) illustrates the shape of the contact line at a length scale corresponding to the bundled yarn of the woven fabric, while (d) captures the tortuosity of the contact line at the scale of the individual fibers within a bundle.
Corning; $\gamma_v \approx 25 \text{ mN/m}$) that has been deposited vertically on the dip-coated oleophobic Fabric G, and subsequently heat treated for 20 minutes at 80 °C to cure. At this higher level of magnification, the inner hierarchical cylindrical structure of the individual fibers is immediately evident. The fibers are densely packed, with radii that are an order of magnitude smaller than the bundled yarn. In Figure 5-1d, we show the topographical details of the wetted perimeter of the cured silicone drop on the collection of individual fibers. These small, tightly bundled fibers play a key role in determining the critical surface tension at which a millimetric liquid drop transitions to the Wenzel state and is subsequently imbibed into the fabric.

The self-similar cylindrical structures that are observed in Figure 5-1(a-d) suggest that Eqn. 5.1 needs to be recursively applied to the smaller individual fibers and larger bundled yarn to predict the apparent contact angles of liquid drops sitting on multifilament woven fabrics. Here, we apply the recursive framework developed by Herminghaus$^{29}$ to expand on the work of Michielsen and Lee.$^{28}$ Thus, systematically developing a set of equations that can model both multifilament woven and nanotextured woven fabrics.

### 5.3.1 Modeling apparent contact angles on multifilament woven fabrics

In Figure 5-2, we illustrate schematically a liquid drop resting on an oleophobic multifilament fabric. The first level of hierarchy ($n = 1$; cf. Figure 5-2a) captures the woven geometry of the yarn which is modeled as an array of parallel cylinders with a radius $R_1$, half-spacing $D_1$ and characterized by the dimensionless geometrical parameter $D_1^* = (R_1 + D_1) / R_1$. The value of $D_1^*$ is related to the weave angle $\alpha$ (between the warp/weft directions and the fabric plane) as $D_1^* = \cot \alpha$. Variations in this geometric parameter $D_1^*$ allows us to account systematically for the wetting effects of various weave constructions and the presence of weave openings on the non-wettability of different fabrics. A small value of $D_1^*$ corresponds to fabrics with a very fine weave, while large values of $D_1^*$ indicate a looser weave with higher incidences of weave open-
ings. At the second level of hierarchy \((n = 2; \text{Figure 5-2b})\), we model the packing of individual fibers into bundles with radius \(R_2\) and mean half-spacing \(D_2\), that are characterized by a dimensionless length scale \(D^*_2 = (R_2 + D_2)/R_2\). A consequence of constructing the yarn as a collection of tightly bundled fibers is that, for multifilament woven fabrics, the value of the inter-fiber spacing \(D_2 \to 0\) (as seen in Figure 5-1d) which leads to \(D^*_2 \to 1\). The local effective contact angle of the liquid meniscus that is established on the array of individual fibers is denoted as \(\theta_2\). For the plain weave multifilament fabrics that we have discussed so far, the hierarchy of equations terminates at \(n = 2\). The equilibrium contact angle that characterizes the nature of the coating applied to the individual fibers is denoted as \(\theta_E\). To define canonically the hierarchical nature of these plain weave fabrics, we denote these two-level cylindrical structures as a CC fabric, as we recursively apply eq 5.1 twice. Therefore, the set of equations that govern the wetting of a liquid drop on a multifilament woven fabric (or CC fabric) with \(n = 2\) is given by eq 5.2a and 5.2b:

\[
\cos \theta_1 = -1 + \frac{1}{D^*_1} \left[ (\pi - \theta_2) \cos \theta_2 + \sin \theta_2 \right] \quad (5.2a)
\]
\[
\cos \theta_2 = -1 + [(\pi - \theta_E) \cos \theta_E + \sin \theta_E] \quad (5.2b)
\]

Eq 5.2a predicts the macroscopic apparent contact angle \(\theta_1\) of a droplet placed on the CC fabric while eq 5.2b governs the apparent contact angle \(\theta_2\) of the liquid meniscus on an array of individual fibers that are tightly bundled (with \(D^*_2 \to 1\)). For a wide range of liquids, the mapping implied by eqs 5.2a and 5.2b amplifies the local equilibrium contact angle \((\theta_E)\) to a new (larger) value of \(\theta_1\) on the hierarchically textured surface, thus enhancing the non-wettability or “repellency” of the fabric. We will extend this model to a third level of hierarchy as shown schematically in Figure 5-2(d).
Figure 5-2: (a) Schematic of an axisymmetric liquid drop on a model sinusoidal non-wetting woven fabric showing different levels of hierarchy. The AA' plane illustrates the cross-sectional view of the periodic woven structure, consisting of bundled yarns of diameter $2R_1$ separated by a distance $2D_1$. The dimensionless geometric parameter $D_1^*$ is related to the angle of weave $\alpha$ as $D_1^* = (R_1 + D_1)/R_1 = \cot \alpha$; (b) Schematic of the second level of hierarchy depicting the location of the contact line resting on the individual non-wetting fibers which compose the yarn. The fibers are modeled as parallel cylinders of diameter $2R_2$ separated by a distance $2D_2$. The packing of the fibers is governed by the dimensionless geometric parameter $D_2^* = (D_2 + R_2)/R_2$ which is taken to be $D_2^* \approx 1$ (corresponding to the tightly woven limit) consistent with the SEM micrographs shown in Figure 5-1d; (c) Schematic of a third level of textural hierarchy, with the individual fibers decorated by an array of spherical micro- or nano-particles of radius $2R_3$ and a mean spacing distance of $2D_3$. The packing of the spherical particles is governed by the dimensionless parameter $D_3^* = (R_3 + D_3)/R_3$. 

\[ D_1^* = \frac{(R_1 + D_1)}{R_1} = \cot \alpha \]

\[ D_2^* = \frac{(D_2 + R_2)}{R_2} \]

\[ D_3^* \gg 1 \]
5.3.2 Pressure-driven transition from the Cassie-Baxter to Wenzel state on multifilament fabrics

The equilibrium contact angle $\theta_E$ can be lowered by (i) depositing liquid drops with lower surface tensions (such as oils) for a given chemical coating on the fibers or (ii) modifying the surface chemistry of the fibers resulting in larger values of surface energy ($\gamma_{sw}$) for a given liquid drop. In either scenario, as $\theta_E$ decreases, the liquid drop will progressively wet larger fractions of the fabric until it eventually undergoes a transition to the fully wetted Wenzel state. The Cassie-Baxter to Wenzel transition is driven by the pressure differential that exists across the composite liquid-air interface, and occurs either by a depinning or sagging mechanism.\textsuperscript{125,126} This transition occurs as a sequential cascade in hierarchical structures, with the larger air pockets trapped between textural features at the larger length scales ($n = 1$) readily prone to collapse. When liquids with large values of $\theta_E$ (i.e., high surface tension liquids) are deposited on multifilament fabrics, they wet only the tops of the woven yarns. This has been demonstrated both by direct visualization and finite element simulations of water on arrays of nonwetting cylinders.\textsuperscript{153} However, upon decreasing the value of $\theta_E$, the meniscus descends into the texture until it transitions to resting on the individual fibers that comprise the warp (weft) yarn that lies underneath two adjacent weft (warp) yarns (see Figure 5-1c). Therefore, the eventual wetting transition to the fully wetted Wenzel state is determined by the smaller length ($n = 2$, fibers) on hierarchical structures such as multifilament woven fabrics. The critical (or breakthrough) pressure difference ($\Delta P_b$) across the liquid-air interface at which the drop irreversibly transitions to the fully-wetted Wenzel state at the largest defect site can be expressed for an array of parallel cylinders as:\textsuperscript{152,153}

$$\Delta P_b = (\gamma_{vc} / R_2) \left[ \sin(\theta_E - \vartheta_c) / (D^*_2 - \sin \vartheta_c) \right]$$

(5.3)

Where $R_2$ is the radius of the fiber at the second level of hierarchy and $\vartheta_c$ is the critical angular position of the contact line on the cylinder at the onset of transition.\textsuperscript{152} At this critical angular position, the transition can occur by either a depinning or a
sagging mechanism.

When a liquid drop of surface tension $\gamma_{lv}$ and radius $r_{\text{drop}} \sim V_{\text{drop}}^{1/3}$ is deposited on an array of cylinders, the Laplace pressure inside the drop is $\Delta P_l = 2\gamma_{lv}/r_{\text{drop}}$. A spontaneous transition to the fully-wetted Wenzel state is expected to occur when the Laplace pressure ($\Delta P_l$) exceeds the breakthrough pressure ($\Delta P_b$). The equilibrium contact angle corresponding to the liquid drop at which this critical wetting transition occurs (leading to a loss of the non-wetting character of the fabric) is denoted as $\theta_E^{(c)}$. A crucial feature of the wetting transition arises from the thermodynamic metastability of the non-wetting Cassie-Baxter state described by eq 5.1 when $\theta_E < 90^\circ$ (e.g., most oils) and a wetting transition can be nucleated by a single localized defect. The inverse dependence of eq 5.3 on the feature length scale ($R_2$) means that the largest defect site in the periodic array acts as the initial nucleation site for the Cassie-Baxter to Wenzel transition. In our calculations below, we assume a defect-free tightly bundled packing of uniform radius fibers with $D^*_2 \approx 1$.

