

**Study of Effects of Surface Wettability on Frosting and Droplet
Manipulation**

by

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To my mother, Enayat

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SUMMARY

Ice formation and build-up cannot be avoided when appropriate environmental conditions are met over prolonged periods. Many electrical/mechanical systems must operate in a relatively ice-free state in order to prevent performance degradation, or, worse, possible catastrophic failure. From 1998-2009, the Federal Aviation Administration (FAA) attributed 886 incidents to icing-related problems, resulting in 202 fatalities. During the same timeframe, the FAA spent nearly \$200 million in airport improvement programs addressing icing-related complications. Such a resource drain has incentivized the development of materials capable of retarding, or, if possible, entirely preventing ice formation and adhesion.

The impact and subsequent freezing of water droplets on solid surfaces is a common mechanism for surface icing and frosting. Despite work in this area, this mechanism has not been thoroughly investigated and thus lacks a thorough fundamental understanding. We aim to investigate this mechanism by decoupling it into two separate phenomena: 1) Impact of droplets on solid surfaces and 2) Freezing, and subsequent frosting, of surfaces under wet conditions. Our goal is to unravel the role that the underlying wettability plays for both of these phenomena. Previous works have reported on these phenomena in a conjoined manner. While what has been put out thus far is quite informative, the underlying physics in both of these phenomena is extensive. We disjoin the two phenomena in order to thoroughly investigate each mechanism.

In the first component, droplet impact on solid surfaces, we will study the impact outcome of water droplets on solid non-uniform wettability surfaces. The vast majority of reports thus

far have focused primarily on solid surfaces with uniform wettability. While in actuality, the vast majority of surfaces in nature possess some type of non-uniformity, whether it be chemical or physical. Impact on non-uniform wettability surfaces can yield interesting outcomes, such as splitting and increased contact time, that can vastly alter the subsequent freezing and frosting mechanisms. In the second part of the thesis, the effect of surface wettability on frosting of wet surfaces will be investigated. Most surfaces will initiate frosting under non-pristine mechanisms. In our case, the wet surface is a result of the impacted droplets. The aim is to understand what role the underlying wettability plays in the frosting of pre-wetted surfaces.

The research offers insight into physical mechanisms necessary to the understanding of the role of surface wettability. It addresses a fundamental problem in a new light that has not been previously conceived. The study was designed to take advantage of recent developments in the wettability engineering, droplet impact, and icing areas.

Nomenclature

Acronyms and Abbreviations

CA	Contact angle
CL	Contact line
CNF	Carbon nano-fiber
DC	Direct current
DWC	Dropwise condensation
FWC	Filmwise condensation
LIS	Lubricant impregnated surfaces
LV	Liquid vapour interface
MFA	Mirror-finish aluminum
PMC	Fluoroacrylic copolymer
POC	Point-of-Care
RH	Relative humidity
SHPO	Superhydrophobic
SL	Solid liquid interface
SLIP	Slippery lubricant impregnated porous
SPHIL	Superhydrophilic

SV Solid vapour interface

WCL Wettability contrast line

WPS Wettability-patterned surface

Dimensionless Groups

$Ca = \frac{\mu U_o}{\sigma}$ Capillary number

$Re = \frac{D_o U_o}{\nu}$ Reynolds number

$We = \frac{\rho D_o U_o^2}{\sigma}$ Weber Number

Greek Variables

α Inclination angle

α_c Critical sliding angle

γ Surface tension of liquid

ΔG_c Critical Gibbs energy change

η Spreading factor

θ_a Advancing angle

θ_c Critical impregnation angle

θ_E Equilibrium angle

θ_E^* Apparent equilibrium angle

θ_r Receding angle

θ_i	Surface i , with wettability θ
θ_a	Advancing angle
ρ_f	Density of fluid
ρ_{ice}	Density of ice
σ_{lv}	Interfacial surface energy of the liquid-vapor phase
τ_c	Contact time
τ_f	Freezing time of a droplet
ϕ	Azimuthal angle that circumnavigates the droplet contact line
ϕ_1	The value of ϕ at the contact line point separating the philic track from the phobic domain
ϕ_s	Solid fraction
ψ	Angle from front end of droplet

Variables

$\tilde{g}_v$	Gibbs energy change between the parent and new phase per unit volume
A	Contact area
A_{ls}	Liquid-solid contact area
A_t	Total surface area
c_f	Specific heat of fluid
c_{ice}	Specific heat of ice

C_n	Time of defrosting cycle
d	Pore spacing
D_o	Impacting droplet diameter
D_{Area}	Diameter of inner region
D_{Max}	Maximum spreading diameter
E_σ	Total free-surface energy
E_{bar}	Cross over energy
$E_{\text{wet-dry}}$	Energy due to the wetting of the solid surface
EK_1	Initial kinetic energy
ES_1	Initial surface energy
ES_2	Final surface energy
F_{a1}	Advancing force contribution by the philic track
F_{a2}	Advancing force contribution by the phobic track
F_a	Advancing force of a droplet
f_i	Solid area fraction
F_{r1}	Rear force contribution by the philic track
F_{r2}	Rear force contribution by the phobic track
F_R	Retentive force of a spherical droplet

F_r	Rear force of a droplet
g	Gravitational constant
$h_{\text{air-ice}}$	Heat transfer coefficient at the air/ice interface
h_p	Pore height
I	Current
J	Heterogeneous nucleation rate
J_o	Kinetic constant
k	Boltzmann's constant
k_f	Thermal conductivity of fluid
k_{ice}	Thermal conductivity of ice
L	Latent heat of fusion for water
m	Mass of water droplet
n	Number of annular regions
P	Power supplied
Q	Joule heat released by surface
$Q_{\text{continuous}}$	Total heat consumed during continuous heating
Q_{melt}	Heat necessary to melt a layer of frost
Q_{pulse}	Total heat consumed during pulsed heating

R	Radius of droplet
r	Droplet radius
R_e	Resistance
r_f	Roughness factor
R_t	Total thermal resistance
t	Time
T_a	Temperature of ambient
T_h	Temperature of heated surface
T_{ice}	Temperature of ice
T_k	Surface temperature in Kelvin
t_{total}	Total time of defrosting
U_o	Impacting droplet velocity
V	Dipping speed
w	Width of track
w_a	Work of adhesion
W_{losses}	Viscous losses
a	Width of pore
b	Thickness of pore
d	Frost thickness

CHAPTER 1

INTRODUCTION

1.1 Fundamentals of Wettability

Wettability(1) is an inherent property of a material based on its resulting interaction with a specific liquid. Consider a single droplet of a known liquid sitting on a solid-material. After enough time has passed, the droplet equilibrates and assumes a semi-hemispherical shape, Figure 1. Where the interface between the liquid and solid makes an angle θ_E , equilibrium angle. At the contact line, CL, the point of contact between the droplet, solid, and vapour, the droplet experiences three forces: one from the solid-vapour (SV) interface, one from the solid-liquid (SL) interface, and one from the liquid-vapour (LV) interface. Assuming the droplet is in equilibrium, the net force equation can be written as,

$$F_{SV} - F_{SL} = F_{LV} \cos \theta_E \quad (1.1)$$

Representing the force terms in terms of surface tension $\gamma \left[\frac{N}{m} \right]$

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_E \quad (1.2)$$

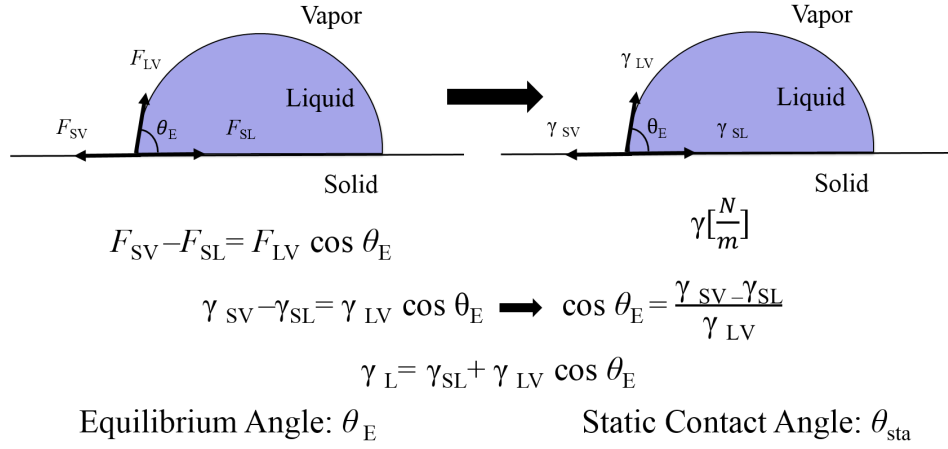


Figure 1. Fore diagram of a static droplet sitting on solid substrate while making an equilibrium angle, θ_E , with the surface. θ_E is oftentimes referred to as θ_{sta}

Rearranging Equation 1.2, we get

$$\cos \theta_E = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1.3)$$

Or what is commonly referred to as the Young's equation(2). Depending on the value of θ_E (sometimes referred to as the static angle, θ_{sta}) the material is commonly referred (Figure 2) to as one of four possible terms: 1) $\theta_E \approx 0^\circ$, superhydrophilic 2) $0^\circ < \theta_E < 90^\circ$, hydrophilic 3) $90^\circ < \theta_E < 150^\circ$, hydrophobic 4) $\theta_E > 150^\circ$, superhydrophobic. As can be deduced from Equation 1.3, when there exists a high energy solid-vapour and low energy liquid-vapour interfaces, materials will generally lie in the superhydrophilic domain(3; 4). While in contrast, for low solid-vapour

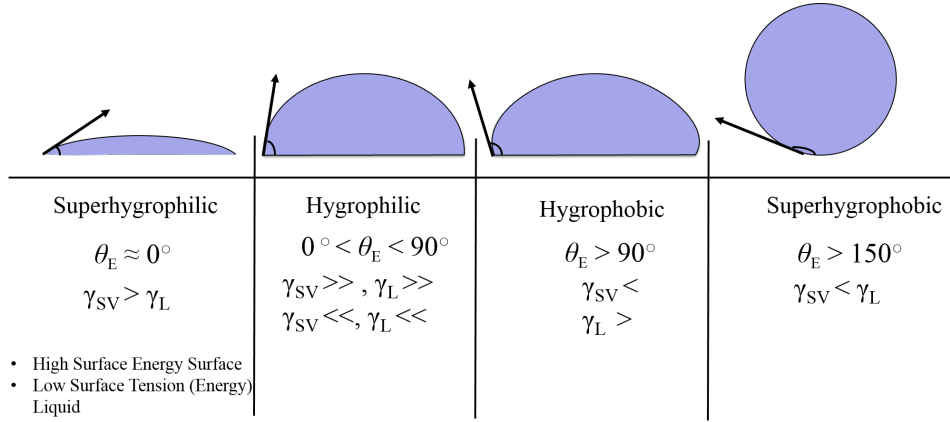


Figure 2. The generally defined regimes of wettability

and high surface energy, materials will lie in the superhydrophobic domain¹. The vast majority of naturally occurring surfaces will either demonstrate hydrophilic (e.g., glass, aluminum) or hydrophobic (e.g., teflon, PDMS) wetting characteristics. Rarely does there exist surfaces that are superhydrophobic/superhydrophilic in nature(5; 6; 7). The scarcity of these two types of materials is due to the need of the existence of an additional layer of complexity to the natural wettability, and that is texture on the microscopic length scale.

The role of the underlying texture of wettability lends itself to two prevailing theories: Wenzel(8) and Cassie-Baxter(9), Figure 3. In the Wenzel theory of wetting, a liquid droplet sitting on textured surface is believed to invade the texture of the surface. Assuming a droplet

¹From now on, we will explicitly refer to a material's interaction with water. All hygro terms will be substituted with hydro.

makes an angle θ_E on a smooth material, if that same material is allowed to be textured, than the new angle a droplet would make by sitting on that material would be

$$\cos \theta_E^* = r_f \cos \theta_E \quad (1.4)$$

Where r_f is the roughness factor, defined as the ratio between the real area, and the projected area of the sample. Note, θ_E^* is what is referred to as the apparent contact angle, the equilibrium angle on a textured material. As a result, and evident from Equation 1.4, if a material is originally hydrophilic and becomes textured, it becomes more hydrophilic. Conversely, if a material is originally hydrophobic and becomes textured, it becomes more hydrophobic. In the Cassie-Baxter theory of wetting, the droplet is believed to sit on top of the texture, rather than invading it. Thus the contact angle of the droplet is a result from the contribution of the material it is in contact with, and the air pockets filling the texture. Under such physical representation, the apparent contact angle is calculated as,

$$\cos \theta_E^* = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (1.5)$$

Where θ_1 is the contact angle of a droplet on the same type of material but smooth, θ_2 is the contact angle of the droplet on air (180°), f_1 and f_2 are the contact area fractions ($f_1 + f_2 = 1$) with the two materials. In addition to the varying static angles, there exists angles that represent dynamic motion of the droplet. Consider a droplet in equilibrium on a flat surface. If the surface is allowed to tilt, the droplet will begin to slide at a critical angle θ_s , known as the sliding angle,

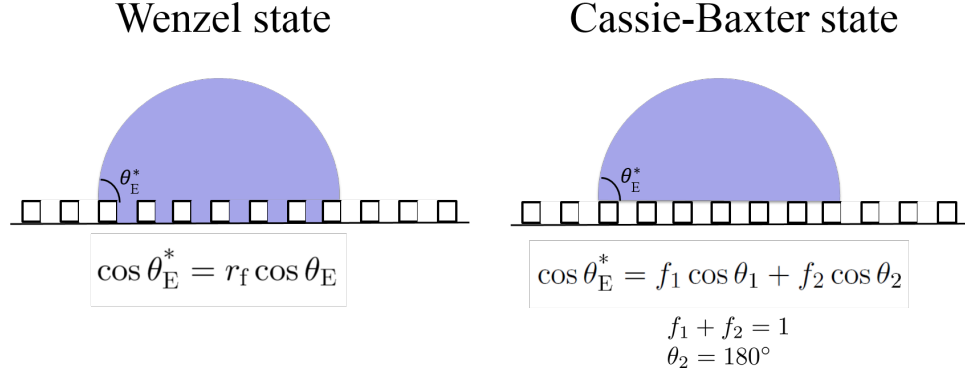


Figure 3. The two prevailing theories of wetting on a textured surface. In the Wenzel state the droplet impregnates the texture, while in the Cassie-Baxter state the droplet rests on top of the texture.

Figure 4. At that instant in time, the droplet begins sliding and the front and rear rims of the droplet assume different interfacial angles. The angle of the rear rim is the receding angle (θ_r), and the angle of the front rim is the advancing angle (θ_a). The difference in these angles are referred to as the contact angle hysteresis(10). A low hysteresis surface possesses high droplet mobility

1.1.1 Lubricant Impregnation

Textured surfaces can get impregnated with low surface tension liquids (lubricants) if circumstances are appropriate. These type of surfaces are referred to as Slippery Lubricant Impregnated Porous (SLIP) surfaces, or Lubricant Impregnated Surfaces (LIS), and have recently become a popular subject of research(11; 12; 13; 14). The design of such a surface is one of a textured material, which can be viewed as a porous medium, with a spreading liquid film (consisting of the aforementioned lubricant) that impregnates the asperities, replacing the solid-

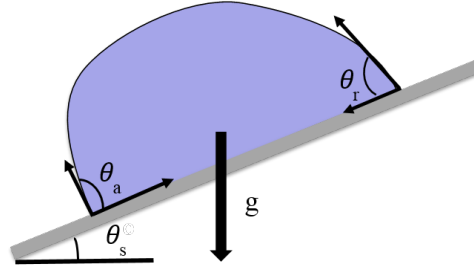


Figure 4. A droplet on a solid surface will slide at angle, θ_s . At the point of sliding, the front rim will possess advancing angle θ_a , and the back rim will possess receding angle, θ_r .

vapor layer with a solid-liquid layer. This exchange of phase occurs if the contact angle of the lubricant on the surface, θ , is less than a critical angle, θ_c defined by $\cos \theta_c = \frac{1-\phi_s}{r_f-\phi_s}$, where ϕ_s is the solid fraction remaining dry, and r_f the solid roughness. Once an appropriate lubricant is designated, there are multiple possible techniques to induce impregnation, such as drop coating or dip coating. Some commonly used lubricants are Krytox, Silicone Oil, and Mineral Oil. To ensure that a continuous lubricating layer is deposited, one should know the height (h_p) and spacing (d) of the surface texture. When dip coating method is utilized, the dipping speed (V) is selected such that the capillary number ($Ca = \frac{\nu V}{\gamma}$) is adjusted to control the lubricant thickness. Ordered structures allow impregnation of surfaces in a way that the lubricant does not overflow the asperities, while unordered surfaces can still be impregnated, but not with the uniformity that is sometimes desired.

1.2 Fundamentals of Droplet Impact

Droplet impact on flat surfaces is a long-studied field dating back nearly 150 years(15) to Worthington's fundamental studies. Ever since, research on droplet impact has greatly ex-

panded(16; 17); Both theoretical and experimental studies have been performed to analyze, evaluate and predict the behavior of impacting droplets.

The field of droplet impact consists of a liquid droplet, generally water, with diameter D_o impacting at a velocity U_o impacting a horizontal surface with wettability θ_E . Once the droplet impacts the surface, the vertical momentum of the droplet is converted into horizontal momentum that causes the liquid droplet to expand horizontally, and converting into a pancake like structure. This period is referred to as the spreading phase, due to the expanding droplet's spreading behavior. After a set amount of time, the spreading ceases. At this point in time, the droplet has achieved what is known as the maximum spreading diameter, $D_{\max}$. The extent to which the droplet spreads, the value of the maximum spreading diameter, is dictated by the D_o , U_o , θ_E , and the properties of the liquid droplet impacting the surface (ρ, σ, μ). Oftentimes, researchers choose to refer to the spreading factor $\eta_{\max} = \frac{D_{\max}}{D_o}$, rather than the maximum spreading diameter.

Once the droplet has reached maximum spreading diameter, the droplet will begin to experience what is known as the receding phase. Due to the fact the droplet has spread beyond its initial diameter, it now experiences a radially inward capillary force forcing it to recede and reduce its diameter. The degree to which the spread droplet recedes is predominantly dependent on the receding angle of the impacted surfaces. One of two most common outcomes occur 1) the droplet recedes and remains in contact with the surface, assuming a diameter less than $D_{\max}$ 2) the droplet entirely recedes and depins. Bouncing of the surface of the impacted material. This outcome generally occurs if the surface impacted is superhydrophobic. In such cases, the total

time that droplet is in contact with the surface (spreading + receding phase) is referred to as the contact time, τ_c .

Prior reports have ranged from studying fundamental parameters affecting spreading(18), receding, and rebound(19; 20; 21) of impacting droplets on surfaces of known wettability, to altering the total contact time(22; 23) between droplet and surface.

1.3 Physics of Frosting/Icing

Frosting is a detrimental commonplace occurrence that impacts everyday electrical and mechanical equipment. As a result, this phenomenon has generated a large amount of research in an attempt to avoid or impede its consequences(24; 25). Atmospheric frosting occurs when suitable environmental conditions are met, and is unavoidable over prolonged time periods(26). Analogous to other thermodynamic phase-change processes, frosting begins (Figure 5) with a nucleation stage wherein water vapor condenses, freezes and induces further crystal growth(27; 28). Nucleation can be heterogeneous or homogeneous(29). Heterogeneous nucleation is initiated via preferential nucleation sites on a surface. Homogeneous nucleation occurs without the existence of preferential nucleation sites, in the interior of a uniform substance. Surfaces that are cooled below the freezing point and accumulate frost over time promote heterogeneous nucleation. The associated heterogeneous nucleation rate(30) is $J = J_o \left(-\frac{\Delta G_c}{kT_k} \right)$, where J_o is a kinetic constant, k is Boltzmann's constant, T_k the surface temperature in Kelvin, and ΔG_c the critical Gibbs energy change, $\Delta G_c = \frac{16\pi}{3} \frac{\sigma_{lv}^3}{\Delta \tilde{g}_v^2} \frac{(2+m)(1-m)^2}{4}$, at a critical embryo size $r_c = \frac{-2\sigma_{lv}}{\tilde{g}_v}$ with $m = \cos \theta$. θ is the contact angle of water on the cooled surface, σ_{lv} the interfacial surface energy of the liquid-vapour phase, and $\tilde{g}_v$ the Gibbs energy change between the parent and new phase per

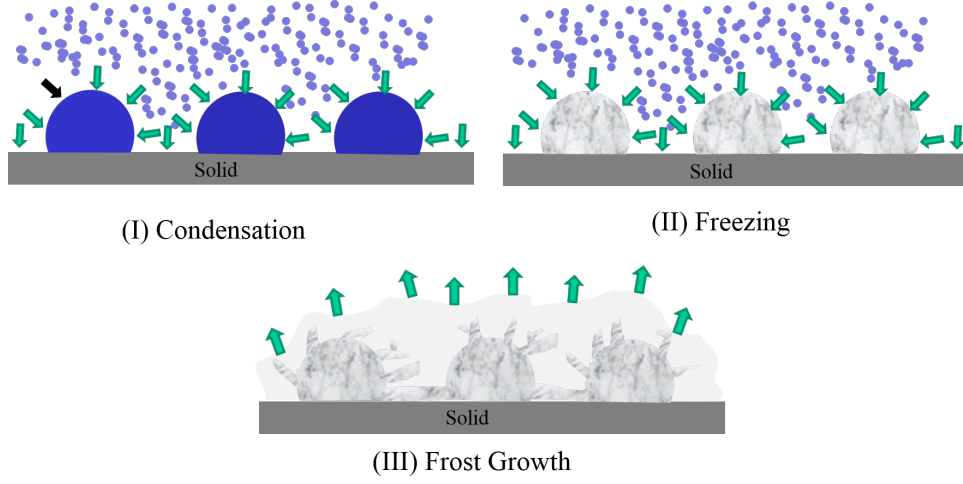


Figure 5. The stages of frost growth on a solid surface.

unit volume. According to the above, surfaces featuring lower contact angles (i.e. that are more wettable) would cause higher nucleation rates. Once liquid droplets have condensed, the next phase in the frosting process is the freezing of the droplets. Freezing time of a droplet, τ_f , is generally governed by the contact the droplet has with the surface. A larger contact area leads to a smaller freezing time. There are two locations from which crystallization can occur, from the liquid solid interface and the liquid air interface. Once the freezing of condensed droplets have occurred, the final phase occurs, and that is frost layer growth and development. Frozen droplets acquire water molecules from the neighboring unfrozen droplets, thus forming a protruding ice bridge. This ice bridge eventually comes in contact with surrounding droplets, causing them to freeze and form ice bridges of their own. Eventually, a thin layer of frost encompasses the entire surfaces. Subsequent frost layer growth on the surface is carried out via

two mechanisms, water vapour deposition and water vapour diffusion. In the case of what vapour deposition, water vapour from the convective environment is directly deposited on the top most layer of frost. For molecular diffusion, water vapour diffuses through the porous frost layer that is formed. Wherein it freezes, releasing latent heat that melt the surrounding frost and refreezes, causing the frost layer to densify overtime. These two processes continue, until the frost layer achieves a maximum thickness, and is no longer able to increase in size.

