Teaching For Social Justice With Standards-Based Secondary English Language Arts Curriculum

Alison George Dover
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CORRECTING MISCONCEPTIONS IN WETTABILITY THEORY AND
UTILIZING FLUID SURFACE TENSION TO CREATE COMPLEX
HIERARCHICAL POLYMER STRUCTURES

A Dissertation Presented

by

DALTON FREDERICK CHENG

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the degree requirements for the degree of

DOCTOR OF PHILOSOPHY

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Polymer Science and Engineering
CORRECTING MISCONCEPTIONS IN WETTABILTY THEORY AND
UTILIZING FLUID SURFACE TENSION TO CREATE COMPLEX
HIERARCHICAL POLYMER STRUCTURES

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I first thank my advisor Professor Tom McCarthy. His guidance and persistence in educating me, getting me to focus on one project and finish something rather than distributing my attention to several projects and not accomplishing much, has been most valuable. He helped me organize myself and my work to be a better scientist, while giving me the freedom to explore and be creative in the lab. It is also through his willingness to take me on as an REU student in Summer 2004 that I was able to gain entry into this program and earn my doctorate degree.

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ABSTRACT

CORRECTING MISCONCEPTIONS IN WETTABILTY THEORY AND UTILIZING FLUID SURFACE TENSION TO CREATE COMPLEX HIERARCHICAL POLYMER STRUCTURES

FEBRUARY 2010

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Nanoimprinting with anodized aluminum membranes was performed to produce nanoposts with controlled diameter and aspect ratio. The polymer nanoposts were found to remain upright and preserve the post-packing structure at low aspect ratios, but succumbed to elastocapillary coalescence at higher aspect ratios, with the morphology of the aggregates directly related to the aspect ratio of the polymer nanoposts. Replication of the replicated nanoposts at low aspect ratio was achieved to reproduce the pore packing structure of the original alumina membrane.

Teflon microparticles were found to be effective stabilizers for inverse foams, producing dry water with excellent flow properties and contact stability and consisting of non-spherical liquid marbles 90-500 microns in diameter. The chemical inertness of the PTFE particles allowed for use of not only water, but also aqueous solutions of acids and bases and organic molecules including ionic liquids and water-soluble polymers. The teflon particle shell stabilized the liquid drop such that two particles containing two solutions which would ordinarily mix and/or react would remain separate.
The wettability studies focused on demonstrating that entrapped gases are not responsible for Cassie superhydrophobic wetting behavior, that the removal of the pockets of air would not lead to Wenzel wetting behavior with an increase in contact angle hysteresis. The measurement of advancing and receding contact angles on surfaces with controlled topography consisting of square posts holes showed that the contact angles remained unchanged despite removal of over 90% of the air. It showed that water was not intruding into the hydrophobic topography because the Laplace pressure was thermodynamically preventing water from increasing its interaction with the topographically-patterned surface. Wettability studies were also aimed at extending our understanding of wettability as a one-dimensional phenomenon from the three-phase contact line perspective, by investigating the ability of hydrophilic arcs, short and long wedges, and the outlines of the wedges, to pin water drops on hydrophobic, low hysteresis surfaces. They were additionally aimed at studying the ability of hydrophilic lines to deform the three-phase contact line of a water drop and kinetically trap a water drop in a distorted shape on a hydrophobic surface.
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CHAPTER 1

INTRODUCTION

1.1. Overview

This dissertation describes fundamental research that was carried out to provide in-depth understanding in several fields related to the surface tension of a wetting fluid. The research on the surface tension effects on polymer structures encompassed the first two parts. The first part focused on negative replication of anodized aluminum membranes through nanoimprinting into thermally cured resists to produce crosslinked polymer nanoposts with controllable diameter and aspect ratio. Controlling the aspect ratio of the nanopores in the alumina membrane allowed for control over the diameter and height of the replicated nanoposts. Lower aspect ratio pores were able to produce well-ordered upright crosslinked polymer nanoposts, which could then be used as a nanoimprint mold to imprint into the same uncured resist to replicate the pore-packing structure of the original alumina membrane. The removal of the alumina membrane from the cured resist by solution etching of the mold and subsequent air-drying of the nanoposts led to elastocapillary coalescence of the higher aspect ratio nanoposts, with the morphology of the nanopost aggregates directly related to their aspect ratio. The morphology of the nanopost aggregates as a result of elastocapillary coalescence was a rough quantitative measure of the aspect ratio of the nanoposts, as the morphology of the aggregates was only a function of the aspect ratio and not related to the diameter of the nanoposts. The modulus of the material was also reduced through the addition of solvent
during the nanoimprinting process, leading to capillary bridging and aggregation of the nanostructures at lower aspect ratio.

The second part addressed the fact that Teflon is actually hydrophilic, that Teflon particles will spontaneously adsorb to and pack on the surface of water, and used that characteristic of Teflon to stabilize water-in-air inverse foams, with Teflon particles forming a particle shell around water drops. Different diameter Teflon particles were used to stabilize inverse foams, which were then characterized for their water content, size, contact stability, thermal stability, flow properties, and change in density between unmixed and mixed states. The chemical stability of Teflon was also used to prepare inverse foams comprising of aqueous solutions of organic molecules, ionic liquids, water-soluble polymers, and acids and bases. The Teflon particle shell encapsulating acidic and basic solutions was effective in preventing the two solutions from contacting one another despite mechanical perturbations. We investigated the possibility of using inverse foams as a polymerization platform and found that HEMA monomers are potentially surface active, adsorbing to the surface of the Teflon particles, rendering them hydrophilic and incapable of remaining on the liquid surface to encapsulate the aqueous polymerizable solution as an inverse foam.

Surface tension is also responsible for producing water drops, which is a well-known phenomena, but misunderstood in certain respects. We focused on correcting two fallacies in wettability theory. First, it was shown experimentally that air pockets are not responsible for superhydrophobic, low-hysteresis wetting behavior, that it is in fact Laplace pressure which allows these air pockets to exist under a water drop on a rough
surface, thus reducing the liquid-solid interface and adhesion of the water drop to the surface. Many publications point to the importance of “pockets of air” or “entrapped gases” in producing superhydrophobic low hysteresis wetting behavior, also described as Cassie wetting behavior, and predict that without the “pockets of air,” water would sink into the rough features of the surface to increase its liquid-solid interaction and exhibit Wenzel wetting behavior with high contact angles and high contact angle hysteresis. The measurements of advancing and receding contact angles at reduced pressure on rough surfaces showed a lack of change in the contact angles and contact angle hysteresis with lower pressure, demonstrating the irrelevance of air pockets in wettability theory.

Our understanding that wettability is a one-dimensional phenomena allowed us to predict and demonstrate that hydrophilic arcs on a hydrophobic, low hysteresis surface would be capable of pinning water drops. By extension, solid hydrophilic short wedges and long wedges were shown to be capable of pinning the same amount of water as their hydrophilic outlines. The contact angle of a water drop on a surface is only a result of the chemistry/topography under the three-phase contact line, not within the solid-liquid interface. We also demonstrated the importance of contact lines versus interfacial areas in wettability theory by patterning hydrophobic surfaces with hydrophilic line patterns to produce water drops which wet the hydrophobic surface. These patterned hydrophilic lines were capable of dictating the shape of the outline of a water drop to distort the shape of a overall water drop and dominate over the influences of surface tension and the hydrophobic surface chemistry which act to reduce the surface area to volume ratio of the water drop and the liquid-solid interfacial area. The contact lines of water drops were
kinetically trapped by these hydrophilic lines to adopt the shape made by the lines, as simple geometric figures, elongated water drops, arches, and other complex unnatural shapes.

1.2. Background

1.2.1. Anodized Aluminum Membranes

Anodized aluminum membranes are produced through a simple and inexpensive means to form an inorganic metal oxide matrix in which hexagonally-packed nanopores run perpendicularly through the material. The diameter and spacing of these pores are easily controlled through the anodization conditions, and the aspect ratio of the pores can also be controlled by understanding the rate at which pores are made through the aluminum. The anodization process is a straightforward one, with the setup displayed in Figure 1.1. With a platinum cathode and aluminum foil as the anode, the two electrodes are connected to a direct current power supply and held in an acidic electrolyte bath. At the anode, aluminum is converted to porous aluminum oxide. At the cathode, hydrogen ions are reduced to hydrogen gas. The pore diameter and pore-to-pore distance are determined by the choice of electrolyte, the concentration of the electrolyte, and voltage, and to a small extent, the temperature of the electrolyte bath. The kinetics of anodization, the rate at which pores burrow through the aluminum foil, is determined primarily by temperature, but exhibits some dependence on the electrolyte solution and the voltage.
Anode: $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$
Cathode: $6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2$

Figure 1.1. Experimental setup for aluminum anodization.

The anodization process is the electrochemical oxidation of aluminum metal, in which aluminum is oxidized in acidic aqueous solution to form aluminum(trihydroxide), some of which is dissolved to form pores, with the remainder undergoing dehydration to form aluminum oxide. Before anodization, the surface of the aluminum is electrochemically polished in a 1:4 v/v perchloric acid:ethanol/H$_2$O bath to smooth the surface and produce a series of pits in the surface. Anodization then uses those pits as starting points for the pores, such that the pores at the top of the membrane are disordered as shown in Figure 1.2 (left). However, as Masuda reported in 1995, these pores order themselves and become increasingly hexagonally packed as the anodization process continues and pores grow longer. This is due to the hydrostatic pressure that occurs as aluminum metal is converted to aluminum oxide, due to the fact that the aluminum oxide
layer is more dense than the starting aluminum metal foil. The expansive forces in the anodization process force the pores to pack and grow perpendicularly through the substrate. The first anodization creates a porous aluminum oxide material that is disordered on the surface and ordered at the bottom of the pores. Dissolution of this membrane reveals the barrier layer of the first membrane, which consists of a well-ordered series of pits in the aluminum foil surface. The second anodization can then be performed to initiate pore growth from the barrier layer of the first membrane and produce an alumina membrane which is ordered on both sides. The process is shown in Figure 1.3.

Pores in anodized aluminum membranes can range from 10 nm to 160 nm in diameter, with spacings 45 nm to over 400 nm. The relationship between voltage and pore-to-pore spacing is approximately 2.5 nm/V. Sulfuric acid, oxalic acid, and phosphoric acid are the acids used in anodization, with anodization in sulfuric acid producing the smallest pores and anodization in phosphoric acid producing the largest pores. The anodization produces one membrane on each side of the aluminum foil, with the remaining aluminum metal sandwiched in the middle. Alumina membranes can be quickly dissolved in NaOH or a chromic acid/phosphoric acid solution, and slowly dissolved in phosphoric acid. Aluminum can be selectively removed using saturated mercuric chloride solution.
Alumina membranes have been referred to by several names, including anodic alumina or anodic aluminum oxide, anodized aluminum, and anodized aluminum membranes. The recognition that these inorganic membranes can be used to replicate well-ordered and/or high aspect nanoscopic features has led to almost 2000 publications citing Masuda’s 1995 two-step anodization work. A discussion of the numerous ways
anodized aluminum membranes have been used in the fabrication of well-ordered nanostructures and the variety of materials used, is much too great for this thesis. Suffice it to say, alumina membranes have been used as evaporation masks to selectively deposit materials on a surface, and etch masks to pattern into a surface. Their temperature stability allowed for the growth of highly ordered arrays of carbon nanotubes and other materials. They have also been used as a template for the growth of nanowires of various metals and metal oxides, as well as polymer nanostructures. The references cited here are just a few of the nearly 2000 publications citing Masuda’s work.

For the synthesis of nanoscopic rod-shaped objects with controllable diameter and dimensions, anodized aluminum membranes are one of the few choices, with their ability to produce them as hexagonally-packed three-dimensional nanostructures. Their simple and inexpensive formation, mild etching conditions, temperature stability, and surface stability are highly advantageous for the formation of inorganic and organic nanostructures. There is little limit to the materials which can be molded with anodized aluminum membranes, as they can be etched by both acids and bases, providing flexibility in the method of liberating the molded materials from the alumina matrix. They can also be used for forming upright nanostructures with a significant aspect ratio, with the heights of the replicated nanostructures ranging from under 100 nm to many microns. The other inexpensive methods for producing well-ordered (hexagonally arrayed) nanostructures are with block copolymer templates or perpendicularly oriented mesoporous channels, and these methods work only for block copolymer/mesoporous films with thicknesses on the order of the domain sizes (tens of nanometers) to several
times larger than the domain size, producing small aspect ratio features which can be
classified as two-dimensional. The ability to produce well-ordered nanorods or
nanotubes with significantly larger aspect ratios (three-dimensional rather than two-
dimensional) is a feature unique to anodized aluminum membranes.

1.2.2. Capillary Bridging and Elastocapillary Coalescence.

Elastocapillary coalescence is a phenomenon in which arrays of structures are
forced to aggregate together in response to encountering the liquid meniscus at the air-
liquid interface, forming larger, complex, hierarchical structures as the liquid wetting
the structures evaporates. The deformation of the structures is a balance between pillar
elasticity and interpillar capillary forces. Like wet carpet fibers, flexible lamellae stick
together after being wet by a wetting liquid and self assemble to form complex
hierarchical patterns. Such capillary adhesion is a function of the material contact angle,
elastic modulus, and the geometry of the fibers as the system minimizes its potential
energy. The meniscus which forms between the pillars resembles a capillary bridge that
is formed between two wetting plates due to capillary force. The shape of the meniscus
between two such wetting plates is such that the hydrostatic pressure of the water directly
underneath the meniscus is less than the atmospheric pressure. The topmost diagram in
Figure 1.4A shows such a capillary bridge between two pillars. For the wetting fluid
meniscus to adopt that shape, the contact angle of the wetting liquid with the material
must be less than 90°. Because capillary forces of a fluid between two structures act to
pull the structures together, a capillary bridge between two pillars will act to pull together
the pillars. If the pillars are anchored to a substrate and can be bent in response to a force acting laterally at or near the top of the structure, then the capillary bridge, with the appropriate interpillar capillary forces and the elasticity of the pillar, can deform the structure and disturb any packing order of the array of the structures.

Figure 1.4. Ordered elastocapillary coalescence from perfectly ordered square array of epoxy nanopillars. With decreasing bending stiffness, the number of pillars per bundle increased from capillary bridging.
This secondary effect forming complex, hierarchical structures from the wetting of arrays of structures is described on the macroscopic length scale by the work of Py,\textsuperscript{11} Bico et al.\textsuperscript{12}, and Boudaoud et al. (Figure 1.5)\textsuperscript{13}. These publications made use of regularly spaced polyester strips which were dipped into a wetting liquid, then pulled up such that the meniscus of the wetting liquid trapped between the strips was a certain height above the bulk liquid. Figure 1.5 shows the polyester strips which were completely dipped into silicone oil and pulled out. Because the strips were flexible, capillary suction bent the lamellae, causing the liquid to rise higher in this more confined environment. They showed (Figure 1.5B) that in the last regime, $L_{\text{wet}}$ increased linearly with $L$ while $L_{\text{dry}}$ remained a constant, due to the balance between capillarity and elasticity. Figure 1.5C showed how the aggregate bundle size as a result of capillary action increased with decreasing wet length and increasing dry length. The publications\textsuperscript{11-13} focused on determining the relationship of the size of a cluster of fibers with increasing length, and on the proportion of fibers that would be wet by capillary bridging. They showed that the maximum number of fibers per bundle was determined by the balance between capillarity and elasticity in the elastocapillary coalescence of flexible lamellas into bundles. This macroscopic capillary bridging was shown to be reversible by Neukirch et al.\textsuperscript{19}, in which they developed a macroscopic model system to examine the bending and buckling response of a vertical elastic rod anchored to a substrate that was slowly raised through a horizontal liquid surface, much like a rod that was originally under water but was slowly exposed due to water evaporation (Figure 1.6). As the air-water interface dropped to the level of the vertical elastic rod, the surface
tension at the air-water interface bent the rod. Further water evaporation caused the middle portion of the rod to be exposed to air as the top of the rod was bent downward. When the air-water interface dropped below a certain level, the rod snapped back into its original upright shape.

Figure 1.5. Elastocapillary coalescence of polyester strips in silicone oil. Taken from Bico et al.\textsuperscript{12} it explains on the macro-scale why carpet fibers bundle when wet, and why paint brush fibers aggregate when dipped into paint. This reversible macroscopic phenomenon can be applied to the nanoscale, where the capillary bridging of two nanoscopic objects results in irreversible change to the overall order of the system.
Figure 1.6. From Neukirch et al.\textsuperscript{19} Bending of a flexible polyester strip by silicone oil. (top) In A, the strip is initially totally immersed, and the fluid level is quasi-statically lowered. When the tip comes in contact with the liquid surface, the strip does not pierce the interface, but instead buckles, and bends gradually as the bath height is reduced (B–C). In D, the strip finally pierces the interface, but both ends remain immersed while its middle part arches out of the liquid bath. The free end finally detaches from the bath (E to F) and the strip recovers its original straight shape. Starting from state F, the experiment is then conducted backward, i.e. the strip is progressively immersed. The sequence of equilibrium states is different: the strip remains straight with its clamped base immersed (G). But when the bath height is large enough it suddenly bends and returns to the equilibrium observed at the beginning of the withdrawal (state B). Initially the strip is completely immersed in the silicone oil. (bottom left) The top of the polyester strip is below the liquid-air interface like in state D. (right) State E of the flexible polyester strip.
On the nanoscale, ordered arrays of carbon nanotubes grown in the vapor phase have been shown to collapse and aggregate into complex disordered hierarchical structures in response to being wet by a fluid (Figure 1.7), irreversibly it seems. Chakrapani et al.\textsuperscript{14} observed through an optical microscope how the evaporation of water caused the upright array of hydrophilic carbon nanotubes to collapse and aggregate to form the structures shown in Figure 1.7 B-D. The mechanism, shown in Figure 1.8, involved the formation of cracks during the evaporation of liquid, followed by enlargement of the cracks as the nanotubes bent and leaned up against one another. Capillary bridges can form not only between individual nanostructures but also between the aggregates of the nanostructures which formed as the result of the initial capillary bridging. The initial crack formation was due to the initial capillary bridging between individual nanotubes. As these nanotubes aggregated, the capillary bridges which formed between the nanotube aggregates acted on the aggregates as a whole, causing the aggregation of the aggregates themselves. This process continues until the separation distance between nanostructure aggregates and the modulus of the aggregates themselves becomes too great for elastocapillary coalescence to occur. Zinc oxide nanowires grown in solution suffer from capillary bridging between nanowires when the wetting agent evaporates.\textsuperscript{15} These nanostructures are deformed to a much smaller extent than the carbon nanotubes due to their significantly lower aspect ratio as the scale bars indicate in comparing Figure 1.7 and Figure 1.9. The lower aspect ratio led to earlier termination of elastocapillary coalescence as the transition of aggregation of the nanowires, to aggregation of aggregates, to aggregation of higher order aggregates, quickly reached a
point at which the elasticity of the aggregates and the distance between the aggregates became large enough to end the disruptive forces of capillary bridging by the wetting fluid.

Figure 1.7. Capillarity-driven assembly of two-dimensional cellular carbon nanotube foams.\textsuperscript{13}
columnar joints formed in cooling basaltic lava (1, 2, 9, 12, 13). Unlike systems in which cracks tend to propagate until stopped by other preexisting cracks (9), crack propagation in the MWNT arrays is usually arrested before cracks meet (Fig. 3a). Consequently, these structures consist of a polygonal network of compacted MWNT rims instead of a polygonal network of cracks (20). These cellular structures do not evolve by means of cell division or coalescence (3). Although image analysis reveals that the average crack length is greater than the average cell width, the growth of an individual crack takes place on a time scale of seconds, whereas the subsequent shrinkage and bending of nanotubes (Fig. 3b and c) is much slower and takes place on a time scale of minutes.

The formation of open cellular structures by the collapse of liquid is illustrated in Fig. 1. (a) Substrate-grown, vertically aligned MWNT arrays with an average nanotube diameter of 30 nm. (b) Scanning electron microscopy image showing a side view of cellular structures formed by the evaporation of water from plasma-oxidized, vertically aligned MWNTs. The arrow depicts the width of a cell. (c and d) Higher-magnification micrographs showing the cellular structures. The micrograph in d illustrates a "crack" along the floor of a nanotube "canyon" as well as the bending of nanotubes that gives rise to the open cellular structures. "Bent" nanotubes occupy the floor of the canyon in regions surrounding the crack. (d Inset) Wall of a cell. It can be seen that the alignment of nanotubes has been preserved.

Figure 1.8. Mechanism for the elastocapillary coalescence of well-ordered upright carbon nanotubes as the wetting fluid evaporated. Chakrapani et al.13
Figure 1.9. Large-scale micropatterned arrays of zinc oxide nanowires wet by ethanol and dried. While no image of these nanowires was taken while they were still wet by ethanol and as a uniform upright array of nanowires, the aggregation of these metal oxide nanowires was clearly a result of elastocapillary coalescence.

The work by Chakrapani and Chaudhuri did not demonstrate any semblance of self-organizational order in the collapse and aggregation of the high aspect ratio nanofeatures. Pokroy et al.,16 (Figure 1.4) produced square arrays of epoxy nanopillars and through the evaporation of ethanol, acetone, toluene, water, and other wetting fluids, they were able to induce elastocapillary coalescence in these nanoposts and cause them to organize as bundles of varying size depending on their bending stiffness. These nanorods not only ordered themselves as monodisperse discrete bundles, but they wrapped...
themselves in a helical form. This was a result of their low aspect ratio and their perfect order in a square array as opposed to the random array of high aspect ratio nanostructures produced by Chakrapani and Chaudhuri.