In the experiments performed, the drop radius of the probe liquid is fixed as $r_{\text{drop}} \approx 1.5$ mm. For a liquid drop of heptane ($\gamma_{lv} = 20.1$ mN/m; $\theta_E = 63^\circ$) resting on a planar array of cylinders corresponding to the smallest length scale in the fabric ($i.e., n = 2$; with a fiber spacing ratio of $D^*_2 \approx 1$ and a fiber radius of $R \sim 10$ $\mu$m), the expected ratio of the breakthrough pressure to the Laplace pressure is $\Delta P_b/\Delta P_l \approx 36$, which suggests that the drop is expected to be stable. However, the tight packing of the bundled fibers provides an alternate route to the Wenzel transition by a wicking mechanism. When the apparent contact angle $\theta_2 \to 0$ on the individual fibers shown in Figure 5-2b with decreasing values of $\theta_E$, the Cassie-Baxter state supported at the second level of hierarchy ($i.e., n = 2$, between the tightly packed fibers) undergoes a wetting transition and the liquid is imbibed completely into the fiber bundle spreading along the individual fiber filaments. Setting $\cos \theta_2 = 1$ in eq 5.2b, we solve this implicit equation to obtain a critical value of $\theta_E^{(c)} \approx 57.2^\circ$ when this wetting transition occurs. Physically, this implies that a liquid drop with an equilibrium contact angle smaller than this critical value will completely wet the individual fibers and be imbibed into the fabric irrespective of the larger scale geometry of the weave. The loss of the Cassie-
Baxter composite state at the $n = 2$ level of hierarchy results in the liquid drop rapidly wicking along the individual fibers until the entire fabric is wetted. Therefore, even if a liquid drop initially exhibits a fairly large macroscopic apparent contact angle on the fabric (i.e., $\theta_1 \gg 90^\circ$), as the equilibrium contact angle $\theta_E$ approaches $\theta_E \approx 57.2^\circ$, it will sharply transition to $\theta_1 = 0$ as the liquid is imbibed into the texture.\textsuperscript{23}

5.4 Results and Discussion

5.4.1 Characterization of dip-coated oleophobic fabrics using goniometric measurements

Contact angle measurements were performed on each of the nine dip-coated fabrics using probe liquids with sequentially decreasing values of surface tension from water ($\gamma_{lv} = 72.1$ mN/m) to n-heptane ($\gamma_{lv} = 20.1$ mN/m). In Table 5.2, we report the measured values of the macroscopic static contact angles ($\theta_1$) on the various dip-coated fabrics. We also list the corresponding values of the equilibrium contact angle ($\theta_E$) measured on flat substrates spin-coated with the same fluorodecyl POSS/Tecnoflon solution. While the equilibrium contact angle on flat surfaces can be measured fairly accurately via goniometry ($\Delta \theta_E = \pm 1^\circ$), difficulties in precisely establishing the position of the three-phase contact line on the textured fabrics results in larger uncertainties in the measurement of apparent contact angles ($\Delta \theta_1 = \pm 5^\circ$).

All dip-coated fabrics are strongly water repellent exhibiting large macroscopic contact angles of $\theta_1 \approx 135^\circ$ with water drops and are also resistant to wetting by low surface tension hexadecane drops ($\gamma_{lv} = 27.5$ mN/m; $\theta_1 \approx 95^\circ$), emphasizing the oleophobic non-wetting character that the dip-coating process confers on the nylon and PET based materials. As mentioned earlier, the dip-coating process that conformally deposits the fluorodecyl POSS/Tecnoflon coating ensures that the value of $\theta_E$ corresponding to a particular probe liquid is systematically controlled. Therefore, the values of $\theta_E$ are identical across all fabrics and any variation in the experimentally measured macroscopic contact angle $\theta_1$ is attributable to the geometry of the outer
Table 5.2: Summary of the surface tension ($\gamma_{lv}$), equilibrium contact angle on a flat fluorodecyl POSS/Technoflon coating ($\theta_E$), and apparent contact angles ($\theta_1$) on the nine PET and Nylon fabrics for the thirteen probe liquids of interest. ($^t$ - Dimethyl methylphosphonate)

<table>
<thead>
<tr>
<th>Probe Liquid</th>
<th>$\gamma_{lv}$ (mN/m)</th>
<th>$\theta_E$ (±1°)</th>
<th>Dip-coated Fabrics</th>
<th>$\theta_1$ (±5°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A  B   C  D  E  F  G  H  I</td>
<td>A  B   C  D  E  F  G  H  I</td>
</tr>
<tr>
<td>Water</td>
<td>72.1</td>
<td>109</td>
<td>130 129 140 142 133 133 132 135 123</td>
<td></td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>43.5</td>
<td>97</td>
<td>114 116 121 115 121 106 109 113 107</td>
<td></td>
</tr>
<tr>
<td>Methylene Iodide</td>
<td>50.8</td>
<td>96</td>
<td>103 105 107 104 116 108 105 115 101</td>
<td></td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>47.7</td>
<td>96</td>
<td>114 113 127 131 132 116 113 103 98</td>
<td></td>
</tr>
<tr>
<td>Rapeseed Oil</td>
<td>35.5</td>
<td>92</td>
<td>111 118 125 111 124 110 108 122 107</td>
<td></td>
</tr>
<tr>
<td>DMMP$^t$</td>
<td>36.7</td>
<td>88</td>
<td>89 94 110 80 91 95 102 93 101</td>
<td></td>
</tr>
<tr>
<td>Hexadecane</td>
<td>27.5</td>
<td>83</td>
<td>0 95 97 91 111 97 92 90 86</td>
<td></td>
</tr>
<tr>
<td>Dodecane</td>
<td>25.4</td>
<td>79</td>
<td>0 92 96 88 97 83 84 81 79</td>
<td></td>
</tr>
<tr>
<td>Decane</td>
<td>23.8</td>
<td>79</td>
<td>0 84 92 76 79 83 80 72</td>
<td></td>
</tr>
<tr>
<td>Tributyl Phosphate</td>
<td>27.8</td>
<td>71</td>
<td>0 84 77 85 64 0 77 84</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>22.1</td>
<td>66</td>
<td>0 84 85 72 82 0 76 84 69</td>
<td></td>
</tr>
<tr>
<td>2-Propanol</td>
<td>23.3</td>
<td>65</td>
<td>0 81 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>20.1</td>
<td>63</td>
<td>0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
</tbody>
</table>

weave, and in particular to the value of $D_1^*$ (related to the yarn weave angle $\alpha$ as $D_1^* = \cot \alpha$). In each of the fabrics, the macroscopic apparent contact angle decreases with lower surface tension liquid drops (i.e., correspondingly smaller values of $\theta_E$), indicative of progressively larger solid/liquid wetted fractions as more of each individual cylindrical fiber is wetted until eventually a wetting transition occurs to the Wenzel state. We perform a non-linear regression of the measured values of $\theta_1$ and $\theta_E$ using eq 5.2a and 5.2b to obtain a best-fit estimate of the dimensionless textural parameter $D_1^*$ that describes the spacing between the yarns for each fabric.

The results of these regression fits are depicted graphically in Figures 5-3(a-d). The cosines of the experimentally measured values of the macroscopic apparent contact angle ($\cos \theta_1$) are plotted against the cosines of the equilibrium contact angles ($\cos \theta_E$) for four representative dip-coated nylon (Fabrics G and I) and polyester (Fabrics B and C) fabrics with differing weaves. We can use the recursive model described by eq 5.2a and 5.2b to obtain two predicted non-wetting curves (corresponding to the warp and weft directions) using values of $R_1$ and $D_1$ that are obtained from microscopy (see Table 5.1). These curves are plotted as solid blue lines in Figures
5-3(a-d), and represent the upper and lower bounds to the microscopy-based model predictions of $\theta_1$ (bounding the region shaded in blue). In Table 5.3, the values of the best-fit textural parameter for all nine fabrics are listed, along with the microscopy based estimates along the warp/weft directions.

Table 5.3: Fitted values of $D^*$ and corresponding values determined from microscopy for the nine PET and nylon fabrics of interest.

<table>
<thead>
<tr>
<th>Fabric</th>
<th>$D^*_1$ from Fitting</th>
<th>$D^*_1$ from Microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$D^*_{1,\text{warp}}$</td>
</tr>
<tr>
<td>A</td>
<td>1.2 ± 0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>B</td>
<td>1.7 ± 0.3</td>
<td>2.4</td>
</tr>
<tr>
<td>C</td>
<td>1.8 ± 0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>D</td>
<td>1.5 ± 0.3</td>
<td>1.7</td>
</tr>
<tr>
<td>E</td>
<td>1.7 ± 0.3</td>
<td>2.0</td>
</tr>
<tr>
<td>F</td>
<td>1.3 ± 0.1</td>
<td>1.8</td>
</tr>
<tr>
<td>G</td>
<td>1.5 ± 0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>H</td>
<td>1.5 ± 0.3</td>
<td>2.2</td>
</tr>
<tr>
<td>I</td>
<td>1.4 ± 0.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

As is evident from Figures 5-3(a-d) and Table 5.3, while the best-fit estimates of $D^*_1$ using the simple hierarchical model of adjacent parallel cylinders qualitatively captures the trends in the non-wetting behavior of the various fabrics, these values are systematically smaller than values that are obtained from microscopy along the warp and weft directions. This result is expected and stems from the fabric possessing three-dimensional structures that protrude into the liquid increasing the real solid fraction of the interface and decreasing the effective $D^*_1$. A more accurate model would require detailed calculation of the topography of the wetted patches that form on the true woven structure using a program such as Surface Evolver. However, despite the significant simplification involved in our 1D cylindrical array model, some important insights underlying the non-wetting behavior of the fabrics can be obtained by application of the hierarchical model. First, despite the differences in fabric construction the values of $D^*_{1,\text{warp}}$ and $D^*_{1,\text{weft}}$ all lie between $1.6 \leq D^* \leq 3.1$. Our best fit values of $D^*_1$ are similar for all fabrics (between 1.2 and 1.8), and this uniformity is expected due to the very similar nature of the weave angles in all plain weave fabrics,
where the geometry of the tight weave offers little flexibility in choosing values of $D_1*$. For example, Michielsen and Lee\textsuperscript{28} estimate a weave angle of $\alpha \approx 30^\circ$ (corresponding to a value of $D_1^* \approx 1.7$). This intrinsic constraint on the magnitude of apparent contact angles that can be attained on a plain weave fabric requires the introduction of an additional micro- or nanotextured length scale to further enhance the nonwetting character of fabrics.