1.4 Thesis Objective

1.4.1 Droplet control on superhydrophobic paper surfaces

- Develop a low-cost method for the fabrication of superhydrophobic paper capable of being wettability patterned
- Demonstrate control of droplet sliding and transport
- Model and predict the demonstrated sliding and transport
- Create a disposable, low-cost Point-of-Care diagnostic device for liquid analysis

1.4.2 Droplet impact on non-uniform wettability surfaces

- Demonstrate varying outcomes possible for droplet impact on non-uniform wettability surfaces
- Develop an analytical theory capable of predicting maximum impact diameters of impacting droplets on non-uniform wettability surfaces

1.4.3 Electrically-conductive superhydrophobic coatings

- Study the frosting behavior of varying types of surfaces under prolonged frosting conditions

- Demonstrate the use of an electrically conductive superhydrophobic coating for Joule heated active deicing
- Mathematically, examine the role of impregnating fluid properties in the active heated process of lubricant impregnated surfaces
- Present the concept of pulsed heating in order to improve energy expenditure in heating of iced surfaces

1.4.4 Frosting and icing of pre-wetted surfaces

- Study the frosting behavior of pre-wetted surfaces of varying wettability
- Explain the role of underlying wettability in the frosting of pre-wetted surfaces
- Re-examine the contribution of the molecular diffusion of water vapour in the freezing of pre-wetted surfaces

1.5 Scope of Work

The presented work encompasses two primary area of focus: study of droplet control on solid surfaces and a study on the role of wettability in frost mitigation. The original motivation of this is the ice formation on solid surfaces. This processes generally begins with sporadic droplets impacting on a cooled surface, resulting in freezing and ice growth. Rather than approaching this complicated problem wholistically, we decomposed it into two separate components. This separation led us down two independent, though externally coupled, tracks of research. Chapter 2 we study the ability to use non-uniform wettability surfaces to control and manipulate static

droplets on solid surfaces. In chapter 3 we examined a more dynamic situation by using non-uniform wettability for studying impacting droplets. Chapters 4 and 5 address the frosting study component of our work. In chapter 4 we study specially synthesized electrically conductive superhydrophobic coatings, and the role wettability plays in combating prolonged frosting. In chapter 5, the focus shifts to when a surface is pre-wetted with water and is subjected to frosting conditions.

CHAPTER 2

CONTROL OF DROPLETS ON SOLID SURFACES VIA WETTABILITY PATTERNING

This chapter and its associated appendix (Appendix A): Elsharkawy, Mohamed, Thomas M.

Schutzius, and Constantine M. Megaridis. "Inkjet patterned superhydrophobic paper for open-air surface microfluidic devices." *Lab on a Chip* 14.6 (2014): 1168-1175. - Reproduced by permission of The Royal Society of Chemistry

2.1 Motivation and Background

Surfaces with water droplet contact angles exceeding 150° and sliding angles below 10° are deemed superhydrophobic and self-cleaning. It has been shown that surfaces demonstrating superhydrophobicity, whether natural or artificial, can be modified to yield domains of varying wettability (*e.g.*, superhydrophobic-hydrophilic). Methods of such modification include, but are not limited to plasma (31), chemical(32), and photo-lithographic treatment(33). In recent years, this superhydrophobic-hydrophilic behavior has formed the basis for producing surface microfluidic devices. Arrangements with patterned wettability have been studied in pool boiling(34), fog capture (32), selective droplet control, droplet splitting, among other applications. Being able to produce microfluidic devices that combine several of these behaviors into a single system, while at the same time maintaining a low-cost of production and easy assembly has implications in the areas of point-of-care (POC) and lab-on-chip analytical devices. One of the

steps in producing low-cost surface-microfluidic devices is choosing an appropriate substrate for patterning. Due to its low cost, flexibility, versatility, light weight, and abundance, paper is already the basis of several household POC diagnostic devices (*e.g.*, pregnancy tests, strips for urinalysis, litmus strips, etc.) Over the past several decades, such diagnostic devices have helped spawn a \$2.1 billion market that spans over 200 companies and has far reaching implications in the clinical, environmental, and bio-defense industries(35). Paper-based, disposable POC devices hold high hopes for utilization in economically developing environments(36). For these devices to be effective and mass applicable, they must be able to store, transport, split, and analyze droplets of a given size and liquid, while simultaneously being low-cost and easy-to-produce with minimal resources; such properties are not inherent to paper materials. In order to produce these desired behaviors, one must develop the ability to selectively pattern varying wettability on paper substrates with the spatial resolution required for each application.

Several techniques have already been reported for the production of surface microfluidic devices on various substrates. Xing et al.(37) reported hydrophobic surfaces that were laser-patterned to produce superhydrophobic channels, which were then primed with water, before droplets were added at the end of the aforementioned channels, eventually coalescing into one another. One method to induce a passive pumping mechanism has mimicked the natural behavior of the cribellate spider, *Uloborus walckenaerius*(38). Watanabe(39; 40) fabricated “surface-directed channels” with superhydrophobic glass substrates (PDMS-coated) that were inkjet patterned with a specially designed solution composed of 2-(2-ethoxyethoxy) ethanol and assembled to produce channels that relied on capillary action to induce droplet mobility and wetting.

Abe et al.(41) demonstrated significant advancement in the field by developing filter paper substrates selectively patterned via inkjet printing for multianalyte and immuno-chemical sensing. The combination of commercially available paper, printers, and ink used to induce varying areas of wettability has been reported by Balu et al.(42), Barona and Amirfazli(43) and Sousa and Mano(44). Balu et al.(42) utilized previously reported model paper substrates that were plasma-treated to induce superhydrophobicity and were then patterned using common printer ink to produce "sticky islands." These islands were analyzed and implemented for droplet storage, transferring, mixing and splitting. Barona and Amirfazli(43) presented a sprayable superhydrophobic nanocomposite film that was patterned via inkjet printing with varying "intensities" of ink. These surfaces were then tested for water repellency and droplet mobility. Sousa and Mano(44) produced superhydrophobic paper which was patterned by inkjet printing and writing. The same type of paper was also modified by poly-(hydroxybutrate) and protein absorbers in demonstrating the viability of such substrates as disposable lab-ware and lab-on-paper devices(45). Finally, Li et al.(46) combined plasma etching and sandpaper to induce controlled droplet splitting on superhydrophobic paper. Noting these previous works, we have developed a cost-effective, comprehensive system that not only mimics the aforementioned behaviors on a single substrate, but also demonstrates potential for further applications in droplet sampling, testing, controlling lab-on-paper reactions, and selectively mobilizing small liquid volumes.

We set out to produce low-cost surface microfluidic devices via inkjet printing onto microtextured silicon carbide paper (sandpaper) that was coated with a fluoroacrylic copolymer to yield a superhydrophobic baseline surface. The sandpaper is used as an example of a myriad of papers

that are available in the open market. The surface microfluidic devices, in combination with the underlying paper substrate, function as a viable platform for paper-based POC diagnostic devices designed on the principles of patterned wettability. The end result is a versatile surface capable of performing a variety of tasks ranging from droplet mixing and sampling, selective droplet mobility, and pumpless surface microfluidics, culminating in the creation of a simple paper-based POC device. Previous papers have reported the design of inkjet based processes, paper microfluidic devices, and POC devices; we build on these previous works and create an easy-to-use, easy-to-produce versatile system capable of demonstrating the aforementioned properties. Paper’s versatility and flexibility make it an ideal surface to be used in combination with common inkjetting techniques. Inkjetting as a patterning technique has gained momentum over the past few years due to its ability to accurately deposit picoliter volume liquids over a range of variant substrates. With their low cost of operation, abundance, ease of use, and good patterning accuracy, paper substrates present themselves as a powerful alternative for modern photolithographic(33) and laser patterning techniques(47)

2.2 Experimental

2.2.1 Materials

Silicon carbide paper sanding sheets (1500 grit; $\sim 10\mu\text{m}$ feature size; McMaster-Carr) were used. An over-the-counter inkjet printer (Kodak Office Hero 1.609) and ink (Kodak black and color ink cartridges, 10 series) were obtained locally. The chemicals utilized are aqueous fluoroacrylic copolymer dispersion (PMC, 20 wt.% in water, Capstone[®] ST-100, DuPont), acetic acid (99.9 wt.%, Fisher Scientific), acetone (ACS reagent, $\geq 99.5\%$; Sigma-Aldrich), alizarin

yellow (ACS reagent, dye content 50%; Sigma Aldrich), bromothymol blue (ACS reagent, dye content 95%; Sigma Aldrich), and methyl red (ACS reagent, dye content 95%; Sigma Aldrich).

2.2.2 Sample Preparation

To produce 10 g of hydrophobizing solution, 0.5 g of acetic acid, 0.5 g of PMC and 9.0 g of acetone were added in a vial. The solution was drop-casted onto the sandpaper and dried by a heat gun for 1 min (Proheat[®] Varitemp[®] PH-1200, 1300 W max). The coated sandpaper was then placed in an oven at 80°C for 60 min to dry completely.

2.2.3 Printing Process and Wettability Patterns

Advancing, receding and sliding angle measurements were performed on the uncoated (control) and coated sandpapers. Areas of varying ink intensity were then deposited on the coated substrates, which were fed through the inkjet printer. Ink deposition was controlled through the alteration of intensity in the printer's vector graphics editor. Within the software, the amount of ink deposited is controlled by a numbering system ranging from 0-100 (referred to as intensity); a 100 set value denotes 100 % intensity (i.e., highest ink deposition rate). We note that the amount of deposited ink is correlated linearly with the intensity. For example, 100 % intensity corresponded to 0.5 g m⁻² ink add-on level, while 50 % intensity to 0.25 g m⁻². At first, only black ink was deposited onto the superhydrophobic paper surface in increments of 25 % (from 0-100) intensity. Afterwards, different colors were deposited at the same intensity increments in order to examine if there is differentiation between colors and the change of wettability they induce. After printing the desired ink patterns on the aforementioned superhydrophobic sandpaper, the printed paper was once again dried with the heat gun and left to dry in the oven (80°C) for an

additional 60 minutes. This protocol assured complete ink drying. If ink had not dried properly, ink dissolution occurred when coming in contact with water. Once the printed areas were thoroughly dried, sliding, receding and advancing contact angle measurements for water were performed. Based on the obtained results, smaller increments of intensity (5 %) were printed in order to hone on intensities that correlate to transitional values (*e.g.*, hydrophobic-hydrophilic, sliding-immobile). The results are discussed in the following section. Next, tracks of varying width were printed with a constant cyan ink intensity, although other primary colors behaved similarly. Using different combinations of track width and ink intensity, a system was designed where droplet sliding could be selectively controlled (in terms of the inclination angle, α). In order to demonstrate the versatility of the produced substrates, different patterns were printed for different microfluidic functions. One pattern demonstrated Laplace-pressure-driven motion, while printed tracks demonstrated water droplet sliding control. In addition, a spot sampling pattern was used to demonstrate rapid droplet splitting and sampling.

2.3 Results and Discussion

In order to develop a biomicrofluidic system based upon tuning droplet mobility, it is first necessary to synthesize superhydrophobic surfaces. It is well established that the two main factors that govern the liquid repellency of a given surface are its chemical nature (surface energy) and topographical microstructure (surface roughness). In general, a substrate is incapable of achieving a superhydrophobic state without a certain extent of underlying roughness and chemical hydrophobicity. Thus, modern techniques utilized in creating superhydrophobic substrates rely on manipulating both the roughness and surface energy of the substrate. Sandpaper already

possesses the necessary underlying roughness, thus requiring only manipulation of its surface energy to attain superhydrophobicity. Scanning electron microscopy (SEM) images of the substrates were taken before and after coating with PMC. Figure 6 presents micrographs of the SiC micro-textured substrate after coating with PMC and shows that it forms a conformal film (roughness features of $10\text{ }\mu\text{m}$), which is advantageous for generating superhydrophobic surfaces.

The required PMC solution concentration for superhydrophobizing the sandpaper was estimated by intending to form a thin, conformal film around the pre-existing silicon-carbide microtexture (feature sizes about $10\text{ }\mu\text{m}$). Acetone readily spread on the silicon-carbide micro-textured surface to form a $\sim 100\text{ }\mu\text{m}$ thick film. Therefore, when a 1 wt.% PMC solution in acetone was deposited onto the micro-textured substrate, after it dried, PMC was estimated to form a $\sim 1\text{ }\mu\text{m}$ film, which is on the scale or below the smallest primary surface feature size, thus ensuring that a large amount of texture remains exposed, as supported by the SEM images in Figure 6. Prior to coating, the sandpaper had advancing contact angle of approximately $106^\circ \pm 4.8^\circ$ and receding contact angle of $\approx 0^\circ$, implying that the uncoated sandpaper already lies in the hydrophobic (but immobile liquid) regime. Coating by PMC resulted in an advancing contact angle of $156^\circ \pm 4.5^\circ$ and receding angle of $130^\circ \pm 6.3^\circ$, with sliding angle of $13^\circ \pm 2.4^\circ$. This transition into the superhydrophobic regime can be attributed to the pre-existing roughness of the sandpaper and the hydrophobic nature of the overlaying PMC film.

Next, black ink was deposited on the superhydrophobic paper via inkjet printing. Deposition of the ink was controlled by prescribing ink intensity in the printer's drawing software. An SEM image of black ink deposited at 100 % intensity on the superhydrophobic (coated) sandpaper

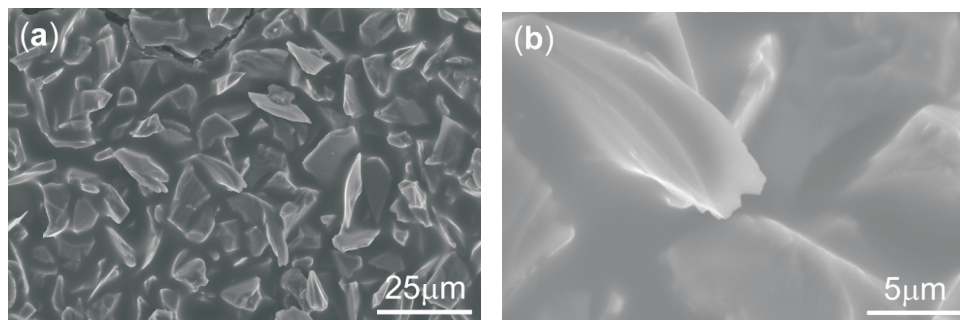


Figure 6. (a) SEM image of 1500 grit sandpaper coated with a fluoropolymer film (PMC). The sandpaper already possesses the necessary underlying surface roughness required to bring about a superhydrophobic state. (b) Magnified detail of a micro-feature spot on (a).

is presented in Figure 7. The excessive amount of ink deposited alters the surface energy of the substrate, thus changing its inherent wettability. Subsequently, black ink intensity was altered in increments of 25; advancing and receding angle measurements were performed and are summarized in Figure 8. For the maximum deposition of black ink (100 %), we recorded an advancing angle of $96^{\circ} \pm 5.4^{\circ}$; the receding angle was practically zero; therefore, the droplets did not display sliding behavior. This sharp decline in liquid repellency and mobility signifies the shift of the superhydrophobic paper state into the hydrophobic, borderline, hydrophilic regime. This change can be attributed to the increase of surface energy of the substrate due to the presence of the ink. As shown in Figure 7, the ink on the coated substrate forms a layer which the overlaying droplet encounters. The presence of the ink lowers liquid mobility, and, in turn, the repellent property of the substrate. By varying the amount of ink deposited, one can modify the degree by which the surface energy of the substrate is altered. In addition, an

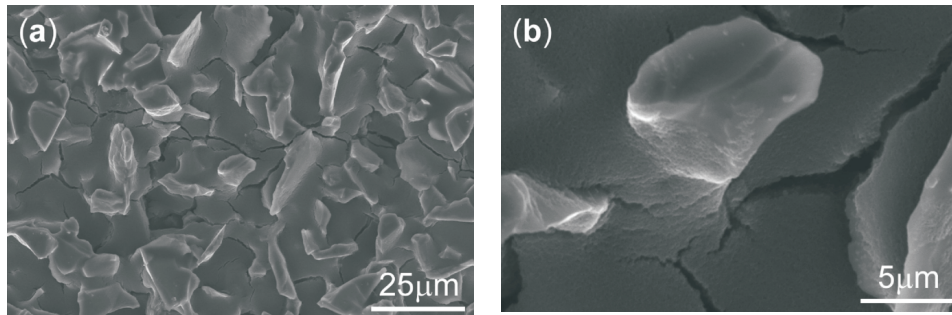


Figure 7. SEM images of superhydrophobic paper covered with black ink dispensed by an inkjet office printer. Magnification increases from (a) to (b). The deposited ink alters the underlying surface energy of the surface. This, in effect, changes the wettability of the substrate. By selectively increasing or decreasing the amount of ink deposited, one can modulate the wettability, as desired.

excessive amount of ink can, theoretically, reduce the amount of surface roughness. Thus, by varying the intensity (*e.g.*, amount) of the applied black ink, one can selectively control droplet mobility and repellency, as previously reported by Barona and Amirfazli(43). Repeating the same experiments with cyan, magenta and yellow inks separately, we noted a similar behavior.

Black ink was inkjetted next using deposition intensity increments of 5, from 25 to 50 (0.125 to 0.25 g m⁻²). The upper bound of this range was selected as the point of transition for droplet sliding (Figure 9). The hypothesis was that this enhanced scale of ink deposition would allow the selective tuning of droplet mobility, as based on the amount of ink deposited. As shown in Figure 9, the sliding angle continued to increase as the amount of ink gradually increased, thus demonstrating the ability to control droplet sliding angle by specifying the amount of ink

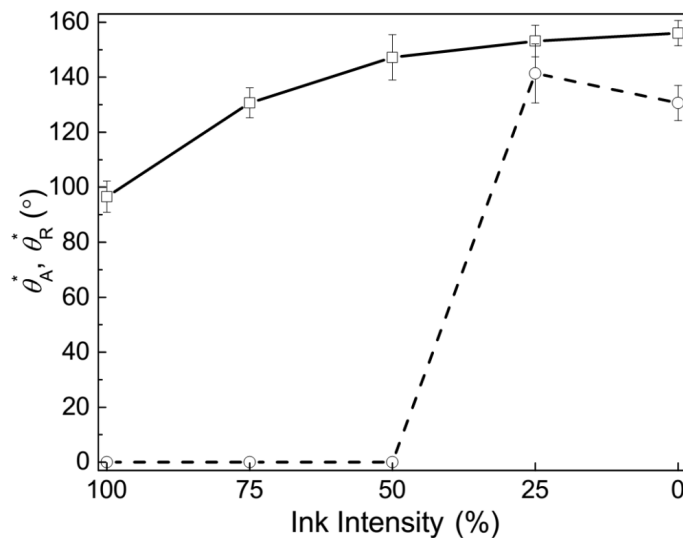


Figure 8. Advancing (squares; solid line) and receding (circles; dashed line) water contact angle measurements on sandpaper printed with different amount of black ink. The amount of deposited ink correlated linearly with the intensity value (100 % corresponded to 0.5 g m^{-2} ink add-on level; 50 % to 0.25 g m^{-2}). As the amount of ink deposited increased, so did the wettability. This is due in part to the increased surface energy provided by the ink, and the partial smoothing of the underlying texture by the formation of the ink layer on the substrate's rough terrain. Furthermore, the steep decrease of receding contact angle between 25 % and 50 % intensity makes possible the manipulation of the sliding angle.

deposited on the substrate. This process presents a "chemical" approach to control droplet mobility on a textured solid. The results indicate that prescribed amounts of ink can effectively alter the surface energy of the substrate, while leaving the underlying microtexture largely unaffected (Figure 7).