1.2.3. Inverse Foams and Dry Water

The irreversible adsorption of hydrophobic particles to water surfaces and their subsequent packing on the water surface has been used to form particle rafts\textsuperscript{20-22} on bulk water and particle shells around water drops,\textsuperscript{21-43} the latter which forms liquid marbles around macroscopic water drops\textsuperscript{29-38} and dry water.\textsuperscript{21-43} “Hydrophobic” is a relative term, and in this context, it is used to describe materials for which the flat surface exhibits higher contact angles than most materials, much like diamond and alumina are harder than most materials. Teflon, perfluorinated alkyl silane monolayers, alkyl silane monolayers are examples of such surfaces. Hydrophobic particles form particle rafts\textsuperscript{20-22} at the liquid-water interface due to capillary forces and the surface tension of the underlying fluid. Mahadevan and coworkers\textsuperscript{44-46} have demonstrated that these particle monolayers can have solid-like qualities, buckling at the flat air-liquid interface similar to how thin polymer films can buckle on rubber substrates due to moduli mismatch, with a buckling wavelength of the particle monolayer forming as a function of the surface tension of the liquid and the diameter of the particles forming the monolayer. The particles used in their experiments were Pliolite, lycopodium, polystyrene powder, and graphite powder. This two-dimensional elastic solid could also support anisotropic
strains through cracking in tension, and could be characterized using a Young’s modulus and a Poisson ratio.

Particle rafts can form around water drops as particle shells, stabilizing them as liquid marbles and water-in-air foams. While publications about the two have only recently begun to appear in the scientific literature, the recognition that hydrophobic particles adsorb and pack on the surface of water or aqueous solutions with a suitable surface tension has existed for decades in patent literature. Using particles to stabilize emulsions was first reported by Pickering in 1907 but water-in-air emulsions stabilized by hydrophobic particles are a more recent phenomena, with the first publication being a 1968 patent demonstrating the use of hydrophobized silica nanoparticles as the stabilizing agent. The term “dry water” describing this mixture was coined in a 1977 patent in which they described the use of 15-20 nanometer diameter silica particles to encapsulate nine times their mass in water. Subsequent patents have described how the use of hydrophobic silica nanoparticles produced a “dry storable source” of water in a finely divided state which would be useful over a wide range of temperatures, able to release water upon heating, and able to retain its flow properties even at temperatures well below the freezing temperature of water. Other patents take advantage of the particle nature of water to incorporate xanthan gum to produce storage-stable aerated gels which can be sprayed like liquids over large distances as a method for controlling insects and other pests. Liquids of high viscosity and liquids with additives have been used and encapsulated in hydrophobized silica nanoparticles for the purpose of fire-extinguishing and detoxification of chemical and biological agents.
The formation of a particle shell around water drops using hydrophobic particles has been demonstrated on the millimetric scale with liquid marbles,\textsuperscript{29-37} where rather than using a high-speed blender to break up bulk water into smaller water drops, a liquid drop is rolled around in hydrophobic silica nanoparticles, lycopodium, monodisperse carboxylate-terminated or oligomeric tetrafluoroethylene or micronic PTFE powder to produce a particle shell around the water drop. The liquids used to date are water,\textsuperscript{29-32,34-35,37} glycerol,\textsuperscript{32} mixtures of the two,\textsuperscript{31} ionic liquids\textsuperscript{32-33} and ferrofluids.\textsuperscript{36} Publications relating to dry water\textsuperscript{38-42} have relied on hydrophobized silica nanoparticles to encapsulate water and weakly basic solutions and have echoed patent literature in describing dry water as a water-storage procedure.\textsuperscript{39} Binks demonstrated the importance of water contact angle of the stabilizing particle in producing dry water\textsuperscript{38} and also began looking at solution effects on dry water by using dilute sodium hydroxide solutions.\textsuperscript{40}
demonstrating that increasing the pH of a solution upwards from neutral pH produced a
transition from dry water to aqueous foams as the increasing pH rendered the
hydrophobized silica hydrophilic. Similar to what is reported in the patent literature, the
use of hydrophobized silica nanoparticles allowed Binks\textsuperscript{38,40} and other researchers\textsuperscript{39} to
encapsulate up to 95\% by mass of water, 19 times greater than the mass of the
hydrophobic powder used in the inverse foam. DeGussa has also converted this process
into a near oil-free cosmetic containing pigments, vitamins, plant extracts, and other
water-dispersable active compounds for use in the cosmetics and commercialized it as
Aqua Foundation.\textsuperscript{41} This formula uses AEROSIL R 812 (silica silylate) to encapsulate up
to 80\% by weight of water, which releases the trapped water when rubbed on skin or by
similar mechanical stresses.

The ability of these micronic and nanoscopic particles to aggregate in an ordered
fashion on the surface of water and aqueous solutions, and not be completely enveloped
by the liquid is due to the contact angle of the material with water, capillary forces\textsuperscript{43} and
the Cheerios Effect\textsuperscript{45}. The contact angle of liquids with particles is similar to the case
with flat surfaces. The wettability of particles introduces the consideration of whether the
particle has a certain region exposed above the surface of the liquid or is fully submerged.
Geometry demonstrates (Figures 1.11 and 1.12, Equation 1.1) that with a smooth contact
angle of 90°, a smooth spherical particle made of the same material will be half-
submerged with $x = r$. With increasing contact angles, more of the particle is exposed. At
the contact angle of 120°, the model particle will sit with 75\% of its diameter exposed.
Decreasing contact angles for more hydrophilic materials results in increasing
submersion of the particle into the liquid phase and the dropping of the center of the particle below the vapor-liquid interface. A particle raft with contact angle greater than 90° will be able to separate two layers of water. This explains how the liquid marble shown in Figure 1.10 is capable of resting on the surface of water: the hydrophobic particle shell separates the two water bodies and prevents them from contacting each another.

Figure 1.11. Interfacial tensions on a particle on the surface of water.

Figure 1.12. The amount of the particle x that is submerged under water.

\[ x = r(\cos \theta + 1) \]  \hspace{1cm} (Equation 1.1)
That Teflon is denser than water would lead to the presumption that Teflon particles
should sink beneath the surface of water, but the fact that they float on the surface of
water is due to the fact that surface tension stops the interface from deforming too much
downward as would happen if the particle were to sink. Mahadevan states that buoyancy
of a small particle prevails over the capillary suction. The surface tension must act
upward to counterbalance the weight of the particle.\textsuperscript{45} Mutual attraction occurs if the
particles have like menisci and repulsion if they have unlike menisci.

1.2.4. Surface Wettability

For an excellent review of wettability, the feature article in Langmuir by Gao and
McCarthy titled Wetting 101\textsuperscript{57} provides a comprehensive analysis of wettability dating
back from when contact angles were first used to describe the wettability of a surface in
1804 to modern day understanding of wettability. Wettability of a surface is the ability of
a surface to be wet by a liquid and for a drop of a liquid to move across a solid. This is a
phenomena which involves both thermodynamics and kinetics.

1.2.4.1. Surface Forces/Energetics

The physics behind a static contact angle is the balance of forces of the three
interfaces.\textsuperscript{47} The solid-vapor interface, the solid-liquid interface, and the liquid-vapor
interface seek to reduce their own surface areas, leading to the balance of the three forces
shown in Equation 1.2 while Equation 1.3, with interfacial energies substituting for
forces, is widely referred to as Young’s equation.\textsuperscript{49}
\[ F_{SV} - F_{SL} = F_{LV} \cos \theta \]  
(Equation 1.2)

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \]  
(Equation 1.3)

Figure 1.13. Interfacial tensions leading to the formation of a water drop.

In 1804, the concept of thermodynamics, of atoms, molecules, and the intermolecular/intramolecular events that give rise to behaviors observed on the macroscopic scale was not known. So when Young wrote his essay on wettability that year,\textsuperscript{48} he viewed wettability from the viewpoint of the balance of forces. He viewed the biphasic interfaces as possessing “contractile forces” acting on the three-phase contact line of the liquid drop. The substitution of forces with energies in the form of surface tension, erroneous as it was, led to the development of the Cassie\textsuperscript{49} and Wenzel\textsuperscript{50} theories of wettability and modern day understanding and misunderstanding of wettability.
1.2.4.2. Surface Chemical Heterogeneity and Surface Roughness

The Wenzel (Equation 1.4)\textsuperscript{49} and Cassie-Baxter (Equation 1.5)\textsuperscript{50} equations were developed to describe the wettability of chemically heterogeneous surfaces and rough surfaces from the thermodynamic viewpoint.

\[
\cos \theta_r = r \cos \theta \quad \text{(Equation 1.4)}
\]
\[
\cos \theta_c = f_1\cos \theta_1 + f_2\cos \theta_2 \quad \text{(Equation 1.5)}
\]

\(r\) is a roughness factor, equivalent to the ratio of the surface area of the rough surface with the surface area of the smooth surface. \(f_1\) and \(f_2\) are the surface area fractions of the two surface chemistries, and \(\theta_1\) and \(\theta_2\) are the contact angles for the respective pure surfaces.

Wenzel described wettability as a purely thermodynamic process, that whether a surface would be spontaneously wetted depended on the magnitude of the free energy change from the replacement of an area of the solid-air interface by an equal area of the solid-liquid interface and the formation of the liquid-air interface with a certain interfacial area. Thus he viewed the wettability of rough surfaces versus smooth surfaces as simply a difference of solid-liquid interfacial areas which would magnify the hydrophobicity of hydrophobic surfaces and the hydrophilicity of hydrophilic surfaces. He viewed contact angles not as a balance of forces as Young described but as a balance of the interfacial tensions with units of energy per unit of interfacial area. His view of water’s interaction with a hydrophobic rough surface has led to some superhydrophobic surfaces described as Wenzel surfaces. These surfaces are characterized by high advancing angles and high contact angle hysteresis. These terms will be defined and discussed in detail later.
Cassie also viewed wettability from a thermodynamic perspective, but rather than viewing a rough surface as simply increasing the solid-liquid interfacial area, he described the wetting of a rough surface as destroying a solid-air interface of area $f_1$ and the gain of energy $f_1 \gamma_{SA}$, which directly led to the equation described in Equation 1.5. The wetting of a rough surface from this perspective would have the water not enter the rough surface features as it would in the Wenzel view. In the case of the Cassie surface, Equation 1.5 can be applied to rough surfaces, such that $\theta_2$ would become 180 and $f_2 \cos \theta_2$ would become $-f_2$. Of course, his equation can also be applied to chemically heterogeneous surface where rather than having air within the solid-liquid interface, the air is replaced by the second chemical component of the surface. Cassie’s view of water’s interaction with a hydrophobic rough surface has led to some superhydrophobic surfaces described as Cassie surfaces. These surfaces are characterized by high advancing angles and low contact angle hysteresis.

McCarthy and Gao pointed out in “The ‘Lotus Effect’ Explained” \textsuperscript{52} and “Wetting 101º” \textsuperscript{57} that on rough surfaces, the thermodynamic effect to wetting on rough surfaces is the Laplace pressure at which water intrudes between the posts. The Laplace pressure is a function of the geometry of the unit cell, its length scale, and the advancing contact angle of the probe fluid with the material surface and operates independently of ambient pressure. Where capillary forces explain why water will spontaneously intrude into narrow spaces where the advancing contact angle with the material walls is less than 90º, Laplace pressure explains why water will not intrude into narrow spaces where the
advancing contact angle with the material walls is greater than 90º, and thus cannot intrude between hydrophobic posts or holes.

1.2.4.3. Dimensionality of Wettability

The original wettability theory by Young did not describe the dimensionality of wettability. However, judging from how Young described wettability in his 1804 essay,48 he recognized that water contact angles seemed to be influenced by forces only at the three-phase contact line. Cassie and Wenzel and their legion of followers have subscribed to the belief that wettability is a two dimensional thermodynamic phenomenon, through the use of energies in the form of interfacial tensions rather than forces. While Pease61 was the first to question the accuracy of Cassie’s and Wenzel’s equations, McCarthy and Gao demonstrated that chemistry/roughness which was within the solid-liquid interface and did not extend out to the three-phase contact line had no effect on the contact angle of the water drop: the contact angle of such a drop was exactly the same as the contact angle of a drop on a surface with the same chemistry/roughness as what was under the contact line of the first drop.53 The diagram shown in Figure 1.14 shows their experiment. Both A and B have the same contact angle, even though A has a region within its solid-liquid interfacial area which is chemically/topographically different from what is under the contact line. Data from McCarthy and Gao and Extrand⁶⁰ showed that the contact angle of the water drop was dependent entirely on the chemistry directly under the three-phase contact line and independent of the chemistry/roughness within the solid-liquid interface, suggesting that wettability was
not a two-dimensional phenomenon. Bartell\textsuperscript{59} also directly questioned Wenzel’s theory in 1953 and showed that the contact angles of drops with roughness within the solid-liquid interface but not under the three-phase contact line had identical contact angles as entirely smooth surfaces. These researchers showed through their experiments that events at the solid-liquid interface were irrelevant and did not modify the contact angle in any way. The importance of only events under the contact line demonstrated that wettability is a one-dimensional phenomenon. The thermodynamic considerations of the solid-liquid interface in Cassie and Wenzel wettability theory were incorrect\textsuperscript{54} and led to faulty intuitions.\textsuperscript{56}

Figure 1.14. Events within the solid-liquid interface do not affect the contact angle at the three-phase contact line. The black line represents the three-phase contact line. The darker grey region represents a region that is chemically and/or topographically distinct from the lighter grey region.
The importance of contact lines and irrelevance of events within the liquid solid interface was also illustrated by Gao and McCarthy in “An Attempt to Correct the Faulty Intuition Perpetuated by the Wenzel and Cassie ‘Laws’” in Demonstration 4 of the paper. That demonstration involved two surfaces, one with $\theta = 180^\circ$, and the second having a 1 m$^2$ circular area with contact angle of 1° in a field with $\theta = 180^\circ$. If 6 L of water were poured onto the perfectly hydrophobic surface and into the 1 m$^2$ circular area with contact angle of 1° in a field with $\theta = 180^\circ$, the water puddle would wet the same surface area in both cases (Figure 1.15A). The area with $\theta = 1^\circ$ would fill up until a contact angle of 180° was reached. Once again, the water ignored the 1° contact angle surface at its solid-liquid interface and was confined by the 180° region at the exterior.

By extension, under the recognition that wettability is a one-dimensional phenomenon, it would be possible to produce the same effect by having a thin ring of 180° surface around the 1 m$^2$ region with contact angle of 1°, followed by another region having 1° contact angle (Figure 1.15B), as long as the emptying of the 6 L of water was slow and careful to prevent the contact line of the water from momentarily crossing over the ring with 180° contact angle to come in contact with the exterior 1° contact angle region.
Figure 1.15. Chemistry at the three-phase contact line determines the contact angle of the drop. The black region represents a surface with $1^\circ$ contact angle, while the grey region represents a surface with $180^\circ$ contact angle. (A) The circular surface with $1^\circ$ contact angle has an area of $1 \text{ m}^2$ surrounded by a surface with $180^\circ$ contact angle. (B) The circular surface with $1^\circ$ contact angle has an area of $1 \text{ m}^2$, with a ring of surface with $180^\circ$ contact angle, followed by a surface with $1^\circ$ contact angle.

1.2.4.4. Dynamic Contact Angle Measurements

There are two different methods for representing the contact angle. One is to obtain the static contact angle. This involves putting a drop on a surface and simply measuring the contact angle of that drop with the surface. The issue with static contact angles is that the method is irreproducible: one could obtain 10 static contact angle values and have them all be different. Static contact angles vary with the method of drop application, the height from which the drop was deposited, the surface, and the time between application of the drop and measurement of the contact angle. Static contact angles result from the formation of metastable drops. With this variation in the static contact angles possibly measured on a surface, it was found that all of these different values varied between an upper and lower limit, regardless of how the drop was
deposited and the time involved. Thus, the more reliable method is to find this upper and lower limit, also know as the advancing (\(\theta_A\)) and receding (\(\theta_R\)) contact angle which are scientifically reproducible values for surfaces (Figure 1.16).

![Figure 1.16](image)

Figure 1.16. (left) A drop of water receding on a surface as a result of evaporation; the drop is pinned at the three-phase contact line until \(\theta_R\) is reached at 2 and \(\theta_R\) remains constant during subsequent evaporation. (right) A drop of water advancing on a surface as a result of condensation; the drop is pinned at the three-phase contact line until \(\theta_A\) levels off at 6.

1.2.4.5. Contact Angle Hysteresis and Kinetics of Drop Movement

For a drop to move on a tilted surface as shown in Figure 1.17, the forward contact line (on the downhill side) must reach the advancing contact angle, and the receding contact line (on the uphill side) must reach the receding contact angle. In the process, the drop distorts from a section of a sphere to a complex shape with different contact angles around the entire perimeter of the drop. The difference between the advancing and receding contact angles is defined as the contact angle hysteresis. The greater the difference between the cosines of the two angles, the greater the drop must distort in order to roll or slide across a surface and the greater the substrate tilt angle will be needed in order to provide enough gravitational force to distort the water drop the
necessary amount to cause it begin moving down the substrate. Chen et al.$^{58}$ developed an equation to account for the relationship between water drop mobility and contact angle hysteresis:

$$F = \gamma_{LV}(\cos \theta_R - \cos \theta_A) \quad \text{(Equation 1.6)}$$

Drop movement can be associated with distortion of the shape of the water drop. The distortion of the water drop from its shape at rest to its shape in motion leads to an increase in the liquid-vapor interfacial area which can be treated as an activation energy barrier and quantified as such, with $E_a = \gamma_{LV}\Delta A_{LV}$ assuming the liquid-solid interfacial area is unchanged.$^{58}$ This leads to the conclusion that water drops will be more unwilling to move when the difference between the two angles is large since moving would require the water droplet to distort and create more interfacial area to move as shown in Figure 1.18. For surfaces on which water drops require a greater gravitational force to move, the hysteresis is larger. Hysteresis is attributed by Gao in Contact Angle Hysteresis Explained$^{51}$ (Figures 1.18 and 1.19) with contact line pinning on the receding end of the drop, with the water drop capable of moving when the receding contact line depins from the surface. Local defects such as a hydrophilic spot along the receding contact line can cause a drop in the receding contact angle, increasing the hysteresis, leading to water drop pinning due to the hydrophilic defect. With low hysteresis, there would be little distortion of the liquid-vapor interface required and the water droplet would be able to move with little effort and small tilt angle.
Figure 1.17. Advancing and receding contact angles of a moving drop. A water drop is only capable of motion after the front end reaches the advancing contact angle and the back end reaches the receding angle.

Figure 1.18. From Contact Angle Hysteresis Explained. For a water drop to move across a surface, the water drop starts and ends at the same ground state, but must distort itself by increasing its liquid-vapor interfacial area to move. This distortion is the activation energy for the drop to move across the surface and describes how wettability is a kinetic phenomenon.
The motion of water drops at the liquid-solid interface under the classic "No Slip" boundary condition from fluid dynamics. The boundary condition simply states that at the liquid-solid interface, liquid molecules do not move. So as the drop rolls across the surface, the water molecules at the interface do not slip across the surface, but remain pinned on the surface until the drop rolls far enough that the water molecules reach the air-liquid interface.

Figure 1.19. The motion of water drops at the liquid-solid interface under the classic “No Slip” boundary condition from fluid dynamics. The boundary condition simply states that at the liquid-solid interface, liquid molecules do not move. So as the drop rolls across the surface, the water molecules at the interface do not slip across the surface, but remain pinned on the surface until the drop rolls far enough that the water molecules reach the air-liquid interface.
1.3. References


42. Wang, W. X.; Bray, C. L.; Adams, D. J.; Cooper, A. I., Journal of the American Chemical Society 2008, 130, (35), 11608-+.


CHAPTER 2

ELASTOCAPILLARY COALESCEENCE AND AGGREGATION OF POLYMER NANOPOSTS WITH VARYING ASPECT RATIO

2.1. Introduction

High aspect ratio features can be defined as having an aspect ratio larger than 1:1, where the features can be characterized as not being mere bumps/grooves on the surface. Besides the formation of carbon nanostructures from a surface,\textsuperscript{1-4} there are few other methods for the formation of free-standing nanostructures with a significant aspect ratio. The use of alumina membranes as a mold for capillary force lithography of molten polymers was demonstrated by Moon and McCarthy.\textsuperscript{5} However, the membranes used in their research had poor pore packing, and a significant pore-size distribution. Nonetheless, anodized aluminum membranes\textsuperscript{6-13} have several advantages in making nanoscopic rods of high aspect ratio. They are inexpensive to produce and much research starting from Masuda et al.\textsuperscript{8-9} has been performed to determine the right conditions to generate well-ordered hexagonally-packed pores of a given diameter and spaced a certain distance apart.

The goal of producing well-ordered hexagonal-packed posts from alumina membranes with aspect ratio sufficiently high has eluded researchers with the exception of a few.\textsuperscript{14} Rods have been made with varying degrees of well-ordered packing from a variety of materials, ranging from polymeric materials such as polystyrene\textsuperscript{6} and carbon nanotubes,\textsuperscript{1} to inorganic materials such as zinc oxide.\textsuperscript{15} However, as many researchers have described, the upright well-ordered nature of these nanostructures succumb to
elastocapillary coalescence during the drying process and are pulled together and aggregate due to the surface tension of the evaporating fluids and capillary forces at the nanoscale level, which has been described in greater detail in Chapter 1.