Figure 5-3 and Table 5.2 also show clearly that for a probe liquid with sufficiently low surface tension, there is a sudden and spontaneous transition to the fully-wetted superoleophilic Wenzel state; the liquid drop readily wicks and spreads along the fabric, resulting in a $0^\circ$ macroscopic contact angle, indicated by the vertical arrow in Figures 5-3(a-d). For the set of fabrics C-E and G-I, this wetting transition occurs upon contact with propanol ($\gamma_{lv} = 23.3$ mN/m; $\theta_E = 65^\circ$), while fabric B wets with n-heptane ($\gamma_{lv} = 20.1$ mN/m; $\theta_E = 63^\circ$).

In each of the fabrics, we also observe that the critical contact angle $\theta_E^{(c)}$ at which a wicking failure occurs is above the predicted limit of $\theta_E^{(c)} = 57.2^\circ$, consistent with the hierarchical CC model of the woven fabric. The variation of the macroscopic contact angle with a variety of liquids on woven fabrics is captured by the single parameter $D_1^*$ in the CC model. However, the tight bundling of the individual fibers from which the yarn is constructed (i.e., $D_2^* \approx 1$) imposes a lower limit on the surface tension of the contacting liquid that can exhibit oleophobicity.

5.4.2 Adding a third length scale of texture to woven fabrics

The undesirable wetting transition, in which the liquid spreads along the closely packed monofilaments of the bundled yarns poses a geometric constraint on the liquid-repellency of woven fabrics. We again emphasize that merely modifying the surface energy by applying various low surface energy coatings is not sufficient to prevent this transition; the introduction of a third level of hierarchy by texturing the individual bundled fibers is required to further amplify the macroscopic contact angle given by the recursive equation set (eq 5.2). This can be achieved, for example, by the introduction of spherical nanoparticles embedded on the fibers. The recursive equations
Figure 5-3: Plot of the cosine of the apparent contact angle $\cos \theta_1$ against the equilibrium contact angle $\cos \theta_E$ on the series of four dip-coated fabrics (a) Fabric B with $D_1^* = 1.73 \pm 0.26$ (b) Fabric C with $D_1^* = 1.75 \pm 0.20$ (c) Fabric G with $D_1^* = 1.51 \pm 0.19$ (d) Fabric I with $D_1^* = 1.41 \pm 0.23$. The best fit curves for $D_1^*$ are plotted as solid black lines for each of the fabrics with the 95% confidence interval band shaded in red. The upper and lower bands, plotted as dashed lines, are used as a measure of uncertainty. The analogous figures for the remaining five fabrics are shown in Appendix B as Fig. B-10–B-14.
Figure 5-4: Plot of the apparent contact angles $\theta_n$ against the equilibrium contact angle $\theta_E$ (predicted by the set of eq 5.4-5.5) on a fabric with $n$ levels of hierarchy. The dotted red line $A$ corresponds to the variation of the contact angle on the individual fibers $\theta_2$ with $\theta_E$ (predicted by eq 5.2b) for the tightly woven limit with $D_2^* = 1$. The solid black curves $B$ and $C$ depict the variation of $\theta_1$ for the two values of $D_1^* = 1.5$ and $D_1^* = 2$, respectively, on the plain-woven fabrics with $n = 2$. The model sinusoidal woven geometries corresponding to curves $B$ and $C$ are shown alongside the plot. The shaded region signifies when the individual fibers are fully wetted ($\theta_E \lesssim 57^\circ$) and is inaccessible to the plain weave fabric with two levels of hierarchy $n = 2$. The dashed black lines show the variation of $\theta_1$ with $\theta_E$ on woven fabrics consisting of textured fibers with $n = 3$ for two nanoparticle spacings $D_3^* = 1.7$ (Curve D) and $D_3^* = 2$ (Curve E).
which determine the apparent contact angle $\theta_n$ at each stage of the $n$ generations of the hierarchical self-similar structure are given by eq 5.4 for a canonical cylindrical geometry (C):\textsuperscript{22,28}

$$\cos \theta_n = -1 + \frac{1}{D_n^*} \left[ (\pi - \theta_{n+1}) \cos \theta_{n+1} + \sin \theta_{n+1} \right]$$ (5.4)

And eq 5.5 for a spherical geometry (S):\textsuperscript{125}

$$\cos \theta_n = -1 + \frac{1}{(D_n^*)^2} \left[ \frac{\pi}{2\sqrt{3}} (1 + \cos \theta_{n+1})^2 \right]$$ (5.5)

In each case the effective contact angle $\theta_n$ that can be achieved depends on the geometry of the texture at this $n^{th}$ scale, and the effective contact angle $\theta_{n+1}$ that is generated by the next, higher order $(n+1)^{th}$ level of texture. In each case the hierarchical equation set is truncated at the finest scale when the surface is locally flat and $\theta_{n+1} \rightarrow \theta_E$. In figure 5-2c, we show one possible realization using spherical nanoparticles to achieve a third generation of hierarchy in the woven fabric, which we denote as a CCS fabric, as we recursively apply eq 5.4 for $n = 1, 2$ and eq 5.5 at $n = 3$. The spherical nanoparticles are embedded into, or deposited onto, the individual fibers of the fabric, and are characterized by a radius $R_3$, half-spacing $D_3$ and a corresponding dimensionless parameter $D_3^* = (D_3 + R_3)/D_3$ characterizing the typical spacing of the individual spherical nanoparticles. We further assume that the chemical coating applied to the spherical nanoparticles is characterized by the same equilibrium contact angle $\theta_E$ that is used for the fibers and yarns. The recursive equations governing the nanoparticle textured CCS fabric (conceptualized in Figure 5-2c) can then be written out explicitly as:

$$\cos \theta_1 = -1 + \frac{1}{D_1^*} \left[ (\pi - \theta_2) \cos \theta_2 + \sin \theta_2 \right]$$ (5.6a)

$$\cos \theta_2 = -1 + \frac{1}{1} \left[ (\pi - \theta_3) \cos \theta_3 + \sin \theta_3 \right]$$ (5.6b)

$$\cos \theta_3 = -1 + \frac{1}{(D_3^*)^2} \left[ \frac{\pi}{2\sqrt{3}} (1 + \cos \theta_E)^2 \right]$$ (5.6c)
where $\theta_3$ refers to the apparent contact angle on the individual nanotextured fibers and we assume a tightly woven structure so that $D^*_2 \to 1$. The introduction of the third level of structure removes the wicking constraint on oleophobicity, and allows for the design and realization of fabrics which can support liquid drops with very low surface tensions in the metastable Cassie-Baxter state. While eq 5.6c is written for a CCS nanotextured fabric, an analogous set of equations can be written for a CCC fabric, where the third generation of nanotexture consists of hairy cylinders. In Figure 5-4, the curves D and E show the variation of the macroscopic apparent contact angle $\theta_1$ with the equilibrium contact angle $\theta_E$ for a spherically nanotextured woven CCS fabric described by eq 5.6a-5.6c with $D^*_1 = 2$, $D^*_2 = 1$ and two different values of $D^*_3$. Larger values of $D^*_3$ result in a lower density of spherical nanoparticles, illustrated by the schematic in the inset of Figure 5-4. The introduction of the nanotextured length scale greatly enhances the apparent contact angle for the CCS fabric that can be achieved when compared to the equivalent CC fabric with the same value of $D^*_1$ (shown in curve C). In addition, the critical equilibrium contact angle at which the wetting transition occurs in the third generation of hierarchy is controlled by the packing of the spheres.

In order to determine the criteria for the pressure driven wetting transition on the array of nanospheres, we adapt the work of Butt et al.\textsuperscript{125} on vertically sintered spheres. In Figure 5-5, we show an illustration of the liquid meniscus between an array of spherical nanoparticles. The position of the contact line on the sphere is a function of the angle $\phi$ between the contact line, the center of the sphere, and the base of the sphere, and is expressed as $y(\phi) = R_3(1 - \cos \phi)$. The value of $\phi$, which sets the location of the contact line, is determined by a balance of the capillary force pulling the interface upwards against the pressure difference across the interface and can be determined from the implicit equation\textsuperscript{125,154}:

\[
\hat{P} = \frac{\sin \phi \sin(\theta_E - \phi)}{(\cos D^*_3 - \sin^2 \phi)}
\] (5.7)
Figure 5-5: (a) Schematic of the meniscus of a liquid drop resting on a sphere of radius $R_3$ possessing an equilibrium contact angle $\theta_E$. The contact line subtends an angle of $\phi$ with the center of the sphere. The pressure differential across the meniscus $\Delta P$ drives the formation of the curved meniscus with a radius of curvature $R_{sag}$ that subtends a half-angle $\beta$ with the vertical. The bottom of the meniscus is at a height $h$ above the bottom surface. (b) Schematic of the top view of an array of spheres arranged in a square and hexagonal lattice. The geometrical lattice parameters $a_l$, $b_l$ are discussed in the main text. (c) Plot of the dimensionless pressure difference $\hat{P}$ vs. the angle $\phi$ subtended by the contact line to the center of the sphere. Initially, in the absence of any pressure differential ($\hat{P} = 0$), the meniscus is flat and is located at $\phi = \theta_E$ (labeled State A). The value of $\phi$ decreases with increasing pressure difference $\hat{P}$ until the pressure reaches a maximum at $\phi = \phi_d$ (labeled State B) which corresponds to a depinning transition. (d) Plot of the minimum meniscus height above the bottom substrate $h$ against the subtended angle $\phi$ showing a gradual decrease until the bottom of the meniscus touches the substrate (i.e., $h = 0$) when $\phi = \phi_s$, signifying a sagging transition (shown in State C). In each of the curves in Fig. 5-5(c,d), the solid, dashed and dash-dot lines correspond to various values of $D_3^*$ and $\theta_E$ as indicated in the figure. Unless otherwise noted, a hexagonal lattice was assumed for the sphere packing.
where $\hat{P} = P/P_{\text{ref}}$ and $P_{\text{ref}} = 2\gamma_{lv}/R_3$ is a reference pressure scale that depends on the liquid surface tension $\gamma_{lv}$ and particle size $R_3$, and $a_l$ is a lattice constant with $a_l = (2\sqrt{3}/\pi)$ for a hexagonally packed array of spheres and $a_l = (4/\pi)$ for a square packing. When there is no external pressure difference (i.e., $\hat{P} = 0$), the liquid meniscus is flat and the contact line wets the spherical nanoparticle at a height determined by $\phi = \theta_{E}$. As $\hat{P}$ is increased, the value of $\phi$ (and therefore, the position of the interface $y$) steadily decreases according to eq 5.7 until the Cassie-Baxter state undergoes a transition to the Wenzel state. This transition can occur in one of the following two ways: (i) a depinning mechanism when the pressure exceeds the maximum capillary force that can be supported by eq 5.7 or (ii) a capillary bulge mechanism when the pressure induces sufficient curvature of the liquid meniscus causing it to touch the underlying substrate on which the spheres are embedded.