The above approach demonstrated control of liquid mobility by way of changing the surface energy of the substrate. We now demonstrate another method for droplet sliding control via contact-area manipulation (Figure 10). Linear tracks of varying width ranging from 0.1 mm to

2 mm were printed with cyan ink at 47 % intensity and tested with 10 μL water droplets. The sliding angle results are presented in Table I. As track width increases, so does the droplet sliding angle. This decrease in mobility is a result of increased contact line distortion between the track width and the receding line(48). Thus, by simply varying the width of the printed lines, we can control the sliding angle of the droplets placed on the substrate. Such a mechanism can be beneficial in systems that require controlled droplet release. Applying Extrand and Gent's(49) analysis of retention of liquid droplets, we can model the ability of the present surfaces to control sliding angle. The retentive force F_R of a spherical droplet on a solid surface is given by

$$F_R = F_r - F_a \quad (2.1)$$

where F_r is the force from the rear of the droplet and F_a from the advancing droplet front. Following Extrand and Gent's(49) derivation,

$$F_a = 2R\gamma \cos \theta_a \quad (2.2)$$

and

$$F_r = 2 \int_0^{\pi/2} R\gamma \cos \theta \cos \phi d\phi \quad (2.3)$$

where R is the droplet radius, γ the surface tension of the liquid, ϕ (see Appendix Figure A1) the azimuthal angle that circumnavigates the droplet contact line from the rearmost point ($\phi=0$) to the side of the drop ($\phi=\pi/2$); due to the geometry, we need to consider only values up to

$\phi=\pi/2$. Following Extrand and Gent, $\cos \theta$ varied linearly around the perimeter between the receding value $\cos \theta_r$ at the rear of the drop ($\phi=0$) and the advancing value $\cos \theta_a$ at the side of the drop ($\phi=\pi/2$)

$$\cos \theta = \frac{\phi}{\pi/2} \cos \theta_a + \left(1 - \frac{\phi}{\pi/2}\right) \cos \theta_r \quad (2.4)$$

In the present situation where the droplet slides on the wettable path and extends outward over the phobic domain, the liquid does not encounter a homogeneous contact surface. Thus, the $\cos \theta_a$ and $\cos \theta_r$ terms vary according to the surface properties underneath the droplet. In order to accommodate for this spatial inhomogeneity, Equation 2.2, Equation 2.3, and Equation 2.4 are modified accordingly. In particular, the integral defined in Equation 2.3 is replaced by the sum of two separate integrals, each corresponding to a different surface under the liquid volume

$$F_r = F_{r_1} + F_{r_2} = 2R\gamma \int_0^{\phi_1} \cos \theta_1 \cos \phi d\phi + 2R\gamma \int_{\phi_1}^{\pi/2} \cos \theta_2 \cos \phi d\phi \quad (2.5)$$

where F_{r_1} is the rear force contribution by the philic track, F_{r_2} the rear force contribution by the phobic paper, $\phi_1 = \sin^{-1} \left(\frac{w}{2R} \right)$ (see Appendix Figure A1) the value of ϕ at the contact line point separating the philic track from the phobic domain, w the width of the track, and $\cos \theta_i$ are modified forms of Equation 2.4; see Appendix Section A.1. In order to calculate the total retentive force, F_R , an analogous analysis for the advancing force is followed

$$F_a = F_{a_1} + F_{a_2} = 2R\gamma \cos \theta_{a_{ink}} \int_0^{\phi_1} \cos \psi d\psi + 2R\gamma \cos \theta_{a_{paper}} \int_{\phi_1}^{\pi/2} \cos \psi d\psi \quad (2.6)$$

where ψ denotes the angle from the front end of the droplet. In line with Extrand and Gent's derivation(49), we assumed that the advancing angle is constant for each of the two surfaces (paper or ink-coated track) which the liquid encounters. Combining Equation 2.5 and Equation 2.6 into Equation 2.1 we determine F_R , which is equated with the gravity force on the droplet along the inclined surface, to obtain

$$F_R = mg \sin \alpha_c \quad (2.7)$$

with m denoting the mass of the 10 μL droplet. This equation is used to estimate α_c , the sliding angle at which the droplet starts moving down the slope. The predicted and experimental sliding angles are compared in Table I. Nearly all predicted values are within one standard deviation of their experimentally-measured counterparts, supporting the argument that droplet sliding is controlled only by wettability forces. To demonstrate a POC-type device, a linear repeated spot pattern was printed as shown in Figure 11a. The circular reservoirs (1.5 mm diameter) were printed with 100 % black ink, while the connecting line (0.1 mm wide) was printed with 35 % cyan ink. The four printed black spots functioned as sticky islands, while the line track acted as a guiding rail for a droplet released down the inclined (20°) plane. The hydrophilic spots were post processed with the water-soluble pH indicators mentioned in the materials section. By placing a 10 μL droplet at the top of the tilted pattern, the droplet rolled down, leaving behind a liquid sample on each of the sticky spots. This procedure successfully separated multiple small volumes (initially $\sim 0.6\mu\text{L}$) from the original droplet at a rate of 50Hz. The

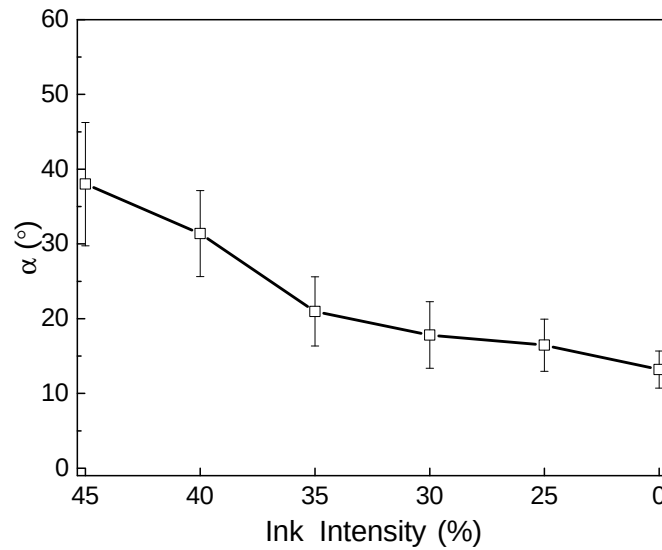


Figure 9. Water droplet sliding angle (α) vs. black ink intensity in increments of 5 % from 25 % to 45 %. As the intensity rose, so did the sliding angle. For intensities equal or greater than 50 %, the droplets remained immobile. These phenomena are supported and understood by the advancing-receding contact angle data in Figure 8.

maximum number of spot volumes that can be sampled from a single droplet depends on the initial liquid volume. The spot samples could be automatically analyzed by the pH indicators present on each spot. Due to the fact that each of the indicators reacts at different pH levels, a neutral droplet of water (pH=7) is expected to induce different color changes in each of the spotted regions; see Figure 11b. This functionality has potential for use in POC devices. For example, post-processing the phillip spots with protein sensors, bacterial indicators or chemical reagents facilitates analytic procedures from a single droplet that is rapidly split as shown in Figure 11. The use of inkjet printing as a patterning technique, and the rapid droplet sampling procedure demonstrated herein in conjunction with post-processing methods, help lay forth

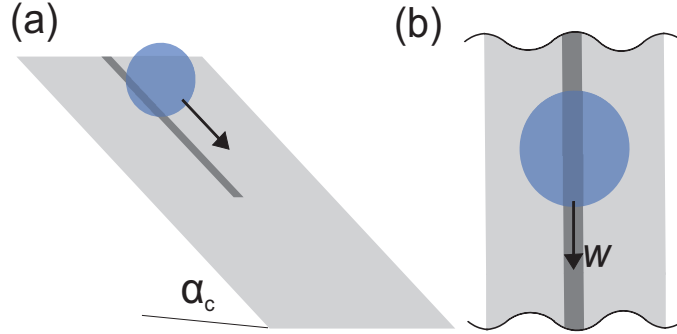


Figure 10. (a) Water droplet placed onto a hydrophilic line track of a known (but varied) width w ; the track was inkjet printed on superhydrophobic paper (light grey). The droplet started sliding down the track when the paper tilt angle reached a threshold value α_c that correlated with the track width w . (b) Top view.

the groundwork. Such simple but reliable droplet analysis procedures are necessary, especially in environments and conditions where supplies are scarce and testing facilities possess limited capabilities.

We now exploit the flexibility of the patterning technique in the design and implementation of surface microfluidic devices capable of capillary-driven fluidic transport and spontaneous droplet splitting. A dumbbell shaped flat pattern (Figure 12), similar to that examined by Xing et al.(37), was printed (100 % black ink) onto the superhydrophobic paper substrate, which was kept horizontal. The pattern consisted of two circular reservoirs, 4 mm and 2 mm diameters, connected with a 25 mm long track of fixed width of 0.75 mm. Droplets of 10 μL and 7 μL were deposited on the reservoirs (large and small, respectively) and the connecting channel was primed by adding water until a thin film formed. The pressure difference in the two volumes

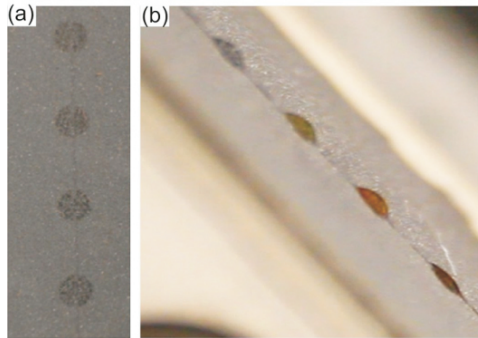


Figure 11. (a) Black ink deposited on superhydrophobic paper at 100 % intensity (0.5 g m^{-2}) to form hydrophilic 1.5 mm diameter spots connected by a 0.1 mm wide line serving as rail for a droplet rolling down the inclined plane. Each circular region was patterned with a separate water soluble pH indicator: alizarine yellow, bromothymol blue, or methyl red. The first (top most) spot was untreated, and thus acted as a control for color. (b) The substrate was angled at 20° and a $10 \mu\text{L}$ water droplet was placed at the top. Due to the superhydrophobic nature of the substrate and its low sliding angle, the droplet slid and rolled over the hydrophilic spots at a rate of 50 spots per second. After making contact with each spot, the droplet released a small volume ($\sim 0.6 \mu\text{L}$) and continued on to the next spot. The liquid left behind on each spot interacted with the pre-deposited pH indicator, and thus changed color accordingly.

drove a flow from the smaller radius reservoir to the larger one, as seen in Figure 13. As Xing et al.(37) described, the flow rate is controlled by several factors, such as reservoir radii, channel width, and channel length. Using the present patterning approach, the above-mentioned factors can be controlled with precision by way of the vector graphics software of the inkjet printer, with minimal wait time. Thus, the present method offers an ideal mechanism for controlled mixing of different liquids on paper.

Due to the ease and flexibility of the patterning process, any imaginable 2D device can be printed. An example of one possible functional surface can be a repeated triangular pattern



Figure 12. Black (100 % intensity), hydrophilic pattern inkjetted on microtextured, silicon-carbide, superhydrophobic paper. The top (large) spot reservoir is 4 mm in diameter and the bottom (small) reservoir is 2 mm in diameter. The connecting line track is 25 mm long and 0.75 mm wide.

that functions as an energy barrier and induces anisotropic droplet sliding. Similar devices have already proven viable when produced on different surfaces(50). Furthermore, if the previously described printed lines were positioned horizontally, and the width and ink deposition were tuned as needed, one could selectively control liquid adherence to the surface simply based on droplet size. Thus, the present approach offers a viable alternative to a recently reported method(51) that created invisible gates to moving water droplets by superhydrophobic metal-polymer hybrid surfaces featuring wettability gradients.

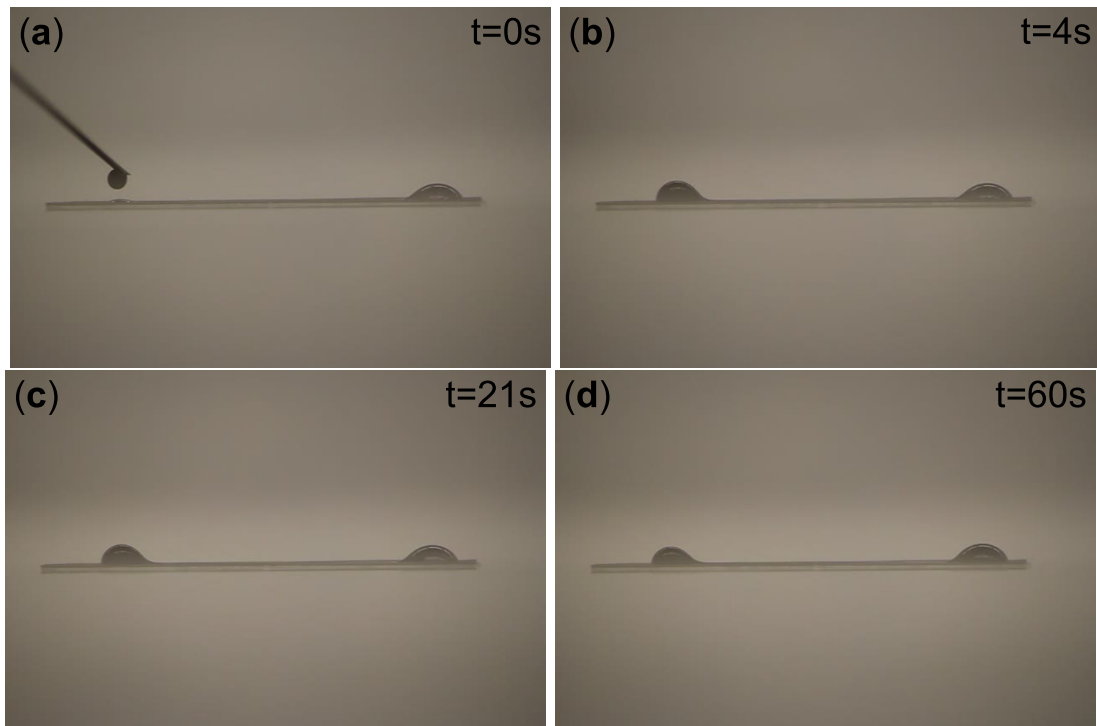


Figure 13. (a) $7\ \mu\text{L}$ water droplet being placed with a syringe and 25 gauge needle onto the 2mm-dia. reservoir shown in Figure 12 (top view). The larger 4mm reservoir (right) contains a pre-deposited $10\ \mu\text{L}$ droplet; (b)-(e) time sequence of images showing the gradual draining of the small droplet (left) into the large droplet (right). The flow is driven by the Laplace pressure difference between the two droplets.

Line width w (mm)	Predicted α_c from (Equation 2.7)	Measured α_c
0.0	11.3°	13.2° ± 2.5°
0.1	21.1°	25.6° ± 3.8°
0.5	25.3°	28.7° ± 6.1°
1.0	30.8°	35.2° ± 5.7°
1.5	36.8°	36.5° ± 8.6°
2.0	43.7°	45.1° ± 4.0°

TABLE I

WATER DROPLET SLIDING ANGLES ON TRACKS OF VARYING WIDTH PRINTED WITH CYAN INK AT 47 % INTENSITY. THE SLIDING ANGLE INCREASED WITH LINE WIDTH, WITH THE DROPLETS LOSING MOBILITY (*i.e.*, SURFACE BECOMES STICKY) ABOVE $W = 2.0$ MM. COMPARISON OF PREDICTED ANGLES WITH THOSE MEASURED EXPERIMENTALLY.

CHAPTER 3

IMPACTING OF DROPLETS ON WETTABILITY-PATTERNED SURFACES

3.1 Motivation and Background

Droplet impact on flat surfaces is a long-studied field dating back nearly 150 years(15) to Worthington’s pioneering studies. Ever since, research on droplet impact has greatly expanded(16; 17); Many theoretical and experimental studies have been performed to analyze, evaluate and predict the behavior of impacting droplets. Prior reports have ranged from studying fundamental parameters affecting spreading(18; 52), receding(53; 54) and rebound(19; 20; 21; 55) of droplets impacting on surfaces of known wettability, to altering the total contact time(22; 23) between droplet and surface. As significant and impactful as all these works have been, the vast majority have only studied impact on uniform-wettability surfaces. In actuality, common-day surfaces are mostly non-uniform. Whether it be via design or nature, most surfaces contain structural or chemical imperfections and heterogeneity that result in the surface to possess domains of varying wettability.

Wettability-patterned surfaces, as they are sometimes referred to in the literature(56), are especially-engineered surfaces that deploy specifically designed spatial distributions of high- and low-surface energy domains on a single substrate to achieve specific tasks. Such tasks include, but are not limited to, high-rate fluid transport(56), enhanced condensation(57), water capture

from the atmosphere(58), selective droplet sliding(59), selective cooling(60), etc. As of now, there exist only a handful of studies examining droplet impact on wettability-patterned surfaces. Kim *et al.*(61) studied the behavior of droplets impacting a superhydrophobic surface with hydrophilic annuli and demonstrated the ability to utilize these patterned-wettability surfaces to achieve varying liquid deposit morphologies. Mock *et al.*(62) studied droplet impact behavior on hydrophobic polymer surfaces that were lithographically patterned to yield circular hydrophilic patterns. They observed a spontaneous self-centering ability that droplets exhibited when impacting the aforementioned surfaces. Michel *et al.*(63) presented a theoretical model to elucidate the hydrodynamics of impacting droplets on Mock *et al.*'s(62) surfaces. Schutzius *et al.*(64) studied the vectoring and shaping of impacting droplets on wettability-patterned surfaces developed via inkjet printing. Sprittles and Shikhmurzaev(65) numerically simulated the impact of droplets on patterned surfaces.

We aim to add to the existing work by analytically studying, and experimentally verifying, axisymmetric droplet impact on a circular region (with specific wettability) surrounded by a region of a different wettability. Specifically, we analyze the spreading behavior of droplets on these surfaces. We put forth a model that is able to predict the spreading behavior depending on the Weber number of the impacting droplet, and the wettabilities of the two regions (as characterized by advancing angle). The work draws upon the previously-reported models of Pasandideh-Fard *et al.*(66), Mao *et al.*(67), and Ukiwe and Kwok(68) in order to build a new analytical understanding for droplet impact on axisymmetrically non-uniform wettability surfaces, something that has not been addressed by these models. From experiments and theory for the

case where the inner domain is more wettable than the surrounding one, we consider the existence of a cross-over energy at the transition line between the two regions of different wettability, leading to three possible regimes of spreading. Lastly, we expand the model to demonstrate its utility when target surfaces feature n -annular regions of non-uniform wettability.

3.2 Experimental: Surfaces and Setup

3.2.1 Sample Preparation

The surfaces used in the present experiments were fabricated via a spray coating and masking technique. Glass slides (75mm x 25mm) were cleaned, rinsed and dried. Masks of varying circular diameters were cut from a vinyl-based adhesive tape using a CO₂ Laser (Universal laser systems V-460, 50 W) and adhered to the glass. The sample was then sprayed with a carbon-nanofiber dispersion to produce a superhydrophobic coating. The coating formulation has been previously reported(69; 70; 26) and is described here only briefly. To mix a typical dispersion, approximately 0.3 g of carbon nanofibers (PR-24-XT-HHT; Pyrograf III, Applied Science, Inc., USA) were placed in 14 g of acetic acid (ACS reagent, ≥ 99.5 wt %, Sigma-Aldrich) and 28 g of acetone (ACS reagent, ≥ 99.5 wt %, Sigma-Aldrich) in a glass vial. The dispersion was stabilized by probe sonication (750 W, probe diameter of 13 mm, amplitude 40%, frequency 20 kHz; Sonics and Materials, Inc., Model VCX-750) for 1.5 min. In a separate vial, 1 g of a fluoroacrylic copolymer (PMC, 20 wt % in water; Capstone ST-100, DuPont) was diluted with 2 g acetic acid and 4 g acetone. The contents of the two vials were mixed and bath-sonicated for 10 min to form a ready-to-spray dispersion. After spraying, samples were dried in an oven at 80° C for one hour.

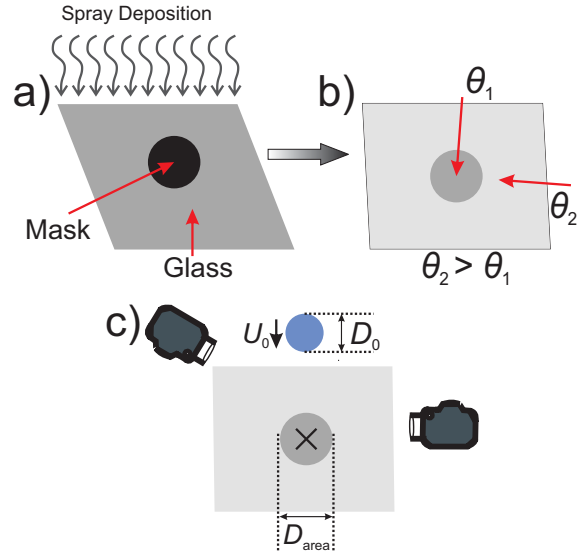


Figure 14. (a) Spray deposition was implemented to produce the experimental samples. Plain glass slides were masked with a Vinyl sheet with adhesive. The sample was then spray coated with a superhydrophobic coating. b) The result was a surface possessing two distinct domains of wettability: $\theta_1 = 115^\circ$ and $\theta_2 = 147^\circ$. c) Droplets of diameter D_o impacted at the center of the circular domain (diameter D_{Area} , wettability θ_1) with velocity U_o . Visualization was performed with a dual camera setup in order to ensure that the droplets impacted centrally and the events remained axisymmetric.