The research presented provides a path for producing well-ordered nanoscopic polymer posts with controllable diameter and aspect ratio through nanoimprinting with anodized aluminum membranes. It is demonstrated here that the pore aspect ratio of alumina membranes can be controlled, leading to control over the height and diameter of polymer posts made through negative replication using alumina membranes as the mold. The elastocapillary coalescence phenomenon of the higher aspect ratio nanoposts was investigated to determine how the morphology of the nanopost aggregates varies with aspect ratio of the primary structures, the nanoposts. Research was performed to investigate the possibility of replicating the pore structure of the original alumina membrane using the replicated nanoposts as the mold. The process of nanoimprinting with alumina membranes to produce polymer nanoposts with specific aspect ratios and diameters required knowledge of the kinetics of pore formation in alumina membranes and performing polymerization of a thermally-cured resist within the pores of the alumina membrane. By capillary force, thermopolymer resists were drawn into alumina membranes to be formed into polymer nanoposts with the aspect ratio of the polymer posts dependent on the aspect ratio of the pores in the alumina membrane mold. At low aspect ratios, the nanoposts were able to remain upright and well-ordered during the drying process and removal of the wetting fluid. Liberating the nanoposts with sufficiently high aspect ratio from the alumina membrane by solvation of the membrane
and drying the nanopost arrays led to the collapse and aggregation of nanoposts. The morphology of the secondary structures formed through the elastocapillary coalescence was found to be dependent on the aspect ratio of the nanoposts and not only their diameter. The curing of the thermopolymer resist with the addition of solvent led to a significant modulus reduction of the material which caused elastocapillary coalescence of the resulting nanoposts at a lower aspect ratio.

2.2. Experimental Section

2.2.1. Produced Anodized Aluminum Membranes

Alumina membranes with pore diameter of 40 nm and pore-to-pore distance of 100 nm were prepared through the two-step anodization process described by Masuda et al.\textsuperscript{10} All chemicals mentioned were used as received. 0.5 mm thick aluminum foil (99.997\% pure) was purchased from Alfa Aesar. The aluminum was cut into pieces 1 cm x 2 cm and electropolished in a 1:4 v/v solution of perchloric acid solution in 200 proof ethanol at 4\(^\circ\)C and 20V. The conditions used for aluminum anodization were 0.3M oxalic acid, 15 \(^\circ\)C, and 40V, producing pores with 40 nm pore diameter, and 100 nm pore-to-pore distance. For pores 10 nm in diameter, spaced 45 nm apart, anodization conditions were 2M sulfuric acid, 19V, and 0 \(^\circ\)C. The anodization process formed two membranes, one on each side of the aluminum foil, and the remaining aluminum sandwiched between the two membranes was allowed to remain to provide mechanical support for the membranes (AAO/Al/AAO). First anodizations were carried out for at least 2 hours. The membrane was then dissolved in a solution of 6 wt\% phosphoric acid and 1.8 wt\%
chromic acid at 60°C for 2 hours and the remaining aluminum foil, with a surface now templated with dents hexagonally packed and spaced appropriately for the anodization condition, was anodized again for the desired time.

2.2.2. Determination of the Kinetics of Pore Formation

Following dissolution of the membrane from the first anodization, the second anodization was carried out for the desired length of time. The aluminum metal trapped between the two newly formed membranes was dissolved with saturated mercuric chloride solution. The freed membranes were dipped in liquid nitrogen, broken, and their cross-sectional thickness was measured using SEM.

2.2.3. Producing Polymer Posts through Nanoimprint Lithography

2.2.3.1. Producing Acrylate Polymer Posts through Nanoimprint Lithography

Posts were made from a thermally-cured resist consisting of 22.9 wt% trimethylol-propanetriacrylate, 1.6 wt% azobisisobutylironitrile (AIBN), and 75.5 wt% of ethoxylated bisphenol-A dimethacrylate. Silicon wafers were cut into 1 cm x 1 cm pieces, rinsed with H\textsubscript{2}O, acetone, and toluene, then oxygen plasma cleaned for 5 minutes. The cleaned Si wafer samples were coated with a layer of 3-(trimethoxysilyl)-propyl methacrylate, made by spincoating the silane at 3000 rpm for 20 seconds, then heating the wafer at 120 °C for 10 minutes. 0.1 ml of the resist was spread onto the treated Si wafer. The AAO/Al/AAO molds were placed carefully on the drop of resist, and the sample vessel was purged with nitrogen for 30 minutes to remove oxygen and water from
the system. An additional 3 hours was given for the resist to fully make its way into the AAO pores. The resist was then cured at 120 °C for 12 hours.

Figure 2.1. Thermoresist formulation, consisting of a difunctional and a trifunctional polymerizable unit, with a thermoinitiator. The resulting mixture, consisting of 22.9 wt% trimethylolpropanetriacrylate, 1.6 wt% AIBN, and 75.5 wt% of ethoxylated bisphenol-A dimethacrylate, is viscous and stored in at -14 °C until its use is required.

Figure 2.2. Procedure for nanoimprinting with anodized aluminum membranes. Following the cleaning of the silicon wafer, the thermoresist described by Figure 2.1 was spread onto the surface. Following imprinting with the alumina membrane, 3 hours was given for the membrane to be filled by the resist. Following curing under nitrogen, the alumina membrane mold was dissolved.
Figure 2.3. Solvation procedure of the anodized aluminum membrane. In order to perform a controlled dissolution of the alumina membrane impregnated with the cured thermoresist, the exposed, unused alumina membrane and the aluminum foil in between the two membranes had to be dissolved selectively. Following imprinting, the exposed alumina membrane is dissolved with 10 wt% NaOH solution. Once the formation of bubbles was observed indicating the solvation of the unused alumina membrane and the start of the reaction of NaOH with aluminum metal to produce hydrogen gas, the exposed aluminum was removed with saturated mercuric chloride solution, leaving the remaining alumina membrane impregnated with the polymer nanoposts. This alumina membrane can be dissolved with 5 wt% phosphoric acid.

The AAO/Al/AAO molds were dissolved stepwise as shown in Figure 2.3. First, the exposed AAO/Al layer was exposed to 10wt% NaOH solution for 15 minutes, until formation of hydrogen gas from the reaction of Al(s) with NaOH was evident. The remaining Al layer was removed with saturated HgCl₂ solution leaving the AAO impregnated with the cured resist. This remaining AAO layer was then dissolved with 5 wt% H₃PO₄ solution.
2.2.3.2. Producing Conductive Polymer Nanoposts

Poly(3-hexyl-triphenylamine) (PHTPA) endcapped with styrene groups of 1 wt\% in toluene was drop-coated into the alumina membrane. After the solvent evaporated, PHTPA films were cured at 200 °C under nitrogen to induce crosslinking of the styrene endgroups. These polymer films on alumina membranes were then transferred to a Si wafer by first selectively dissolving the Al, replacing the mercuric chloride solution with water followed by methanol, then floating the AAO/polymer film in methanol onto a Si wafer and dissolving the membrane in a 1:1 volume mixture of ethanol and 10 wt% \( \text{H}_3\text{PO}_4 \) solution. The solvation solution was then slowly replaced with ethanol and the samples dried at 50 °C overnight.

2.2.4. Replication of the Pore Structure of the Alumina Membrane

The pore structure of the original alumina membrane mold was replicated using imprinted polymer nanoposts as the mold as shown in Figure 2.4. Using the same thermopolymer resist, the mold was imprinted into the resist layer. Curing conditions were the same as in Section 2.2.3. Separation of the mold and cured resist layer was performed using a razor blade to force the two layers apart. This procedure was also performed with gold-coated nanorods as the mold. There was no discernible difference in the ease of separating the two layers with or without the gold coating.
2.3. Nanoimprinting with Anodized Aluminum Membranes

2.3.1. Kinetics of Anodization and Predictions for Polymer Post Heights

In order to predict and control the height of polymer posts formed from nanoimprinting with anodized aluminum membranes with one end of the pore closed, knowledge of the kinetics of anodization and the variables within the capillary force equation were needed. Within the capillary force equation, the advancing contact angle of the resist with the aluminum oxide surface was required, and assumed to be ~80° at the air-thermopolymer resist-metal oxide surface interface. The radius of the pore was set by the anodization conditions at 20 nm using anodization conditions of 0.3M oxalic acid, 40V, and 15 °C. With one end of the pore closed and the open end pulling in the thermopolymer resist, it was calculated that the thermal resist would be able to fill up
81% of the volume in the 40 nm diameter pores, with the air originally filling up the entire pore now compressed to 19% its original volume after the pressure from the capillary forces pulling the resist into the alumina membrane pores equilibrated with the pressure of the compressed air originally trapped in the pores and now displaced and compressed by the incoming resist. Controlling the time spent anodizing the aluminum sample produced pores of predictable lengths which set the upper limit on the height and aspect ratio of posts produced from that membrane mold. The anodization kinetics of pore growth specific for the anodization conditions used (0.3M oxalic acid, 40V, 15°C) were found to be about ~133 nm/min or ~8 µm/hr using the thickness of the membrane. By general approximation, for each minute of anodization using the conditions mentioned and the thermopolymer resist, the height of the imprinted nanoposts would increase 107 nm.

Table 2.1. Using anodization time to control pore-replicated post height.

<table>
<thead>
<tr>
<th>Anodization Time</th>
<th>Predicted Post Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 seconds</td>
<td>54 nm</td>
</tr>
<tr>
<td>60 seconds</td>
<td>107 nm</td>
</tr>
<tr>
<td>120 seconds</td>
<td>215 nm</td>
</tr>
<tr>
<td>300 seconds</td>
<td>537 nm</td>
</tr>
<tr>
<td>600 seconds</td>
<td>1075 nm</td>
</tr>
</tbody>
</table>
2.3.2. Polymer Nanoposts

Varying the anodization time allowed for control over the pore depth and consequently polymer post height. Figure 2.5 shows the crosslinked polymer posts after the membrane support was dissolved. The imprinting with an AAO/Al/AAO mold, with zero seconds of anodization (barrier layer only) produced a series of well-ordered hills on the surface spaced 100 nm apart center to center. Increasing the anodization time to 30 seconds (~50 nm, 1:1.35) and to 300 seconds (~500 nm, 1:13.5) produced well-ordered posts that were able to remain upright following solvation of the alumina membrane with 5 wt% H$_3$PO$_4$ solution. The crosslinked polymer material possessed the necessary modulus to resist the effects of capillary bridging by water at these aspect ratios.
2.3.3. Polymer Nanopores

Replicating the AAO pore structure using the same thermal-polymer resist proved rather simple. For these experiments, the mold was the well-ordered polymer posts from Section 2.3.2 which were estimated to be 100 nm tall. Using the procedure described in section 2.2.3, the gold-coated mold assembly was easily separated from the cured resist.
Inspection of the polymer posts mold by SEM showed that the posts were still intact, and had not fractured during the forceful separation as the micrographs in Figure 2.6 demonstrate. The replicated pores in the crosslinked polymer matrix were hexagonally packed, mimicking the pore structure of the original alumina membrane mold. This mold of gold-coated low aspect ratio posts was able to continue making more porous polymer films out of the same thermally-cured resist formulation and this was demonstrated for two additional cycles. Moreover, the post mold could be washed with organic solvents without concern over solvation or disturbing the hexagonal packing of the polymer posts due to their crosslinking. Attempts to do the same with molds of larger aspect ratio failed. The adhesive forces between the gold-coated posts and the cured thermopolymer resist prevented separation of the mold from the newly formed pattern due to the increase in surface area with larger aspect ratio polymer posts, and all attempts resulted in the breaking of the mold or substrate with the replicated patterns.
Figure 2.6. (A) Posts from a membrane formed through 60 second anodization of aluminum (AR ~2.7). (B) Pores in the acrylate resist made from posts shown in (A). The diameter of these pores/posts are not exactly 40nm, due to the 20 nm thick gold layer required for SEM imaging. The 100nm pore-to-pore distance which originates from the alumina membrane, however, has not been changed.

2.4. Elastocapillary Coalescence and Polymer Nanopost Aggregation

2.4.1. Elastocapillary Coalescence of 40 nm Diameter Polymer Nanoposts

Imprinting with membrane molds made from anodization times of 10 minutes and more produced polymer nanorods which aggregated due to elastocapillary coalescence. The crosslinked polymer lacked the appropriate modulus to withstand capillary bridging at the higher aspect ratios and produced secondary structures due to the surface tension forces pulling the posts together during the drying process. From an alumina membrane which had been anodized for 10 minutes, the 40 nm diameter polymer replicated posts, estimated to be 1075 nm tall (Table 2.1), collapsed upon drying to form clumps of posts 500 nm to 1 micron in diameter, randomly distributed across the sample as seen in Figure 2.7A, B. Inspection of some of these posts which had broken off instead of collapsing
and aggregating together showed that the approximation of ~107 nm increase in post height per minute of anodization was fairly accurate. Figure 2.7C shows polymer posts which are 1100 nm in length, corresponding well to the theoretical value in Table 2.1.

Increasing the anodization time incrementally to 120 minutes showed the gradual transition of post aggregation to form clumps to the formation of lines of greater length and height. From 10 minutes of anodization, the resulting posts collapsed to form small clumps (Figure 2.7). At 20 and 30 minutes, the density of the clumps decreased, but the overall size of aggregates had lengthened in one direction to form 1-D linear aggregates (Figure 2.8).

With 40 and 50 minutes of anodization, the posts aggregated to form lines exhibiting more order and spaced further apart (Figure 2.9, Row A and B). These lines increased in connectivity with one another as they coalesced to form longer lines and began to intersect to form 2-D structures. At 60 and 120 minutes, the posts made from these anodized aluminum membranes all become connected with one another and the aggregates themselves had increased in height (Figure 2.9, Row C and D) to form taller ridges and deeper valleys. The final outcome of the sequence of secondary structures formed through elastocapillary coalescence sequence was a series of cone-shaped voids with walls made of 40 nm diameter posts as displayed in Figure 2.10A. Due to the thickness of the membrane, the alumina was dissolved with 10 wt% NaOH solution to avoid an estimated two to three month wait for the 5 wt% phosphoric acid to etch through 64 microns of alumina. Cone-shaped voids were observed with posts made from membranes created from 8 hours of anodization. The approximation of post height made
from these membranes was about 52 microns, giving an aspect ratio of 1300, and measurement of these posts were in good agreement at 50 microns in height (AR ~1250). Figure 2.10B shows the packing of the nanoposts that made up the walls of the cone-shaped voids. The posts in interior of the walls, shown in Figure 2.10C, had collapsed in a disordered fashion. The side view in Figure 2.10 D-F demonstrated bending and buckling of the nanoposts while maintaining their attachment to the substrate by the bottom end.

Figure 2.7. Collapse and aggregation of posts made from membranes produced by 10 minutes of anodization. The elastocapillary coalescence for these posts with AR ~27 produce clusters of nanoposts (A, B). Posts were also observed to have broken at their base (C), and their measured lengths are in good agreement with the predicted lengths shown in Table 1 (1075 nm predicted versus 1083 nm measured).
Figure 2.8. (Row A) Posts from membrane made from 20 minutes of anodization (AR ~54). (Row B) Posts from membrane made from 30 minutes of anodization (AR ~81). These higher aspect ratio features exhibited aggregation which resulted in longer aggregates with increasing aspect ratio.
Figure 2.9. (Row A) Posts from membrane made form 40 minutes of anodization (AR ~108). (Row B) 50 minutes of anodization (AR ~134). (Row C) 60 minutes of anodization (AR ~161). (Row D) 120 minutes of anodization (AR ~323). With increasing aspect ratio (from A-D), the density of aggregates decreased as they merged with larger features to form the intersecting winding lines in D. The middle column of features also showed that the increasing aspect ratio of the primary nanopost features increased the height of the aggregates. The column on the right shows no increase or decrease in the orientation of the collapsed nanoposts with increasing aspect ratio.
Figure 2.10. Ultra-high aspect ratio crosslinked acrylate posts. (A) Cone-shaped voids resulting from aggregation of the 40 nm diameter nanoposts. (B) The tops of the walls of the voids are made up of 40 nm diameter nanoposts. (C) The wall of one of the voids. (D) Side view of the entire carpet of nanoposts. (E) The bases of the nanotubes are anchored to the substrate. (F) The tops of this carpet of nanoposts press up against one another. The membrane mold was anodized for 8 hours, producing posts ~50 µm tall and AR ~1300, in good agreement with the predicted 52 µm. Despite being pressed against one another, elastocapillary coalescence of these ultra-high aspect ratio nanoposts did not result in posts which packed against each other in an ordered fashion. This could be explained by the disorder in the packing of the nanoposts along their length (C). Conical shaped voids are the result of the aggregation and collapse of these long nanoposts. As observed in E, the posts remain anchored to the substrate but bend and buckle due to their modulus and their aspect ratio and elastocapillary coalescence.
2.4.2. Modulus Reduction Through Solvent Inclusion

The pores of the AAO membrane mold were filled with a solution of the thermopolymer resist in propylene glycol methyl ether acetate (PGMEA) to investigate the effects of solvent on nanopost collapse and aggregation. Figure 11A,B shows that with aspect ratios of 5, both cured materials, without and with solvent inclusion, respectively, produced rods with a sufficient modulus to withstand the capillary bridging forces and were able to remain upright. However, increasing the aspect ratio to 13.5 displayed in Figure 2.11 C,D revealed that the solvent has reduced the modulus of the cured thermopolymer resist such that the rods collapsed to aggregate into clumps. The size scale of these aggregates with aspect ratio 13.5 (Figure 2.11D) was smaller than that of aggregates with twice the aspect ratio (Figure 2.7) and were more uniform in size. While no modulus measurements were performed to determine how much the modulus of the material cured in the presence of solvent would differ from the original thermopolymer resist, the inclusion of solvent should be recognized to reduce the modulus of the material as the curing of the polymerizable components and diffusion and evaporation of PGMEA from the cured resist should leave behind empty voids within the polymer matrix.
Figure 2.11. (A) and (B) are rods composed of 100 vol% thermopolymer resist with A having aspect ratio of 5.4 and B having aspect ratio of 13.5, the same as Figure 2.5C-D, respectively. (C) and (D) are rods formed from having the pores of the alumina membrane filled with a mixture of 50 vol% thermopolymer resist and 50 vol% PGMEA and cured. The rods at aspect ratios of 5.4 were able to preserve the replicated structure of the AAO membranes, but at aspect ratios of 13.5, the rods succumbed to capillary bridging, as the inclusion of solvent into the resist during curing led to a significant reduction in the modulus of the cured material.

2.4.3. Elastocapillary Coalescence of 10 nm Diameter Polymer Nanoposts

10 nm diameter posts made by nanoimprinting with alumina membranes with the same pore diameter exhibited a similar trend in the hierarchical structures formed with increasing aspect ratio through elastocapillary coalescence. Kinetics of the anodization conditions which produced 10 nm diameter pores was determined to be ~16 microns per hour, or 267 nm/min of anodization. By capillary force calculations for 10 nm diameter
pores with one end of the pores closed, the thermopolymer resist was predicted to fill 95% of these pores as opposed to 81% for the 40 nm diameter pores due to the larger capillary force with a smaller pore diameter. At lower aspect ratios of ~25, as seen in the top row of Figure 2.12, the nanoposts aggregated to form clusters similar to those with comparable aspect ratio for posts with 40 nm diameters (Figure 2.7). At twice that aspect ratio, shown in the bottom row of Figure 2.12, the nanopost aggregates had collapsed to form more elongated secondary structures, similar to those shown in Figure 2.8 Row A. The trend for the elastocapillary coalescence of nanoposts with 40 nm and 10 nm diameters was the same for aspect ratios of 25 to 50, and can be expected to be the same up to ultra-high aspect ratio posts.
2.4.4. Conducting Polymer Nanoposts

The crosslinking of spuncoat PHTPA, a hole-conducting polymer synthesized by Prof. Kenneth R. Carter was performed in alumina membranes with pore depth ~266 nm. While the crosslinking was successful in producing the conducting polymer nanoposts, the material was not capable of withstanding the capillary bridging, which pulled the nanoposts together as seen in Figure 2.13 even at an aspect ratio estimated to be ~5. This is probably due to the thin support layer of the conducting polymer which provided no mechanical support at the base of the nanoposts, allowing the film base to be deformed.
and the posts pulled together to compensate for the forces behind capillary bridging. While the nanorods were not capable of withstanding capillary bridging forces, this method provided a path for the formation of nanoposts with a thin base layer.

Figure 2.13. 40 nm crosslinked poly(hexyl-triphenylamine) nanoposts. The collapse of these conducting polymer nanorods formed through spincoating onto an alumina membrane with pore depth of ~266 nm to form posts with aspect ratio of 5 can be attributed to a low modulus of the material and elastocapillary coalescence.