In Figure 5-5c, we plot $\hat{P}$ determined from eq 5.7 as a function of $\phi$ for different values of the equilibrium contact angle $\theta_{E}$ and the dimensionless spacing parameter $D_3^*$. In each of the curves, we see that there is a maximum value of $\hat{P} = \hat{P}_{\text{max}}$ at a particular value of $\phi = \phi_d$ (i.e., $d\hat{P}/d\phi|_{\phi=\phi_d} = 0$). For a given value of $D_3^*$ and $\theta_{E}$, the maximum pressure difference that can be supported is larger for a hexagonal packing of spheres compared to a square array. If the dimensionless pressure difference $\hat{P}$ across the meniscus is larger than the value $\hat{P}_{\text{max}}$, the capillary force acting at the contact line will be unable to balance the pressure force at the interface for any point on the sphere. The composite interface therefore depins and wets when the meniscus physically corresponds to state B depicted in the inset of Figure 5-6. The depinning transition $\hat{P}_{\text{dep}}$ is therefore the maximum value of $\hat{P}$ at which $d\hat{P}/d\phi = 0$. An expression for the depinning angle $\phi_m$ is provided by Butt et al.. However, while estimating the capillary bulge pressure, Butt et al. assume that the location of the contact line is determined by $\phi = \theta_{E}$, an assumption which is valid only when $\hat{P} \ll 1$. We can derive a more general analytical expression for the height $h$ of the bottom of the curved meniscus (with radius of curvature $R_{\text{sag}}$) above the substrate (as shown in Fig. 5-5a) as:
\[ h = R_3(1 - \cos \phi) - R_{sag}(1 - \cos \beta) \]  
(5.8a)

\[ \sin \beta = \left( \frac{R_3}{R_{sag}} \right) [b_4(D_3^* - 1) + 1 - \sin \phi] \]  
(5.8b)

\[ \hat{P} = \left( \frac{R_3}{R_{sag}} \right) \]  
(5.8c)

with \( b_4 = 1 \) for a hexagonal lattice and \( b_4 = 1/\sqrt{2} \) for a square lattice. We show the variation of the height \( h \) with \( \phi \) as an external pressure difference is applied in Figure 5-5d. Initially, when there is no external pressure (\( \hat{P} = 0 \)), the bottom of the meniscus starts at a height \( h = R_3(1 - \cos \theta_E) \) above the substrate, depicted by State A in the inset of Figure 5-5d. As the pressure is gradually increased, the meniscus curvature increases and height decreases. Eventually the meniscus can touch down on the substrate, corresponding to \( h = 0 \), even if the pressure is still increasing (i.e. \( d\hat{P}/d\phi < 0 \) in Fig. 5-5). This corresponds to a sagging transition, and at this point the contact line on the sphere subtends an angle \( \phi = \phi_s \). The value of \( \phi_s \) corresponds to the intersection of the curves in Figure 5-5d with the x-axis, and can be numerically obtained from eq 5.8a-5.8c. The value of the dimensionless pressure difference \( \hat{P}_{sag} \) at which the touchdown of the meniscus first occurs is given by:

\[ \hat{P}_{sag} = \frac{2(1 - \cos \phi_s)}{(1 - \cos \phi_s)^2 + (b_4(D_3^* - 1) + 1 - \sin \phi_s)^2} \]  
(5.9)

In summary, when there is no external pressure applied, the meniscus initially sits flat at a height \( h \) corresponding to \( \phi = \theta_E \) (state A in Fig. 5-5). As the pressure is gradually increased, the meniscus bends and deforms downward and \( \phi \) decreases. The mode of transition from the Cassie-Baxter state to the Wenzel state is determined by the larger of the two angles \( \phi_s \) and \( \phi_d \) (corresponding to the depinning and sagging failure mechanisms, respectively). In Figure 5-6a, we illustrate this behavior for an array of hexagonally packed spheres characterized by \( D_3^* = 1.5 \) and \( \theta_E = 60^\circ \) as the imposed pressure difference \( \hat{P} \) is increased. The solid line shows the evolution of the location of the meniscus with applied pressure from an initial value of \( \phi = \theta_E \) determined by eq 5.7. The horizontal dashed line indicates the value of \( \phi_d \) at which
Figure 5-6: (a) Plot of the location of the contact line characterized by $\phi$ against dimensionless pressure difference $\hat{P}$ for hexagonally packed spheres with $D_3^* = 1.5$ and $\theta_E = 60^\circ$. The solid curve describes the evolution of the meniscus with pressure via eq 5.7, where the meniscus initially evolves from $\phi = \theta_E$ when $\hat{P} = 0$. The horizontal dashed line corresponds to the depinning transition limit of $\phi = \phi_d$. The dotted curve plots the variation of the pressure as a function of $\phi$ corresponding to a sagging transition (eq 5.9). The intersection of the solid line and the dotted line determines the sagging transition limit of $\phi = \phi_s$; for these parameter values the depinning transition is encountered first (as shown by the solid black circle). (b) Contour plot of the dimensionless breakthrough pressure for various values of the dimensionless geometric spacing $D_3^*$ and equilibrium contact angle $\theta_E$. The breakthrough mechanism corresponds to a depinning transition over the entire range of $D_3^*$ and $\theta_E$ shown.
the depinning transition occurs and the dotted line is a plot of eq 5.9 as a function of $\phi$. The sagging transition, and the value of $\phi_s$ is found from the intersection of this curve with eq 5.7. As the value of $\phi_d > \phi_s$, the depinning transition occurs first for this particular configuration. By performing a series of such calculations varying $1 \leq D_s^* \leq 4$ and $0 \leq \theta_E \leq 90^\circ$, we observe that the Cassie-Baxter to Wenzel transition occurs primarily by the depinning transition, even on a single monolayer array of spheres. Our calculations show that as the contact line descends along the surface of the wetted spheres, the smaller wetted perimeter is unable to support the additional pressure force on the curved liquid-vapor surface area and leads to a depinning transition before the lowest point of the meniscus touches the underlying substrate ($h = 0$ or state C in Fig. 5-5d). This observation of the depinning behavior on an array of spheres is also consistent with the result of Butt et al., who show that the depinning transition is the dominant mode on higher aspect ratio structures, such as an array of two vertically sintered spheres. In Figure 5-6b, we show contour plots of the dimensionless pressure $\tilde{P}_d(\theta_E, D_s^*)$ at which depinning occurs. For a fixed surface coating (which fixes the value of $\theta_E$), the value of the depinning pressure $\tilde{P}_d$ steadily decreases as the dimensionless spacing ratio increases. Following the procedure of Butt et al., we can obtain an analytical estimate of the breakthrough pressure in the limit of large $D_s^* \gg 1$. Eq 5.7 simplifies to the expression, $\tilde{P} \approx \sin \phi \sin(\theta_E - \phi)/(a_l D_s^{*2})$ and we can obtain an expression for the dimensional depinning pressure in this limit as:

$$P_d = \left(\frac{2\gamma_{lv}}{R}\right) \left(\frac{1}{a_l D_s^{*2}}\right) \sin^2(\theta_E/2)$$  \hspace{1cm} (5.10)

The pressure at which the depinning transition occurs scales directly with the liquid surface tension ($P_d \propto \gamma_{lv}$), and inversely with the radius of the spherical microstructures ($P_d \propto 1/R$) and with the square of the dimensionless spacing ratio ($P_d \propto 1/D_s^{*2}$). This implies that small, densely-packed spherical particles decorating individual fibers are needed to construct robustly superoleophobic fabrics. The Laplace pressure inside a liquid drop of radius $r_{drop}$ ~ $(V_{drop})^{1/3}$ deposited on the spherically nanotextured fabric is $P = 2\gamma/r_{drop}$. Equating this pressure with the de-
pinning pressure from eq 5.10, we can obtain an estimate of the maximum radius of the sphere $R$ that can sustain a low surface tension liquid drop in the Cassie-Baxter state as $R \lesssim (r/a_i)(1/D^*_3)^2 \sin^2(\theta_E/2)$.

5.4.3 Spray-coating of micron scale texture on woven fabrics

In order to test the prediction that a third level of structure with a sufficiently small length scale can widen the range of oleophobicity for a selected fabric, we use a spray technique to deposit corpuscular beads onto a dip-coated woven fabric (Fabric E) from a 50/50 wt% poly(methyl methacrylate)/fluorodecyl POSS solution. The spherical beads are formed during the capillary-driven atomization of the non-Newtonian polymer solution by a judicious choice of the solution concentration and molecular weight of the polymer. In Figure 5-7(a,b) we show SEM images of a spray-coated Nylon fabric (Fabric E) at two different magnifications. The spherical beads are randomly deposited on the fibers with a broad distribution in both the radius ($5 \mu m < R_3 < 15 \mu m$) and mean dimensionless spacing $D^*_3$.