At the conclusion of this process, the resulting surface possessed two domains of wettability (Figure 14a). The vinyl mask shielded the covered areas from the spray-coating process, thus allowing the underlying glass to retain its natural hydrophilic nature. On the other hand, the deposited coating induced a superhydrophobic state throughout the spray-exposed (unmasked) regions. When the vinyl mask was a disk of diameter D_{Area} , the resulting sample had a wettable disk area surrounded by a non-wettable domain. When the vinyl mask was a sheet with a hole of diameter D_{Area} , the resulting pattern was a nonwettable disk surrounded by a wettable domain.

3.2.2 Visualization

In order to ensure that the droplets accurately impacted at the center of the circular region 1, a dual camera visualization setup was utilized (Figure 14c). The setup consisted of a floating optical table, with a light source (Fostec 8375), and two high-speed cameras (Redlake MotionPro; Vision Phantom M310) used in a synchronized fashion to capture each impact event.

3.3 Analytical Formulation

In classical impact on flat uniform-wettability surfaces, a droplet of diameter D_o impacting with velocity U_o is characterized by the Weber number $We = \frac{\rho U_o^2 D_o}{\sigma}$, where ρ , σ are, respectively the density and surface tension of the fluid. The inertial forces from the impact cause the formation of a liquid rim, which continues to advance and spread laterally on the surface. The rim advances while forming an angle θ with the surface; this angle is the dynamic advancing angle¹. The rim eventually equilibrates and assumes a maximal spreading diameter

¹See section B.0.2 in Appendix B for a discussion on the role of static and dynamic contact angles

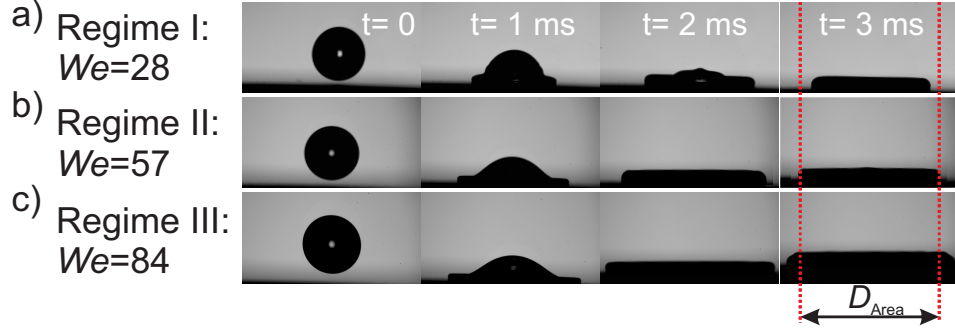


Figure 15. When water droplets impact a circular wettable domain of $D_{\text{Area}} = 5.4$ mm, there are three possible outcomes depending on the impact velocity U_o (which designates the value of We). a) Regime I - Droplet spreading occurs entirely within the circular domain, thus $D_{\text{max}} < D_{\text{Area}}$. b) Regime II - Spreading droplets get pinned at the wettability contrast line (WCL) at the periphery of the inner domain, thus $D_{\text{max}} = D_{\text{Area}}$. As the impact velocity increases further, the liquid remains anchored at the WCL until the energy becomes high enough to extend beyond the WCL. c) Regime III - The droplet impacts and spreads past the WCL, thus $D_{\text{max}} > D_{\text{Area}}$. The three cases depicted in this figure are characteristic of the three regimes, which occur over specific ranges of We .

D_{max} . The maximal spreading factor, defined as $\eta_{\text{max}} = \frac{D_{\text{max}}}{D_o}$, has been the object of many prior works on the spreading behavior of impacting droplets. Multiple studies have shown a strong correlation between the theoretical predictions put forth, and independent experimental results. These reports demonstrated the spreading behavior to be a complex interplay between inertial, capillary, and viscous forces, with a strong dependence on the underlying wettability of the impacted surface(54). In our experiments, droplets of diameter D_o and velocity U_o (Figure 14c) impacted at the center of disks of diameter D_{Area} with wettability represented by θ_1 surrounded by a region of wettability represented by θ_2 , where $\theta_2 > \theta_1$. Under these conditions, three outcomes are possible, depending on the value of We (Figure 15). The first

outcome occurs for the lower range of We (Figure 15a), where spreading of the impacting droplet occurs entirely within the inner region. The second outcome occurs for a medium range of We , where the droplet spreads, encounters the boundary between the two wettability regions, and does not possess enough energy to spread outside the inner region, resulting in $D_{\max} = D_{\text{Area}}$ and $\eta_{\max} = \eta_{\text{Area}}$ (Figure 15b). The last outcome occurs when the droplet spreads beyond the circular region, Figure 15c. Henceforth, we will denote these three regimes as 1) Regime I - Interior Spreading, 2) Regime II - Entrapment, and 3) Regime III - Exterior Spreading. In the following section, we derive analytically and show experimentally under which We these regimes are observed.

3.3.1 Regime I - Interior Spreading

In this regime, the impacting droplet does not possess enough energy to surpass, or even reach, the wettability contrast line (WCL), where the wettability step occurs (Figure 16a). The maximum spreading can be modeled and predicted using the existing energy approach models of droplet impact on uniform-wettability surfaces. For the sake of completeness, we briefly restate this derivation. Considering a droplet with diameter D_o and velocity U_o , the kinetic and surface energies are expressed as $E_{K1} = \frac{1}{2}\rho\left(\frac{\pi D_o^3}{6}\right)U_o^2$, $E_{S1} = \pi D_o^2\sigma$. Upon impact, the droplet spreads, and momentarily ceases upon reaching its maximum spread. Assuming the kinetic energy of the droplet to be zero at its maximum spread, the total energy of the system before contact and at maximum spread can be expressed as

$$E_{S1} + E_{K1} = E_{S2} + E_{\text{wet-dry}} + W_{\text{losses}} \quad (3.1)$$

where E_{S2} is the surface energy of the droplet (of the liquid-vapour interface) at maximum spread, W_{losses} are the viscous losses sustained during spreading, and $E_{\text{wet-dry}}$ is the energy due to the wetting of the solid surface. The above energy representation has been reported multiple times, with one of the most accurate depictions put forth by Ukiwe and Kwok(68). Following certain mathematical and geometric assumptions, the above terms can be expressed¹ as $E_{S2} = \left(\frac{\pi}{4} D_{\text{max}}^2 + \frac{2}{3} \pi \frac{D_o^3}{D_{\text{max}}} \right) \sigma$, $E_{\text{wet-dry}} = -\sigma \frac{\pi}{4} D_{\text{max}}^2 \cos \theta_1$ ², and $W_{\text{losses}} = \frac{\pi}{3} \rho U_o^2 D_o D_{\text{max}}^2 \frac{1}{\sqrt{Re}}$, where Re is the Reynolds number $Re = \frac{U_o D_o}{\nu}$. Substituting the above terms into Equation 3.1 and rearranging, one obtains

$$(We + 12)\eta_{\text{max}} = 8 + \eta_{\text{max}}^3 \left[3(1 - \cos \theta_1) + 4 \frac{We}{\sqrt{Re}} \right] \quad (3.2)$$

as reported by Ukiwe and Kwok(68). If the impact conditions (We) and wettability (θ_1) of the surface are known, then the maximum spreading factor (η_{max}) for droplets spreading entirely within the innermost region can be evaluated readily using Equation 3.2.

3.3.2 Regime II - Entrapment

Liquid entrapment occurs when the total energy of the impacting droplet is high enough for it to reach the WCL, but low enough to overcome the cross-over energy required to surpass the WCL. As long as the impact velocity (or the height from which the droplet is released) is below

¹For detailed derivations, see Pasandideh-Fard *et al.*(66), Mao *et al.*(67), and Ukiwe and Kwok(68)

²See section B.0.2.2 in Appendix B for elaboration on the use of dynamic advancing angle to define wettability

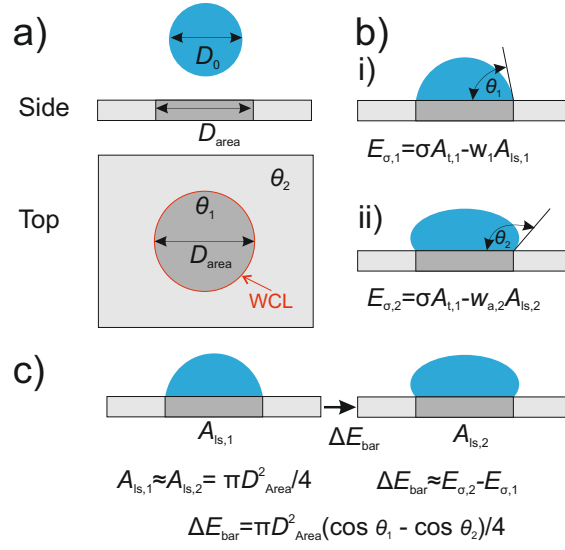


Figure 16. (a) A droplet of diameter D_0 strikes the center of a circular region of wettability θ_1 and diameter D_{Area} . This area is surrounded by a region of wettability $\theta_2 > \theta_1$. The border between these two regions is referred to as the wettability contrast line, WCL. For the impacting droplet to spread outside the inner-most region (D_{Area}), the spreading droplet must be able to change its contact angle from that of the inner region (b-i) to that of the outer region (b-ii). (c) During this change of the liquid-vapour interface, the liquid/solid contact area (A_{ls}) can be assumed to be constant. The energy required for this transition is denoted by ΔE_{bar} .

a threshold value, an impacting droplet remains trapped within the innermost region. Beyond the threshold impact velocity, the droplet can cross the WCL barrier and continue its spreading over the exterior region (contact angle θ_2).

The minimum Weber number, $We_{\min}$, at which the droplet covers the entire area 1 can be determined from Equation 3.2. Since D_{Area} is known, we retroactively solve for $We_{\min}$. Thus, with $D_{\max} = D_{\text{area}}$ and $\eta_{\max} = \frac{D_{\text{area}}}{D_o} = \eta_{\text{Area}}$, $We_{\min}$ can be computed from Equation 3.2.

As impact velocity rises further, impacting droplets remain entrapped at the WCL, but fail to reach into the exterior region 2. This behavior persists until We exceeds a critical value, $We_{\max}$, when the liquid front spreads onto the exterior surface. To help understand entrapment, we consider a static droplet sitting on a surface of uniform wettability, θ . The total free-surface energy, E_{σ} , can be expressed as

$$E_{\sigma} = \sigma A_t - w_a A_{\text{ls}} \quad (3.3)$$

where A_t is the total surface area of the liquid-vapour interface, w_a is the work of adhesion defined as $w_a = \sigma(1 + \cos \theta)$, and A_{ls} the liquid-solid contact area. Looking at the pinned spreading droplet in a static sense, and analyzing two instances in time, right before the rim traverses the WCL (Figure 16b-i), and right afterward (Figure 16b-ii). The surface free energy of both of these instances can be expressed as follows, $E_{\sigma,1} = \sigma A_{t,1} - \sigma(1 + \cos \theta_1) A_{\text{ls},1}$ and $E_{\sigma,2} = \sigma A_{t,1} - \sigma(1 + \cos \theta_2) A_{\text{ls},2}$. Assuming that the time between these two instances is extremely small, so that the total distance traversed by the rim is minimal, then the area wetted of wettability θ_2 is negligible when compared to the total area wetted of θ_1 . This allows us to assume $A_{\text{ls},1} \cong A_{\text{ls},2} = A_{\text{ls}}$, and $A_{\text{ls},1}$ can be expressed in terms of the width of the circular

area of region 1, $A_{ls,1} = \frac{\pi D_{\text{Area}}^2}{4}$. Subtracting the above two equations, the difference between the energy of these two states (Figure 16c) can be expressed as

$$\Delta E_{\text{bar}} = E_2 - E_1 \cong E_{\sigma,2} - E_{\sigma,1} \cong \frac{\sigma \pi D_{\text{Area}}^2}{4} (\cos \theta_1 - \cos \theta_2) \quad (3.4)$$

This ΔE_{bar} is the cross-over energy that must be overcome by the expanding droplet in order to traverse beyond the WCL. The existence of this cross-over energy can also be explained in terms of the need of the droplet to adjust its contact angle to continue its advancement on the exterior region. We have observed the change in contact angle experimentally as shown in Figure 17. Figure 17a shows how a droplet spreading from a hydrophilic to a hydrophobic semi-infinite domain must increase its contact angle from 115° to 147° between the snapshots at $t = 0.7$ and 1.1 ms. On the contrary, Figure 17b shows how a droplet traversing from a hydrophobic to a hydrophilic domain must decrease its contact angle from 147° to 115° between the snapshots at $t = 0.8$ and 1.2 ms. Note, however, that from Equation 3.4, whenever θ_2 is greater than θ_1 (i.e. region 1 is more wettable than region 2), ΔE_{bar} is positive, meaning that the liquid transitions from lower energy state to a higher one, and thus if this energy differential is not provided, the expanding droplet would not spread onto the exterior region. In order to determine We_{max} , the point at which an impacting droplet possesses sufficient energy to escape entrapment, we must first discuss Regime III- Exterior Spreading. It is important to note in this context that the spray deposition technique as described in Figure 14 creates a physical step from the uncovered glass to the coated side. Thus, there exists a vertical energy barrier (positive, if the inner region

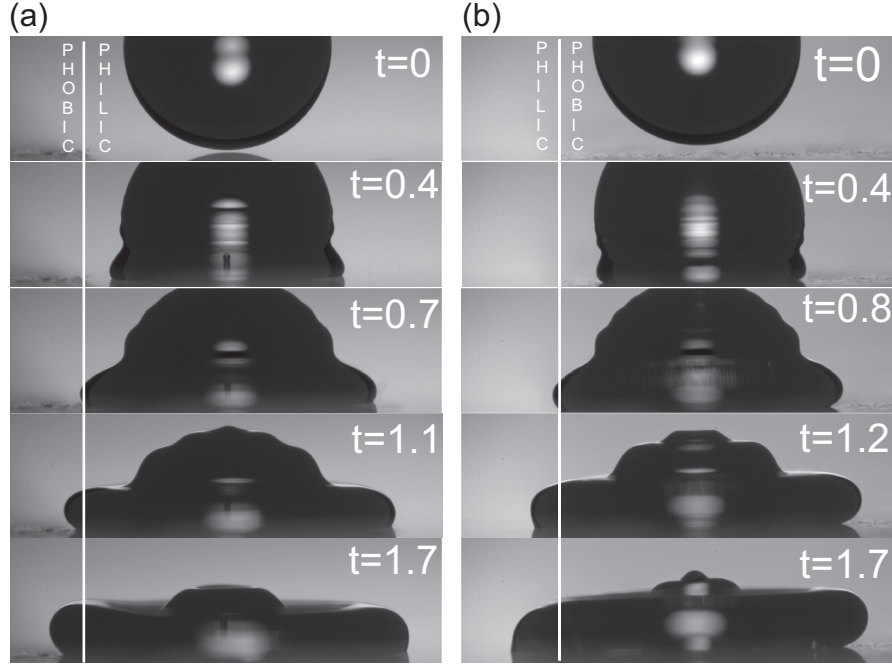


Figure 17. Impact of a 2.1 mm-diameter water droplet on a straight wettability step marked by the white line. The wettability changes from one side of this line to the other. (a) Impact on a predominantly hydrophilic area. After an initial phase of lateral spreading ($t=0.4$ ms) exclusively on the hydrophilic domain, the droplet reaches the wettability contrast line ($t=0.7$ ms). Before the droplet can continue its spreading into the hydrophobic region (far left), the fluid must change its advancing contact angle to the higher value corresponding to the hydrophobic domain (left). Note the stark contrast in contact angles between the right- and left-hand sides of this droplet at $t=1.1$ ms and afterwards. Similar phenomena are observed when the droplet impacts on a hydrophobic domain and eventually the fluid spreads onto a hydrophilic one (b). All timestamps are in milliseconds.

is uncoated glass, and negative otherwise) that has to be overcome in order for the droplet to continue its spreading beyond the WCL. Since we know that this step size is of the order of 100 microns, an order of magnitude analysis using Equation 3.4 shows that the vertical energy barrier¹ is $O(10^{-9})$ J, while $\Delta E_{\text{bar}} \sim O(10^{-6})$ J. This implies that the vertical energy barrier can safely be neglected for the present analysis.

3.3.3 Regime III - Exterior Spreading

Based upon the aforementioned analysis, we expect that for all We greater than We_{max} , an impacting droplet will experience Regime III, i.e. exterior spreading. The analysis for Regime I clearly indicates that the maximum spreading diameter depends on the wettability of the underlying substrate. We next examine if the maximum spreading diameter in Regime III depends on the contact angles of the two underlying regions. In order to predict the maximum spreading when a droplet experiences exterior spreading, we modify Equation 3.1 to account for non-uniform wettability. This modification can be performed by altering only $E_{\text{wet-dry}}$ in the energy equation. The initial surface and kinetic energy terms remain the same due to the initial conditions being the same. The final surface energy and viscous losses aren't altered due to the fact that they are originally derived with only consideration given to the geometric shape, and no dependence on the wettability. Thus, in order to evaluate how the non-uniform wettability of a surface alters the maximum spreading diameter, one only needs to consider the energy needed for the liquid to wet the multiple wettability regions. In addition, we must

¹Difference in z -height between inner and outer region. This physical step alters the potential energy on each side of the WCL.

take into consideration the role of the cross-over energy, ΔE_{bar} which must be overcome for the fluid to reach area 2. The cross-over energy, as already explained, arises from the need for the liquid-vapour interface to change from one shape to another with a pinned contact line. This implies that ΔE_{bar} is of retarding nature, and must be accounted for in the energy equation. Thus, modifying Equation 3.1 to account for a droplet impacting a dual-wettability region,

$$E_{S1} + E_{K1} = E_{S2} + E_{\text{wet-dry-1}} + E_{\text{wet-dry-2}} + W_{\text{losses}} + \Delta E_{\text{bar}} \quad (3.5)$$

where Equation 3.5 has the same form as Equation 3.1, but also takes into consideration the cross-over energy (ΔE_{bar}) and the fact that the droplet extends over two regions of distinct wettabilities. It is $E_{\text{wet-dry-1}} = -\sigma \frac{\pi}{4} D_{\text{Area}}^2 \cos \theta_1$, and $E_{\text{wet-dry-2}} = -\sigma \frac{\pi}{4} (D_{\text{max}}^2 - D_{\text{Area}}^2) \cos \theta_2$. Substituting in Equation 3.5, we deduce

$$E_{S1} + E_{K1} = E_{S2} - \sigma \frac{\pi}{4} D_{\text{max}}^2 \cos \theta_2 + W_{\text{losses}} \quad (3.6)$$

which is Equation 3.1 for a droplet impacting a uniform-wettability surface (θ_2), and η_{max} can be determined using Equation 3.2 for θ_2 . Yet, this solution holds only if We exceeds We_{max} . We now return to the question posed when discussing Regime - II. At what point does an impacting droplet transition from the entrapment regime to the exterior spreading regime? To resolve this, we merely carryout the same procedure in the previous section. Knowing that the transition

from Regime II to Regime III occurs when $\eta_{\max} = \eta_{\text{Area}}$, we use the solution of Equation 3.6, retroactively solving the following equation for $We_{\max}$

$$(We_{\max} + 12)\eta_{\text{Area}} = 8 + \eta_{\text{Area}}^3 \left[3(1 - \cos \theta_2) + 4 \frac{We_{\max}}{\sqrt{Re}} \right] \quad (3.7)$$

Based on the above equations, it stands that the spreading of a droplet impacting a dual-wettability surface is unaffected by the wettability of the innermost region (θ_1). In other words, the spreading on the outermost region (θ_2) is independent of the wettability of the inner region. The only effect that the wettability of the innermost region has is in dictating at what We the impacting droplet is able to transition from the entrapment regime to the exterior spreading regime. An impacting droplet can not reach the exterior region unless it possesses enough excess energy to change its liquid-gas interface until it attains the advancing angle characteristic of the exterior region. All excess energy is redistributed in this surface-area change. Once the transition has occurred, the maximum spreading diameter on the outer wettability region would be independent of the inner region. Or, the same maximum diameter would be achieved as if the droplet impacted on a surface of uniform wettability θ_2 . Simply, Equation 3.2 solved either for $We_{\max}$ or $We_{\min}$ designates the dynamic domain over which entrapment occurs ($We_{\min} - We_{\max}$).