2.5. Mechanism of Nanopost Aggregation

Research conducted by other researchers mentioned in Chapter 1 described how elastocapillary coalescence from capillary bridging between nanostructures causes bending of the nanorods. Ordinarily, it can be expected that for the top of a nanorod to come in contact with one of its neighbors, it undergoes deflection due to a load acting on the untethered end and bends along its length such that its top travels half the distance between itself and one of its neighbors. Similar to the macroscopic structures, this would
occur in the dry state due to gravitational forces at an aspect ratio which would be
determined by the bending modulus of the material. With well-ordered nanoposts 40 nm
in diameter and spaced only 60 nm apart from inner edge to inner edge (100 nm center to
center distance), the nanostructures would only need to deflect 30 nm for the tops of a
pair of neighboring nanoposts to come in contact. This would naturally occur at a critical
aspect ratio of these particular nanorods made from the cured thermopolymer resist.
However, capillary bridging between nanoposts creates a large load acting in the
horizontal direction which causes them to bend and deflect along their length at much
smaller aspect ratios due to the magnitude of capillary forces acting at the nanoscale.
Such a load acting on the nanoposts causes them to easily bridge the 60 nm distance
starting from the top of the nanorods as the wetting fluid meniscus dips to the level of the
tops of the nanostructures. As the meniscus travels down the length of the nanorods as
the wetting fluid evaporates, it pulls the nanorods together along their length until it can
no longer do so due to the fact that the nanoposts are anchored at their base, similar to the
macroscopic event shown in Figure 1.5.

From the data, it could be recognized that clusters were the initial structures
formed by elastocapillary coalescence of nanoposts. These clusters of nanoposts shown
in Figures 2.7, 2.8, 2.11, 2.12, 2.13 had the capability themselves of succumbing to
elastocapillary coalescence, forming tertiary structures consisting of couplets of clumps.
Figure 2.12 (bottom row) shows clearly how the aggregation of the individual clusters of
nanoposts can lead to the longer structures.
If the nanorod aspect ratio were already larger than the critical aspect ratio at which the nanoposts begin to bend and deflect from their own size independent of capillary bridging, the mechanism for collapse would be different. These nanorods would already possess the necessary aspect ratio to naturally deflect to bridge the distance separating the nanoposts in the absence of capillary bridging. The nanoposts would be bending and coming in contact with each other once the alumina matrix was dissolved and became free-standing nanoposts in a continuous phase of water. Capillary forces would be simply acting on nanoposts which had already been disturbed from their well-ordered packing structure and were already aggregating due to their dimensions.

It is clear that at higher aspect ratios, the longer aggregates that formed as a result of elastocapillary coalescence lacked the appearance of being formed by the coupling of individual clusters of these nanorods like in Figure 2.12 (bottom row). For example, in Figure 2.9D, with aspect ratio of >300, the edges of the aggregate structures were smooth. The ridges did not possess the choppy appearance of the structures in Figure 2.9A with aspect ratio of ~100 or in the bottom row of Figure 2.12. It is impossible at this point to determine just by judging from the structure of the aggregates where elastocapillary coalescence of well-ordered nanoposts ended and elastocapillary coalescence of disordered bending nanoposts began, to pinpoint the aspect ratio at which the natural bending and buckling of the nanorods became significant to influence their aggregation structure. Whether the natural bending and buckling of the nanoposts influences the secondary structures they form through elastocapillary coalescence is also unknown.
2.6. Cluster Size

The variation of cluster size with aspect ratio, diameter of the nanorods, spacing between the nanorods is difficult to quantify. The morphologies of the aggregates in Figures 2.7-2.10 showed a wide distribution of feature sizes for nanorods of the same aspect ratio. The situation was further complicated by the ability of the aggregates to themselves aggregate with one another. What is apparent is that between the aggregates shown in Figure 2.9D and 2.10, the diameter of the irregularly shaped aggregates is similar to the diameter of the cone-shaped voids. This suggests that the packing of the nanoposts determines the size scale of the aggregates. The smaller the nanopost, the smaller the aggregates, as is apparent in comparing Figures 2.7 and 2.8A and Figure 2.12. Between two sets of nanoposts with the same diameter but different spacing, the different spacing can be hypothesized to lead to the eventual formation of conical shaped voids with larger diameters as the density of the nanoposts decreases and the volume of air within an array of nanoposts increases.

2.7. Conclusions

Polymerizations within alumina membranes are possible, and by controlling the aspect ratio of the pores in the alumina membrane mold, crosslinked polymer posts of controlled diameter and aspect ratio could be formed. At lower aspect ratios, the hexagonal packing of the nanoposts was preserved and no aggregation or collapse was observed. Using these low aspect ratio nanoposts to replicate the pore structure of the original alumina membrane mold was achieved. The aggregation of the higher aspect
ratio nanoposts due to elastocapillary coalescence created secondary structures whose size and morphology directly correlated with the aspect ratio of the nanoposts, the primary structure in this system. With increasing aspect ratio, the nanoposts aggregated to form clusters and then lines. The lines increased in length and height with increasing aspect ratio until they began to intersect and form irregular shapes. These irregular shapes grew taller as the primary structures themselves were greater in height. Eventually, at aspect ratio of >1000, the nanoposts aggregated to form conical-shaped voids with walls made up of the nanoposts. This trend appeared to be independent of post diameter and only a function of the post aspect ratio. The addition of solvent to dilute the polymerizable material within the alumina membrane pores reduced the modulus of the cured nanoposts such that they succumbed to elastocapillary coalescence at a much lower aspect ratio.

While it is evident that over the range of aspect ratios, elastocapillary coalescence initially acts upon well-ordered nanorods and eventually acts upon nanorods which had already begun to bend and buckle from their own dimensions, it is impossible to pinpoint the aspect ratio at which this occurs and judge whether the disorder of the nanorod structure affects the aggregate structures. Chakrapani’s work with the aggregation phenomena of vertically aligned carbon nanotubes displayed similar aggregate structures on a greater length scale to those shown in Figure 2.9D, and under an optical microscope, he was able to view the formation of the aggregates as the wetting fluid evaporated from the carpet of carbon nanotubes. The similar morphologies on a greater length scale are likely due to the modulus of the carbon nanotubes being orders of magnitude greater than
the crosslinked polymer used in the studies described in this thesis chapter. Further studies in the formation of the arrays of hexagonally-packed nanorods with varying aspect ratio should focus on the preservation of the packing structure of the nanorods to understand how individual nanoposts and arrays of nanoposts would behave in the absence of elastocapillary coalescence. While the use of anodized aluminum membranes limits researchers to the formation of rod-like structures or porous structures by double-replication techniques, by current day lab techniques, anodized aluminum membranes are one of the few ways known to form well-ordered 3-D vertical nanostructures with controllable aspect ratio and feature dimensions. As the research in this chapter demonstrates, the effects of surface tension on well-ordered 3-D vertical nanostructures presents challenges for any further chemical modification of high aspect ratio nanoposts. The preservation of high aspect ratio 3-D nanofeatures has been performed with freeze-drying, but this method limits the potential for further modification of the nanostructures to the vapor phase and to the use of supercritical fluids, as attempts to rewet the nanorods for solution phase modification would induce capillary bridging and disruption of any deliberately preserved packing order. One could envision maintaining the nanorods constantly in a liquid phase. By simply replacing the wetting fluid with the reaction solution and then perform freeze-drying after the rods had been modified, elastocapillary coalescence would be avoided. As freeze-drying can be a harsh process, this presents the need for a gentler method for the absence-of-surface-tension removal of the wetting fluid. Transforming the wetting fluid into a supercritical fluid would be one such method. The wetting fluid does not have to be the solvent in which the reaction is performed. Wetting
fluids can be gradually replaced until the nanorods are wet by a fluid which can be transformed into a supercritical fluid under mild temperatures. With these two methods for absence-of-surface-tension removal of fluids wetting high aspect ratio free-standing nanofeatures, research can be performed to produce core-shell vertical nanoposts or interdigitated structures for purposes such as ordered heterojunctions for solar cell applications. The deposition of other nanostructures such as nanoparticles or nanorods with smaller dimension onto the surface of the well-ordered nanoposts also would be interesting. As for elastocapillary coalescence, the research in this thesis was performed on neutral polymers. Polymers with charged surfaces would likely exhibit different morphologies from elastocapillary coalescence. Sulfonation of polystyrene nanorods to transform the posts surface into polystyrene sulfonate would be an effective method for understanding how surface charges affect the nanopost aggregation from capillary bridging with the wetting fluid.
2.8. References


CHAPTER 3

TEFLON-SUPPORTED DRY WATER

3.1. Introduction

In research reported to date, the formation of an inverse foams has utilized hydrophobized silica nanoparticles as discussed in Chapter 1. The use of these hydrophobized nanoparticles has allowed for the transformation of bulk water to dry water with only 5 wt% of the stabilizing agent. However, as Binks demonstrated, the introduction of a basic solution as the liquid intended for encapsulation in the dry water form, rendered it impossible to produce the inverse foam using these hydrophobized silica nanoparticles as the solution reacted with the particle surfaces to make them hydrophilic. Silica is inherently reactive. In this chapter, it is demonstrated that PTFE microparticles can effectively stabilize water-in-air inverse foams. PTFE-particle stabilized inverse foams were characterized for their size, thermal stability, density change between mixed and unmixed states, flow properties, and their overall stability to mechanical pertabations. Due to the unreactivity of PTFE, it was possible to produce inverse foams from aqueous solutions of reactive compounds such as the basic solutions used by Binks discussed in Chapter 1, in addition to other water-soluble compounds previously unreported as being encapsulated in the dry water form.
3.2. Experimental Section

3.2.1. Materials

Poly(tetrafluoroethylene) powder with 1 micron, 12 micron, and 35 micron diameters was purchased from Aldrich. Sodium hydroxide was purchased from Aldrich. Sulfuric acid, hydroxyethylmethacrylate, glycerol, and ethanol were purchased from Fisher Scientific and used as received. Bis(hydroxyethyl)dimethylammonium methanesulfonate (TEGO 2) was acquired from Evonik and used as received.

3.2.2. Dry Water Formation

The synthesis of dry water was carried out using an Oster 12-speed blender model 6802 and the Mini-Jar accessory #4937 with ~220 ml fill capacity. Water and powder were added into the Mini-Jar, and the two components were mixed using the “Ice Crush” blend method. Vortex mixing of samples was performed on a Fisher Scientific Vortex Genie 2 for the purpose of breaking up aggregates and making the dry water powder more uniform in size. Samples were vortex mixed 10 times for periods of less than 5 seconds to eliminate the risk of destabilizing the mixture.

3.2.3. Characterization of Dry Water

Powders were passed through meshes, whose sizes were verified through optical microscopy. Individual powder particles were observed through an Olympus BX-51 Reflected Fluorescence System optical microscope for size verification. Images of the remaining dry water powder which could not pass through the mesh due to their size
were obtained with a Nikon D80 camera with a Nikon 105mm f2.8 VR Macro lens and tripod attached.

20 ml glass scintillation vials were filled completely with the dry water powder, to prevent condensation of water on exposed glass surfaces. Samples were capped, then sealed with Teflon tape. Heat tests were performed by placing the sealed samples in an oven at 105 °C overnight. Samples were taken out and allowed to return to cool to room temperature. Cold tests were performed in a freezer at -14 °C overnight. Samples were taken out and allowed to warm to room temperature. Samples were examined for changes in morphology and presence of liberated water.

To measure density change between the unmixed and dry water forms, 20 mL glass scintillation vials were filled with the dry water sample, and the mass of the dry water required to fill the vials was obtained. Assuming powder composition was unchanged from the unmixed state, the equivalent mass of powder and water was added to a graduated cylinder and the volume determined and density calculated.

Powder flow was conducted using a polyethylene funnel with a 5 mm opening.

3.2.4. Dry Liquid Formation

Bulk mixtures of the aqueous solution and PTFE powder were turned into inverse foams by vortex mixing 2 gram batches of water and 12 micron diameter PTFE powder in 20 ml polystyrene vials for 2 minutes. PTFE powder concentration was maintained at 20 wt%. Aqueous solutions were tested for inverse foam encapsulation potential in increments of 10 wt% of the solute.
3.3. Teflon-Supported Dry Water Physical Properties

The synthesis of dry water has been performed using several methods described by the references cited in Chapter 1. Besides the blending and vortex mixing methods described in this thesis, in general, any procedure which is intended for the formation of dry water will need to be able to catastrophically break up bulk water into tiny water drops in the presence of a stabilizing hydrophobic powder. Using the blender, a requirement for the formation of dry water was that the blending container with water and powder also contain a large volume fraction of air to provide water the adequate space to be broken up into tiny water drops. The requirement regarding the volume of air in the dry water container also applied to the polystyrene vial and the vortex mixing used to produce dry liquids as described in section 3.2.4.

Following the blending and vortex mixing of the PTFE particles and bulk water, the resulting dry water consisted of small heterogeneous particles, with small water drops coated with the PTFE particles to form the PTFE particle shell similar to those formed in liquid marbles and particle rafts as discussed in Chapter 1. The 1 µm PTFE-supported dry water displayed in Figure 3.1 was indistinguishable from dry water made from 12 micron diameter PTFE powder. 35 micron diameter PTFE particles were incapable of stabilizing dry water, likely due to their size since their surface properties were the same as the 1 micron and 12 micron diameter particles. The properties of dry water made from 1 micron and 12 micron PTFE powder also appeared to be very similar. Following blending and vortex mixing to produce the dry water, the inverse foam consisted of particles with the same size regardless of the diameter of the stabilizing hydrophobic
powder as shown in Table 3.1 and Figure 3.2, with Figure 3.2D demonstrating that an individual dry water particle was simply a non-spherical liquid marble. Dry water stabilized by both 1 micron and 12 micron diameter PTFE particles is shown in Table 3.1 to have particle sizes ranging from 90-500 microns. The distribution of dry water particle sizes is unknown. The values reported are simply the smallest and the largest values of the observed diameters of the dry water particles. The PTFE powder itself, while listed as having particle diameters of 1 micron and 12 micron, exists as aggregates of these primary polymer particles, and it was these aggregates which packed on the surface of the water drops and stabilized the inverse foam. It can be expected that the water drop sizes and size distribution produced by a blender, using the same blender, same blending mode, and same volume of water in the same container, will be the same regardless of the stabilizing particle sizes. The similar range of particle sizes of the inverse foam despite the different stabilizing powder diameters is likely an indication that the stabilizing aggregates of PTFE particles are of similar sizes even though the primary particles are of different sizes.

Dry water made from 1 and 12 micron diameter PTFE powder flowed very well through a 5 mm diameter funnel, which was to be expected. PTFE particles themselves flow very well through the funnel, and when these particles form a particle shell around a small water drop, it can be expected that the resulting heterogeneous particle will also exhibit similar flow properties due to the same chemical nature of the outer shell and the small size of the particles compared to the diameter of the funnel. Inverse foams were also remarkably stable when poured onto a water absorbent surface such as a paper towel.
No water release was observed. The thermal stability of dry water stabilized by PTFE powder was excellent in heat, and poor in cold (Table 3.2). The purpose for such experiments was due to comments in the patent literature discussed in Chapter 1 on the advantages of storing large volumes of water in the dry water form. In the patent literature, inverse foams were touted as an advantageous method for storing water in extreme temperatures compared to bulk water. In the form of dry water, water could be frozen and maintain its flow properties as a powder as opposed to bulk water which would become a large ice block and difficult to transport. Any need to liberate the water could be performed simply by heating the water out of the inverse foam and condensing it elsewhere. By heating the Teflon-stabilized inverse foam in a filled, closed container to temperatures above the boiling point of water and returning it to room temperature, no change in the physical properties of the dry water was found. The morphology, flow properties, and contact stability remained unchanged. By freezing the dry water, some changes were observed. While much of the inverse foam remained unaffected, some aggregates were formed. These aggregates consisted of flakes of PTFE powder and water which had poor contact stability and released water when placed in contact with a water absorbent material such as a paper towel. These aggregates negatively impacted the flow properties of the inverse foam through a 5 mm diameter funnel due to their size being on the millimeter scale. The formation of such aggregates was likely due to the expansion of water during the freezing process. In the process, the particle shell was broken, allowing for water within individual dry water particles to bridge and merge with water within neighboring particles. The aggregates formed by the freezing of Teflon-
stabilized dry water, demonstrated to impact the flow properties of the heterogeneous powder through a funnel, would be a concern if someone were planning to flow frozen dry water through a narrow diameter funnel. However, for large scale processes, the aggregates formed due to the freezing of dry water would be of little concern as there would be no need to pass frozen dry water through funnels or filtering devices.

There were significant differences between the two sets of inverse foams. It was determined that with the 12 micron diameter PTFE particles, at least 12 wt% PTFE powder was required to fully encapsulate all the water in an inverse foam as displayed in Figure 3.3, whereas 15 wt% PTFE powder was needed to completely produce the inverse foam using 1 micron diameter powder. The properties of dry water stabilized by micronic PTFE particles and 20-30 nm diameter hydrophobized silica nanoparticles were similar in their appearances and flow and contact properties, but the PTFE particles lacked the ability to encapsulate 19 times their weight in water like the hydrophobized silica nanoparticles were capable of doing. All attempts to produce dry water using a lower weight percentage of powder resulted in the incomplete encapsulation of the water and the formation of unstable aggregates of PTFE powder and water which released water when placed in contact with another object, similar to the aggregates formed by freezing the inverse foam. However, following removal of excess water, vortex mixing of these unstable aggregates in polystyrene vials resulted in a formation of dry water powder with properties similar to those of dry water powder formed when enough stabilizing PTFE powder was used during the blending process. There was also a decrease in density from the unmixed state to the mixed state of PTFE powder and water,
with a 15% change and 12% change for dry water made from 1 micron and 12 micron PTFE powder, respectively, pointing to the importance of the incorporation of a significant volume of air as the continuous phase of the inverse foam. The 15% density decrease using the 1 micron powder suggested a greater incorporation of air as the continuous phase of the foam compared to the dry water stabilized by the 12 micron powder. Their stability to mechanical perturbations in the form of vortex mixing also differed greatly, with dry water stabilized by 1 micron diameter particles being stable indefinitely, and dry water stabilized by 12 micron diameter particles lasting less than 1 minute. Dry water stabilized by 12 micron powder could not withstand the chaotic motions of the Vortex Genie, which resulted in the large scale release of water. This could be due to the inefficient packing of the aggregates of the 12 micron PTFE powder on the water drops producing heterogeneous particles only 7.5 to 40 times greater in diameter than the primary particles, whereas the aggregates of the 1 micron powder, having been made of significantly smaller diameter particles, were capable of producing a more complete particle shell which could withstand collisions with the polystyrene wall and with other dry water particles without disrupting the particle shell and spilling water.
Figure 3.1. 1 micron, 10 wt% powder. The heterogeneous powder is the morphology of the inverse foam formed from blending, the vortex mixing the sample. The powder was directly poured out of the vial following vortex mixing onto the paper. No wetting of the underlying paper was observed.

Table 3.1. Dry water particle sizes from different diameter PTFE powder.

<table>
<thead>
<tr>
<th>Powder Size</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 micron</td>
<td>90 - 500 micron</td>
</tr>
<tr>
<td>12 micron</td>
<td>90 - 500 micron</td>
</tr>
</tbody>
</table>
Figure 3.2. (A) 12 micron, 10 wt% powder on a 200 micron mesh. This sample has been blended and vortex mixed. (B) 12 micron, 10 wt% powder. (C) 1 micron, 10 wt% powder, blended and vortex mixed. Dry water particles which could not pass through the 200 micron mesh are measured, with tick marks spaced 0.5mm apart (B and C). (D) 5x magnification of dry water particles resting on 200 micron mesh (1 micron PTFE powder, 10 wt%). The heat from the light source in the optical microscope caused the dry water particle on the right to shrink as the water within it evaporated.

Table 3.2. Temperature effects on the physical properties of dry water stabilized by 1 micron and 12 diameter PTFE powder.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Hot</th>
<th>Cold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Stability</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Morphology Change</td>
<td>No</td>
<td>Flakes + Powder</td>
</tr>
</tbody>
</table>

Table 3.3. Change in density between the unmixed states and mixed states of 15 wt% powder with 85 wt% water for 1 and 12 micron diameter PTFE powder. Stability to vortex mixing of dry water made from 1 micron and 12 micron diameter powder.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Density Change</th>
<th>Stability to Vortex Mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 micron</td>
<td>-15%</td>
<td>1 hour +</td>
</tr>
<tr>
<td>12 micron</td>
<td>-12%</td>
<td>No more than 1 min</td>
</tr>
</tbody>
</table>
Figure 3.3. Volume of free water remaining after the mixture was blended at various wt% of 1 micron and 12 micron PTFE powder in 30 gram batches. 1 micron diameter PTFE powder was inferior to the 12 micron PTFE powder in the encapsulation of water, encapsulating only 5.7 times its mass in water compared to 7.3 times for the 12 micron powder.