The spray-coated textured fabric exhibits an enhanced liquid-repellent behavior. In Fig. 5-7c, we plot the cosine of the macroscopic contact angle $\cos \theta_1$ against the cosine of the equilibrium contact angle $\cos \theta_E$ (analogous to Figure 5-3) for two samples Fabric E that have either been dip-coated to increase the equilibrium contact angle on the fibers $\theta_2 \rightarrow \theta_E$ (black circles) or spray-coated to yield a third level of structure $\theta_3 \rightarrow \theta_E$ (red circles). The effect of introducing the third length scale is apparent in the larger values of the macroscopic contact angle on the spray-coated fabric for the various low surface tension liquids when compared to the dip-coated woven fabric. The differences in the roll-off angles between the spray-coated and dip-coated fabrics are shown in Figure 5-7d. The textured spray-coated fabrics consistently show smaller roll-off angles for the range of liquids used, indicating a superior oleophobic character. In Figure 5-7e, we show liquid drops of octane and hexadecane that are deposited onto the spray-coated fabric resulting in macroscopic contact angles of $\theta_1 = 108^\circ$ and $\theta_1 = 133^\circ$, respectively. By contrast, the same sized drop of octane ($V \approx 10 \mu L$) completely wets the dip-coated fabric E. The
Figure 5-7: (a) Scanning Electron Micrograph (SEM) of a dip-coated nylon fabric (Fabric E) spray-coated with a 50/50 PMMA/fluorodecyl POSS solution to introduce a spherical microtexture on individual fibers. (b) Magnified SEM showing the spherical PMMA/fluorodecyl POSS microtexture. (c) Plot of the effective contact angle ($\cos \theta_1$) against $\cos \theta_E$ for the dip-coated plain weave fabric (black line) $D_1 = 1.7 \pm 0.29$ and the spray-coated fabric with $D_3 = 1.26 \pm 0.15$ (red line). (d) A plot of the roll-off angle $\omega$ (in degrees) on the dip-coated plain-woven fabric (black) and spray-coated fabric (red) for a range of different liquids. (e) Liquid drops of Hexadecane ($\gamma_{lv} = 27.8$ mN/m) and Octane ($\gamma_{lv} = 21.6$ mN/m) vertically deposited on the sprayed fabric shown in (a,b) exhibiting contact angles of $\theta_1 = 133^\circ$ and $\theta_1 = 108^\circ$, respectively.
dimensionless spacing ratio of the weave was calculated previously (cf. Table 5.3) as \( D_1^* = 1.57 \pm 0.27 \) and is shown as the solid black line in Figure 5-7c. Using this value of \( D_1^* \), which characterizes the geometry of the weave, we can perform a regression of the contact angle data on the spray coated fabric using eq 5.6a, 5.6b and 5.6c to obtain an estimate of the mean spacing ratio of the spherical beads as \( D_3^* = 1.49 \pm 0.23 \). We also observe that the transition to the Wenzel state on the spray-coated fabric occurs for n-heptane \( (\gamma_{lv} = 20.1 \text{ mN/m}; \theta_E = 62^\circ) \). This best-fit estimate of \( D_3^* \) approximates the corrugated and polydisperse corpuscular beads with varied radii and interparticle spacing (as seen in Figure 5-7) as a model system of uniformly-spaced, hexagonally-packed array of spheres. By applying the simple model presented in the previous section using this value of \( D_3^* \approx 1.5 \), we obtain an estimate of the maximum feature size that should be able to support a 1 mm liquid drop of n-heptane as \( R_{\text{min}} \approx 100 \mu\text{m} \), which is an order of magnitude larger than the 5 – 15 \( \mu\text{m} \) structures observed in Figure 5-7b. However, the origin of this discrepancy can be attributed to the broad distribution of the interparticle spacing in the real spray-coated fabric, and the metastability of the non-wetting Cassie-Baxter state. Local regions of the spray-coated fibers containing a low density of corpuscular spheres and large interbead spacing, act as nucleation sites for the Cassie-Baxter to Wenzel transition. For liquids with \( \theta_E < 90^\circ \), the Wenzel state is the overall minimum energy state and a local transition propagates until the entire substrate is wetted. Indeed, by using a value of \( R = 10 \mu\text{m} \) for the corpuscular structures (consistent with SEM images), we see that the 1 mm drop of n-heptane will locally wet regions where the value of \( D_3^* \gtrsim 4.7 \) (i.e., \( D_3 = R(D_3^* - 1) \approx 37 \mu\text{m} \)). An example of potential nucleation sites with large interbead spacing can be seen in Figure 5-7b. Therefore, it is critical to develop processing techniques which can deposit a uniform and conformal layer of densely packed spherical structures with minimal defect sizes. This will help prevent wetting transitions on oleophobic fabric surfaces, and allow for even lower surface tension liquids to be supported in the non-wetting state. Our simple spray-coating method clearly demonstrates the benefits of introducing a third re-entrant length scale when designing oleophobic fabrics, as revealed by the ability of the three-scale
5.5 Conclusions

In this work, we initially performed a series of contact angle measurements on a set of nine dip-coated omniphobic woven fabrics with varying yarn radius ($R_1$) and half-spacing ($D^*$) using probe liquids of decreasing surface tensions (from water, $\gamma_w = 72.1$ mN/m, to heptane, $\gamma_v = 20.1$ mN/m). The trends of macroscopic apparent contact angles and the transition to the fully-wetted Wenzel state are similar across all nine dip-coated woven fabrics despite the differences in weave construction. Fitting a modified version of the hierarchical two-level model outlined by Michielsen and Lee to the measured contact angle data allows us to obtain a single dimensionless geometrical parameter ($D^*$) that characterizes the observed wetting behavior on each woven fabric. This dimensionless parameter is related to the weave angle of the fabric, and can rationalize the experimentally measured trends in the apparent contact angles as well as the onset of a spontaneous wetting transition to the fully-wetted Wenzel state. For the particular case of tightly bundled fibers in the fabric yarns, our model further predicts the existence of a critical value of the equilibrium contact angle of $\theta^{(c)}_E \approx 57^\circ$, below which a liquid drop will spontaneously transition to the fully wetted Wenzel state by a wicking mechanism. This is consistent with the observed transition data. We have demonstrated that the introduction of an additional micro/nano-textured length scale on the fibers ($n = 3$) is necessary to overcome this limit and we have developed a three level hierarchical model to rationalize this effect. We have extended previously developed ideas on pressure-driven Cassie-Baxter to Wenzel transitions in order to provide a framework that guides the selection of particle size, feature density and surface coating at all three length scales. Finally, we provide an example of how introducing a spherical microtexture on the individual fibers using a spray-on technique can be used to extend the range of liquid repellency for a given fabric. The hierarchical equation set given by eq 5.6, in conjunction with the analysis of stability against meniscus depinning and sagging (eq 5.7-5.10), can be used to
understand how to maximize the oleophobic character of a woven fabric system.
Chapter 6

Fog harvesting mesh design and scale-up

Access to clean drinking water is essential for human survival. In today’s world our water resources are becoming increasingly stressed due to increasing population, urbanization, and standard of living. Furthermore, in arid regions of the world this water stress is exacerbated by groundwater abuse, water-intensive crop cultivation, and rapid industrialization. However, some of these arid regions, particularly mountainous coastal areas, are frequently shrouded with dense fog. This fog is a largely untapped resource capable of augmenting limited local water supplies.

Previous work has investigated how mesh geometry affects deposition of fog droplets onto the mesh substrate and how the substrate surface chemistry affects the efficiency of drainage from the mesh surface.\textsuperscript{155,156} In this chapter, I explore how the geometry of the mesh wires influences the efficiency of water drainage and, in particular, how wires with sharp edges alter the prevalence of clogging within the mesh interstices. Additionally, fog harvesting meshes (\(\sim 30 \times 30\) cm) that were investigated in the lab are scaled up (to \(1 \times 1\) m) for field testing.
6.1 Introduction

6.1.1 Motivation

Water is rapidly becoming our most scarce resource. 35% of the world’s population lives in drylands and depend on groundwater, which can often be unsuitable for drinking, or water supply tankers, which are expensive and intermittent. According to WHO statistics, less than 0.007% of the water on the earth is readily accessible for human consumption and approximately a billion people lack access to safe drinking water. This water insecurity is one of the leading causes for school dropouts, especially among girls, and more than 200 million working hours are spent daily for the collection of domestic water. According to a December 2011 report from the Food and Agriculture Organization of the United Nations (FAO) “Fog collection technology appears to be an extremely promising and low-cost water harvesting system for drinking water ... It does not require energy input to operate and utilizes clean and abundant water ... The system is easy to construct and expandable, it reduces the burden of carrying water from a distance and generates time savings that the community can invest in income-generating activities and education of children.” These devices can be manufactured locally and employ local unskilled labor. Their local deployment has a substantially smaller carbon footprint than traditional truck-based transport to remote locations. As a result, fog harvesting can fill the need for water in coastal arid regions that typically rely on water that is transported (typically by carbon-intensive transportation methods) from elsewhere.

6.1.2 Background

While fog harvesting using synthetic mesh structures is a relatively recent undertaking, various plants and animals have meet their hydration needs with fog-based water for thousands of years. Bosque de Fray Jorge National Park in the Limarí Province of Chile consists solely of fog harvesting flora shown in Fig. 6-1. The park receives less than five inches of annual average rainfall, as a result all of the vegetation
is sustained by fog water. Natural systems, such as Fray Jorge National Park, have driven interest in synthetic analogs, particularly in regions where water scarcity is an enduring issue. Researchers are currently striving to maximize the efficiency $\eta$ (defined as the fraction of water collected from the total flux of liquid water through the mesh) with which mesh-based fog collectors extract water from the ambient fog-laden air stream.$^{155,162-165}$

Fog harvesting meshes are typically fibrous retiform structures characterized by a fiber radius $R$ and half spacing $D$, which are shown schematically in Fig. 6-2. The relative openness of the mesh can be described by the dimensionless spacing ratio $D^* = (R + D)/R$. In the fog harvesting literature the shade coefficient $SC$ (defined as the fraction of the projected area of the mesh that is occluded by the fibers) is commonly used to describe the mesh openness and is related to the dimensionless spacing ratio $D^*$ as $SC = 2(1 - 1/2D^*)/D^*$. If we also nondimensionalize the wire radius as $R^* = r_{fog}/R$ where $r_{fog}$ is the radius of a fog droplet, then we can completely describe a model fog harvesting mesh (depicted in Fig. 6-2) with two dimensionless parameters ($D^*$ and $R^*$).