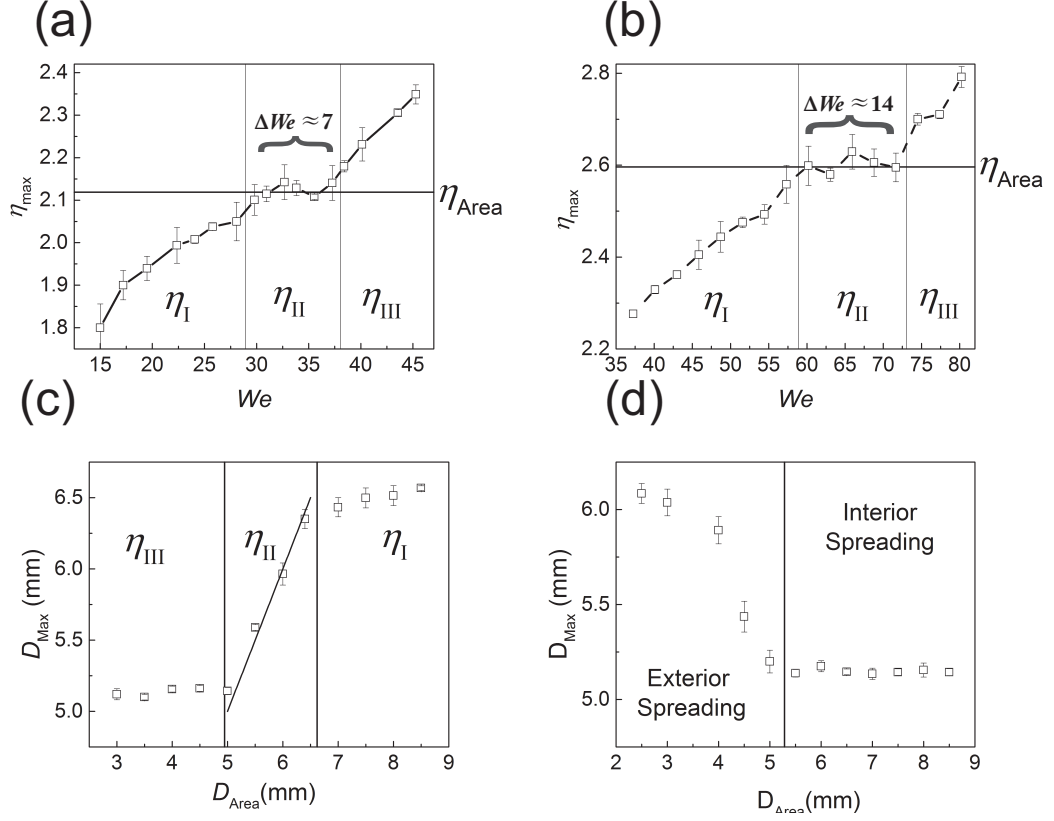


Figure 18. Droplet impact with varying We on disks with $\theta_1 = 115^\circ$ and diameter $D_{\text{Area}} =$ (a) 4.5 mm, or (b) 5.5 mm. The surrounding domain (area 2) had $\theta_2 = 147^\circ$. In both cases, the maximum spreading factor continues to increase as We rises. At a certain point (indicated by the leftmost vertical line), the droplets become trapped at the disk periphery. After another We (We_{max} , rightmost vertical line), the droplet escapes entrapment and spreads onto the exterior non-wettable region. (c) At constant $We = 77$, a droplet impacts on disks of varying diameters, where $\theta_1 = 115^\circ$ and $\theta_2 = 147^\circ$. As the inner region diameter is increased progressively, the maximum spreading factor stays unchanged until the point where the droplet becomes entrapped ($D_{\text{Area}} \approx D_{\text{Max}}$). After a larger D_{Area} (≈ 6.5 mm), the spreading D_{Max} remains relatively constant. (d) Spreading behavior for $\theta_1 > \theta_2$ and constant $We = 77$. Droplets impact on disks of varying diameters, where $\theta_1 = 147^\circ$ and $\theta_2 = 115^\circ$. As D_{Area} rises, the maximum spreading diameter continues to decrease until when the inner region is large enough for the entire spreading to occur within it.

3.4 Summary of Analysis

The above analysis can be summarized, in terms of how maximum spreading varies with We , as follows

$$\eta_{\max} = \begin{cases} \eta_{\text{I}} & We < We_{\min} \\ \eta_{\text{II}} & We_{\min} < We < We_{\max} \\ \eta_{\text{III}} & We > We_{\max} \end{cases}$$

where η_{I} is the spreading factor in Regime I (Interior Spreading), as determined from $(We + 12)\eta_{\text{I}} = 8 + \eta_{\text{I}}^3 \left[3(1 - \cos \theta_1) + 4 \frac{We}{\sqrt{Re}} \right]$. η_{II} is the spreading factor in Regime II (Entrapment), which is designated by the size of the inner disk so that $\eta_{\text{II}} = \frac{D_{\text{Area}}}{D_{\text{o}}}$. η_{III} is the spreading factor in Regime III (Exterior Spreading), as determined from $(We + 12)\eta_{\text{III}} = 8 + \eta_{\text{III}}^3 \left[3(1 - \cos \theta_2) + 4 \frac{We}{\sqrt{Re}} \right]$. $We_{\min}$ and $We_{\max}$ are the limits separating the three regimes; the respective values can be obtained from $(We_{\min} + 12)\eta_{\text{Area}} = 8 + \eta_{\text{Area}}^3 \left[3(1 - \cos \theta_1) + 4 \frac{We_{\min}}{\sqrt{Re}} \right]$ and $(We_{\max} + 12)\eta_{\text{Area}} = 8 + \eta_{\text{Area}}^3 \left[3(1 - \cos \theta_2) + 4 \frac{We_{\max}}{\sqrt{Re}} \right]$. The We range for entrapment (Regime II) is $We_{\min} - We_{\max}$.

3.5 Experimental Results

3.5.1 Spreading Regimes

We have verified the theoretical formulation by studying experimentally droplets of $D_{\text{o}} = 2.1$ mm impacting with varying velocities (likewise We) on samples with inner wettability¹ of $\theta_1 = 115^\circ$ and outer wettability $\theta_2 = 147^\circ$; see Figure 14. We begin with a circle of $D_{\text{area}} \approx 4.4$ mm,

¹All reported angles are the experimentally-observed dynamic advancing angles

corresponding to $\eta_{\text{Area}} \approx 2.1$. Figure 18a shows the three domains of spreading. First interior spreading, followed by entrapment occurring at $We \approx 30$ and $\eta_{\text{max}} = \eta_{\text{area}}$, followed by exterior spreading starting at $We \approx 37$. Expanding the diameter of the inner disk to $D_{\text{area}} \approx 5.4\text{mm}$ (corresponding to $\eta_{\text{Area}} \approx 2.6$), the same trend is observed. However, the start of entrapment in the latter case has changed from $We \approx 30$ to $We \approx 60$. Furthermore, the range of We over which entrapment occurs is larger in the case of the larger disk.

After solving for We_{max} and We_{min} using the above equations, one can determine $\Delta We = We_{\text{max}} - We_{\text{min}}$. For $\eta_{\text{area}} = 2.1$ (Figure 18a) we obtain $\Delta We = 6$, while the experimentally observed value (Figure 18a) is $\Delta We \approx 7$. For $\eta_{\text{area}} = 2.6$, we calculate $\Delta We = 14$, which is the same with the experimentally-observed value (Figure 18b). As seen from these results, there is strong agreement between the analytically-predicted values and those observed experimentally for the range of We where the liquid transitions from barely reaching the wettability contrast line to when the liquid starts spreading beyond the wettable disk. Thus, Figure 18a,b demonstrates all the main behaviors predicted by the prior analysis. For low values of We , the droplet impacts and spreads. At a specific higher value of We , the droplet becomes entrapped at the WCL, and fails to change its spreading factor. Then, at a specific higher value of We , the droplet is able to overcome the pinning at the WCL, and continues its spreading over the less wettable outer region. We conclude that the We range over which the droplet becomes entrapped increases for larger diameters (Figure 18b).

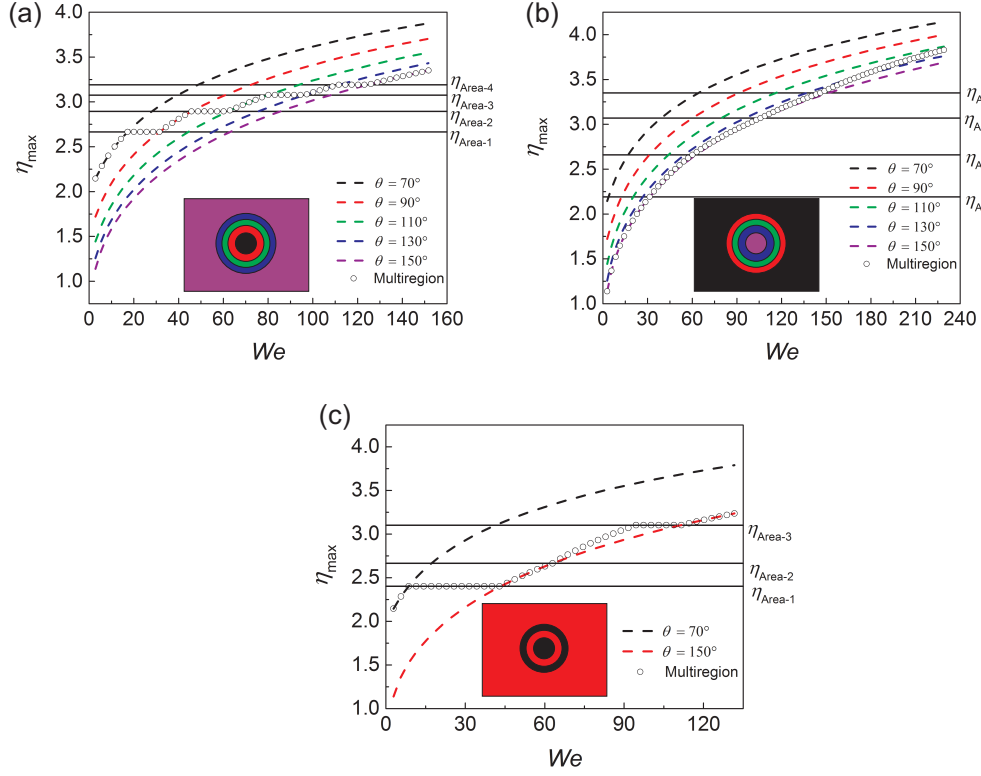


Figure 19. Theoretical plots for droplet impact on multi-region non-uniform wettability surface. (a) Radially decreasing wettability, (b) Radially increasing wettability, and (c) Alternating wettability. The dotted lines represent the theoretical trends for the spreading factor on the uniform surfaces. Empty circles (o) mark the theoretically-predicted behavior for the multiregion surface (composed of the wettabilities represented by the dotted lines) as predicted by Equation 3.13 and Equation 3.14, respectively and iteratively.

3.5.2 Insensitivity to Interior Wettable Region in Regime III

It is already apparent from Equation 3.6 and the related discussion that the spreading behavior in Regime III is insensitive to the wettability of the inner region and its area. This was corroborated by the experimental observations. We have found no variation of the maximum spreading diameter ($D_{\max}$) in the third regime, regardless of the size of the inner wettable domain. While this behavior is hinted in Figure 18a,b, we verify this by impacting droplets of constant $We = 77$, on disks of varying diameter, D_{area} .¹ As seen in Figure 18c, at lower values of D_{area} (≤ 5.0 mm), the observed $D_{\max}$ does not change. In these cases, the small wettable domain cannot arrest the liquid, which extends beyond the WCL and eventually ceases, before it starts receding. For larger D_{Area} (> 5.0 mm), the droplet becomes entrapped (Regime II), and $D_{\max} = D_{\text{Area}}$. Beyond D_{Area} (~ 6.5 mm), the spreading happens entirely within the inner (wetable) region and thus, the maximum spreading diameter varies with We .

3.6 Impact on non-wettable disk surrounded by wettable domain

In all cases considered up to now, we considered that $\theta_1 < \theta_2$. We now explore situations where the reverse is true, i.e. $\theta_1 > \theta_2$. We begin by physically interpreting such circumstances, where a spreading droplet is impacting centrally on an area that is more phobic than the outer region. Intuitively, and based upon the above energy analysis, the impacting droplet would never experience an entrapment regime. If the droplet were to spread into the exterior region, the contact angle would have to transition from a higher energy state to a lower energy state,

¹ $\theta_1 = 115^\circ$ and $\theta_2 = 147^\circ$

which is energetically favourable, and thus can occur spontaneously. The ΔE_{bar} term for such cases would be non-existent. In essence, there would be only two regimes of spreading, interior and exterior. For interior spreading, the maximum spreading diameter can be calculated by solving the aforementioned equation,

$$(We + 12)\eta_{\text{I}} = 8 + \eta_{\text{I}}^3 \left[3(1 - \cos \theta_1) + 4 \frac{We}{\sqrt{Re}} \right] \quad (3.8)$$

The maximum spreading diameter in the exterior spreading regime can be calculated from Equation 3.5 without the ΔE_{bar} , with all other terms as previously defined

$$E_{\text{S1}} + E_{\text{K1}} = E_{\text{S2}} - \sigma \frac{\pi}{4} D_{\text{Area}}^2 \cos \theta_1 - \sigma \frac{\pi}{4} (D_{\text{max}}^2 - D_{\text{Area}}^2) \cos \theta_2 + W_{\text{losses}} \quad (3.9)$$

As seen, Equation 3.9 includes terms dependent on both θ_1 and θ_2 . Thus, in the case where $\theta_2 < \theta_1$, the wettability of the inner region influences spreading in the exterior region. In contrast, Equation 3.6 for $\theta_2 > \theta_1$ had no dependence of θ_1 . We verified our analysis experimentally by impacting water droplets on hydrophobic disks surrounded by a hydrophilic region. We see from Figure 18d, in the case of constant We and varying circle sizes, the wettability of the inner region does affect maximum spreading diameter in the exterior spreading regime. As the diameter of the inner region (with $\theta_1 = 147^\circ$) increases, the maximum spreading diameter declines. This effect can be mathematically observed in Equation 3.9, which includes $\theta_1 = 147^\circ$, in turn influencing the calculation of the maximum spreading diameter.

3.7 Spreading over multiple concentric rings of varying wettability

We now expand the basic configuration Figure 14 by considering surfaces with n - annular regions of varying wettability (*i.e.*, concentric annuli). Adopting the previous approach to accommodate such circumstances, we begin by modifying Equation 3.5 to account for n annular regions whose wettability declines with radial distance from the point of impact, *i.e.* $\theta_i < \theta_{i+1}$. The modified equation takes the form

$$E_{S1} + E_{K1} = E_{S2} + E_{n\text{-wet-dry}} + W_{\text{losses}} + \Delta E_{n\text{-bar}} \quad (3.10)$$

where $E_{n\text{-wet-dry}}$, and $\Delta E_{n\text{-bar}}$, respectively, take into consideration the surface energy change and cross-over energy in the n -regions. We then obtain

$$E_{n\text{-wet-dry}} = \frac{-\sigma\pi}{4} \sum_{i=1}^n (D_i^2 - D_{i-1}^2) \cos \theta_i \quad (3.11)$$

and

$$\Delta E_{n\text{-bar}} = \frac{\sigma\pi}{4} \sum_{i=1}^n D_i^2 (\cos \theta_i - \cos \theta_{i+1}) \quad (3.12)$$

with $D_0=0$, $D_n = D_{\text{max}}$ and D_1 to D_n represent the diameters (known by design) of the different wettability regions. Combining Equation 3.11 and Equation 3.12 with Equation 3.10, rearranging and simplifying, we deduce

$$E_{S1} + E_{K1} = E_{S2} - \sigma \frac{\pi}{4} D_n^2 \cos \theta_{n+1} + W_{\text{losses}} \quad (3.13)$$

where θ_{n+1} is the wettability of the outermost domain (surrounding the largest ring). As seen from Equation 3.13, the same outcome as for two wettability regions (with $\theta_1 < \theta_2$) is deduced. The droplet maximum spreading diameter is dependent only on the wettability of the outermost region (θ_{n+1}). Note, that this extrapolation assumes that the spreading droplet crosses all the cross-over energies and reaches the outermost regime. In order to determine whether a droplet is able to do that or not, one would have to carry out an iterative check for each of the areas, as demonstrated earlier.

Lastly, we expand Equation 3.9 for n -region spreading with $\theta_i > \theta_{i+1}$,

$$E_{S1} + E_{K1} = E_{S2} + \frac{-\sigma\pi}{4} \sum_{i=1}^n (D_i^2 - D_{i-1}^2) \cos \theta_i + W_{\text{losses}} \quad (3.14)$$

where $D_0 = 0$ and $D_n = D_{\text{max}}$.

Equation 3.13 and Equation 3.14 are derived for situations where, respectively, the wettability is monotonically decreasing radially (e.g., $\dots > \theta_3 > \theta_2 > \theta_1$) or increasing (e.g., $\dots < \theta_3 < \theta_2 < \theta_1$). These equations do not account for circumstances where the concentric circles alternate between lower and higher wettabilities (e.g., $\theta_3 > \theta_2 < \theta_1$). In order to solve for such circumstances, these two equations would have to be solved in conjunction, and iteratively. In Figure 19 we present theoretical plots for: (a) continuously decreasing wettability (Equation 3.13), (b) continuously increasing wettability (Equation 3.14), and (c) alternating (Equation 3.13 and Equation 3.14). In the case of continually decreasing wettability, Figure 19a, the maximum spreading diameter increases as function of the We , becomes entrapped until the

corresponding We is high enough to continue the spreading phase onto the exterior region, at which point, the fluid spreads and becomes entrapped once again, and so forth. Thus, the maximum spreading diameter of the spreading droplet will either lie in the entrapped region or on the trendline of a uniform material. In the case of continually increasing wettability, Figure 19b, the spreading droplet will initially lie on the trendline of the inner-most region. Once the fluid comes in contact with the first outer region, the spreading profile will deviate into an intermediary value that lies between the trendline of the first and second region. This is a predicted behavior, due to the fact that the spreading under such circumstances is a combination of both wettabilities (see Equation 3.9). As the spreading continues onto more and more regions, the spreading behavior will continue to deviate from anyone specific uniform trendline, due to the fact that the spreading is a combination of all the wettabilities of the encountered region (Equation 3.14). In the case of alternating wettability, Figure 19c, the spreading behavior is a combination of both aforementioned cases. The fluid becomes entrapped when encountering a lower wettability (higher contact angle) ring, while its spreading continues as the fluid encounters higher wettabilities with distance from the point of first impact.

CHAPTER 4

FROST REMOVAL VIA SUPERHYDROPHOBIC ELECTRICALLY-CONDUCTIVE SURFACE COATINGS

This chapter is reprinted with permission from Elsharkawy, M., Tortorella, D., Kapatral, S., & Megaridis, C. M. (2016). Combating frosting with Joule-heated liquid-infused superhydrophobic coatings. *Langmuir*, 32(17), 4278-4288. Copyright 2016 American Chemical Society

4.1 Motivation and Background

Frost formation is a ubiquitous phenomenon observed when suitable environmental conditions of pressure, temperature and humidity are met. The pervasive nature of frost is detrimental to the functionality and performance of modern mechanical and electrical systems (71) (*e.g.*, aircraft, wind turbines, power transmission lines, etc.). Thus, there is an ever-present need to develop surfaces capable of retarding, or if possible, preventing frost formation and adhesion. Recent efforts have shifted to the functionalization of bio-inspired materials capable of extreme water repellency (*i.e.*, superhydrophobic (SHPO))(72). Superhydrophobicity is achievable by designing low-energy surfaces also possessing micro/nanoscale texture. The structure's hydrophobic chemistry, in conjunction with the ability to entrap air pockets, result in water contact angles above 150° and sliding angles below 10° . In addition to impeding frost formation(73), such materials have been shown to help facilitate droplet coalescence and shedding

(74), jumping (75), as well as trampolining(21). A key shortcoming of such surfaces is their tendency to become severely compromised due to a transition into the impaled Wenzel state when exposed to high-humidity frosting conditions (76). This causes increased adhesion due to ice crystals anchoring on the surface texture, and thereby hampering any defrosting efforts (77). An alternative anti-frosting approach is the use of slippery lubricant-infused porous (SLIP) surfaces, which possess ultra-low contact angle hysteresis. SLIP surfaces impede frost formation by taking advantage of oil-water immiscibility, allowing small condensate droplets to slide off the surface before freezing, and presenting nucleating droplets with an atomically smooth surface to nucleate upon(78). These combined properties result in reduced nucleation rates. The performance of SLIP surfaces is limited by oil drainage caused by capillary forces arising from dendritic frost on frozen droplets (79) and cloaking (80). Furthermore, SLIP surfaces require a calculated design of texture-lubricant pair and external oil sources in order to retain/replenish the depleting lubricating liquid upon exposure to repeated frosting-defrosting cycles.

Both of the above-mentioned approaches are passive; they rely solely on surface wettability to mitigate frosting. Despite extensive research on passive approaches(81), frost accumulation is unavoidable over prolonged periods of sub-freezing exposure. Edge effects (82) and surface defects (75) result in local reductions of energy barriers, causing heterogeneous or homogeneous nucleation, thereby initiating a propagating freezing front leading to frosting of the entire surface (83). Hence, there is a need for surfaces which not only passively delay frost formation, but can also actively remove the formed frost.

Research has been performed on electrothermal methods utilizing Joule heating by passing electrical current through conductors for frost removal (84). Only few studies explored self-heating, carbon-based (polymeric) nanomaterial coatings as an active approach to address the frosting problem(85; 86). We report spray-deposited, electrically-conductive, superhydrophobic nanocomposite coatings that can actively mitigate condensation frosting on demand by Joule heating. The coatings are comprised of a fluoroacrylic-carbon nanofiber (CNF) dispersion sprayed on glass slides to form conductive superhydrophobic coatings after drying (69; 70).

The present coatings are not only superhydrophobic, but double up as heating elements (by providing skin heating), helping to defrost surfaces by directing the supplied heat to the substrate-frost interface, and in turn, making it easier to partially melt and dislodge the frost. The aforementioned surfaces provide a low-cost, light-weight, energy-saving alternative by eliminating the need for external heating elements or systems that can only locally heat the frost-air interface instead of the substrate itself. Expanding upon our current capabilities, we infuse our nanostructured coatings with lubricants, in effect producing electrically-conductive SLIP surfaces. This novel material makes use of the passive mitigation properties inherent in SLIP surfaces, in conjunction with the demonstrated Joule heating properties of the coating that intervenes between the underlying solid surface and the formed frost.

We first utilize condensation frosting to demonstrate the failure (in preventing frost buildup) of SHPO and SLIP surfaces in high relative humidity environments over prolonged periods (> 120 minutes). We analyze the passive frosting delay on the SHPO coatings as well as on the SLIP surfaces. Secondly, after frost formation, we demonstrate the active capabilities of both

types of materials. Two mechanisms of active defrosting are demonstrated: end-of-cycle and periodic thermal defrosting. In addition, we examine experimentally and analytically the role of the impregnating lubricant of a SLIP surface on the heat transfer across the material/frost interface. The experimental results are interpreted by drawing analytical parallels between the current system and heat diffusion through 1-D layers of the impregnating lubricant and the frost. The heat equation with appropriate boundary conditions is solved and the results are compared with the experimental findings.