3.4. Dry Liquids

Due to the inherent unreactivity of PTFE, it was possible to use acidic and basic solutions as the aqueous phase of this inverse foam. Binks et al. reported the use of weakly basic solutions for making dry water, up to solutions with a pH of 9.0. He showed that by pH 10, air-in-water foams had begun to form and by pH 11, the change was complete, with a milky white solution being formed instead of an inverse foam. The demonstration by Binks of the gradual transformation from dry water to foam with increasing basicity of the aqueous solution was due to the gradual base-catalyzed
hydrolysis of the silicon-oxygen-silicon bonds on the surface of the hydrophobic particles, rendering them more and more hydrophilic. Changing the stabilizing agent to unreactive PTFE allowed for the use of extremely basic solutions. Figure 3.4 shows acidic dry water and basic dry water, made from 1 wt% sulfuric acid and 1 wt% sodium hydroxide solution, respectively, using 15 wt% 12 µm PTFE powder. Clearly the PTFE powder was unaffected by the solution and maintained its hydrophobic nature. There is even a small basic liquid marble in the upper left corner of Figure 3.4 (left) which is resting on the acidic dry water with no apparent mixing due to the lack of color change. Mixed together without the particle shell, these two solutions would have created an exothermic reaction, but due to their separation by the PTFE particle shells, the solutions trapped within the particles in the two inverse foams remained separate and incapable of reacting with each other, even after being mixed together in a Vortex Genie and poured back out on to a petri dish as shown in Figure 3.4 (right). Pushing on the mixture of two inverse foams in 3.4 right with a gloved finger led to the release of the acidic and basic solution and the immediate exothermic reaction between the two. Attempts to make dry water from 10 wt% NaOH solution using 15 wt% 12 micron powder was unsuccessful - very little solution encapsulation occurred. Most of the solution stayed out of the dry water morphology.
The formation of particle rafts, liquid marbles and dry water are based on the same principle of taking a high surface energy liquid and coating it with hydrophobic, low surface energy powders which stabilize the air-water interface. This phenomena could also be performed with other high surface energy liquids/solutions. However, several organic solutions which could produce liquid marbles failed to produce dry liquids using 1 and 12 micron powder at 20 wt% powder. Initial scouting experiments were performed to determine which solutions could be encapsulated as dry water and which could not. It has been reported that liquid marbles have been made with glycerol and glycerol/water solutions.\(^1\) Attempts to produce dry water from aqueous solutions of
glycerol were successful at 30 wt% glycerol and below using 12 µm PTFE powder. Increasing the concentration of glycerol to 40 wt% resulted in the formation of a white viscous solution. The white color of the liquids suggested the incorporation of the PTFE microparticles in the solution. Instead of producing an inverse foam with a continuous phase of air, the resulting product consisted of a white solution with a continuous liquid phase. Success was found in making liquid marbles with ethanol/water solutions up to 50 wt% ethanol, yet the solutions failed to produce dry water by blending and vortex methods in concentrations at and greater than 10%, producing similar white solutions, but with less viscosity than that of the glycerol solutions. Experiments involving ionic liquids demonstrated that a high concentration of these organic compounds could be encapsulated in inverse foams. Bis(hydroxyethyl)-dimethylammonium methanesulfonate (TEGO 2), a viscous ionic liquid with a surface tension similar to that of glycerol and large contact angle with PTFE surfaces,\textsuperscript{2,3} was able to reach as high as 70 wt% concentration in aqueous solutions before the blending process produced the white viscous liquid at 80 wt% concentration, which characterized failures of producing inverse foams with certain aqueous solutions.

For the purposes of investigating the possibility of an inverse foam polymerization which would involve the polymerization of water soluble monomers in aqueous solutions encapsulated as dry liquids to produce polymer particles coated with the Teflon particles which stabilized the original unpolymerized dry liquid, experiments were performed using aqueous solutions of hydroxyethylmethacrylate (HEMA). Liquid marbles were made using HEMA/water solutions up to 100 wt%, and polymerization of
HEMA within these platforms was achieved using azobisisobutyronitrile (AIBN) as the thermal initiator at 80 °C for 6 hours under nitrogen. However, any solution with more than 10 wt% HEMA was incapable of producing a dry liquid using 15 wt% of the 12 micron diameter PTFE powder. At 1 wt% HEMA, dry liquids could be formed using 15 wt% powder but the concentration of polymerizable monomer in the liquid phase was too low for polymerizations to occur. It appears that the water soluble monomer was surface active and rendered the PTFE particles hydrophilic much the same way that poly(vinyl alcohol) (PVOH) can irreversibly absorb from aqueous solutions to hydrophobic substrates. Work by Kozlov and McCarthy points to the irreversible absorption of PVOH to the surface of Teflon particles from water which was likely the phenomenon which prevented the formation of dry water with more than 0.001 wt% of PVOH polymer in water. Above 0.001 wt% concentration of PVOH in water, the blending of such solutions with 15 wt% PTFE powder produced a white liquid with the hydrophobic particles within the aqueous phase. The PVOH in solution absorbed to the PTFE powder surface, making them hydrophilic and incapable of stabilizing inverse foams. While HEMA is not a polymer, the inability of 10 wt% solutions of the monomer to be encapsulated as a dry liquid and the observation that the Teflon powder had been completely pulled into the liquid phase points to the possible surface activity of HEMA. The addition of 10 wt% HEMA to any of the aqueous solutions which were capable of being encapsulated as inverse foams, also rendered those solutions incapable of doing so.
Table 3.4. Comparison of ability to produce liquid marbles and dry liquids from various aqueous solutions.

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>Liquid Marble</th>
<th>Dry water</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-50 wt% EtOH</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>0-30 wt% glycerol</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>40+ wt% glycerol</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>10-100 wt% HEMA</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>0-70 wt% TEGO 2</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>70+ wt% TEGO 2</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

3.5. Conclusions

Dry water made from PTFE powder exhibited similar behavior to powders made from hydrophobized silica nanoparticles. The contact stability and flow properties of these inverse foams were similar to those made from hydrophobized silica as reported by other researchers discussed in Chapter 1. 12 micron powder was capable of encapsulating a larger volume of water than the 1 micron powder and incorporated less air in between particles leading to a smaller density decrease between the unmixed and dry water form, yet the dry water stabilized by 1 micron powder was immune to mechanical perturbations in the form of vortex mixing. While a larger weight percentage of PTFE powder was required to completely encapsulate water compared to hydrophobized silica nanoparticles, the PTFE powder exhibited excellent stability to acidic and basic solutions, allowing for the production of dry sodium hydroxide solutions and dry sulfuric acid solutions. Experiments comparing the use of aqueous solutions of organic compounds to form liquid marbles and dry solutions (inverse foams) showed that the ability of a solution to form a liquid marble did not necessarily indicate that it could
also be encapsulated as an inverse foam, for reasons unknown. However, there is potential application for producing microparticles of polymers using dry water or liquid marbles as reaction platforms, as HEMA was polymerized within liquid marbles. The failure of HEMA incorporation into dry water was possibly due to the surface activity of HEMA in aqueous solutions when it is placed in contact with a hydrophobic substrate. What is needed for an inverse foam polymerization is a water soluble monomer that is not surface active when placed in contact with a hydrophobic surface.

The results demonstrated how the use of micron-sized PTFE powder led to a decreased ability to encapsulate water compared to hydrophobized silica nanoparticles. The amazing ability of the silica nanoparticles to encapsulate many times their mass in water was certainly one property that the PTFE powder from Aldrich lacked. Future research into dry water stabilized by PTFE powder should investigate the use of PTFE nanoparticles to see if water encapsulation is increased by reducing the size of the stabilizing particles and their aggregates. Another avenue of research would be to increase the number of solutions which can be encapsulated as dry water. With liquid marbles and dry water utilizing the adsorption and packing of hydrophobic particles on the surface of liquids, the differences in the formation of the two led to differences in the solutions capable of being encapsulated using the same stabilizing powder. The experiments performed here demonstrated the wide range of liquids and solutions which could be encapsulated as liquid marbles which were formed by gentle means. Dry water, made through the catastrophic inversion of bulk liquids and powder, was made through much more chaotic means. Clearly, producing individual liquid marbles on the size scale
of dry water particles would produce an inverse foam, eventually. A desirable dry water synthesis technique would be one which could encapsulate the same solutions and liquids as liquid marbles were capable of doing, but in the time frame that dry water was typically made. With such a method, the potential of dry water/dry liquids as a polymerization platform would be realized.
3.6 References


4.1. Introduction

There has been the notion that rough surfaces exhibit higher contact angles because the water drop rests on pockets of air, which directly allows for a decreased solid-liquid interaction and inserts liquid-vapor interfaces into the solid-liquid interface which increase the contact angle. Now suppose that a Cassie superhydrophobic surface, one with high advancing contact angle and low contact angle hysteresis, were brought into the vacuum of space. Would the rough surface exhibit the same wetting properties in the vacuum of space as on Earth? The idea that “entrapped air” is responsible for producing Cassie wetting behavior would lead one to the conclusion that removing that “air” would lead to a transition in wetting behavior from the Cassie wetting behavior to the Wenzel, as many authors have noted. The water drop would lack the cushion of air to prevent it from interacting with the surface features and the water-air interface would become a water-solid interface, leading to Wenzel wetting behavior. But the basic unproven assumption is that air actively causes Cassie wetting behavior and is not a bystander in the whole system. Analysis of “entrapped air” has led to attempts to establish criteria for the entrapped gas and statements implying that the air inside a polystyrene nanotube and the air between the nanotubes is different, even though they are at the same pressure. The Wenzel state has also been described as “sucking disk behavior” with the idea that a water drop can discharge air between the drop and the
surface. Transitions from Cassie wetting behavior to Wenzel wetting behavior have been attempted by compressing a drop on a surface with triangular spikes\textsuperscript{7}, by controlling pore size and pore-to-pore distance in anodized aluminum membranes\textsuperscript{4}, and by placing a water drop on a surface from different heights.\textsuperscript{2}

These studies have only utilized static contact angles to demonstrate the transition from Cassie to Wenzel wetting behavior while providing no data on the actual advancing and receding contact angles of their experimental surfaces. By showing a water drop on a surface with a higher static contact angle in one case than in the other, their attempts to demonstrate a Cassie to Wenzel surface transition were merely showing that the surface had hysteresis, with the two contact angle values stated existing between the advancing contact angle and the receding contact angle. Figure 4.1 theorizes what the dynamic contact angle data would look like if air was indeed responsible for preventing a Cassie surface from turning into a Wenzel surface. There would be no change in the advancing angle with decreasing pressure, but with the removal of air, the water drop would increase its interaction with the features of the surface due to the removal of the air cushion, leading to a decrease in the receding contact angle and a corresponding increase in the contact angle hysteresis.

The other explanation for Cassie wetting behavior is that the Laplace pressure,\textsuperscript{13-14} described by equation 4.1, of the hydrophobic surface features prevents water from having intimate contact with the entire chemically hydrophobic rough surface. This largely-ignored thermodynamic phenomena is what prevents water from entering a capillary with an inner surface with water advancing contact angle greater than 90°.
Laplace pressure, being independent of ambient pressure, would predict that the removal of air from within those surface features would have no effect on the dynamic contact angle of water or another probe fluid on the surface as shown in Figure 4.1. A Cassie surface at atmospheric conditions would remain a Cassie surface regardless of the pressure; there would be no transition to the Wenzel wetting behavior upon reduction of pressure and removal of air. The impact of Laplace pressure of these surface features would also be observed by exceeding the Laplace pressure of the surface features and forcing the water to intrude into the rough surface hydrophobic features. This would be marked by no change in the advancing contact angle, but a severe drop in the receding contact angle and increase in contact angle hysteresis as the pressure difference between the air under the drop and the air above the drop would prevent the water from leaving from within the hydrophobic features, effectively pinning the drop at that location.
This research demonstrated that entrapped air was not responsible for Cassie superhydrophobic wetting behavior. New techniques for the measurement of advancing and receding contact angles were developed to measure the wettability of a surface at reduced pressures, since the experimental setup would not allow for the direct addition or removal of water for direct dynamic contact angle measurement. It was also demonstrated how exceeding the Laplace pressure of the hydrophobic surface features influenced contact angles and contact angle hysteresis.
\[
\Delta P = - \frac{p \gamma_{lv} \cos \theta_A}{A} \quad \text{(Equation 4.1)}
\]
\[
- \frac{4 \gamma_{lv} \cos \theta_A}{s} \quad \text{(Equation 4.2)}
\]
\[
- \frac{4 \gamma_{lv} \cos \theta_A}{3s} \quad \text{(Equation 4.3)}
\]

In Equation 4.1, \( p \) is the perimeter, \( \gamma_{lv} \) is the surface tension of the probe fluid, \( \theta_A \) is the advancing contact angle, and \( A \) is the area. Equation 4.2 describes the Laplace pressure for a surface with square holes of side length \( s \). Equation 4.3 describes the Laplace pressure for a surface with square posts of side length \( s \).

### 4.2. Experimental Section

#### 4.2.1. Rough Surfaces

The surfaces which were modified were Si wafers with square holes 70 microns on each side, and a Si wafer with square posts 25 microns on each side. From Equation 4.2 and assuming that \( \theta_A = 120^\circ \), the Laplace pressure of the surface is 15.43 torr. Based on Equation 4.3 and assuming that \( \theta_A = 120^\circ \), the Laplace pressure of the surface is 14.4 torr. Their contact angle responses to the reduction in pressure was compared to those of a smooth Si wafer.
4.2.2. Modification of Surfaces

The surfaces mentioned in section 4.2.1 were used to measure contact angles of hydrophobic surfaces at reduced pressures. The surfaces of these wafers were washed with deionized water, acetone, and toluene, and then oxygen plasma-cleaned for 10 minutes. The clean surfaces were then modified with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-dimethylchlorosilane in the vapor phase at 70 °C for 24 hours.

4.2.3. Measurement of Receding Contact Angles at Reduced Pressures

Receding angles were measured through evaporation of a water drop at the reduced pressures (Figures 4.3 and 4.4). A water drop was placed on the sample. The pressure was reduced to the desired value, and then the entire assembly was gently
rocked to move the water drop to a new location. The receding contact angle was recorded after it was evident the water drop was evaporating such that the contact angle at the three-phase contact line was a constant. At each pressure, receding contact angles were measured once on each surface. The use of water evaporation to accurately determine receding contact angles is intuitive. On a water drop pinned on a surface, water evaporates from the drop, thus shrinking the drop until the three-phase contact line has a contact angle equivalent to the receding contact angle of the system as shown in Figure 4.3. Afterwards, the water drop will evaporate while maintaining the receding contact angle at the three-phase contact line. Confirmation of this method in measuring receding contact angles is also shown in comparing data in Table 4.1 and Figure 4.8.
Figure 4.3. Evaporation of a water drop from a static contact angle $\theta$ to the receding contact angle $\theta_R$. This method allows for the measurement of the receding contact angle of a water drop without physically removing water from the drop.

Figure 4.4. Measuring receding contact angles at reduced pressures. The water drop was placed on the wafer at atmospheric pressures. After the desired pressure was reached, the water drop is moved to another position on the wafer and the water allowed to evaporate.
4.2.4. Measurement of Advancing Contact Angles at Reduced Pressures

A hydrophilic linear defect 2 mm long and 1 mm in width was intentionally scratched into the modified silicon wafer and a drop of water ~3 mm in diameter was placed on the hydrophilic defect. The silicon wafer was mounted on a glass rod at 90° vertically and placed in the viewing chamber of the glassware as shown in Figure 4.5 and by Kalinin and coworkers\textsuperscript{15}. Reduction in pressure was performed by controlling air inlet and vacuum rate. Equilibrium reduced pressure was reached in several minutes. After equilibrium reduced pressure was reached, the entire assembly was carefully rotated 180° to deposit the advancing side of the water drop to a new position on the wafer at the reduced pressure (Figure 4.5, 4.6 B-C) while making sure it was still pinned at the same point. Immediately after rotation, the advancing contact angle of the drop was measured at the lower side of the water drop. At each pressure, advancing contact angles were measured once on each surface.

In the measurement of the advancing and receding contact angles, air bubbles were observed to appear between the water drop and samples with rods and square holes while the pressure was being reduced. Once the drop was moved to a new location either by rotation of the sample as in the measurement of advancing angles, or by simply tapping the drop to a new location on a horizontal wafer for the measurement of the receding angle, there were no longer air bubbles under the drop.
Figure 4.5. Experimental setup for measuring contact angles of surfaces at reduced pressures. Maintenance of constant reduced pressure in the chamber was performed by leaking air in while keeping the valve to the vacuum open.

Figure 4.6. Measuring advancing contact angles at reduced pressures. (A) At atmospheric conditions, the water drop is placed on the defect and angled at 90° to horizontal (B). The water drop remains pinned at the defect on the top end of the drop. (C) After the desired reduced pressure is reached, the sample is rotated 180°, thereby depositing the drop onto a new position on the wafer at reduced pressures. Initially, the water drop will be at the advancing contact angle at the bottom side of the drop. The hydrophilic linear defect is marked by ■, as it is in Figure 4.5. This method allows for the measurement of the advancing angle of a water drop without physically adding water to the drop. The rotation of the sample is to eliminate air bubbles within the liquid-solid interface during pressure reduction and simulate the deposition of a water drop onto a surface at the reduced pressure.
This method for the determination of the advancing contact angle of a surface at reduced pressures is accurate due to an understanding of water drop fluidics. Water drops are capable of moving when the forward end of the drop reaches the advancing angle and the back end of the drop reaches the receding contact angle as described in Chapter 1. Due to the hydrophilic line scratched into the surface, the drop was unable to slide down the sample due to the inability of the back end of the drop to reach the 0° receding contact angle of a water drop on a native oxide layer of silicon. Therefore, upon initial tilting of the surface to 90° to the horizontal plane, the water drop, with its back end on the hydrophilic line, advanced its forward contact angle immediately to a value equal to the advancing contact angle of the surface as shown in Figure 4.7. The preciseness of this method was affirmed by comparing the advancing contact angles of all three surfaces measured by a goniometer and by the method described, both at atmospheric conditions.

Figure 4.7. Schematic of surface tensions on a water drop pinned on a hydrophilic line at 90° to the horizontal.
4.2.5 Utilizing Laplace Pressure to Change Contact Angle Hysteresis

To demonstrate the influence of Laplace pressure on wettability, a drop deposited at 60 torr on both of the rough surfaces was quickly returned to atmospheric pressure of 760 torr, placing a pressure of 700 torr on the water drop and forcing water from the water drop into the square holes or in between the square posts within the solid-liquid interface. Advancing contact angles, receding contact angles, and contact angle hysteresis were then measured again using a goniometer for water drops trapped in this state.

4.3. Wettability of Rough Surfaces at Reduced Pressures

The measurement of contact angles following removal of air shows that dynamic contact angles are independent of air pressure: Cassie wetting behavior characterized by high advancing contact angle and low hysteresis is not a result of the water drop rolling over pockets of air. While there are pockets of air trapped at the solid-liquid interface, they play no role in producing Cassie wetting behavior. It can be seen in Figure 4.8 that the advancing and receding contact angles for the smooth surface, the surface with rods, and surface with square holes do not change with a decrease in pressure. Moreover, there is no change in hysteresis with decreasing pressure as would be expected if this were the case, as is shown in Figure 4.9. If water drop movement over a rough surface was dependent on the presence of entrapped air as many authors have stated, a decrease in the pressure of the air to less than 8% of the original pressure would have resulted in a decrease in the receding contact angle and an increase in hysteresis as the reduction in air
pressure/density allowed water to intrude further into the topographical features and more fully interact with the surface. The water drop would not have rolled off the surface with small tilt angle at reduced pressures as it does at ambient pressures. By the sucking disc theory, the water should have been able to easily displace the remaining air and increase its interaction with the rough features. The fact that water drop movement is independent of pressure indicates that Laplace pressure is responsible for superhydrophobic behavior, by preventing water from entering into the rough hydrophobic features and displacing these pockets of air. Roughening a surface merely produces a surface covered with features on which water cannot enter due to thermodynamic reasons.

The data shown in Figures 4.9 and 4.10 show a variation in the advancing and receding contact angles, but this can be attributed to natural contact angle variations on a surface. The method for measuring the advancing contact angle of a surface by pinning the back end of a water drop and tilting the surface such that the front end of the water drop is at the advancing angle was difficult to carry out reproducibly compared to using the goniometer. Gao and McCarthy, among others, have maintained that advancing and receding contact angles are the only reproducible manner of measuring the wettability of a surface. At both the advancing and receding contact angles, the contact line of the drop is in a metastable state. Any minor perturbation of the drop would disturb the delicate contact line of those two forms, causing a contact angle change to a random static contact angle between the advancing and receding angles. Causing the bottom portion of the contact line of the drop (Figure 4.6C) to advance to the metastable state of the advancing angle required rotating the drop from the horizontal position to the 90° tilt
in such a manner as to not perturb the drop from that state. Any extraneous movement immediately caused the advancing contact line of the drop to slip down the sample, decreasing the “advancing contact angle” which was what made the reproducibility of this method more difficult. However, with the recognition that contact angles can vary across any sample, it was impossible to differentiate between natural variations and disturbances of the advancing contact line. Therefore, all advancing contact angle values were reported as measured. Nonetheless, as shown in Table 4.1, when performed correctly, the advancing contact angle could be accurately measured to match the value obtained on the goniometer, which was the case for the posts surface. This does not occur 100% of the time (Table 4.1, flat surface and surface with square holes) which was what led us to describe this method as measuring the pseudo-advancing angle. For receding contact angles, the excellent reproducibility and accuracy of the evaporating drop method is shown in Table 4.1. It demonstrated that the values obtained for the receding contact angle by water drop evaporation were extremely close to traditional measurements on the goniometer and could be considered accurate, indicating the usefulness of such a technique when traditional methods for measuring receding contact angles are difficult or impossible given the experimental setup.