The theoretical collection efficiency for a fog harvesting mesh is the product of the aerodynamic collection efficiency ($\eta_a$) and the deposition efficiency ($\eta_d$). The deposition efficiency $\eta_d$ quantifies the fraction of fog stream that is deposited on an
Figure 6-2: (a) Schematic of an ambient fog-laden air stream moving at a velocity of $v_0$ passing through a fog harvesting mesh with wire radius $R$ and half spacing $D$. (b) Enlarged image of an individual wire of the mesh shown in (a) with fog droplets of radius $r_{fog}$. At high velocities fog droplets deviate from the air stream lines and impact the wire due to their inertia. Reproduced from Park et al.\textsuperscript{156} (c) Image of a Raschel fog collection mesh on a hillside in Spain. Reproduced from Klemm et al.\textsuperscript{162}
individual mesh wire and was initially investigated by Langmuir and Blodgett. They found that the deposition efficiency could be described well by the simple empirical expression $\eta_d \approx \frac{St}{(St + \pi/2)}$ where $St$ is the Stokes number. The Stokes number describes the response time of a particle (e.g., a fog droplet) to that of the surrounding flow $St = \frac{t_{\text{particle}}}{t_{\text{flow}}}$. For the case of an ambient fog stream the Stokes number becomes $St = \frac{2\rho_{\text{water}} r^2_{\text{fog}}}{9 \mu_{\text{air}}} \left( \frac{R}{v_0} \right) = \frac{(2\rho_{\text{water}}/9\rho_{\text{air}}) Re_R (r_{\text{fog}}/R)^2}{\rho_{\text{water}}/9\rho_{\text{air}}}$ where $\rho_{\text{water}}$ and $\rho_{\text{air}}$ are the water and air densities, respectively, $\mu_{\text{air}}$ is the viscosity of air, $v_0$ is the upstream velocity of the unperturbed air stream, and $Re_R = \rho_{\text{air}} v_0 R/\mu_{\text{air}}$ is the Reynolds number for the air flow past the mesh wire.

The aerodynamic collection efficiency $\eta_a$ describes the fraction of the fog flow that is directed towards the solid fibers of the mesh. This has been previously evaluated by Rivera as $\eta_a = SC/(1 + (C_0/C_D)^{1/2})$ where $C_0$ is the pressure drop coefficient for a woven mesh, which is a function of $SC$ (and consequently $D^*$), and $C_D \approx 1.18$ is the drag coefficient for the mesh structure. Decomposing the overall efficiency into the aerodynamic and deposition efficiencies reveals that the dependence on the two dimensionless geometric parameters ($D^*$ and $R^*$) can be decoupled with the aerodynamic collection efficiency depending only on the dimensionless wire spacing $\eta_a = \eta_a(D^*)$ and the deposition efficiency depending only on the ratio of the radius of the fog droplets to the radius of the mesh wire $\eta_d = \eta_d(R^*)$. The resultant overall collection efficiency $\eta$ can be expressed as:

$$\eta = \eta_a(D^*) \eta_d(R^*) = \left[ \frac{SC}{1 + \sqrt{C_0/C_D}} \right] \left[ \frac{St}{St + \pi/2} \right]$$

This expression for the overall collection efficiency informs the rational design of fog harvesting meshes. Park \textit{et al.} employ eq 6.1 to reveal that an optimal mesh spacing exists for $D^*_{\text{opt}} \approx 3.1$ which maximizes the aerodynamic efficiency of the fog harvesting mesh. Furthermore, Park \textit{et al.} highlight that for a given value of $D^*$ and a fixed wind velocity (i.e., constant $Re$) the overall collection efficiency can be enhanced by maximizing $R^*$ (i.e., moving to finer meshes for a given fog condition). Two constraints that depend on the surface wettability of the mesh arise in practice: (i)
re-entrainment of deposited fog droplets into the effluent fog stream and (ii) clogging of the mesh interstices due to contact line pinning which alters the local aerodynamics of the mesh. These two phenomena are shown schematically in Fig. 6-3a-b. Re-entrainment occurs when the aerodynamic drag force on the drop becomes greater than the adhesive force holding it to the mesh. In general larger wind velocities (i.e., larger Re and thus larger St) will lead to enhanced deposition of fog onto the mesh, but droplet re-entrainment also becomes more prevalent at higher wind velocities, especially for larger droplets pinned on the mesh surface. Clogging occurs when the hysteretic wetting force pinning the droplet in the mesh interstices is greater than the gravitational force which acts to drain the liquid drop. This occurs for meshes with large contact angle hysteresis and small mesh openings (i.e. small D*). Using scaling arguments for the various forces acting on the drop, Park et al. are able to define a relation for $D_{\text{crit}}^* = \left( {D_{\text{crit}} / f_{\text{fog}}} \right) R^* + 1$ above which clogging will not occur ($D_{\text{crit}}$ is the critical value of D for a given mesh below which clogging will occur). For the lab-scale fog experiments conducted in this thesis, re-entrainment is not observed due to the low superficial fog velocities investigated. In the following section I will explore how the geometry of the fiber cross-section (round versus rectangular) affect the prevalence of clogging in lab based for experiments.

6.2 Lab-Scale Mesh Design

6.2.1 Materials and methods

Sample preparation

Round wire mesh samples were prepared by cutting commercially available woven wire meshes (McMaster-Carr, corrosion-resistant 304 stainless steel woven wire cloth) into 30 mm × 30 mm square pieces. Analogous rectangular wire meshes were fabricated using a Form 1+ 3D printer (Formlabs) with wire spacing $2D$, width $2R$, and thickness $2H$. A schematic of a 3D printed mesh with square wire cross-section is shown in Fig. 6-4. One wire diameter/width ($2R = 890 \mu m$) and two mesh spacings ($D^* = 3.5$ and
Figure 6-3: Schematics of (a) droplet re-entrainment and (b) clogging of the mesh. Plots identifying the range of droplet sizes for which (a) re-entrainment and (b) clogging will occur. Reproduced from Park et al.\textsuperscript{156}
Figure 6-4: Schematic of a 3D printed rectangular cross section mesh wire spacing 2D, width 2R, and thickness 2H.

$D^* = 4.8$ were investigated for the meshes with round and rectangular cross-section wires. Three wire half-thicknesses ($H = 0.5R$, $R$, and $1.5R$) were investigated for the meshes with rectangular cross-section wires. Table 6.1 lists a summary of the 3D printed mesh parameters that were investigated in this work.

Table 6.1: Summary of the wire radius $R$, half-spacing $D$, dimensionless spacing $D^*$, and half-thickness $H$ for the six 3D printed meshes investigated in the lab-scale fog collection experiments.

<table>
<thead>
<tr>
<th>$R$ (μm)</th>
<th>$D$ (μm)</th>
<th>$D^*$ (μm)</th>
<th>$H$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>445</td>
<td>1113</td>
<td>3.5</td>
<td>223</td>
</tr>
<tr>
<td>445</td>
<td>1113</td>
<td>3.5</td>
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<td>445</td>
<td>1113</td>
<td>3.5</td>
<td>668</td>
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<td>445</td>
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Dip-coating of meshes

The meshes were all dip-coated using previously described protocols\textsuperscript{156} to impart a constant surface chemistry across the various meshes. Briefly, the mesh samples were dip-coated in a 50 wt% 1H,1H,2H,2H-tridecafluorooctyl polyhedral oligomeric...
silsesquioxane (fluoroctyl POSS), 50 wt% poly(ethyl methacrylate) (PEMA, $M_w = 515$ kDa, Sigma-Aldrich) solution in the volatile hydrochlorofluorocarbon solvent Asahiklin AK-225 (Asahi Glass Company) with a total solids concentration of 10 mg/mL. The meshes were dipped for 5 min in the solution and air dried to allow for complete solvent evaporation, resulting in a smooth hydrophobic coating. The advancing and receding smooth surface water contact angles were previously reported as $\theta_{adv} = 121^\circ$ and $\theta_{rec} = 117^\circ$.\(^{156}\)

**Experimental procedure**

The fog harvesting experiments were conducted in a controlled environment glovebox (environmental chamber, Electro-Tech Systems) at a temperature of $T = 26.4 \pm 0.5^\circ$ and a relative humidity of $RH = 100\%$. A schematic of the fog harvesting system is shown in Fig. 6-5. The mesh samples were placed 1 cm in front of the end of a 30 mm diameter tube through which fog was advected. The fog (with mean droplet radius $r_{fog} \approx 3 \mu m$) was generated using a medical nebulizer (Omron Compair XLT Nebulizer Compressor Kit NE-C25, $Q = 16$ mL/h) and advected toward the mesh sample by an air stream of velocity $v_0 \approx 2$ m/s generated by a variable speed fan (Thermaltake mobile fan II external USB cooling fan). The water draining off of the mesh was collected in a container (5 cm x 5 cm) located 5 cm under the mesh sample. The amount of water collected was recorded every 30 minutes for 2 hours.

**6.2.2 Round vs rectangular cross-section mesh wires**

Fog harvesting meshes with round and square cross-section fibers were investigated to explore the effect of sharp edges on droplet pinning and clogging of the mesh. The fog harvesting experimental apparatus was run at the fixed fog conditions described above allowing the different fog harvesting meshes to be compared based on the absolute amount of water collected over the 30 minute experimental time intervals. Computational research being conducted at Oxford (in the laboratory of Julia Yeomans) has suggested that meshes possessing wires with sharp edges (e.g., rectan-
Figure 6-5: Schematic of the experimental setup for fog harvesting experiments. The fog is generated by a medical nebulizer and advected at a superficial velocity of $v_0 \approx 2.0 \text{ m/s}$ towards the mesh sample. The liquid water flux through the mesh is $Q = 16.1 \pm 0.7 \text{ mL/hr}$.

Gular cross-sections) will be less prone to droplets pinning within the mesh interstices, which leads to clogging. The work in the Yeomans’ lab shows that a droplet is much more likely to reside on the face that it deposits on than move around the discontinuous edge presented by the sharp corner. As the mesh thickness decreases the droplets become even less likely to transition to an inner face (a face parallel to the flow direction and within a mesh interstice) of the mesh because there is less surface area for deposition relative to the outer face of the mesh. Fog collection experiments were conducted for meshes with two different $D^*$ values ($D^* = 3.5$ and $D^* = 4.8$) and four different wire cross-sections (one round and three rectangular). The results of these experiments are shown graphically in Fig. 6-6.