The present materials add a new dimension to existing surface technologies by combining passive anti-frosting approaches with active frost-removal techniques to combat frost formation over prolonged time periods. Coating application offers a facile, scalable, substrate- and geometry-independent approach for developing functional materials with superior long-term anti-frosting properties. It is also noted that the present materials and techniques can be readily adapted in anti-icing efforts.

4.2 Experimental Section

4.2.1 Dispersion Preparation

The coating formulation has been previously reported in Refs. (69; 70), and is described only briefly below for completeness. In a typical batch, approximately 0.3 g of carbon nanofibers (PR-24-XT-HHT; Pyrograf III, Applied Science Inc., USA) were treated with 14 g of acetic acid (ACS reagent, ≥ 99.5 wt.%, Sigma Aldrich) and 28 g of acetone (ACS reagent, ≥ 99.5 wt.% Sigma-Aldrich) in a vial. The nanofiber dispersion was then stabilized by probe sonication (750W, 13 mm probe dia., 40% amplitude, 20KHz frequency, Sonics and Materials, Inc., Model

VCX-750) for 1.5 min. In a second vial, fluoroacrylic copolymer (PMC, 20 wt.% in water, Capstone ST-100, DuPont) was diluted with 2g acetic acid and 4g acetone. The contents of the two vials were mixed and bath sonicated for 10 minutes to form a ready-to-spray dispersion.

4.2.2 Materials

Glass slides ($7.5 \times 2.5 \times 0.1$ cm) were cut to 30mm in length and had copper tape electrodes (2.5×40 mm) applied to both ends. The dispersion was then sprayed on top of the glass/electrode sample. This resulted in a coated surface of about 25×25 mm. Power supply leads were applied to the 10mm portion of the protruding electrodes.

4.2.3 Spraying

Spraying was done using an air brush (Paasche, VL-Set Siphon feed, 0.73 mm spray nozzle, operated at 40 psi pressure) from a distance ≈ 15 cm and dried at 80°C in a convective oven for two hours to completely vaporize the solvents.

4.2.4 Coated Surface and Frost Characterization

4.2.4.1 Weight and Electrical Conductivity

Each glass slide was weighted before and after spraying to calculate the mass deposited using a precision scale (LE26P, Sartorius AG). Using a multimeter (AKTAKOM AMM-3031) and the two point measuring method, resistance was recorded for each sample: immediately after drying, before frosting took place, and after defrosting was complete. Resistance measurements immediately prior and after frosting were performed on the mounted samples by way of the cables connected to the power supply.

4.2.4.2 Wettability

Contact angles were measured using $7\mu\text{l}$ water droplets viewed by a digital camera (Mintron MHD-13MG5SH-D) coupled with a high-magnification lens (OPTEM Zoom 100). The images were acquired by a computer software (Kinovea), that allows for real-time angle measurements. For every new measurement, droplets were placed at a different location on the coating; five different measurements were made on each sample to produce each value.

4.2.4.3 Infusing

SHPO sprayed glass samples were infused with varying lubricants. Infusement was performed via controlled dip coating using a Vexta Stepping motor PX245-01AA and VXM stepping motor control. Ascend and descend speeds of the process were equivalent and designated to ensure the dominance of interfacial forces. The lubricants used to infuse the SLIP surfaces were Krytox (Dupont), and PMX-200 (CST Viscosity 100, Krayden Inc).

4.2.4.4 Frosting Setup

An environmental test chamber (Espec SH-641) with both temperature and humidity control was used. Inside the chamber, a Peltier cell (TeTech, CP-061) was mounted on a rotary stage. The samples were placed on top (vertically or horizontally, as needed) of the Peltier cell. To improve thermal contact, thermal paste (OT-201, Omega Engineering Inc.) was applied underneath the glass samples. Over the thermal paste and beneath the samples, electrically insulated thermocouples were placed (Type K, OMEGA). The thermocouples were connected to a digital acquisition system (OM-DAQ-USB-2400, OMEGA) to record temperatures at a frequency of 4 Hz. The electrodes hanging from the samples were extended to the outside of the chamber and

from there to a regulated DC power supply (Sorensen DCR 40-13B, AMETEK Programmable Power, Inc.) whose voltage varied between 0-40 V.

4.2.5 Frosting Procedure

After each sample was properly mounted, the chamber temperature was set to 10° C and humidity to 0% RH, with the Peltier being turned off. In all cases, except in those where frost visualization was necessary, the sample was mounted horizontally. Once the chamber had reached thermal equilibrium, the Peltier cell was turned on and cooled to $-7.5(\pm 0.5)^{\circ}$ C. After that, the chamber humidity was raised to 80% RH at which point frosting conditions became favorable. These conditions were maintained for however long each experiment was carried out (10 min, 15 min, 120 min, 300 min, etc.). At the conclusion of the frosting period, the humidity was turned off, and the chamber was cooled to -2° C. Upon thermal stabilization of the chamber, the Peltier was shut down and allowed to reach ambient temperature. This step brought the entire environment to a uniform temperature. This procedure was followed to impose the boundary conditions listed in our analysis (see Figure 25).

4.2.5.1 Frost Mass Measurement

Weight measurements were performed after placing the sample on a completely horizontal (eliminating the need for adhesive) Peltier and allowing the sample to accumulate frost for the allotted time. Afterwards, the sample was quickly removed from the chamber and immediately weighed (Sartorius LE26P). The frost-free samples had also been weighed before placement in the chamber. The difference between the post and pre-frosting measurements defined the mass of the accumulated frost.

4.2.6 Joule Heating

The heating was performed by applying constant DC voltage via an external power supply (Sorensen DCR 40-13B). Alligator clips connected the power supply to the electrodes on the sample.

4.2.7 Frost Visualization

Video recording was performed using a DSLR digital camera (Canon EOS T3i). During experimentation, all samples were maintained at 0 ° angle with respect to the horizontal. For visualization purposes, they were rotated by 90° (vertically) to be visible through the chamber window.

4.3 Results and discussion

4.3.1 Material Element

The spray-deposited coating consists of carbon nanofibers dispersed in a fluoroacrylic copolymer (PMC, DuPont, 20 wt.% dispersion in water, Capstone ST-100) matrix. The PMC copolymer serves as a low surface-energy material, providing the chemical hydrophobicity, while the CNFs provide hierarchical micro/nano structure and electrical conductivity when deposited in concentrations above the percolation limit. This combination of low surface energy and hierarchical roughness leads to water contact angles of about 160°, well within the superhydrophobic regime.

The method of spray deposition (Figure 20a) offers several advantages. The first is the accessibility of tools and machinery already present in manufacturing facilities where spray

processing is common. This translates to reduced costs compared to photolithographically-produced superhydrophobic surfaces requiring 3D molds. Secondly, the approach has repair capabilities (Figure 20b). After the surface wears, or suffers local damage (*e.g.*, scratch), it is possible to restore it to its original state by simply spraying an added layer on the damaged area. The added layer functions to return the surface’s non-wettable properties, while at the same time further enhancing its electrical conductivity.

The coating’s conductivity can be fine-tuned via the mass added (Figure 20c), which is controlled by the number of spray passes over the substrate. By increasing the total mass deposited, there is an improvement in the electrical conductance of the material (*i.e.*, lower resistance). This is attributed to the increased CNF amount deposited, effectively improving the percolation network (Figure 20b), and raising electrical conductance. Furthermore, coating mass addition causes a parallel increase in the contact angle of water on the surface (*i.e.*, more hydrophobic), Figure 20d. However, after a critical add-on mass of 0.3 mg cm^{-2} , the CA remains relatively constant at about 160° , even as more mass is added. No such bound was observed for the electrical conductance (Figure 20c). Due to limitations of our experimental setup, we utilized only surfaces with sheet resistances of $40 - 100 \Omega$ (add-on levels of $0.5 - 1.1 \text{ mg cm}^{-2}$) in our experiments.

4.3.2 Prolonged Frosting on Passive Surfaces

SHPO and SLIP surfaces are known to passively delay frost formation in high relative-humidity environments over relatively short periods (5 minutes(87), 9 min(88), 20 – 30min(89; 90; 79), 60 min(91), 100 min(78; 92)) of exposure. Albeit via different mechanisms, both types of

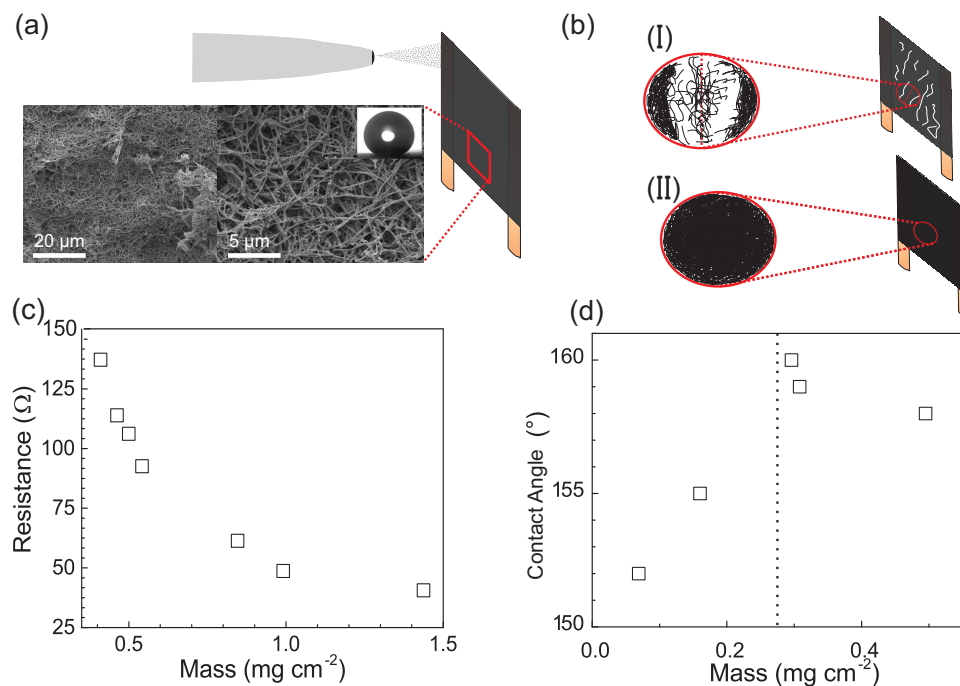


Figure 20. (a) A dispersion comprised of carbon nanofibers (CNF) and a fluoroacrylic copolymer (PMC) in solvents is sprayed onto a plain glass slide with copper electrodes attached. The end result is a porous re-entrant (SEM images in bottom) and superhydrophobic (inset image) coating. (b) Spray deposition allows for repair of damaged (*e.g.*, scratched) surfaces (**I** to **II**). The add-on mass allows for tunability of physical properties, such as electrical resistance (c) and wettability (d). (c) Graph of electrical resistance vs. coating mass deposition. Increasing add-on mass results in lower resistance. This is attributed to the continued enhancement of the percolation network with the added deposition of CNFs. (d) Graph of water contact angle vs. coating mass deposition. As coating mass rises, there is a parallel increase in contact angle until a critical mass of about 0.3 mg cm^{-2} , above which the contact angle remains relatively constant.

surfaces act to reduce the frost nucleation rate, thus delaying frost buildup. Even after numerous studies performed on frost delay and prevention, there is a lack of work addressing the behavior of passive surfaces under prolonged (> 120 minutes) exposure to high relative-humidity frosting environments. We begin addressing this gap by analyzing the behavior of such surfaces when exposed to prolonged frosting periods (300 minutes).

Following the same experimental protocol (Figure 21a), four types of samples were tested: Untreated glass, sprayed SHPO, Krytox-infused SLIP and PMX-200 infused SLIP. After 300 minutes of continuous frosting, we observed no difference in the visual appearance (Figure 21b) of the four samples, which were all covered in thick frost. Furthermore, the total mass of frost accumulated on each sample was found to be the same, a point to be elaborated on later. The aforementioned results can be interpreted in light of the unique delay mechanisms of each surface. SHPO surfaces decrease frost nucleation by reducing the number of nucleation sites available. These surfaces often present a reduced contact area (due to the presence of trapped air in the texture), and from nucleation theory, a proportionally lower nucleation rate(25). But once the first layer of frost has formed on the surface, the continuous passive delay capabilities cease to matter, and frost nucleation is independent of the underlying material, which is no longer seen by the ambient vapor (which feeds subsequent frost growth). An analogous argument can be made for SLIP surfaces(79). Once the first frost layer is formed, the passive nature of the surface (due to its atomic-level smoothness) and water-oil immiscibility cease to be of importance, as the frost nucleation rate is influenced only by the top frost layer, which masks the underlying material, presenting the humid ambient environment with a thin layer of frost to nucleate upon.

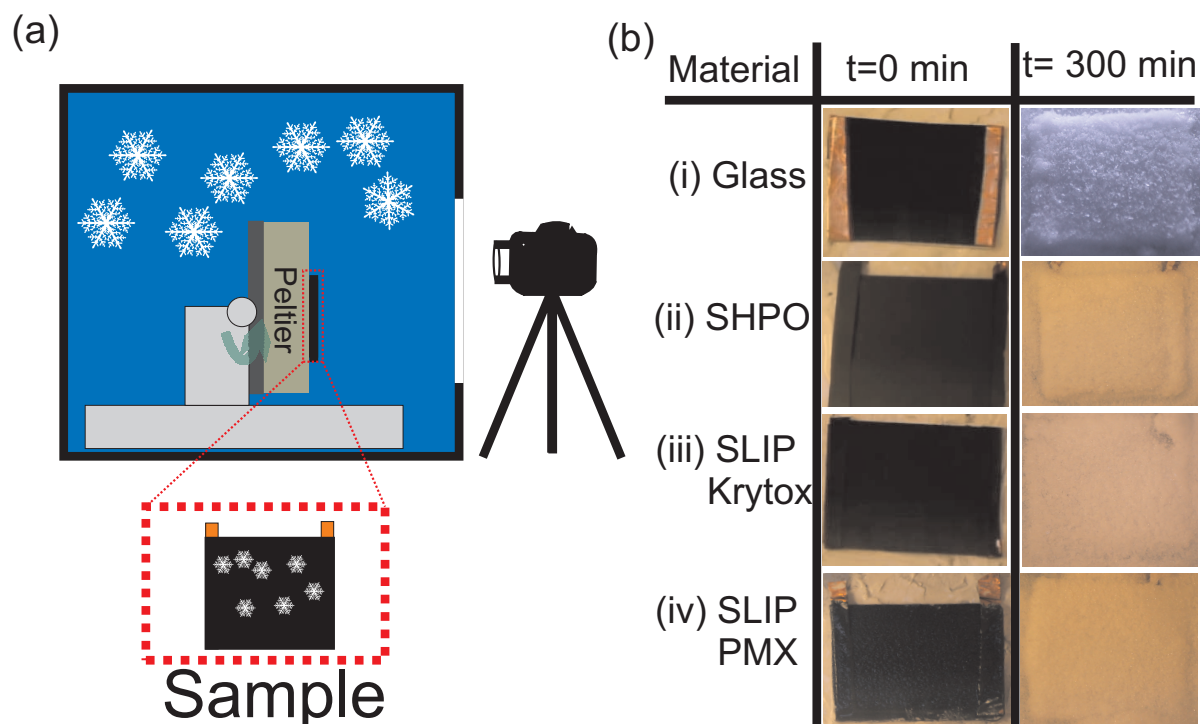


Figure 21. (a) Schematic of experimental setup. The sample (in black) is attached via thermal paste to a Peltier with rotating capabilities. The assembly is located within a humidity- and temperature-controlled chamber (see experimental section). Visualization is performed by a camera aimed at the sample through a transparent window. DC voltage is applied to the sample electrodes via an external power source. (b) Various surfaces (i-iv) are exposed to high relative-humidity frosting conditions for prolonged periods. After 300 minutes of continuous frosting, there is no discernible difference in the visual appearance of any of the samples (right column). In addition to the similarities among plain glass, SHPO and SLIP, there is no difference in behavior between the two SLIP surfaces (Krytox, PMX-200). This was consistent for all tests performed with these oils.

As time passes and frost builds up (Figure 22a-d), any passive delay capabilities that initially existed, become gradually less prominent, until they are entirely negligible (infinite time). For short periods of frosting (0-60 minutes), there is a significant, but decreasing, difference in the amount of frost accumulated on the SHPO and SLIP surfaces when compared to the glass substrate. At such short time scales, the first layer of frost has yet to form, thus the passive characteristics of the SHPO and SLIP persist.

Observing the frosting behavior of the various samples in the early period (Figure 23a), and utilizing the black/white contrast (between the underlying dark surface and the overlying frost) to quantify frost area coverage vs. time (Figure 23b), we compared the different samples during the early stages of frosting. In the case of glass, the backside of the slide was covered with thin black plastic tape to create a dark background against which frost could be discerned with accuracy. Naturally, the tape introduced added thermal resistance to the cooling of the surface by the underlying peltier. For this reason, the surface of the glass slide with the tape would be at a slightly higher temperature compared to a similar glass slide mounted on the peltier without it (the latter was impractical, since it provided no contrast between the frost and the transparent glass surface). Consequently, the measured frost area coverage for glass provides a lower bound for the coverage of the control sample, where only the mounting paste was present underneath the glass slide. The results in Figure 23b show the early frost coverage of glass to be consistently higher than all coated surfaces. Between the two SLIP surfaces, frost area coverage was consistently higher for the PMX-200 case.

In separate experiments, we also measured the frost mass accumulated on the different samples over various time intervals. For these tests, the dark background on the glass surface was not needed, so the uncoated glass was mounted on the peltier plate without the black background tape. The results are presented in Figure 23c by percentage of frost mass on a coated sample differing from the frost mass collected on uncoated glass during the same time period (*i.e.*, a relative change of 0 % indicates similar behavior). We see that for the early frosting period, glass collects the highest amount of frost, followed by SHPO, and the two SLIP samples. The same trend was seen for the frost coverage rates (Figure 23b). As time progresses, (60-300 minutes) the difference in frost mass collected on all samples becomes negligible. By around 180 minutes, an almost identical amount of frost has been collected on all four samples. Thus, the key distinction among the surfaces lies in the early stages of frosting (up to 60 min). This leads one to conclude that for prolonged periods (several hours) of frosting exposure, there is no discernible difference between the samples, and thus no benefit in having SHPO and SLIP surfaces over plain glass material.