Dynamic contact angles can vary across surfaces with the same chemistry and topography. With the recognition that the technique for measuring advancing angle is only precise a percentage of the time, variations in the advancing contact angle and therefore the contact angle hysteresis may also be due to human error during the gathering of advancing contact angle data. While this affects to some degree the
quantitative credibility of the advancing angle and contact angle hysteresis data, receding contact angle data is unaffected. The lack of change in the receding contact angles of all three sample across the spectrum of pressures demonstrates the irrelevance of air pockets and entrapped gases in Cassie wetting behavior. The fact that water drops rolled off the two rough surfaces at low tilt angles at both 760 torr and 60 torr rather than requiring a much larger tilt angle at 60 torr, is a qualitative measure of the lack of change of the contact angle hysteresis at reduced pressures and reinforces the understanding that “pockets of air” are simply bystanders in superhydrophobic wetting behavior. With this observation, the hysteresis data in Figure 4.9 and advancing angle data in Figure 4.8 are fully qualitatively and pseudo-quantitatively correct as a whole as they described no relationship between hysteresis/advancing angle and pressure.

Table 4.1. Advancing and receding contact angles measured on a goniometer and using the methods described in this paper, both at atmospheric pressure. The value listed first is data gathered using the goniometer (θ_A^G, θ_R^G, (θ_A-θ_R)^G), and the second value is the data gathered using the methods described in this paper (θ_A^*, θ_R^*, (θ_A-θ_R)^*). Both sets of contact angle data were measured once at on each surface and reported as measured. See Appendix A for further explanation.

<table>
<thead>
<tr>
<th></th>
<th>θ_A^G/θ_A^*</th>
<th>θ_R^G/θ_R^*</th>
<th>(θ_A-θ_R)^G / (θ_A-θ_R)^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat</td>
<td>103°/98°</td>
<td>93°/92°</td>
<td>10/6</td>
</tr>
<tr>
<td>Holes</td>
<td>152°/145°</td>
<td>137°/136°</td>
<td>15/9</td>
</tr>
<tr>
<td>Posts</td>
<td>165°/165°</td>
<td>132°/134°</td>
<td>33/31</td>
</tr>
</tbody>
</table>
Figure 4.8. Advancing and receding contact angles for surfaces with no topography (smooth silicon wafer), square holes, and square posts with decreasing pressure. The reduction of air pressure and removal of air did not affect dynamic contact angle measurements the way it would have had air pockets played a key role in promoting superhydrophobic behavior in rough surfaces.
Figure 4.9. Contact angle hysteresis with reduced pressure. While there was clear variation in the hysteresis over the range of pressures, the variation was random, as can be expected with dynamic contact angle measurements. Removal of air in the system did not result in increased liquid-solid interaction.
The mathematical description of Laplace pressure is the same as capillary pressure. The only difference is whether cosine $\theta$ is positive or negative. Capillary force, for which the general equation is shown as Equation 4.1, is a negative value when the advancing contact angle of the wetting fluid with the surface is less than 90º. This indicates that it is energetically favorable for water to enter into narrow regions of space with zero difference between the air pressure inside the space and atmospheric conditions. For a capillary with inner surface advancing contact angle $< 90^\circ$, water will spontaneously wet the walls of the tube and enter the capillary. Capillary force is due to the curvature of the liquid meniscus. Because the meniscus is concave from the contact angle of the fluid with the walls, the surface curvature for the liquid is negative and the pressure in the liquid immediately below the interface is less than the air pressure outside by the amount:

$$\Delta P = -2\gamma \cos \theta / r \quad \text{(Equation 4.4)}$$

To prevent water from entering a capillary with one end closed, a larger pressure inside a capillary compared to outside would be needed, with the difference in pressures equivalent to or larger than the collective pressure from the capillary pressure of the tube and the pressure from the mass of water due to force of gravity weighing on the capillary. For the size of drops used in wettability measurements which are on the millimetric scale, the consideration of the pressure due to the mass of water is minute compared to capillary pressure. Equation 4.4 applies to a cylinder using Equation 4.1 as the general equation. The liquid rises until the pressure at the base of the liquid from the column of water above it equals that of the air outside. Equation 4.1 and 4.4 can also be used to calculate
the hydrostatic pressure of a water drop, in which the internal pressure of a water drop is larger than the atmospheric pressure. ΔP is the pressure difference between atmospheric pressure and the internal pressure of the water drop. For this case, $\theta = 180^\circ$ for a water drop contact angle with air. For advancing contact angles $>90^\circ$, Equation 4.4 switches to positive values, indicating the need to apply pressure to force the liquid into the tube.

$\Delta P$ is now described as the Laplace pressure. For these cases, the surface curvature of the liquid is positive and the pressure in the liquid immediately below the air-liquid interface is greater than the air pressure, similar to the case with water drops. While the curvature of the water would cause the meniscus of the water to bulge into the space, water would not wet the tube like it would in the case of capillary pressure. Water would not intrude into a space where the walls surrounding that space had an advancing angle $>90^\circ$. For water to intrude into a tube with walls with advancing angle $>90^\circ$ that was closed on the opposite end, a pressure differential, greater than the Laplace pressure of the tube, between the tube and outside the tube, with the pressure greater outside the tube than inside the tube, would be required to force the water to enter the hydrophobic tube. It would be impossible for water to intrude into a tube when the advancing angle is greater than 90° at equivalent pressures (inside the tube and atmospheric conditions). The same can be said with a roughened surface, chemically modified with hydrophobic chemical groups. Cassie wetting behavior occurs when the surface features have a length scale small enough such that the Laplace pressure becomes large enough to prevent the intrusion of water from the gravitation forces acting on the water drop. It is also necessary that these surface features be tall enough to prevent the meniscus of the water...
from wetting the bottom of the features. Figure 4.10 (left and center) shows a deep feature and a shallow feature, both with walls with contact angle $> 90^\circ$. The contact angle of the water with the hydrophobic walls causes the water meniscus to point towards the bottom of the feature. In the case of the deeper feature, the water meniscus is unable to wet the bottom while it is able to in the shallow feature, leading to Wenzel wetting behavior.

Figure 4.10. (left and center) For $P_1 = P_0$, intrusion of water into hydrophobic features due to the shape of the water meniscus despite Laplace pressure. The contact angle at the pore walls is greater than $90^\circ$, leading to water within the pore, but without water advancing into the pore at the water-solid interface. In the case of capillary force, the meniscus would be pointing in the opposite direction, away from the bottom of the pore since the contact angle is less than $90^\circ$. However, capillary action would allow for water to slide down the walls and wet the walls of the pore. (right) Exceeding the Laplace pressure of the hydrophobic feature would cause water to intrude into the feature until the air pressure under the water meniscus were the same as the ambient pressure.
4.4. Effect of Laplace Pressure on Wettability

Based on equations 4.1 - 4.3, it can be calculated that as long as the surface is rough and modified with chemical groups that would provide a smooth surface with an water advancing contact angle greater than 90°, and the surface features are deep enough as to prevent the water meniscus from wetting the bottom of the features, the surface will exhibit Cassie wetting behavior as long as the pressures of the air pockets and the air above the water drop are the same. Figure 4.10 (left) shows the expected profile of a water drop resting on top of, but not advancing into a surface feature due to Laplace pressure.

It has been argued that the air within the surface topography and the rest of the air is different while at the same pressure, that as the water drop attempted to remove itself from the tops of these pockets of air within the polymer nanotubes, the volume of the air pocket would have to expand unfavorably and this expansion would cause adhesion of the water drop to the surface. The claim that air within polystyrene nanotubes and outside the tubes are different while being at the same pressure is ridiculous. For this effect to take place, the water meniscus would have to invert itself and point away from the substrate (like the meniscus of water for $\theta_A < 90^\circ$) as the water drop was detaching from the surface, in order to increase the volume of the air pocket and create a region under the drop with an air pressure less than ambient conditions. Polystyrene has a contact angle greater than 90° which would make the inversion of the meniscus impossible.
As described in Section 4.2.5, water was forced into more contact with the surface topography. This experiment is described in Figure 4.10 (left and right). Starting from Figure 4.10(left), $P_0$ and $P_1$ were reduced to 60 torr. Then the vacuum was released, returning $P_0$ to atmospheric conditions with a pressure of 760 torr, thus putting an external pressure of 700 torr onto water drops on the surface with rods and with square holes by the procedure described in Section 4.2.5. With this external pressure greater than the Laplace pressure acting on the water drop on the rough surfaces, water was pushed into the surface topography until the pressure of the “entrapped gases” equilibrated with the atmospheric conditions. For water to remove itself from within the pocket, the air pressure in the pocket would have to decrease to account for the increase in air volume, which was not possible while the ambient pressure remained unchanged. Figure 4.11 demonstrates how the external pressure acting on a water drop affects dynamic contact angle measurements from that drop. Following application of the 700 torr of external pressure on the water drop, no noticeable change in the drop was observed. Advancing angles measured by a goniometer starting from the contact line in Figure 4.11B were unchanged as shown in Figure 4.11C and Table 4.3, as the advancing contact line proceeded over the rough surface without intruding into the surface topography due to the Laplace pressure of the surface features. Receding the contact line from the Figure 4.11C to B, the receding contact angles also remained unchanged as was expected. The surfaces over which the water contact line was advancing and receding going from Figure 4.11 B to C and back to B were identical to those measured at normal conditions. However further removal of water (4.12 B to D) demonstrated how the 700
torr of pressure acting on the water drop over the original liquid-solid interface caused receding angles to drop to zero in both rough surfaces and form a film of water over the original liquid-solid interfacial area of the water drops shown in Figure 4.11A and B, as the contact lines of the drops were not allowed to recede due to being pinned down into the surface features by the external pressure. This demonstrated the true effect of increased interaction between water and the surface topography and the existence of the Laplace pressure for small spaces with walls with $\theta_A > 90^\circ$. From the film of water in Figure 4.11D, water could be added to reproduce the water drops in Figures 4.12 B and C.

While the following experiment was not carried out, based on the understanding of Laplace pressure, the reduction of pressure back down to 60 torr on the entrapped water film from Figure 4.11D would cause the water originally forced into the square holes and in between the square posts, to be forced back out and eventually coalesce as a small water drop or several water drops with a volume or collective volume equal to the water originally trapped in the surface topography. The entrapped air pockets at 760 torr beneath the entrapped water would be able to expand in volume until its pressure was 60 torr, pushing water back to the surface. Once out of the square pores or out from between the square posts, the water would not remain a film: instead the water would coalesce into a drop or drops reflecting the chemistry and topography of the surface, with the static contact angles of the drops between the advancing and receding contact angles of the surfaces.
Table 4.2. Laplace Pressure for features of certain shape, size, and material contact angle.

<table>
<thead>
<tr>
<th>Feature Size and Shape</th>
<th>Contact Angle</th>
<th>Laplace Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square holes 70 x 70 micron</td>
<td>120º</td>
<td>15.4 torr</td>
</tr>
<tr>
<td>Square posts 25 x 25 microns</td>
<td>120º</td>
<td>14.4 torr</td>
</tr>
</tbody>
</table>

Table 4.3. Change in contact angle after exceeding the Laplace Pressure.

<table>
<thead>
<tr>
<th>Feature Size and Shape</th>
<th>Receding Contact Angle</th>
<th>Advancing Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square holes 70 x 70 micron</td>
<td>0º</td>
<td>153º</td>
</tr>
<tr>
<td>Square posts 25 x 25 microns</td>
<td>0º</td>
<td>165º</td>
</tr>
</tbody>
</table>
Figure 4.11. Exceeding the Laplace pressure. (A) Water drop on rough surface at low pressure (60 torr). (B) Laplace pressure of surface is exceeded by returning the air pressure above the water drop to atmospheric pressure creating a pressure differential of 700 torr between the air under the drop and the air above the drop. (C) Adding water to the drop causes the three-phase contact line to advance at the same advancing angle as at reduced pressures and at atmospheric pressure. (D) Evaporation of the water drop demonstrates that the receding contact angle in this situation is zero following overcoming the Laplace pressure of the surface. Water remains trapped in the surface features. All of these changes are reversible.
4.5. Conclusions

Entrapped air/pockets of air are not responsible for the low hysteresis behavior of Cassie wetting behavior and preventing the transition to Wenzel wetting behavior. Laplace pressure thermodynamically explains why water cannot enter narrow spaces where the walls themselves have advancing contact angles greater than 90º and rationalizes how contact angles are independent of air pressure. As the water rolls over the hydrophobic rough features on a Cassie surface, Laplace pressure prevents the water from fully interacting with the solid surface. In doing this, it allows the contact line of the moving water drop to utilize the water-air interface to reduce adhesion to the surface, therefore resulting in a low hysteresis surface. It is not to be said that air does not exist under the drop resting on a rough hydrophobic surface, merely that it does not play a role in preventing water from intruding into the surface rough features. Contact angles explain how water can still encounter the bottom of a rough feature to produce Wenzel wetting behavior while still obeying Laplace pressure. Exceeding the Laplace pressure can force water into hydrophobic features and cause the water drop to be completely pinned with a zero degree receding contact angle.
4.6. References


CHAPTER 5

WETTABILTY IS ONE-DIMENSIONAL: CONTACT LINE PINNING AND WATER DROP DEFORMATION

5.1. Introduction

The understanding that surface wettability is a one-dimensional phenomena dominated by events at the contact line leads to the understanding that hydrophilic patterns on a hydrophobic surface will be capable of pinning water drops if appropriately shaped, and that hydrophilic patterns on a hydrophobic surface should also be effective in deforming the three-phase contact line of water drops such that the solid-liquid interface of the water drop is non-circular. McCarthy and Gao are not the only researchers who have come to this realization. Bartell, Extrand, and Pease have published data establishing this fact.

A water drop forms due to the surface tension of the liquid. The water molecules at the air-water interface lack the ideal number of hydrogen bonds that water molecules within the drop have. The liquid surface can be thought of as a stretched membrane with the surface tension opposing its distortion. Due to the curvature of the interface, the internal pressure of the water drop is greater than ambient pressure. This hydrostatic pressure for a spherical water drop can be described by Equation 5.1. For a generalization to any surface, the increase in hydrostatic pressure $\Delta P$ across the air-liquid interface is equal to the product of the surface tension and curvature of the surface $C$ in Equation 5.3. $R_1$ and $R_2$ are the radii of curvature of the surface and can be positive or negative.
Capillary length is the characteristic length scale for a fluid subject to gravity. $g$ is the acceleration due to gravity, $\rho$ is the density of the fluid, and $\gamma$ is the surface tension of the fluid. Equation 5.4 describes capillary length and is the solution to the Young-Laplace equation shown in Equation 5.2 with gravity completely absent. When the largest dimension of the water drop is below the capillary length, the water drop will remain a section of a sphere. When it is larger than the capillary length, gravity distorts the drop, flattening it more of a puddle as the water volume increases. The capillary length of water is $\sim 2.7\text{mm}$.

$$\lambda_c = \sqrt{\frac{\gamma}{\rho g}}$$  \hspace{1cm} (Equation 5.4)

A useful experiment to demonstrate that wettability is dictated by contact lines would be the apparent wettability of Teflon. Using a flat circular surface that has a radius of 50 mm, let's produce three cases, each with 2% of the surface area hydrophilic with silica with receding contact angle 0° and the remaining 98% of the surface area hydrophobic with Teflon with advancing contact angle 120°. Case 1 has the solid hydrophilic circle in the center with a radius of 7.05 mm, with the remainder of the surface hydrophobic. Case 2 has the surface speckled with hydrophilic defects on the nanoscopic scale, with the remaining 98% of the surface hydrophobic. Case 3 has a 500
micron thick hydrophilic line running along the edge of the circular surface, with the remainder (interior) of the surface hydrophobic. Outside of the 100mm diameter circle is a perfectly hydrophobic surface with 180°/180° advancing and receding contact angles. In all three cases, we produce a puddle of water that covers the entire 100 mm diameter circular surface. If the assumption that wettability is a two-dimensional phenomenon is applied, then Cassie’s equation from Chapter 1 could be used to predict the contact angles of these large puddles. Case 1 and Case 2 and Case 3 using Cassie’s equation would all be predicted to have the contact angle of the 100 mm diameter puddle decrease by 2.0% from that of the pure Teflon surface due to the inclusion of 2.0% hydrophilic surface area within the solid-liquid interface of the water drop on the surface. If we assume that wettability is one-dimensional, that only the chemistry at the three-phase contact line defines the contact angle of the entire drop/puddle, Case 1 would have the same receding contact angle as Teflon, and Case 2 might exhibit a small decrease due to the small fraction of the hydrophilic defects which have fallen under the three-phase contact line. Removal of water from the puddle in Case 3 would produce a thin film of water with a contact angle of 10°, equivalent to the receding contact angle of the hydrophilic chemistry pinning the three-phase contact line. Any further removal of water to reduce the contact angle below 10° would cause the contact line to de-pin from the hydrophilic ring and the water film would pull itself in to form a thicker puddle with a smaller diameter, with a contact angle of 120°. All three cases would have a 180° advancing contact angle from the edge of the 100mm diameter circle. The distribution of the seemingly small amount of hydrophilic surface area on a hydrophobic surface as a thin
hydrophilic ring, the entirety of which is in contact with the three-phase contact line of the water drop/puddle, would drastically change the contact angle in a way which is impossible to predict using the assumption that wettability is two-dimensional but simple to predict knowing that wettability is one-dimensional. Using the hydrophilic ring, it would be possible to produce a thin film of water on the hydrophobic Teflon surface with a contact angle that is representative of the hydrophilic chemistry at the three-phase contact line and completely ignores the hydrophobic chemistry at the solid-liquid interface.
Figure 5.1. All 3 surfaces with diameter of 100 mm are 2% hydrophilic by surface area as marked by the black regions. (top left) Case 1 has a solid hydrophilic circle with a 7.05 mm radius. (top right) Case 2 has 200 hydrophilic 1mm diameter spots randomly scattered across the surface. (bottom) Case 3 has a 500 micron thick hydrophilic line running along the edge of the circular surface. With wettability being a one-dimensional phenomena, a puddle of water 100 mm in diameter will act differently on these three surfaces due to the distribution of the hydrophilic domains.

As described in Chapter 1, there have been a number of publications which emphasize that wettability is a one-dimensional phenomena. It is incorrect to analyze wettability from an interfacial area perspective, as was the case for Wenzel and Cassie. The objective of this research was to use the understanding that wettability is a one-dimensional phenomena to pin and deform water drops using hydrophilic contact lines on hydrophobic substrates. First, research was conducted to investigate how arcs, short wedges, and long wedges would be capable of pinning water drops. In order to perform
this research, a method was developed to produce hydrophilic patterns on a surface while preserving a low hysteresis hydrophobic surface functionality, such that in the absence of the hydrophilic pattern, the water drop would roll off the surface effortlessly at the tilt angle that measurements were performed at. The volume of water pinned by arcs, short wedges, and long wedges of different lengths and dimensions was measured and compared to the volume of water pinned by the outlines of those short and long wedges to reinforce the one-dimensionality of wettability. The deformation of water drops using hydrophilic contact lines on a hydrophobic surface was performed using perfluorinated surfaces patterned with hydrophilic patterns. Water drops were deformed using hydrophilic lines to form a variety of shapes with different curvatures to demonstrate the dominance of the hydrophilic lines on the shape of the water drop and absolute disregard of the liquid phase for the hydrophobic chemistry within the liquid-solid interface. In addition, it was shown that a perfluorinated surface could appear deceptively hydrophilic with a wetting film of water whose contact line was pinned on a thin hydrophilic line at the edge of the surface, an experiment that was described in greater detail earlier.

5.2. Experimental Section

5.2.1. Producing Hydrophilic Patterns on a Hydrophobic, Low Hysteresis Surface

Before spincoating the resist onto the surface, substrates were oxygen-plasma cleaned for 15 minutes. The photoresist was spuncoat onto silicon wafers for 60 seconds at 4000 rpm. Substrates were then heated at 115 °C for 60 seconds to remove the solvent. Exposure was performed using 365 nm UV light from a 500 W OAI UV lamp for 15
seconds. Exposed substrates were developed in MICROPOSIT MF-321 developer for 50 seconds to remove resist from the exposed regions and clean the silicon wafer. The substrates were then rinsed with deionized water for one minute, then oxygen-plasma treated for 5 minutes. The developed regions were then modified with tetramethyldicyclosiloxane (D₄H) at 80 °C for 3 days to produce the low hysteresis surface with contact angles 106°/104°. The mask was washed away with acetone, exposing the hydrophilic silica patterns and slightly changing the contact angles of the hydrophobic low hysteresis surface to 106°/102°.

Figure 5.2. Procedure for the formation of hydrophilic (silica) patterns on a low hysteresis hydrophobic surface.
5.2.2. Producing Hydrophilic Patterns on a Perfluorinated Surface

Before spincoating the negative photoresist, the substrates were oxygen-plasma cleaned for 15 minutes. The photoresist was spuncoat onto silicon wafers for 60 seconds at 4000 rpm. Substrates were then heated at 115 °C for 60 seconds to remove the solvent. Exposure to 365 nm UV light was performed using a 500 W OAI UV lamp for 15 seconds. Exposed substrates were developed in MICROPOSIT MF-321 developer for 50 seconds to remove resist from the exposed regions and clean the silicon wafer. The substrates were then rinsed with deionized water for one minute, then oxygen-plasma treated for 5 minutes. The developed regions were then modified with (tridecafluoro-1,1,2,2,tetrahydrooctyl)-dimethylchlorosilane in the vapor phase at 70 °C for 3 days, producing a surface with 114°/109° contact angles. The mask was washed away with acetone, exposing the hydrophilic silica patterns.
5.2.3. Water Drop Pinning

A comparison between the influence of surface areas compared to contact lines was carried out using the patterns shown in Figure 5.4. Using the procedure for producing hydrophilic patterns on a low hysteresis hydrophobic surface described in Figure 5.2, experiments were performed to determine the maximum volume of water that each of the individual features could pin at a 90° tilt angle. The patterns in Figure 5.4A compared pinning ability of hydrophilic arcs of different lengths with their solid hydrophilic counterparts in the form of short wedges and long wedges. The short wedges had the edges originating from the center of the circle while the long wedges had edges originating from the opposite side of the circle. Figure 5.4B consisted of the same arcs,
but now contained the outlines of the short wedges and long wedges. All arc lines were 500 microns in width. The arcs, short wedges, and long wedges were based on circles with diameters of 2 mm, 4 mm, and 6 mm. Their counterparts in Figure 5.4B were based on circles 4 mm and 6 mm in diameter.