The round cross-section meshes exhibit higher (or equivalent) fog water collection than the analogous square cross-section meshes for both values of mesh spacing. This likely results from increased clogging in the case of the square cross-section mesh. While it was hypothesized that the sharp edges would make it more difficult for drops depositing on the face normal to the fog flow to migrate into the mesh interstices, it also makes it more difficult for clogged portions of the mesh to drain and unclog. This is illustrated in Fig. 6-7(a-b) where multiple portions of the square wire mesh (Fig. 6-7b) exhibit clogging but only one instance of clogging is observed for the round wire mesh. The fog droplets ($r_{fog} \approx 3 \mu\text{m}$) are much smaller than the mesh.
Figure 6-6: Incremental amount of water collected over 30 min time intervals for the two hour fog collection experiments. Round (i.e., circular), square ($H = R$), thick ($H = 1.5R$), and thin ($H = 0.5R$) wire cross-sections were investigated for meshes with dimensionless spacing of (a) $D^* = 3.6$ and (b) $D^* = 4.8$.

Wires ($R \sim 1$ mm), so the droplets readily deposit on the surfaces inside the mesh openings in addition to the surface normal to the fog flow. As more droplets deposit in the mesh interstices the drops coalesce and grow with the same sharp edges that prevent the droplets on the outer face from migrating into the mesh openings pinning the drops within the interstices. It is therefore desirable to minimize the area that drops can deposit onto within the mesh openings (i.e., decrease the mesh thickness) to prevent clogging.

Fig 6-7(b-d) depicts the prevalence of clogging as a function of the mesh thickness for $D^* = 4.8$. The thin mesh ($H = 0.5R$) exhibits no noticeable clogging while the thick mesh ($H = 1.5R$) has many instances of fully- and partially-clogged openings. As a result of the lack of clogging, the thin mesh exhibits the highest amount of water collected for the $D^* = 4.8$ meshes (see Fig. 6-6b). For the more closely spaced meshes ($D^* = 3.5$, Fig. 6-6a) all of the meshes exhibit noticeable clogging; however, the thick mesh collects the most water and the thin mesh the least (this is exactly opposite of what was observed for the $D^* = 4.8$ meshes). This could be a result of the increased clogging across all of the meshes affecting the collection efficiency or the inherent variability in the experimental system. More data should be collected to validate the observed trends and determine their statistical significance. Fig. 6-8
Figure 6-7: Images of four meshes with $D^* = 4.8$ after two hours of fog harvesting. The four mesh samples are: (a) round, (b) square ($H = R$), (c) thick rectangular ($H = 1.5R$), and (d) thin rectangular ($H = 0.5R$) wire mesh. For the rectangular cross-section mesh samples, local clogging increases with the thickness of the mesh.
Figure 6-8: Cumulative water collected over 30 min time intervals for two hour fog collection experiments. Round and square cross-section meshes were investigated for $D^* = 3.5$. Error bars represent one standard deviation.

shows the cumulative water collected with standard deviation error bars for the round and square $D^* = 3.5$ meshes. The cumulative collected water is the same for these meshes within standard error.

6.3 Scale-up and Field Deployment

To investigate the real world performance of the fluoroPOSS/PEMA coated stainless steel meshes developed in the Cohen/McKinley lab we have entered into collaboration with Professors Juan de Dios Rivera, Pilar Cereceda, and Robert Holmes at the Pontificia Universidad Católica de Chile and Professor Richard LeBoeuf at the Universidad de los Andes in Santiago, Chile, and with Professor Daniel M. Fernandez at California State University, Monterey Bay (CSUMB). Our initial collaboration with the team in Chile gave us unique insights into the practical issues that arise when harvesting fog in the field. More recently we have deployed meshes to Northern California in collaboration with CSUMB, which promises to deliver high quality fog
harvesting data from the field coupled with meteorological data from local weather stations.

6.3.1 Scale-up and deployment of dip-coated stainless steel meshes

The woven stainless steel fog harvesting meshes described in the last section are typically coated by immersion in a vat of coating solution. While this approach is amenable for small meshes (\(\sim 3 \text{ cm} \times 3 \text{ cm}\) mesh and \(\sim 50 \text{ mL}\) of coating solution), it does not scale to the standard fog collector (SFC) size meshes (\(1 \text{ m} \times 1 \text{ m}\)) required for field deployment. Both the hydrochlorofluorocarbon solvent and the low surface energy molecule (fluorodecyl POSS) used in the coating are precious commodities with the former being relatively expensive and the latter not commercially available. To minimize the required amount of both of these components a coating apparatus consisting of a narrow slot (\(\sim2-4\) times the thickness of the mesh) was fabricated minimizing both the total volume of coating solution required and the liquid surface area available for evaporation. A schematic of this device is shown in Fig. B-15 in Appendix B and an image of the dip-coater in use (within a walk-in fume hood for appropriate ventilation) is shown in Fig. B-16. In addition to using a narrow slot to minimize the amount of coating material, a ratio of 80/20 (wt\%) PEMA--fluorodecyl POSS was used to further reduce the fluorodecyl POSS requirement. Previous work\textsuperscript{151} has shown that this ratio exhibits the same surface wettability (\(i.e., the same advancing \(\theta_{\text{adv}}\) and receding \(\theta_{\text{rec}}\) contact angles) as the 50/50 ratio used for lab scale experiments.

304 stainless steel meshes with three different spacings (McMaster-Carr Mesh 22 \(\times\) 22, wire diameter = 0.0135"; McMaster-Carr Mesh 16 \(\times\) 16, wire diameter = 0.018"; McMaster-Carr Mesh 14 \(\times\) 14, wire diameter = 0.02") were coated and sent to Prof. Fernandez for deployment across Northern California. A map detailing the locations where meshes from MIT have been deployed is shown in Fig. 6-9.
6.3.2 Preliminary field results

The SFCs from MIT were deployed in late fall of 2014 after the end of the traditional fog season in Northern California. As a result, only limited fog collection data is available from isolated fog incidents in 2014. Fig. 6-10 shows a comparison between the fog collection of a Chilean (Raschel) and an MIT (McMaster-Carr Mesh 14 x 14, wire diameter = 0.02") mesh at the University of California – Santa Cruz field site for a fog event on September 17-18, 2014. There is a strong correlation between the onset of fog collection and the amount of water collected is very similar for both meshes. As a result, a similar collection efficiency was observed for both meshes during this fog event. The strong correlation of the water collection could be a result of the patchiness of the fog during this discrete fog event. Data collected during more sustained dense fog events will hopefully show meaningful differences between the meshes.

This data set is limited due to the sparse nature of the fog and the lack of corre-
Figure 6-10: Comparison of the (a) marginal and (b) cumulative water collected by the Chilean (Raschel)\textsuperscript{164} and MIT (Mesh 14 × 14) meshes at the University of California – Santa Cruz field site for a fog event on September 17-18, 2014. There is a strong correlation between fog collection in the MIT and Chilean meshes with a similar amount of water collected by both meshes.

6.4 Conclusion

Previous work by Park \textit{et al.} provides a framework for how fog harvesting meshes should be designed to optimize their collection efficiency with respect to the mesh geometry and wettability. Here, I have extended the work beyond the model round wire meshes previously investigated to see if meshes with sharp wire edges can inhibit the onset of clogging. For meshes with square or thick ($H = 1.5R$) rectangular wire cross-sections clogging was not reduced, but instead may have been enhanced due to the sharp edges of the wire trapping water within the mesh openings and resisting drainage. The mesh with a thin ($H = 0.5R$) rectangular cross-section did show reduced clogging relative to the other rectangular wire and the round wire meshes. More data is required to determine if these meshes yield significantly higher fog collection efficiencies.

A dip-coating device has been fabricated to allow for the coating of fog harvesting
meshes at the SFC scale. Meshes with three different spacings have been deployed in Northern California in a collaboration with Prof. Daniel Fernandez at CSUMB. Preliminary data has been recorded for isolated fog incidents at the end of 2014. Better data will be obtained with the onset of the fog season in late summer through fall of 2015.
Chapter 7

Conclusions and future work

7.1 Conclusions

Well engineered surfaces can significantly augment how a material interacts with its surroundings extending its capabilities or even adding new functionality. This thesis initially looks to extend a surface characterization technique (dynamic tensiometry) to provide a more comprehensive understanding of the phenomena and interactions taking place at the interface between a solid and liquid. In Chapter 2, I demonstrate how dynamic tensiometry can be used to go beyond the traditional measurement of apparent advancing and receding contact angles to quantify wetting hysteresis, investigate wetting state transitions and probe the characteristic topographical length scales of textured nonwetting surfaces. By interrogating the entirety of an immersed sample, as opposed to the contact line of a small droplet with goniometry, an integrated value of wetting hysteresis $H$ can be obtained which can provide additional insight over the traditional single point definition of contact angle hysteresis $CAH$. The tensiometer system is also an ideal platform for probing the pressure driven transition from the metastable nonwetting Cassie-Baxter regime to the wetting Wenzel regime. The transition between the wetting states can be detected very clearly in an immersion/emersion cycle by a sudden and pronounced change in the hysteresis, which allows for the ready determination of the breakthrough depth for a single experiment.
While goniometry and tensiometry are most commonly employed to investigate surfaces with immutable surface chemistry, they can also provide useful information on the molecular rearrangement of switchable surfaces. In Chapter 3, goniometry is used to measure the time evolution of water contact angles on a switchable polymer film over a range of temperatures. This allows for the extraction of the activation energy for the rearrangement of the surface from a hydrophobic state (when exposed to air) to a hydrophilic state (when exposed to water). Utilizing dynamic tensiometry the kinetics of the surface rearrangement could be probed in more detail by immersing (and subsequently withdrawing) glass substrates coated with the switchable coating into (and out of) a reservoir of water at various speeds and over a range of temperatures. Modeling the forward and reverse surface reconstruction with a first-order rate equation, the activation energies for both of these processes can be determined. The dynamics of this reversible surface switching process could be understood in terms of a single dimensionless grouping $\alpha_f = \tau_f V/\ell_{cap}$ that represents a ratio of the time scale for molecular rearrangement ($\tau_f$) to a characteristic tensiometric time scale for the advancement of the solid-liquid-air interface ($\ell_{cap}/V$).