4.3.3 Defrosting by End-of-Cycle Joule Heating

As shown above, the leading passive approaches in the literature have no success in combating long-term frost formation and accumulation. Instead, an active (*i.e.*, energy-consuming) approach must be utilized to avert frost over prolonged time periods. The present methodology takes advantage of the high electrical conductivity of the present coatings and facilitates the study of two previously unaddressed landscapes in active defrosting: 1) electrically-conductive SHPO materials, 2) electrically-conductive SLIP surfaces. The technique utilizes surface-skin

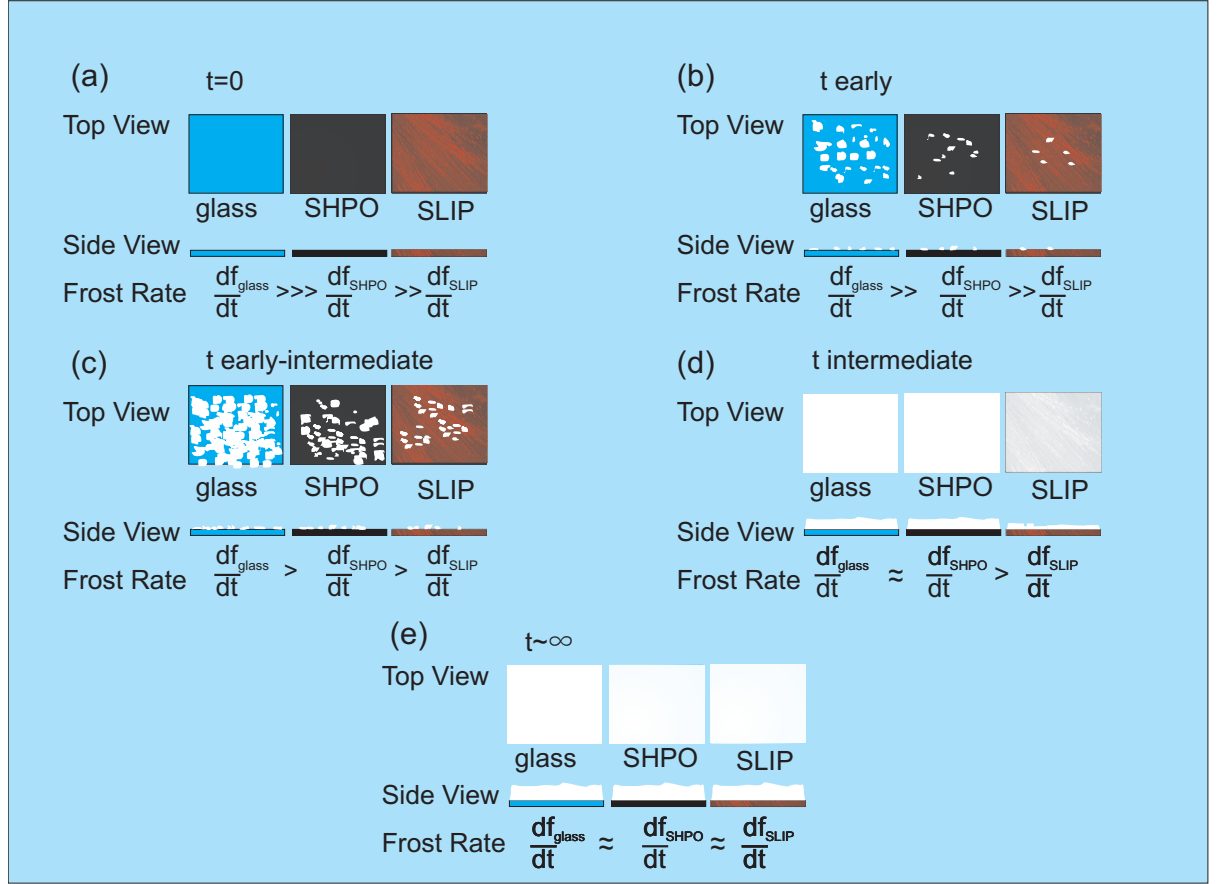


Figure 22. Frost formation on three types of surfaces. (a) During the initial frosting stage (marked $t=0$), the intrinsic properties of each material are dominant, thus having a strong effect on the rate of frost growth ($\frac{df}{dt}$). SLIP surfaces display the strongest delay in early stage frosting, followed by the SHPO material, and the uncoated glass. As time progresses (b)-(c), frost begins to form on the samples, affecting the subsequent frosting rate. (d) After some time, a uniform layer of frost has formed on the SHPO and glass substrates. From this time on, the frost growth becomes independent of the underlying material (assuming a truly uniform layer has formed) and the frost growth on glass and SHPO substrates are equivalent. SLIP surfaces have yet to form a uniform frost layer, thus the growth rate is still affected, albeit at a lesser extent, by the underlying material. (e) Once enough time has passed, all surfaces, regardless of their frost-delay capabilities, get covered by a thick frost layer, which negates their passive capabilities, and results in similar frost growth rates from this point forward.

heating, and thus can be applied only with electrically insulating substrates (glass in the present case). As in the previous section, four types of samples (uncoated glass, SHPO, Krytox SLIP, PMX-200 SLIP, all oriented vertically) were exposed to identical frosting/humidity conditions (10°C, 80% RH), thus ensuring that an equivalent amount of frost accumulated on all samples (maintained at -7.5°C) after 300 mins. Skin-heating was then activated at a power density of 1.5 W cm⁻². As seen in the examples of Figure 24a, after approximately 3.5 minutes of heating, the heated samples became clean of frost, which melted from the bottom up as the heat input persisted. The Joule heat Q released by the coating is

$$Q \propto Pt \propto I^2 Rt \quad (4.1)$$

where P is the power supplied over time t . In the present case, Q is consumed mainly to melt the accumulated frost, which is the same for all samples (Figure 23c). Thus, for constant Q , one expects a $t \propto 1/P$ correlation. To confirm this, we repeated the same defrosting experiments ($t = 300$ minutes), but varied the supplied power density. As seen from Figure 24b, the t vs. P relationship predicted by Equation 4.1 (red curve) is generally confirmed. The slight deviation is attributed to differences in dissipative heat transfer (through the substrate) which changes with applied power level, sample-edge effects and inaccuracies in determining the instant when defrosting is completed.

It is also worth noting that at fixed power, there is no difference in time to defrost between the SHPO and the SLIP surfaces. All the defrosting times were found to be comparable to one another. We expand upon this observation in the following section.

4.3.4 Role of Impregnating-Fluid Properties

Due to many scientific and industrial applications that can be contrived from SLIP surfaces, there is a need to understand and analyze the underlying physical forces governing the behavior of these materials. We aim to add to the literature by studying the role of the impregnating lubricant in controlling heat transfer through the SLIP interface. As seen from Figure 24a, there is little to no difference in the defrosting behaviors of the SHPO and the SLIP surface (similar behavior observed for varying SLIP surfaces). This is non-intuitive, considering the varying thermal properties of the lubricants used herein, Table II. Henceforth, we will refer to the impregnating lubricant as impregnating fluid.

To understand the role of the impregnating fluid, we draw parallels between our system and heat transfer through a simple 1D composite system, Figure 25a, consisting of a geometrically textured solid, an impregnating fluid (air or liquid), and a frost layer of constant thickness (no ongoing phase change). For simplicity, we assume the underlying structure of the coated substrate to be a laterally-repeated porous rectangular pattern. We assume the solid structure to be the same for SHPO and SLIP surfaces, thus there is only a need to analyze what is occurring at the pores, where fluid impregnation occurs. In addition, we assume the impregnating fluid to not over-impregnate, remaining confined within the interstitial regions only. Let us consider a typical pore of width a and depth b , impregnated with a fluid of known density (ρ_f), thermal

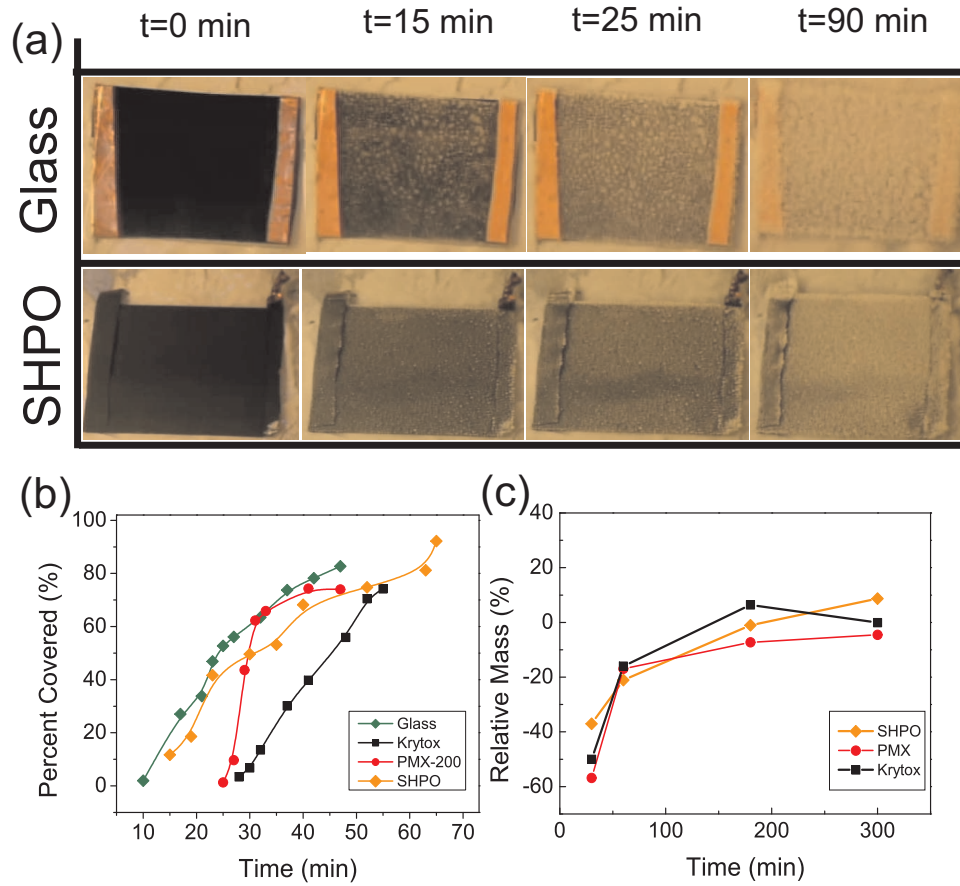


Figure 23. (a) Images of uncoated-glass and SHPO samples during the early stages of frosting (< 90 min). During this period, there is a discernible difference in the visual appearance of these samples. To track frost accumulation on the glass surface, the backside of the slide was covered with thin black plastic tape to create a dark background against which frost could be discerned with accuracy. SLIP surfaces demonstrated the least amount of frost growth, followed by SHPO, and then glass. (b) Surface coverage by frost vs. time by performing a black/white contrast analysis of the previous images. In all cases, black marks the underlying surface and white marks the overlying frost. All samples reached 100% frost coverage by 90 minutes. The time period after complete frost coverage corresponds to comparable frost nucleation for all samples. To test this hypothesis we measured the mass of frost accumulated on each sample with time (c). Frost mass is plotted relative to mass accumulated on plain glass. Prior to the frost-layer formation, there are significant differences among the samples in frost mass collected. As time progressed, the differences became less significant, thus indicating very similar frosting behaviors.

conductivity (k_f) and specific heat (c_f), with a layer of frost of thickness d formed on top of the pore. The entire system is initially in thermal equilibrium at a temperature T_a . Mimicking the self-heating behavior of the material, we assume that the bottom of the pore ($x = 0$) is instantaneously heated and maintained at a constant temperature T_h , such that $T_h > T_a$. The above situation can be represented via the following system, which applies in the limit $a \gg b$

$$\alpha_f \frac{\partial T_f^2}{\partial x^2} = \frac{\partial T_f}{\partial t}, \quad \text{when } 0 \leq x < b, t > 0 \quad (4.2)$$

$$\alpha_{ice} \frac{\partial T_{ice}^2}{\partial x^2} = \frac{\partial T_{ice}}{\partial t}, \quad \text{when } b \leq x < b + d, t > 0$$

with boundary conditions,

$$\begin{aligned} T_f &= T_h & \text{at } x = 0, t > 0 \\ T_f &= T_{ice} & \text{at } x = b, t > 0 \\ k_f \frac{\partial T_f}{\partial x} &= k_{ice} \frac{\partial T_{ice}}{\partial x} & \text{at } x = b, t > 0 \\ k_{ice} \frac{\partial T_{ice}}{\partial x} + h_{air-ice}(T_{ice} - T_a) &= 0 & \text{at } x = b + d, t > 0 \end{aligned} \quad (4.3)$$

and initial condition,

$$T_f = T_{ice} = T_a \text{ for } t = 0, 0 < x < b + d \quad (4.4)$$

where α_f and α_{ice} are the thermal diffusivities of the fluid and frost, respectively. $T_f(x)$, $T_{ice}(x)$ are the local temperatures of the fluid and frost, respectively. In addition, $h_{air-ice}$ is the heat

transfer coefficient at the air/ice interface. We note, $h_{\text{air-ice}}$ is not known for our system, and was taken to be a fixed value for this analysis. The above system can be homogenized and solved using the procedure outlined in Ref.(93) The system was solved using the properties of the two impregnating fluids (*i.e.*, Krytox, PMX-200). For the case of SHPO surfaces, air was taken to be the impregnating fluid. A graph of the heat flux (q') difference at the fluid-frost interface ($x=b$) as a function of time is presented in Figure 25c, which shows little to no difference between the two impregnating fluids. These predictions are counter-intuitive, especially when considering the disparate thermal conductivities and diffusivities of the two lubricating fluids (see Table II). We note, the thermal conductivity of ice varies, but for simplicity we utilized the value listed in ref.(94).

Seeking to expand our understanding, we consider the total thermal resistance (Figure 26a) of the composite system,

$$R_t = \frac{b}{Ak_f} + \frac{d}{Ak_{ice}} \quad (4.5)$$

where R_t is the total thermal resistance and A is the contact area, which is assumed to be the same for both the fluid and the frost layer. Letting $b=1\mu\text{m}$, $d=3\text{mm}$, and substituting for the varying thermal conductivities of the fluids (Table II), we produce the data in Table III, which provides a comparison of the total thermal resistances for the three impregnating fluids (air for SHPO, Krytox or PMX-200 for the SLIP surfaces). For the sake of simplicity, we compare the calculated total thermal resistances with the thermal resistance of air. We see that for the above-specified values, there is a maximum 1.7% difference among the three impregnating fluids. As the value of b is increased, so does the difference in total thermal resistances among

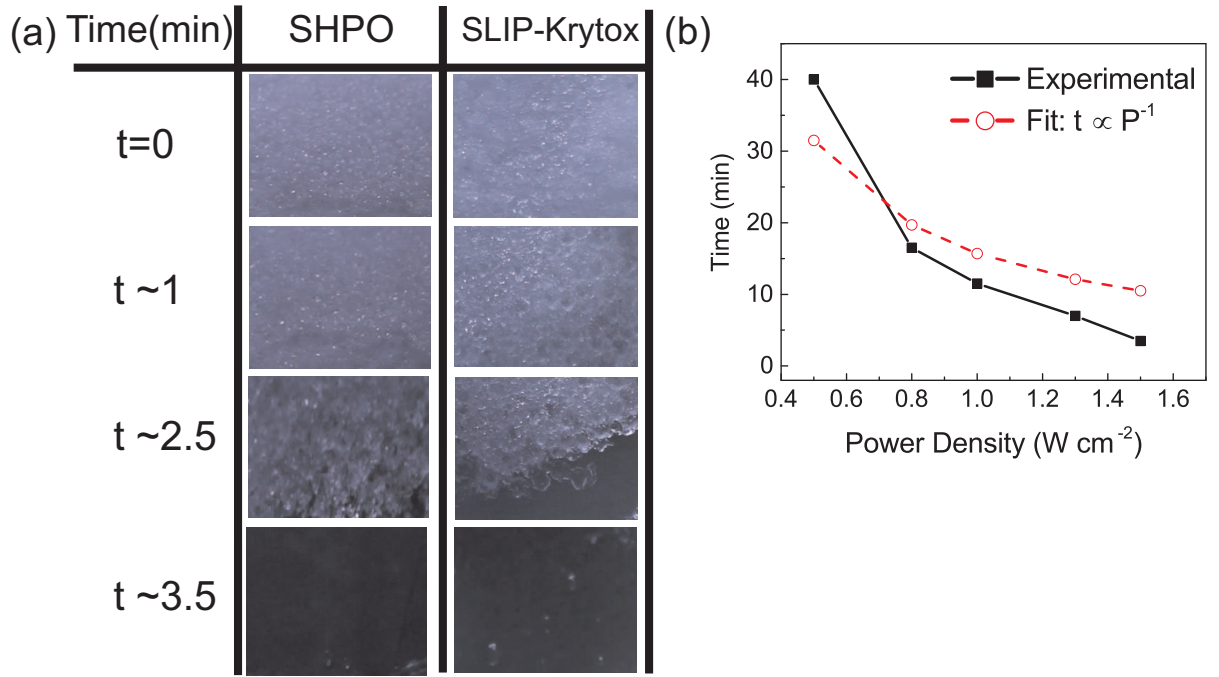


Figure 24. (a) Active defrosting of two samples after 300 minutes of continuous frost buildup. These samples were then heated at a power density of 1.5 W cm^{-2} until each surface became frost-free (due to Joule heating). There is no difference in the behavior or time it takes to defrost these two samples. (b) By varying the power density, we could control the time it took to completely defrost each sample. Equation 4.1 predicts an inverse behavior between power density and defrosting time for a fixed mass of accumulated frost; this trend is shown by the red curve and is in good agreement with the present experimental measurements.

the impregnating fluids (Figure 26b). Thus, for small pore depths, the thermal conductivity of the impregnating fluid bares little effect. Based on Equation 4.5, the specified values of d (3 mm) and k_{ice} ($1.6 \text{ Wm}^{-1}\text{K}^{-1}$) cause the frost-layer resistance term to be dominant. Any change in the first term, due to the change in thermal conductivity of the fluid, bares little effect on R_t . Little change in the total thermal resistance would correspondingly result in miniscule changes in the heat flux for different impregnating fluids, effectively explaining the results in Figure 25. On the other hand, if the second term in Equation 4.5 became less dominant (*i.e.*, smaller values of d , thinner frost layer), a change in the value of the first term (*i.e.*, different fluid conductivities or varying pore depths) would yield a more significant impact on heat flux being transferred through the interface ($x=b$) for SLIP surfaces with different impregnating fluids. We confirm this by calculating the total thermal resistance for the above system for constant $b=1\mu\text{m}$ and decreasing values of d , beginning with $d=3\text{mm}$, and graphing the difference in total thermal resistance among the different impregnating fluids (Figure 26c). As d decreases, the dominance of the frost term in Equation 4.5 declines, and the differences in total thermal resistance become more pronounced with changes in the impregnating fluid. The previous heat transfer analysis, albeit 1-D, offers fundamental insight on the relative importance of the presence of the impregnating fluid as well as the overlaying frost layer. Of course, early on only the fluid is present, but as frost gradually builds up (starting from the tips of the protruding asperities of the textured surface), the importance of the frost layer rises. In general, the heat transfer rate is dependent on the temperature profiles within both the fluid and the frost regions, therefore it is important to take both into consideration when estimating the thermal resistance of the entire

composite system. As the results show, the thickness of the frost layer affects heat transfer, and the thinner this layer, the more important the thermal conductivity of the impregnating fluid becomes.

4.3.5 Defrosting by Periodic Joule Heating

Although plain SHPO and SLIP surfaces can delay frost formation, they prove inadequate in preventing frost buildup in the long term. When frost forms on the present surfaces, their ability to induce Joule heating offers an advantage, as skin heating can be activated to melt the deposited frost layer. It is worth investigating whether intermittent (pulsed) heating offers a more efficient methodology to avert frost. An optimal active technique should take advantage of the passive capabilities of the SHPO and SLIP surfaces for frost growth delay. In another series of experiments under the same ambient conditions (10°C, 80% RH), a thermal pulse was applied at a constant DC power density (1.5 W cm^{-2}) every 30 minutes. Each power pulse is intended to melt thin discontinuous frost layers that have formed, instead of a thick uniform frost layer at the conclusion of a long-term frosting phase. The melting of thin frost layers allows for the surface to be periodically renewed to a relatively frost-free state, thus presenting the nucleating frost with a more energetically unfavorable environment, allowing the user to take prolonged advantage of the passive capabilities of the low-energy surface.

Melting nascent frost layers requires high enough power densities in order to supply sufficient heat. The heat (Q_{melt}) necessary to melt a layer of mass m is

$$Q_{\text{melt}} = mL \tag{4.6}$$

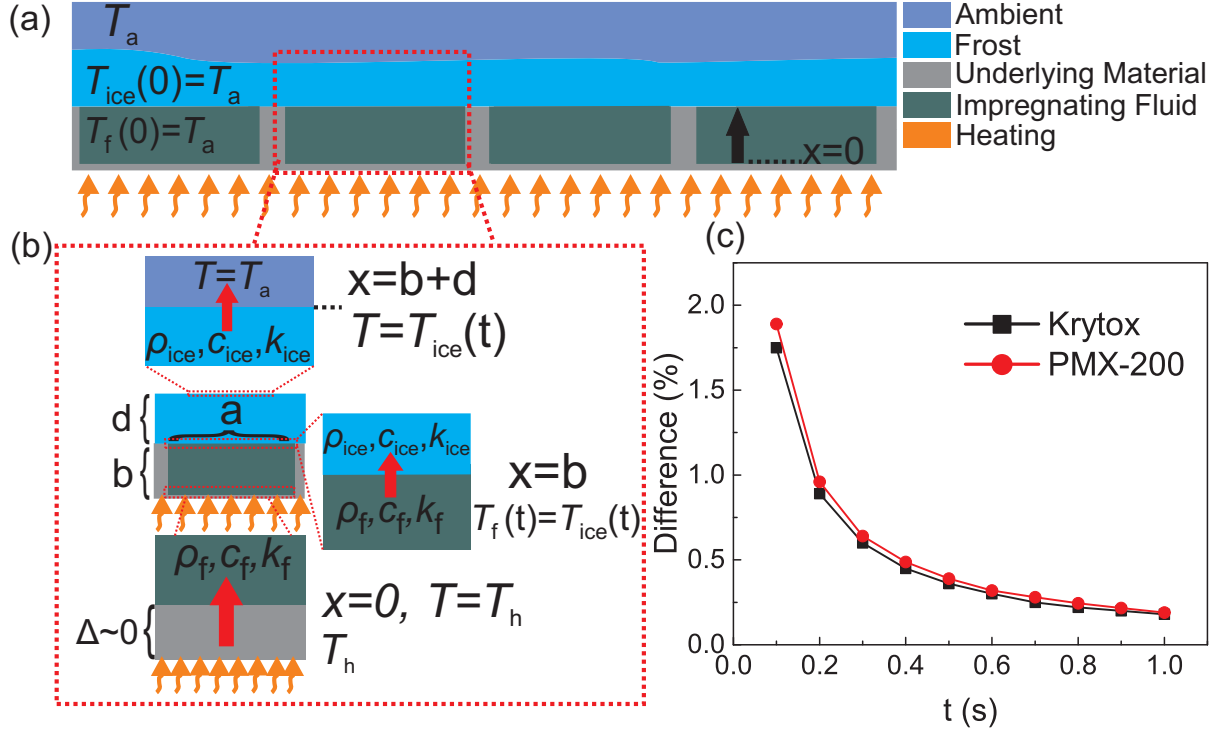


Figure 25. Diagram (not drawn to scale) demonstrating the parallels drawn between a SLIP surface and a 1-D composite heat transfer system. (a) We assume the underlying structure of the SLIP surface to be a repeating rectangular pattern (gray regions). The spaces between the rectangular regions are infused by a fluid (in dark green) of known thermophysical properties. A frost layer (light blue) sits on top of the surface. The entire system is initially in thermal equilibrium, that of ambient T_a , before being heated uniformly from the bottom (orange arrows). (b) Zooming on a singular pore filled with the impregnating fluid. The pore of width a , depth b , with a frost layer of thickness d on top. The 1-D approximation is justified in the limit $a \gg b$. Three interfaces exist: frost/ambient (top zoomed schematic), frost/fluid (right zoomed schematic), and fluid/solid (bottom zoomed schematic). The respective boundary conditions are listed in the text. For simplicity, we assume that the underlying material (gray) possess no thickness, and serves to perfectly transmit the heat which is generated in its own volume. Red arrows represent the direction of heat flow. (c) Differences in predicted heat flux at $x = b$ for two impregnating fluids, as determined by solving the transient system described above. There is little difference in the heat flux at the interface when the impregnating fluid is changed. The system was solved for $b=1\mu\text{m}$, $d=3\text{ mm}$, $T_a = 10^\circ$, and $T_h = 20^\circ$.

where L is the latent heat of fusion for water. Thin layers require lower quantities of heat to melt, and because $Q_{\text{heat}} \propto P$ (Equation 4.1), lower power densities. By pulsing at constant power P every 30 minutes, we melt a thinner frost layer, as compared to that after the 5-hour frost cycle. When pulsing periodically, we allow the surfaces to operate within their most efficient range (see Figure 23c), and take permanent advantage of their passive capabilities to delay frosting. As a result, the total amount of frost that accumulates on the surface over ten 30-minute frost/defrost cycles is drastically reduced compared to that accumulated after one 5-hour frosting period. Thus, the total energy expended to melt the frost via the pulse heating approach is less than that in the end-of-cycle case. We confirm this by comparing the energy expenditure of the continuous vs. periodic pulse defrosting for the SHPO case, $\frac{Q_{\text{pulse}}}{Q_{\text{continuous}}} = \frac{P \sum_{n=1}^{10} C_n}{P(t_{\text{total}})} = \frac{137}{210} = 0.65$, where Q_{pulse} , $Q_{\text{continuous}}$ denote the total heat consumed during pulsed and continuous heating, respectively; C_n is the time of each defrosting cycle, and t_{total} is the total time of defrosting for the continuous case. The cyclic pulsing method allows for 35% energy savings when compared to the end-of-cycle case.