![Diagram of patterns representing hydrophilic patterns on a low hysteresis hydrophobic surface. In the vertical direction, arcs have the same length and curvature as the upper edge of the short and long wedges below them, as is shown by the red line in Figure 5.5. Each of the arcs have two defects, the two ends of the lines, so in the comparison between the arcs and the outlines of the short wedges and long wedges, we sought to retain the defects by cutting off the outlines at the bottom and leaving them incomplete. 180, 120, 90, 60, and 30 represent the degree of the arc.]

**Figure 5.4.** Patterns representing the hydrophilic patterns on a low hysteresis hydrophobic surface. In the vertical direction, arcs have the same length and curvature as the upper edge of the short and long wedges below them, as is shown by the red line in Figure 5.5. Each of the arcs have two defects, the two ends of the lines, so in the comparison between the arcs and the outlines of the short wedges and long wedges, we sought to retain the defects by cutting off the outlines at the bottom and leaving them incomplete. 180, 120, 90, 60, and 30 represent the degree of the arc.

### 5.2.4. Water Drop Deformation on Hydrophobic Surfaces Through Contact Line Pinning

Pinning of water drops along contact lines that completely enclosed hydrophobic areas was performed on hydrophilic lines patterned onto a perfluorinated surfaces. Drops were deposited and elongated and pulled using a microscope slide until the entire contact line was in contact with the hydrophilic line.
5.3. Water Drop and Puddle Pinning using Hydrophilic Patterns

The key issue in this section was to demonstrate that hydrophilic lines could pin water drops on a low hysteresis surface. By the two-dimensional argument, as the surface area increased among the arcs, short wedges and long wedges (Figure 5.4), the volume of water which could be pinned on the patterns would increase with increasing surface area of the hydrophilic patterns. Under the premise that wettability is a one-dimensional issue, the amount of water which could be pinned on the arcs, short wedges, and long wedges would depend on the shape of the outline of the hydrophilic pattern.

The pinning of water drops on these hydrophilic patterns despite the low hysteresis surface could be understood using dynamic contact angle analysis. Following the deposition of the D₄H monolayer on the silicon wafer surface to produce a low hysteresis surface with 106°/104° advancing and receding contact angles, respectively, the rinsing of the surface with acetone to remove the organic resist mask caused the receding contact angle to decrease slightly to 102° leading to an increase of the hysteresis of the surface to 4°, which is still a relatively low contact angle hysteresis. The thickness of the D₄H monolayer was 1 nm by ellipsometry. Everywhere on the surface, water drops adopted a shape typical of hydrophobic surfaces and moved with ease due to the low hysteresis. However, when the back edge of the water drop came in contact with the hydrophilic patterns on the hydrophobic substrate as depicted in Figure 5.5, the receding contact angle of that water drop decreased to the receding contact angle of the hydrophilic pattern, which, being silica, was at or close to zero and potentially increased the contact angle hysteresis of that drop at that position on the substrate to 106°. This
result was predicted by Gao and McCarthy\textsuperscript{4} in 2006 when they discussed the potential use of hydrophilic spots on a hydrophobic surface to pin water drops and stop their movement across the hydrophobic surface. The basis of this phenomenon is that wettability is based on contact lines as the drops were not pinned until the back edge of the contact line of the water drop came in contact with the hydrophilic patterns.

Figure 5.5. (A) Hydrophilic patterns patterned on a low hysteresis hydrophobic surface. (B) Pinning of water drops on hydrophilic arcs, short wedges, and long wedges, based on the original circle with diameter of 2 mm, with the substrate held at 90° to the horizontal. The water drops vary in volume. The sole purpose of this diagram was to illustrate the pinning of water drops on arcs, short wedges and long wedges tilted at 90°. The 6 water drops pinned on the hydrophilic patterns on the left half of B show visible deformation of the top of the contact line due to the hydrophilic patterns.
Figures 5.6-5.8 show the maximum volume of water which can be pinned at 90°
tilt angles on the hydrophilic arcs, short wedges, and long wedges from original circles of
diameters 2 mm (Figure 5.6), 4 mm (Figure 5.7) and 6 mm (Figure 5.8). For patterns
based on a 2 mm diameter circle, with the exception of the features based on the arc
length 180° in Figure 5.6, the short wedges pinned the same volume of water as their
counterparts. All long wedges pinned larger volumes of water than their
counterparts. For the features based on 4 mm diameter circles, the long wedges
predominantly pinned more water than the corresponding short wedges and arcs. The
pinning of water on features based on the 6 mm diameter circle showed the definitive
trend that going from the arcs to short wedges to long wedges, larger volumes of water
could be pinned on the features with greater hydrophilic surface area.

While this data lends credibility to the Cassie and Wenzel theories that wettability
is related to surface area, Figures 5.9 and 5.10 clearly show that the incomplete outlines
of the short wedges and the long wedges were capable of pinning similar amounts of
water as their solid counterparts. The similarities are most noticeable by comparing
Figures 5.8 and 5.10. These features based on 6 mm circles showed the same increase in
the volume of water pinned on the arcs, short wedges, and long wedges. In fact, the
volumes of water pinned differed by no more than 1 microliter between the solid and
outlines of the solid features, with the outlines pinning the larger volume of water than
their solid counterparts. This did not mean that outlines of the wedges were better at
pinning water drops: it only meant that the silica was cleaner for the wedge outlines than
the silica in the solid wedges. This led to a smaller receding contact angle and larger
hysteresis, increasing the ability of the cleaner silica patterns to pin water drops with larger mass. The outline of the same hydrophilic patterns, with hydrophobic centers, pinned similar volumes of water as the solid hydrophilic patterns, since the chemistry at the solid-liquid interface clearly made no difference. Surface area was further shown to be irrelevant in Figure 5.11 where the surface area of the features was plotted against the maximum volume of water capable of being pinned on the hydrophilic patterns. The two points showing the pinning of 40 and 41 microliters of water had one feature which contains only 30% of the surface area of the other. The pinning of 47 microliters of water with the long wedge of surface area of 28 mm$^2$ appeared to be possible with an arc with the surface area of approximately 5 mm$^2$ by extrapolating from the data for the arc lines. Figure 5.12 clearly shows that with increasing length of the arc, larger volumes of water could be pinned.
Figure 5.6. 2 mm - Solid features. Volume of water pinned on hydrophilic arcs with line thickness 500 microns, short wedges, and long wedges, based on a circle 2 mm in diameter. In all cases, the long wedges were capable of pinning greater volumes of water than the short wedges and the arcs.

Figure 5.7. 4 mm - Solid features. Volume of water pinned on hydrophilic arcs with line thickness 500 microns, short wedges, and long wedges based on a circle 4 mm in diameter. The majority of these patterns also demonstrated a greater ability of long wedges to pin larger water drops than that of short wedges and arcs.
Figure 5.8.  6 mm - Solid features. Volume of water pinned on hydrophilic arcs with line thickness 500 microns, short wedges, and long wedges based on a circle 6 mm in diameter. The majority of these patterns demonstrated a greater ability of long wedges to pin larger water drops than that of short wedges, which was better than that of arcs.

Figure 5.9.  4 mm - Feature Outlines. Volume of water pinned on hydrophilic arcs with line thickness 500 microns, incomplete outlines of short wedges and long wedges based on a circle 4 mm in diameter. This figure can be compared to Figure 5.9 and the volumes of water pinned by corresponding wedges matches.
Figure 5.10. 6 mm - Feature outlines. Volume of water pinned on hydrophilic arcs with line thickness 500 microns, incomplete outlines of short wedges and long wedges based on a circle 6 mm in diameter. This figure can be compared to Figure 5.9 and the volumes of water pinned by corresponding wedges matches.
Figure 5.11. Relationship between the maximum volume of water pinned and the surface area of the hydrophilic pattern. This combines the data shown in Figure 5.8-10. There is no relationship between hydrophilic surface area and the volume of water pinned by the hydrophilic surface.
Figure 5.12. Relationship between the maximum volume of water pinned and the arc length of the hydrophilic arcs only. This combines the data for the arcs shown in Figure 5.8-10. There is a clear relationship between the arc length and the maximum volume of water that arc could pin, with increasing arc length leading to a linear increase in the volume of water pinned.
The increase in volume of water pinned by long wedges and short wedges than the corresponding arcs despite having the same arc length was due to the presence of defects in the hydrophilic arc patterns. The presence of defects at the two ends of the arc provided points at which the water drop would be capable of depinning from the hydrophilic pattern. In the case of the solid short wedges and long wedges, their lack of such defects along the edge of the pattern allowed them to pin larger volumes of water (Figure 5.13). The exact relationship between the arc length and the volume of water pinned is unclear, but the correlation is apparent. We believe that the volume of water pinned will not only depend on the length of the hydrophilic line but also on the angle of the arc pattern. Wettability is a one-dimensional phenomenon, not two-dimensional. Chemistry within the solid-liquid interface can be ignored, as they play no role in the wettability of a surface.

Figure 5.13. Pinning of water drops (blue) on hydrophilic arcs, short wedges, and long wedges on hydrophobic surfaces at 90° tilt angles. The arc lengths in the three features (shown in red) are the same at 90° while the hydrophilic surface area increases from arcs to short wedges to long wedges.
The analysis of the different pinning abilities of arcs and short wedges and long wedges must start from the distorted shape of the water drop just prior to depinning from the pattern. In Figure 5.5B, the single drop in the upper leftmost corner shows an example of the distorted shape. The top of that contact line of the drop is distorted such that it mimics the hydrophilic arc pattern (Figure 5.14, left). Upon further addition of water, the water drop distorts into the shape of the middle diagram in Figure 5.14 with a distortion marked “A” protruding from the main body (B) of the water drop. The contact line of the top of the water drop pinned by the arc is linked to B by the two red contact lines shown in Figure 5.14. As more water is added, the distortion of the contact line of part A of the water drop becomes more pronounced with the elongation and narrowing of the two “red” contact lines until the top portion of the water drop necks as displayed by the dotted line in Figure 5.14, left. Eventually, the water at the boundary between regions A and B of the pinned water drop necks completely and the majority of the water drop (B) breaks away leaving a small volume of water still pinned on the hydrophilic arc, short or long wedge. This mechanism of water drop depinning from the pinning patterns explains why solid and outlines of hydrophilic long wedges are capable of pinning larger volumes of water than short wedges (solid and outlines), which are better than arc lines. The angle $\phi$ of the two hydrophilic lines leading from the arc controls the rate of necking of the water in section A. The hydrophilic edge of the long wedge stabilizes and is better able to follow the “red” contact lines of the distortion in the water drop (A) pinned at 90° to the vertical. The edge of the long wedge links the pinning arc to the main body of the water drop and controls the necking of section A. With a larger $\phi$, the necking of the
water in section A is slower compared to a shape with a smaller $\varphi$ such as the short wedges. Eventually the mass of the main body of the water drop causes the water drop to neck between sections A and B and break into two drops. The short wedge, having a smaller $\varphi$ (Figure 5.15), is not designed as well to stabilize the “red” contact line of the distorted drop in the vertical direction. The necking and detachment of section A of the water drop occurs at a lower water drop mass due to the lower $\varphi$. The arc, having no hydrophilic contact line support for the “red” contact lines in the distortion of the water drop, has the lowest pinning ability. Between the pinning arc and the necking water drop, the lack of hydrophilic lines allows section A to neck naturally and without hinderance from hydrophilic contact lines leading from the corners of the arc. The detachment of the water drop from the hydrophilic pattern leads to the part B of the water drop rolling away from the hydrophilic pattern, and section A remaining pinned on the pattern. It was observed that the volume of water drop A on the short wedges, long wedges and arcs with the same arc length differed. It is possible that the differences between the volumes of water remaining pinned on the pattern will match the differences between the water drop volumes shown in Figures 5.6 - 5.10, such that subtracting the difference will cause the data to collapse and the volume of water pinned on patterns with the same arc length to even out. This assumes that section B of each water drop is dependent on the arc length of the pattern, that any additional water from the pattern being a short or long wedge will be in section A of the pinned water drop.
Figure 5.14. Depinning mechanism of a water drop from hydrophilic arcs, short wedges and long wedges. As the drop is pinned on the arcs or wedges and the mass of the drop increases from the original shape of a water drop pinned at 90° to the vertical (left), section A of the water drop begins to appear, with B being the main body of the water drop (middle). Eventually, section A necks completely leading to the depinning of section B from the hydrophilic pattern (right).

Figure 5.15. Parameters of the pattern based on a circle for pinning a water drop. The pinning ability of the hydrophilic pattern depends on the length of the arc as Figure 5.12 shows, and the angle $\phi$ of the two lines leading from the arc. Short wedges and their outlines have a smaller $\phi$ than long wedges and their outlines, while arcs lack the two lines.
5.4. Contact Line Deformation of Water Drops and Puddles

5.4.1. Simple Shapes

The understanding that the wettability of a surface is dominated by contact lines leads to the conclusion that hydrophilic lines, properly placed, can lead to deformed water drops and puddles. The McCarthy groups, among others, has mentioned that within the surface area of the solid-liquid interface, chemistry is unimportant and does not affect the overall drop shape. Thus within a circular solid-liquid interface, if 20% of the surface area was hydrophilic and the contact line was in contact with hydrophobic surface, the contact angle of the drop would remain unchanged. However, if that 20% hydrophilic surface area were distributed in the form of 4, 500 micron thick, 10 mm long, hydrophilic lines making up the four sides of a square that was 10 mm long on each side, with the interior still hydrophobic, the hydrophilic lines would be capable of distorting a puddle such that the three-phase contact line remained pinned on the 4 lines, causing the solid-liquid interface of the water puddle to distort into the shape of a square as can be seen with the largest square in Figure 5.16. A passerby could make the observation that it seemed the entire surface area under the square puddle was hydrophilic allowing it to distort as such when in reality, only 4 hydrophilic lines were required.

Figure 5.16 demonstrates the ability of hydrophilic lines to distort water drops and puddles into simple geometric figures with a variety of sizes on a Teflon-like surface, formed by the reaction of silica surfaces with (tridecafluoro-1,1,2,2,tetrahydrooctyl)-dimethylchlorosilane. All lines were 500 microns thick. The triangles and squares started with sides 2 mm long, and increased in increments of 2 mm to 10 mm long. The
pentagons and hexagons started with sides 1 mm long, with increments of 1 mm up to 5 mm long per side. For the hydrophilic surface area percentage of the entire solid-liquid interfacial area including the three-phase contact line, triangles ranged from 98% to 32% hydrophilic from the smallest triangle to the largest triangle, squares from 75% to 19%, pentagons from 93% to 27%, and hexagons from 82% to 22%. One can recognize that without these hydrophilic lines, the liquid-solid interface of a drop on this hydrophobic surface would remain a section of a sphere and the water drop would exhibit a hydrophobic contact angle. Again, however, the hydrophobic chemistry under the drop played no role in preventing the distortion of the water drop as the hydrophilic contact lines determined the shape of the three-phase contact line in contact with the hydrophilic lines and therefore the overall water puddle shape.
Figure 5.16. 500 micron wide hydrophilic lines forming simple geometric figures on a perfluorinated surface. Regardless of the size of the feature and the hydrophobicity of the surface, water drops/ puddles were still distorted by the hydrophilic lines. Triangles and squares range in size from 2mm sides to 1cm sides. Pentagons and hexagons range in size from 1mm sides to 5mm sides. The triangles and square, able to distort the water drop/ puddles to match their shapes, were unable to form sharp corners at the three-phase contact line. Pentagons and hexagons were better at deformation of the water drop/ puddle including the formation of sharp corners. This is an issue of curvature, such that as the shape approaches that of a circle with increasing number of sides, the water drop/ puddle is better able to conform completely with the hydrophilic lines.

The understanding that wettability is a one-dimensional phenomenon also allowed us to produce elongated water puddles on the perfluorinated surface described earlier, due to the hydrophilic contact lines patterned onto the hydrophobic surface. 60 mm long puddles could be confined to spaces with widths as small as 2 mm (Figure 5.17 left). With increasing width of the puddle, the water contact line was more capable of adopting the shape of the square and half circle ends of the pattern (Figure 5.18). This is likely due
to the larger hydrostatic pressure within narrower puddles, making it more difficult for
the hydrophilic contact lines to deform the water puddle and cause the water contact line
to completely conform with the hydrophilic pattern, corners and all. The left side of
Figure 5.19 shows contact line-stabilized elongated water puddles 60 mm long, 4 mm
wide. Regardless of the line thickness ranging from 100 microns to 500 microns, the
elongation of water puddles to form those shown in Figure 5.19 (left) was possible.

The right side of Figure 5.19 shows two arcs, 40 mm wide, and 40 and 60 mm tall
for the smaller and larger arc, respectively. Again, because hydrophilic contact lines
dictate the shape of a puddle regardless of the chemistry of the solid-liquid interface,
water puddles could be elongated and bent to follow the hydrophilic contact lines and
form stable arch-shaped water puddles. The arch-shaped puddles had both convex and
concave edges. Figure 5.20 and 5.21 shows a series of concentric rings and concentric
half rings, respectively, with a 45 mm radius at the largest, with the contact lines of the
distorted water puddles pinned using 500 micron thick hydrophilic lines. Again the
surface was hydrophobic due to the perfluorinated silane monolayer, except for the lines
which were hydrophilic silica. The hydrophilic contact lines allowed for the formation of
these donut-shaped water puddles with widths of 4 mm. All of these patterns distorted
puddles into unorthodox shapes. Due to the curvature of a water puddles, there exists a
hydrostatic pressure of that water puddle which is a function of the curvature of the
puddle. Within each of the distorted puddles, the hydrostatic pressure must be the same,
leading to the conclusion that the curvature of the water puddles must also be the same
everywhere.
Figure 5.17. Patterns 2 mm, 3 mm, 5 mm, and 7 mm wide with lines 500 microns thick. The top end of the patterns (②) were made hydrophilic with 10 wt% NaOH solution to bridge the two parallel lines with a hydrophilic feature. A drop of water was added at point ①, and water was added between the lines while the growing water puddle was pulled with a microscope slide to the region made hydrophilic by the NaOH solution, forming the stable elongated water puddles shown in the bottom half.
Figure 5.18. The rectangular and half circle ends of the elongated water puddles shown in the bottom half of Figure 5.19. (A) 2 mm, (B) 3 mm, (C) 5 mm, (D) 7 mm. The two narrower water puddles showed pinning by the hydrophilic contact lines, but the edges of the water puddle were not as sharp or well-defined as the 2 wider water puddles. This is likely due to the larger hydrostatic pressure of the narrower water puddles, while the wider puddles with lower hydrostatic pressure are more capable of adhering to the entire contact line.
Figure 5.19. (left) 60 mm long puddles, 4 mm wide, with line thickness 500 microns, 250 microns, and 100 microns. The arcs in the interior of the pattern could be used to form puddles that are not as elongated as the ones shown, and do not affect the ability to produce the contact line stabilized elongated puddles. (right) Arcs 40 mm wide from edge to edge and 40 and 60 mm tall for the smaller and larger arc respectively. The half circles at the base of each arc are 4 mm wide, with lines 500 microns thick. Due to the hydrophilic contact lines that formed complete shapes, such elongated and curved water puddles could be formed. On the left, the arcs within the pattern were used for the formation of shorter elongated puddles and did not aid in the formation and stabilization of the long elongated puddles shown.
Figure 5.20. Concentric circles with hydrophilic line thickness 500 microns and diameters ranging from 6 mm (including the line) to 90 mm (including the line). The rest of the surface is perfluorinated. These ring-shaped water puddles were 4 mm wide.
Figure 5.21. (top) Concentric half rings of water 4 mm wide using the pattern in Figure 5.20. (bottom) Colored water was used to make the half ring-shaped water puddles.
Finally, we carried out the experiment described in the introduction of this chapter, only with a 90 mm diameter water puddle. A 0.5 mm thick circular hydrophilic silica line was produced on the edge of the 90 mm diameter surface and the inner circle with diameter of 89 mm was made hydrophobic using the procedure described in Figure 5.4. A puddle of water 90 mm in diameter was formed such that the entire contact line of the puddle was in contact with the thin hydrophilic ring (Figure 5.22 top). The maximum mass of water which could be held within the 90 mm hydrophilic ring was 28.9g. The minimum was 4.1g through water evaporation. The film of water shown in Figure 5.22 (bottom) had a contact angle of 8°. To estimate the thickness of that thin film of water stabilized by the hydrophilic contact line on the hydrophobic surface, it was assumed that the water film was a thin cylindrical disc with mass 4.1g and diameter 90 mm, From this, it was calculated that the approximate thickness of the water film was 644 microns, possible on a circular surface that was 98% perfluorinated and only 2.2% hydrophilic by surface area because the 2.2% hydrophilic portion of the surface was patterned on the exterior of the 90 mm diameter pattern as a hydrophilic ring to stabilize the contact line of the 90 mm diameter water puddle. Of course, using the results shown in Figure 5.19, we can change the line thickness of this circle to 100 microns, making the entire pattern only 0.4% hydrophilic by surface area, and expect the same result.
Figure 5.22. (top) 90 mm diameter water puddle on a surface that has an 89 mm diameter hydrophobic circle, encircled by a 500 micron thick hydrophilic ring. (bottom) Following removal of the majority of the water with a pipette, evaporation of the same water puddle was used to form a thin film of water, the contact line of which is stabilized by the hydrophilic ring. The two figures appear to be to be two different surfaces due to the nature of the water puddle. The top water puddle is typical of a hydrophobic surface with the >2.5 mm thick water puddle, while the bottom deceptively appears to be a water film wetting a hydrophilic wafer. For such a water puddle, the advancing angle would be that of the perfluorinated chemistry at 114, and the receding would be that of a silica surface, which was measured to be 8° on this sample, due to the contact line resting on the patterned hydrophilic ring.
5.4.2. Complex-Shaped Water Puddles from Hydrophilic Contact Line Pinning

The understanding that contact lines determine the wettability of a surface and shape of the water puddle led to the formation of uniquely-shaped water puddles using uniquely patterned hydrophilic lines. Figures 5.23 and 5.24 show water puddles with varying height due to the shape of the liquid-solid interface which was due to the hydrophilic pinning lines at the three-phase contact line of the water puddle. In both cases, the water puddle had a higher height profile where the width of the water puddle was greater, and a lower height profile where the width (diameter) was smaller. This is due to the equilibration of hydrostatic pressure within the water puddle. With hydrostatic pressure inversely proportional to the diameter of a water drop, water within the curved interface with a smaller radius would have a larger pressure acting upon it than water within a curved interface with a larger radius. The pressure within a water drop is directly related to its curvature. By connecting a water drop with greater curvature (and greater hydrostatic pressure) to one with less curvature (and less hydrostatic pressure), the resulting water drop equilibrates to have the same curvature throughout its entire liquid-air interface and therefore the same hydrostatic pressure. The overall water puddle maintains equivalent hydrostatic pressure by pushing water from the narrower regions to the wider region(s) due to the initial differences in curvature and therefore, hydrostatic pressure, on the water at the two ends of the water puddle. This led to the uneven elongated water puddles as seen in Figures 5.23 and 5.24. Deliberate addition of water to the narrower regions (right side of Figure 5.23, middle of Figure 5.24) visibly led to the
transfer of liquid to the wider regions immediately, to the effect of watching water travel “uphill.”