After exploring how dynamic tensiometry can enhance the understanding of textured, nonwetting surfaces and switchable polymer coatings in Chapters 2 and 3, I turn to three applications that employ engineered coatings to enhance their functionality in the final three chapters. In Chapter 4, I describe how a spray-on superhydrophobic surface can be used to reduce skin friction in turbulent Taylor-Couette flows. A custom Taylor-Couette cell was fabricated to allow Reynolds numbers up to $Re_{\text{max}} = 8 \times 10^4$ to be accessed. A maximum skin friction reduction of 15% was observed for a closed system. The maximum skin friction reduction can be increased up to 22% when the system is open and the plastron can be augmented with air from the environment. A modified form of the Prandtl-von Kármán skin friction law is used to show that the extent of friction reduction attainable is directly related to the dimensionless effective slip length $b^+ = b/\delta_v$ where $b$ is the dimensional slip length, which is a material parameter. As a result, superhydrophobic surfaces can reduce skin friction in turbulent flows when the viscous sublayer is of comparable thickness.
to the effective slip length ($b \approx 19 \mu m$ in this work).

In Chapter 5, I explore how the inherent two-level hierarchical texture of plain woven fabrics can be combined with an additional textural length scale and low surface energy to become robustly oleophobic. Nine dip-coated woven fabrics were investigated and a modified version of the hierarchical two-level model outlined by Michielsen and Lee$^{28}$ is fitted to measure contact angle data which allows for a single dimensionless geometrical parameter ($D^*_1$) to be obtained that characterizes the observed wetting behavior on each woven fabric. For the common case of tightly bundled fibers ($D^*_2 \rightarrow 1$) in the fabric yarns, the model further predicts the existence of a critical value of the equilibrium contact angle of $\theta_E^{(c)} \approx 57^\circ$, below which a liquid drop will spontaneously transition to the fully wetted Wenzel state by a wicking mechanism. The introduction of an additional micro/nano-textured length scale on the fibers ($n = 3$) is necessary to overcome this limit. A new three level hierarchical model is developed to rationalize this effect. Finally, a demonstration is given of how introducing a spherical microtexture on the individual fibers can be used to extend the range of liquid repellency for a given fabric.

In the final application, described in Chapter 6, I extend previous work that provides a framework for designing fog harvesting meshes to optimize their collection efficiency with respect to their mesh geometry and wettability. In particular, I investigate how the wire geometry of the mesh affects the prevalence of clogging and observe that thin rectangular wires (similar to the Chilean Raschel mesh) show promise in reducing the effect of clogging for a given mesh spacing $D^*$. I also demonstrate how the lab scale coating methodology can be scaled up to coat SFCs which are being deployed in the field for real world testing.

### 7.2 Future Work

In this thesis, I move from describing and extending a characterization technique to utilizing engineered surfaces to tackle three real world applications. While making headway in these areas this work highlights a number of opportunities for future re-
search. The superhydrophobic surfaces employed for skin friction reduction in Chapter 4 are often not mechanically durable and are susceptible to wetting failures due to pressure perturbations or local defects. The Achilles' heel of most superhydrophobic surfaces is their mechanical durability, but recent work with etched metal systems and thermoset polymers has shown promise in yielding robust superhydrophobic systems. The efficacy of these systems for drag reduction should be investigated. Surface porosity is key to obtaining the 'connected' plastron which augments the observed friction reduction. As a result, porous or actively heated systems that allow for the plastron to be sustained are of acute interest. Actively heated systems are the subject of ongoing research in the Cohen/McKinley lab.

The results presented in Chapter 5 highlight the necessity of additional levels of micro/nano-texture for obtaining robustly oleophobic fabrics. Techniques for depositing nanoparticles onto fibers or extruding fibers with built-in nanotexture should be pursued with extra focus paid towards techniques that covalently link the particles to each other and the fiber substrate to ensure long-term viability (i.e., mechanical and chemical durability) in real-world use.

In Chapter 6, I demonstrate that thin rectangular wires show promise in reducing the prevalence of clogging in fog harvesting. Further experimentation is required to verify this hypothesis; if it holds, these wires can be used for further experimentation with various mesh geometries, such as spiral or vertical wires. Meshes with vertical wires may further prevent clogging by eliminating pinning points that act transverse to the direction of drainage. The recently deployed SFCs also provide an opportunity for the collection of real world field data. The current deployment will provide a side-by-side comparison of the fog harvesting performance between the MIT and Chilean meshes with the relevant local weather information also being measured (e.g., wind speed and direction, temperature, humidity, and liquid water content). As the fog season gets underway the performance of the variously spaced MIT meshes can be compared with each other and with the other co-located meshes to determine the most viable real world fog harvesting system.
Appendix A

Minor projects

A.1 Asahiklin replacement and fluoroPOSS recovery

The HCFC solvent Asahiklin has been used to great effect throughout our labs research with fluorinated POSS molecules. However, as of January 1st, 2015, its sale and distribution within the U.S. has been banned by the EPA. To continue research with fluorinated POSS molecules, which have been a staple of our superomniphobic coatings, a suitable replacement must be found. Several HCFC solvents marketed under the Vertrel brand by DuPont were screened and Vertrel MS-757 was found to co-dissolve PMMA, a polymer we commonly blend with POSS, and fluoroocetyl POSS. The resulting solution could then be sprayed resulting in the surface structures shown in Figure A-1. The spray-coating was observed to have the same wetting characteristics as the analogous Asahiklin-based solution.

The fluorinated POSS molecules used in our superhydrophobic coatings are not commercially available and thus only made available to us through a collaboration with the Air Force Research Lab at Edwards Air Force Base. As we move to scale-up many aspects of our research, fluoroPOSS has become a scarce commodity. As such a procedure to recover fluoroPOSS for previously used solutions was developed.

Previously used solutions were distilled using rotary evaporation and the resulting PMMA/fluoroPOSS material was redissolved in a solvent selective to the polymer (acetone was used to dissolve the PMMA, leaving the fluoroPOSS undissolved). This
Figure A-1: (A) and (B) show two examples of the structures produced by solution spraying of PMMA/fluoroctyl POSS in Vertrel MS-757.

Undissolved fluoroPOSS can then be recovered and repurposed by vacuum filtering the acetone solution. Implementing this procedure for solutions used in dip-coating fog harvesting meshes led to the recovery of 60% of the initially used fluoroPOSS. The overall recovery is expected to be very high, which indicates roughly 40% of fluoroPOSS is consumed when dip-coating SFC scale fog harvesting meshes.
Appendix B

Additional figures

B.1 Designing hierarchically textured oleophobic fabrics

B.1.1 Fabric SEMs
Figure B-1: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric A) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.

Figure B-2: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric B) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.
Figure B-3: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric C) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.

Figure B-4: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric D) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.
Figure B-5: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric E) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.

Figure B-6: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric F) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.
Figure B-7: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric G) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.

Figure B-8: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric H) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.
Figure B-9: Scanning Electron Micrograph (SEM) of a plain-woven polyester fabric (Fabric I) which has undergone a hydrophobic treatment by dip-coating in a 50/50 fluorodecyl POSS/Tecnoflon solution.

B.1.2 Wetting plots
Figure B-10: Plot of the cosine of the apparent contact angle $\cos \theta_1$ against the equilibrium contact angle $\cos \theta_E$ for Fabric A with $D_1^* = 1.18 \pm 0.18$. The best fit curves for $D_1^*$ are plotted as solid black lines for each of the fabrics with the 95% confidence interval band shaded in red. The upper and lower bands, plotted as dashed lines, are used as a measure of uncertainty.

Figure B-11: Plot of the cosine of the apparent contact angle $\cos \theta_1$ against the equilibrium contact angle $\cos \theta_E$ for Fabric D with $D_1^* = 1.51 \pm 0.26$. The best fit curves for $D_1^*$ are plotted as solid black lines for each of the fabrics with the 95% confidence interval band shaded in red. The upper and lower bands, plotted as dashed lines, are used as a measure of uncertainty.
Figure B-12: Plot of the cosine of the apparent contact angle $\cos \theta_1$ against the equilibrium contact angle $\cos \theta_E$ for Fabric E with $D^*_{\text{E}} = 1.70 \pm 0.29$. The best fit curves for $D^*_{\text{E}}$ are plotted as solid black lines for each of the fabrics with the 95% confidence interval band shaded in red. The upper and lower bands, plotted as dashed lines, are used as a measure of uncertainty.

Figure B-13: Plot of the cosine of the apparent contact angle $\cos \theta_1$ against the equilibrium contact angle $\cos \theta_E$ for Fabric F with $D^*_{\text{F}} = 1.31 \pm 0.11$. The best fit curves for $D^*_{\text{F}}$ are plotted as solid black lines for each of the fabrics with the 95% confidence interval band shaded in red. The upper and lower bands, plotted as dashed lines, are used as a measure of uncertainty.
Figure B-14: Plot of the cosine of the apparent contact angle $\cos \theta_1$ against the equilibrium contact angle $\cos \theta_E$ for Fabric H with $D_1^* = 1.52 \pm 0.29$. The best fit curves for $D_1^*$ are plotted as solid black lines for each of the fabrics with the 95% confidence interval band shaded in red. The upper and lower bands, plotted as dashed lines, are used as a measure of uncertainty.

B.2 Fog harvesting mesh design and scale-up
Figure B-15: Schematic of standard fog collector (SFC) mesh coater. The coater is made with welded aluminum 5052 and is designed with a narrow spacing to minimize evaporation of the solvent used in the solution for dip-coating and to minimize the volume of solution required. Schematic and design notes are courtesy of Maria Z. Tou.
Figure B-16: SFC coater in use within a walk-in fume hood for ventilation. The mesh is sequentially dipped four times rotating 90° in between each dip to ensure the entire mesh is coated.
Bibliography


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