Figure 5.23. Water puddle pinned on hydrophilic lines 500 microns wide, with a 4mm diameter half circle on one end and 8mm diameter half circle on the other. The uneven nature of the water is due to hydrostatic pressure being larger on the narrower end than on the wider end, leading to the transfer of water from one end to the other.

Figure 5.24. Water puddle pinned on hydrophilic lines 500 microns wide, with half circles 8mm in diameter on both ends, tapering to 4mm across in the middle. The hydrophilic contact line completely determines the shape of the water, and the uneven hydrostatic pressure within this water puddle leads to water being forced to the wider areas.
5.4.3. Hybrid Contact Lines

Looking at the elongated water puddles in Figure 5.19 (left), the question arose of what would happen if the straight hydrophilic contact line was broken up into shorter hydrophilic segments with hydrophobic spacings in between? The elongated water puddle relied on a complete hydrophilic contact line to pin the contact line of the water puddle and trap the puddle in the elongated shape. Would a hybrid contact line be capable of also stabilizing the contact line of the elongated water puddle? What role would hydrophobic spacing and length of the hydrophilic segments play in allowing for the formation of water puddles shown in Figure 5.19 (left). At what point would the hybrid contact line be unable to kinetically trap and stabilize the contact line of the water puddle?

Using the same experimental procedure to produce hydrophilic patterns on a perfluorinated surface, patterns were made with varying lengths of hydrophilic segments and perfluorinated hydrophobic spacings to provide a preliminary look at the use of hybrid contact lines to mimic a fully hydrophilic line. Figures 5.25 and 5.26 show two examples of patterns which were capable of pinning the contact line of a water puddle and trapping it in its elongated form. The images were shot after the water puddle had evaporated to more fully reveal the hydrophobic segments within the contact line. The defects in the contact line of these puddles from the hydrophobic regions within the contact line were always visible regardless of how much water was held within the pattern.
Figure 5.25. 4 mm wide water puddle pinned on the pattern shown with 4 mm long hydrophilic sections which are 500 microns thick, separated by 500 microns long hydrophobic section. The water puddle shown has been allowed to evaporate to make the hydrophobic sections along the contact line more evident. The hydrophobic sections cause the contact line to deviate from the otherwise straight contact line, but cannot do so completely due to the pinning of the rest of the contact line on the hydrophilic sections.

Figure 5.26. 4 mm wide water puddle pinned on the pattern shown with 500 micron long hydrophilic sections separated by 250 microns long hydrophobic section. The lines are 500 microns thick. The jagged contact line is due to the alternating hydrophobic and hydrophilic chemistry along the contact line. The hydrophobic chemistry works to prevent this straight contact line from occurring on the hydrophobic surface which is obvious where the contact line cuts into the puddle, but the hydrophilic chemistry prevents the depinning of the entire contact line and maintains the overall stability of the elongated water puddle.
Table 5.1. Hybrid contact line pinning ability of elongated water puddles.

<table>
<thead>
<tr>
<th>Line Length (mm)</th>
<th>Spacing (mm)</th>
<th>Puddle Elongation Possible (Yes/No)</th>
<th>Line Length (mm)</th>
<th>Spacing (mm)</th>
<th>Puddle Elongation Possible (Yes/No)</th>
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</thead>
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</tr>
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<tr>
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<tr>
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<tr>
<td>2</td>
<td>0.5</td>
<td>Yes</td>
<td>4</td>
<td>2</td>
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</tr>
</tbody>
</table>

Table 5.1 sheds some light on the stabilizing of the contact line of a water puddle on a hydrophobic surface with the hybrid patterns. The failure of puddle elongation and stabilization by the pattern of alternating hydrophilic/hydrophobic segments was indicated by the inability to form a stable elongated water puddle using the pattern. Placing a water puddle at one of the two ends of the pattern and pulling on the water puddle while adding water through a pipette led to the break-up of the water puddle. The water puddle would initially begin necking at the first hydrophobic section, then break into two drops/puddles, with a volume of water remaining pinned on the half-circle contact line, and the rest as a glob of water pinned to the hydrophilic microscope slide. With hydrophobic spacing greater than 1 mm, no length of hydrophilic segment was
capable of stabilizing the elongated water puddle contact line well enough to bridge the hydrophobic gap. For 1 mm hydrophobic spacings, stabilization of the contact line required the hydrophilic segments to be equal to or longer than 1 mm. When the hydrophilic segment length dropped to 0.5 mm, the water puddle depinned from the patterns. With hydrophobic spacings of 0.5 mm and 0.25 mm, hydrophilic segments 0.5 mm long were capable of stabilizing the water contact line well enough for the water contact line to bridge the gap and produce a stable elongated water puddle. The requirements for stabilization of water puddle contact lines using hybrid pinning lines from Table 1, using the combination of the hydrophilic silica and hydrophobic perfluorinated surface chemistry, is that the hydrophobic spaces cannot be greater than 1 mm long, and that the hydrophilic segments must be equal to or longer than the hydrophobic spaces. These initial scouting experiments demonstrated success in the use of discontinuous hydrophilic patterns for stabilizing the contact line of deformed water puddles. Whether the requirement that the hydrophilic segments be equal to or longer than the hydrophobic spaces, will apply with micron sized or nanosized features is unknown. These initial scouting experiments were performed with pairings of perfluorinated surfaces and silica surfaces. It is highly unlikely that pairings of surfaces with different chemistries will have the same requirements for hydrophilic line length and hydrophobic spacings for the stabilization of the contact lines of elongated water puddles. However, with regard to hybrid pinning lines, the patterns that produced the water drops/ puddles shown in 5.16-5.24, 5.27 can also be produced using the same hybrid pinning lines that were shown to work in Table 5.1. From that, we can expect the three-phase
contact lines of the water drops/ponds in Figure 5.16-5.24, 5.27 using hybrid pinning lines to have the same dimples as those in Figure 5.25 and 5.26.

Figure 5.27. PSE (Polymer Science and Engineering)-shaped water puddles. The dominating influence of the hydrophilic contact lines over the shape of the water puddle are such that such complex shapes such as these letters can be formed. The water puddles are 4 mm wide, with 500 micron thick hydrophilic pinning lines dictating the shape of the water puddles.

5.5. Conclusions

The pinning ability of hydrophilic patterns is independent of surface area and dependent on the length of the arc-shaped pinning contact line. While wedges are capable of pinning larger volumes of water than their corresponding arcs, it is due to the lack of defects at the edge of the wedges that allowed them to pin larger volumes of water before
they depinned. Solid hydrophilic wedges and hydrophilic outlines of the wedges were capable of pinning similar volumes of water. The deformation of water drops/puddles on hydrophobic surfaces as simple geometric figures, as elongated water puddles, as arch-shaped and donut-shaped water puddles was predictable through the understanding that wettability is a one-dimensional issue, therefore making water drops/puddles entirely influenced by events underneath the contact lines and not within the solid-liquid interface. Contact angles of water drops are entirely dependent on the chemistry at the contact line, such that a perfluorinated surface can appear to be hydrophilic using a hydrophilic contact line. The fact that water can wet a low energy surface such as a perfluorinated surface has implications for research where the wetting of a low energy surface with a fluid with higher surface energy is required. This research would suggest that a simple hydrophilic contact line surrounding the entire low energy surface would be sufficient to produce a thin film of the desired wetting fluid on the surface. For example, if the process described in section 5.2.2 was to be applied to a perfluorinated surface instead of a silica surface to produce a surface with perfluorinated lines on a surface functionalized with alkyl groups, a simple hydrophilic line patterned beforehand onto a perfluorinated surface could be used to pin a thin film of the S1813 positive photoresist across the low energy surface to allow for the formation of the resist layer on which UV lithography could be performed. This would avoid the use of a large puddle of the photoresist to wet the entire perfluorinated surface only to have most of it go to waste as it is spuncoat off the surface.
With the understanding that wettability is a one-dimensional issue, the deformation of water puddles into the shapes in Section 5.4 was predictable. The contact line of water drops can recognize molecular level roughness and chemistry, evident through contact angles and contact angle hysteresis. The question to ask here is what is the thickness of the water drop contact line? Is it 1 angstrom? 1 nm? 100 nm? Will a perfect 100 nm thick hydrophilic line be able to deform a water drop like a line 100 microns thick? For true one dimensionality of wettability, it should be possible to deform water drops using nanometer (or angstrom) thick hydrophilic lines on a hydrophobic surface. We view wettability as a one-dimensional phenomenon from the length scale of the size of the water drop used to measure contact angles and determine the wettability of a surface. But from the length scale of the diameter of a water molecule, a one-dimensional contact line would be a line that was one water molecule wide, which may or may not be capable of exerting its influence over a drop many orders of magnitude larger in diameter. From the viewpoint at those molecular length scales, the contact line of a water drop is a turbulent place, with water molecules entering and exiting the liquid phase from the vapor phase, and intra-molecular vibrations and inter-molecular interactions. The contact line is also not distinct at those length scales: between the completely liquid phase and the vapor phase, their would exist a layer in which the concentration of water was not quite vapor and not quite liquid either. The precise patterning of such patterns to determine contact line thickness would be difficult (and expensive) or even impossible by current technology to produce. With thinner and thinner lines, the issue would not only be with the formation of the patterns
but the effects of defects on the continuity of hydrophilic chemistry under the water drop contact line. These defects can result from the lithographic process and from thermodynamics. In our experimental procedure, we utilized the hydrophilicity of silica surfaces to deform water drops and puddles. However silica surfaces, having high surface energy, very quickly lose their hydrophilicity from the adsorption of compounds in the air to lower that high solid-air interfacial energy. Thinner hydrophilic silica patterns will have a higher likelihood that the adsorption of compounds to the surface produces a sizable hydrophobic interruption in the hydrophilic pattern large enough to disturb the stability of the contact line. Extending the lifetime of the hydrophilic patterns can always be accomplished by using different hydrophilic surface chemistry. In a perfect world, such an experiment to determine contact line thickness would involve the formation of hydrophilic patterns, which would not stop at 100 microns in thickness, but continue down to 1 nm or 1 angstrom in thickness or until the water drop could no longer be deformed into the shapes shown in this thesis.

The experiments using hydrophilic patterns with dimensions hundreds to thousands of microns in length and width demonstrated that discontinuous hydrophilic lines with hydrophobic spacers could still stabilize the contact line of a water puddle. This research can be extended into Cassie’s wettability theory of chemically heterogeneous surfaces. Cassie’s theory hinged on the assumption of wettability being a two-dimensional phenomenon. We now know that wettability is one-dimensional. Most experiments aimed at proving Cassie’s theory and checking its accuracy involved experiments on surfaces with either random or ordered patches of chemically
heterogeneous regions, with the size of patches being much smaller in dimension than that of the water drop. For the incorrect assumption that surface area could influence the contact angle of a water drop, such surfaces were ideal for testing Cassie’s wettability equation. For testing for the true influence of chemically heterogeneous regions on the wettability of a surface, what is needed is a surface for which the chemical composition directly under the contact line of a water drop can be accurately calculated. The random or ordered patterning of a surface with two-dimensional regions of chemically heterogeneous regions is not ideal for such measurements, as the contact line can easily deform itself from a circular shape and become more jagged as it latches onto the more hydrophilic regions during receding angle measurements and is hindered by the more hydrophobic regions during advancing angle measurements, making calculations of the chemical composition under the irregularly shaped contact line impossible. Moreover, we need to be able to measure advancing and receding contact angles for surfaces with both chemical functionalities A and B, for which the chemical composition under the contact line can vary from 100% A / 0% B to 0% A / 100% B. Circular patterns up to 5 mm in diameter should be produced. Within each of these circular patterns, radiating from the center, slices of the circle should be chemically patterned either A or B, with the arc angle of the slices varying to produce the desired range of chemical compositions under a circular contact line of a water drop placed in the center of the circular patterns. For a water drop millimeters in diameter placed in the center of the circular patterns, its contact line will be composed of alternating arc lengths of A and B chemistries, with the arc lengths varying to produce desired variations in the chemical composition under the
contact line of the water drop. The arc length of each of the slices is a function of the arc angle and the diameter of the water drop. In order to limit distortion of the contact line by hydrophilic regions during receding contact angle measurements and hydrophobic regions during advancing contact angle measurements, the arc angles of the slices must be small. That way, the contact line will “feel” the composite circular contact line chemistry and remain circular rather than the individual chemistries which will distort the contact line from a circular shape. The surface functional groups A and B should also vary away from very hydrophilic and very hydrophobic chemical pairs which is what the preliminary experiments in this chapter worked with. For example, the wedges can consist of silica and carboxylic acid terminated groups, alkyl and perfluorinated groups, perfluorinated and carboxylic acid terminated groups, ranging from 0% to 100% of both. Pairing of the surface functional groups should include alcohols, carboxylic acids, amines, esters, ethers, phenyls, alkyl, silicones, perfluorinated groups. Surface functional groups known for producing low hysteresis surfaces should also be included in the pairings to determine their impact on the advancing and receding contact angles.

The comparison of pinning ability of arcs versus short wedges versus long wedges indicated the importance of the two hydrophilic lines leading in the downward direction of the pinned water drop. While Figure 5.12 showed that increasing the arc length led to an increase in the maximum volume of water pinned, the data was inconclusive on how the arc angle influenced the pinning ability of an arc of a certain length, as patterns with the same arc length but smaller arc angle did not necessarily pin more or less water than one with a larger arc angle. Future research on water drop pinning should focus on how
the parameters determining the shape of the hydrophilic pinning pattern can affect the
volume of water pinned by patterns. Based on the parameters shown in Figure 5.15, the
“knobs to be turned” in this research would be the arc length, the arc angle $\theta$, and the
angle $\phi$.

The data gathered from the two previous proposed projects/future research and the
data presented in this chapter will aid in the patterning of surfaces for anisotropic wetting
behavior. A surface exhibiting anisotropic wetting behavior, for example, would be a
surface on which a water drop rolled with great ease in one direction but was pinned
going the opposite direction at the same direction. The surface would have to be
patterned in such a way that the receding contact angle of a water drop in one direction
was lower than for water drop receding contact angles in other directions. The results of
the experiments in drop pinning demonstrated that hydrophilic arcs were effective for
inhibiting drop movement. Arcs pointing in the opposite direction were not capable of
pinning water drops. By patterning sub-millimetric hydrophilic outlines of half-circles on
a perfluorinated surface, a surface with anisotropic wetting behavior should be produced.

The parameters for such a surface would have to be investigated. They would include the
diameter of the half-circles, their spacing, and how they were arranged across the surface.
They could be lined up across the surface in a line, with the ends of the arc patterns
touching each other, or separated by a distance. The lines made up of the half circle arcs
would also have to be separated from one another in the perpendicular direction by a
certain length or range of lengths. The half circle arcs could also be hexagonally
arranged on a surface with varying lattice spacing, or in a square arrangement. The
appropriate spacing of these patterns would benefit from the project proposed earlier by understanding how hydrophobic spacers between hydrophilic patterns can affect the stabilization of the contact line in such a way as to reduce the receding contact angle. The formation of surfaces with anisotropic wettability is not limited to patterning with half circle arcs. Experiments should be performed using patterns with different arc angles and arc lengths to investigate how the patterning and spacing of the hydrophilic arcs can affect wettability of a surface for drop movement in one direction versus another.
5.6. References


A.1. Chapter 4

The experimental section in Chapter 4 described a different method for measuring advancing and receding contact angles. This method was devised due to the experimental apparatus restriction that water could not be manually added or removed to measure the advancing and receding contact angles, respectively. For each measurement only one measurement was taken. The issue at hand was that over time, the wettability of the modified surfaces exposed to air changed. A previous attempt at measuring contact angles of rough surfaces at reduced pressures had involved modifying all three surfaces in the same glass vessel at the same time, then performing measurements on them one at a time. Initially contact angles for all three surfaces were measured on the goniometer following removal from the surface modification vessel. Following the measurement of contact angles of the smooth surface and the surface with posts at reduced pressures using the methods described in Chapter 4, one measurement per sample per contact angle per pressure, it was found using the contact angle goniometer that the surface with square holes, the last to be measured, had experienced a drop of \(-10^\circ\) in the advancing angle and \(-5^\circ\) in the receding contact angle from the time that the surface modification had been terminated and the samples removed from the glass vessel. While the reason for this is unknown, it is possible that contaminants in the air, particularly siloxane oligomers,
coated the surface thereby reducing the advancing and receding contact angles.

Siloxanes have been observed to readily wet perfluorinated surfaces.

Ordinarily, it would have been preferred if advancing and receding contact angles could be measured for each surface and each pressure three times, and the average of the three values used to plot the relationship between the wettability of a surface with topography and pressure. In the time that it took to perform one series of measurements on the first two surfaces (two in total), the data from the measurements on the third surface as the third series of measurements already exhibited the reduction in contact angles due to surface contamination. The reduction of advancing and receding contact angles of a surface simply by leaving it exposed to air would have corrupted my data and artificially implanted a reduction in advancing and receding contact angles if the experiment had proceeded in a fashion where multiple measurements are taken at each pressure starting from atmospheric pressure down to low pressures, since the measurements at low pressures would have shown lower contact angles not because of the reduced pressure but because of longer exposures to air. Given the influence of time on contact angles, it was decided each surface would be modified one at a time, and that only one measurement would be performed for each surface, for each advancing contact angle and receding contact angles at each pressure. If air truly was responsible for Cassie wetting behavior, then the data would reflect that relationship in the contact angle hysteresis calculated from these pairs of measurements. The data for the smooth surface, the Si wafer surface with square holes, and the Si wafer surface with square posts is listed in Tables A.1, A.2 and A.3, respectively.
Table A.1. Advancing and receding contact angles on a flat Si wafer modified with (tridecafluoro-1,1,2,2,tetrahydrooctyl)-dimethylchlorosilane from 760 torr to 60 torr.

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Table A.2. Advancing and receding contact angles on a Si wafer with square holes 70 microns on each side, modified with (tridecafluoro-1,1,2,2,tetrahydrooctyl)-dimethylchlorosilane from 760 torr to 60 torr.

<table>
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<tr>
<th>Pressure (torr)</th>
<th>$\theta_A$</th>
<th>$\theta_R$</th>
<th>Hysteresis ($\theta_A$-$\theta_R$)</th>
</tr>
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<tr>
<td>760</td>
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<td>138</td>
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<td>138</td>
<td>14</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>139</td>
<td>11</td>
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</table>
Table A.3. Advancing and receding contact angles on a Si wafer with square posts 25 microns on each side, modified with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-dimethylchlorosilane from 760 torr to 60 torr.

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>$\theta_A$</th>
<th>$\theta_R$</th>
<th>Hysteresis ($\theta_A$-$\theta_R$)</th>
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<tbody>
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<td>137</td>
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<td>60</td>
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<td>136</td>
<td>27</td>
</tr>
</tbody>
</table>

Allen, B. Dry water. Patent assigned to The United States of America as represented by the Secretary of the Army, US 4008170 (1977).


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