As seen from Figure 27, the various samples (SHPO, Krytox, and PMX-200) require slightly different times to defrost during each defrosting cycle. This behavior can be explained in light of the different nucleation rates and thermal conductivities of the impregnating fluids. From Figure 23c, the SHPO and SLIP surfaces accumulate different amounts of frost in the 30-minute window, with the SHPO surface accumulating more frost than either SLIP surface. This increased frost mass would require a higher heat to be supplied, resulting in increased defrosting time for the SHPO surface. Secondly, thinner frost layers negate the dominating effect of

the second term in Equation 4.5, thus causing the thermal conductivities of the impregnating fluid to become relevant in the defrosting. The combination of these two factors results in the surfaces to require different times to defrost. Taking this into consideration, one should expect SHPO surfaces to require the longest time to defrost (*i.e.*, most heat) for each cycle. In regards to SLIP surfaces, we can not make any definitive statements, but if one were to assume nucleation behaviors were comparable, or only slightly different for the two SLIP surfaces, then we would expect the PMX-200 SLIP surfaces to perform best due to their fluid's higher thermal conductivity. Even though this is not what is observed in Figure 27, the performance of all three tested samples is too similar to make more definitive statements with regards to enhanced thermal performance.

The mechanism by which the frost melts and reforms throughout these cycles is important to explore further. As we see from Figure 27, when heating is applied at the conclusion of the first 30-minute frosting cycle, small droplets of water remain pinned to each vertically-placed surface and do not become dislodged. Once heating is stopped, and the second 30-minute frosting cycle begins, these droplets begin to freeze, and frost nucleation begins on and around them. Due to the pre-existence of these droplets, the second frost cycle yields a larger mass of frost accumulation. As a result, the total time to defrost after the second 30-minute cycle is longer. Similar to the first cycle, at the conclusion of the heating in the second cycle, small droplets remain on the surface. By now, the droplets have grown further in size, resulting in their dislodgement and sliding down the vertically-held surface. It is important to note that droplet dislodgement did not occur on the SHPO surface, and occurred from the second cycle

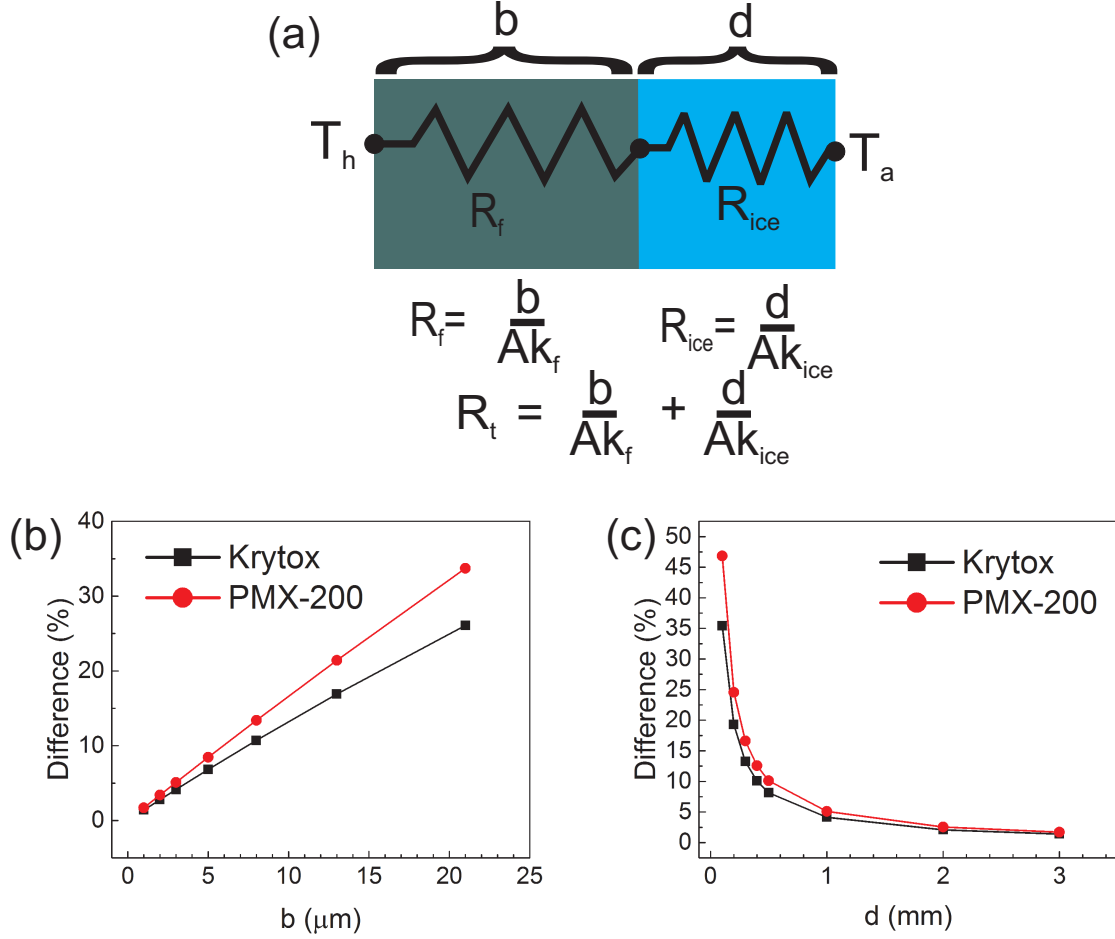


Figure 26. (a) Diagram (not drawn to scale) of the total thermal resistance present in a fluid-impregnated pore of depth b . A frost layer (blue) of thickness d is present above the pore. The total thermal resistance (R_t) of the system can be written in terms of b , d , the thermal conductivity of the fluid (k_f), thermal conductivity of ice (k_{ice}), and cross sectional area (A), not pictured. (b) For a frost layer with $d = 3\text{mm}$, and varying values of b , we show how the total thermal resistance changes with the impregnating fluid's thermal properties (*i.e.*, k_f). The results are presented in relation to the total thermal resistance when the impregnating fluid is air (*i.e.*, SHPO). As b increases, so does the difference in total resistance, with larger pore depths demonstrating larger thermal resistance differences. (c) For fixed pore depth $b = 1\mu\text{m}$, and varying the value of d , we show how the total thermal resistance changes. The thicker is the frost layer, the smaller the difference in total thermal resistance across the fluid/frost layers.

onwards for both SLIP surfaces. This can be attributed to droplet pinning on the texture of SHPO surfaces and the low hysteresis of SLIP surfaces. Droplet dislodgement helps to enhance the cleanliness of the surfaces, and assists the subsequent heating cycles due to less frost on the surface. That explains why the time to defrost does not increase significantly after the second cycle for both SLIP surfaces. It is noted that droplet dislodgement would most likely result in oil drainage from the SLIP surface if carried out for extended time periods. However, the SLIP degradation due to this long-term mechanism was not investigated in the present study.

One can foreseeably expand upon the periodic pulse heating approach by decreasing the time between successive pulses. Smaller time intervals would expectedly result in thinner frost layers being formed, and correspondingly lower energy to remove them. One important factor pertaining to the validity of the present results is the role of the underlying substrate material. If the material were not thermally insulating, the fundamental assumption that the heat being supplied is predominantly consumed to melt the frost layer, would be invalid and the analysis carried out in Equation 4.2-Equation 4.4 would be incomplete. In that case, one would have to also account for the heat flowing through the underlying material. Finally, it is important to emphasize that the skin heating approach can only be implemented experimentally with electrically-insulating substrates (so that the applied current flows only through the coating and not the underlying material). These issues are out of the scope of the present study and thus are not elaborated further.

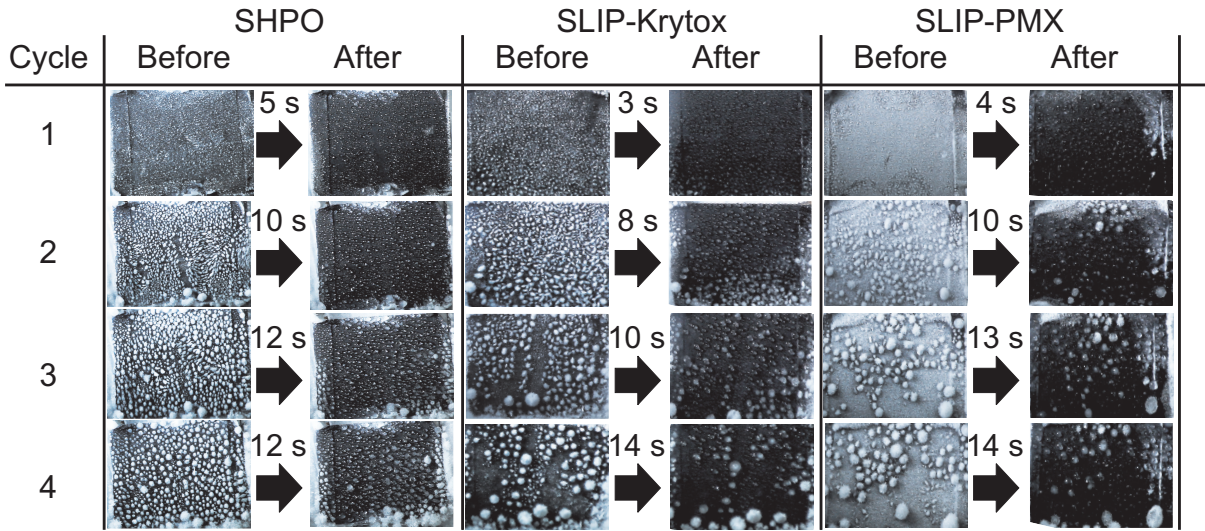


Figure 27. Three materials (SHPO, SLIP-Krytox, and SLIP PMX-200) were placed in a 10°C and 80% RH environment and Peltier-cooled to -7.5°C. Each sample was thermally pulsed every 30 minutes at power density of 1.5 W cm⁻² until the surface became relatively frost-free. The periodic heat pulses melt the thin nascent frost, rather than waiting to the conclusion of an extended frosting period when the frost layer is much thicker. By melting the thin frost every 30 minutes, the underlying surface is re-exposed, thus continuously taking advantage of its inherent passive frost-delaying capabilities. Pictured are before and after images for four pulse cycles on each surface; the number above each black arrow denotes the length of time that Joule heating was applied during that cycle.

Fluid	Density ρ [kg m ⁻³]	Thermal Conductivity k [Wm ⁻¹ K ⁻¹]	Specific Heat c [J kg ⁻¹ K ⁻¹]	Thermal Diffusivity α [m ² s ⁻¹]
Air	1.28	.026	1000	2.1E - 5
Krytox	1900	.083	900	4.9E - 8
PMX-200	960	.16	1500	1.1E - 7
Ice	920	1.6	1900	8.9E - 7

TABLE II

PHYSICAL PROPERTIES OF THE FLUIDS IMPREGNATING THE CNF-POLYMER
COMPOSITE COATINGS

Fluid	Thermal Conductivity k [Wm ⁻¹ K ⁻¹]	$\left \frac{R_{\text{air}} - R_{\text{f}}}{R_{\text{air}}} \right \times 100\%$
Air	.026	0
Krytox	.083	1.4
PMX-200	.16	1.7

TABLE III

DIFFERENCE IN TOTAL THERMAL RESISTANCE OF A COMPOSITE SYSTEM FOR
DIFFERENT IMPREGNATING FLUIDS. VALUES ARE TAKEN RELATIVE TO WHEN
THE SYSTEM IS IMPREGNATED WITH AIR (SHPO).

CHAPTER 5

FROST FORMATION ON PRE-WETTED SURFACES

5.1 Motivation and Background

There have been numerous studies (both modeling(95; 96; 97) and experimental(98; 99)) performed to analyze and predict atmospheric frost formation behavior on varying types of surfaces subjected to continuous periods of frosting. All of these studies have considered surfaces initially in a dry (pristine) state. As important as these works are, there is still an entire class of surfaces that remain unexplored. These surfaces begin their frosting in a pre-wetted (unpristine) state. In fact, rarely does a surface that experiences frosting start in a pristine state. Predominantly, the surface will possess some type of non-uniformity or defect. In the case considered here, the non-uniformity appears in the form of pre-existing water. Examples of such surfaces appear in heat pumps, heat exchangers, or air conditioners that are subjected to cyclical bouts of frosting and defrosting(100; 101; 102). These cycles are brought on by the need to maintain the devices in a frost-free state. Cyclic heating melts the formed frost layers, yielding water which is partially removed by gravity. At the same time, some remnant water remains adhered to the surface, yielding operation under wet conditions(103; 104; 105). The shape/form that the remnant water assumes is dependent on the wettability (sessile contact angle θ) of the underlying material(106; 107; 90). The leftover water yields a pre-wetted state and thus, subsequent frosting cycles commence under non-pristine circumstances.

Frosting of pre-wetted surfaces has rarely been studied(108). To fill this gap, we study the mechanisms by which deposited water affects the nucleation and subsequent frosting on a metal surface. Analyzing three types of aluminum surfaces, namely, superhydrophilic, hydrophilic, and hybrid hydrophilic-superhydrophilic (termed wettability-patterned), we report how the wettability of each surface affects the water retention and subsequent frosting cycles. Using a combination of mass measurements and image analysis, we draw conclusions regarding the overall performance of the materials studied, which could be viewed as examples of surfaces encountered in practice.

5.2 Experimental

Three types of surfaces were used in this work: 1) Mirror-finish aluminum (MFA) (multi-purpose polished aluminum alloy 6061, 2 mm thick, McMaster Carr) with $\theta = 78^\circ$, 2) MFA chemically-etched with hydrochloric acid (Sigma Aldrich, 37% in 5 M aqueous solution) to produce a superhydrophilic (SPHIL) surface ($\theta \approx 0^\circ$), and 3) Wettability-patterned surface (WPS) combining spatially-distributed domains of hydrophilic and superhydrophilic behavior(57; 109; 110; 111; 112). All experiments were performed in an environmental chamber (ESPEQ, SH-641) maintaining temperature of 10°C and 75% Relative Humidity (RH). The samples were mounted on a Peltier cooler (TeTech, CP-061HT) and cooled to -15°C . The experimental setup is pictured in the schematic of Figure 28a.

5.3 Results

We first measured the frost-mass accumulation for the three types of surfaces (MFA, SPHIL, WPS) over varying time intervals. Samples were subjected to the frosting conditions described

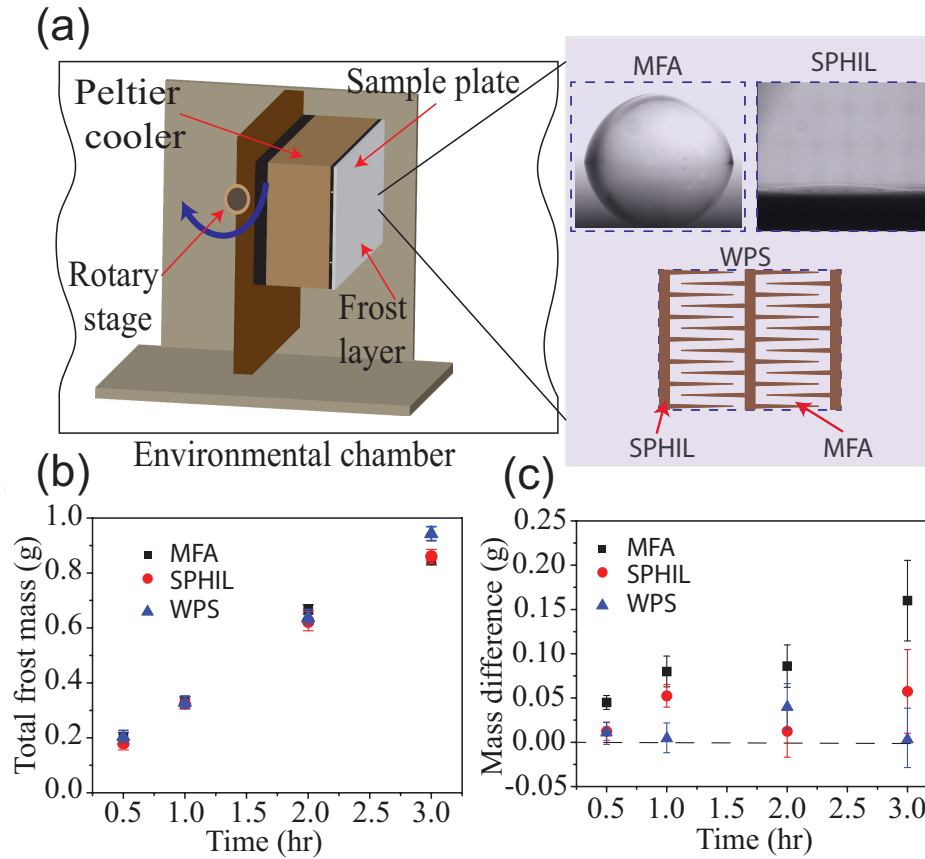


Figure 28. (a) Frosting experiments were performed in an environmental chamber. The surfaces used were Mirror Finished Aluminum (MFA, $\theta = 78^\circ$), Superhydrophilic Aluminum (SPHIL, $\theta = 0^\circ$), and Wettability-Patterned Aluminum (WPS, combining MFA and SPHIL domains). (b) The chamber was set to 10°C and 75% Relative Humidity, with the peltier set to -15°C . Dry samples of each surface were mounted horizontally and exposed to the preset ambient for varying time periods (0.5, 1, 2, 3 hours). As seen from the graph, there is little to no difference in the frost accumulated on the three surfaces when starting dry. (c) The samples were then pre-wetted with an equivalent and known mass of water and were allowed to frost. As seen from this figure, which plots the frost net mass difference from the frost mass on the respective dry surface, MFA displayed the largest frost mass increase followed by the WPS and SPHIL surfaces.

above for 0.5, 1, 2 and 3 hours. Each sample was weighed with high precision prior and after frosting, with the measured frost-mass accumulation being the difference. Each measurement was repeated for three experiments, each performed under the same conditions. As seen from Figure 28b, the frost mass on the three samples for all time intervals were comparable to one another. This implies that for frosting periods above 0.5 hours (and for the environmental conditions these samples are subjected to), frost accumulation is independent of the wettability of the underlying surface. These results support prior reports that the surface wettability only affects the formation of the initial thin layer of frost,(30; 26) and plays little role in subsequent frost accumulation, which sees only the overlaying frost layer. Next, we tested surfaces pre-wetted with a known mass of water. The added mass used to pre-wet the surfaces was determined as follows: a SPHIL substrate was placed horizontally and water was added until saturation. The saturated substrate was turned vertically for excess water to drain down. The substrate was then weighed to determine the mass of the remnant water on the sample. An equal mass was added, using a syringe, to the MFA surface in the form of water droplets randomly placed throughout the surface until the mass was equal to that measured earlier for the SPHIL substrate. For the WPS samples, the added water (same amount as in the MFA and SPHIL cases) stayed predominantly in the SPHIL regions, with sporadic drops left on the MFA areas. It is important to note that the procedure used to pre-wet each surface is consistent with defrosting experiments described later. The results of frosting experiments performed under the same environmental conditions as for the initially-dry samples are presented in Figure 28c, which plots the temporal frost mass difference from the frost accumulated on the respective dry surface over the same period. As seen,

all three pre-wetted surfaces accrue more frost over time than the corresponding dry surfaces, a result that makes sense intuitively. The pre-existence of the liquid on the pre-wetted surfaces increases the mass accumulation, as the pre-wetting liquid has entirely bypassed the nucleation stage (vapor to liquid, which adds recalescent heat locally). This causes the pre-wetted surface to freeze at an earlier time than the dry surface, thus decreasing the time required for freezing. This, in turn, allows more time for frosting in the frost growth and crystallization phase.

When comparing the presuffused (pre-wetted) sample data, we note that the SPHIL and WPS surface had the lowest increase (on average across all tests). Thus, although there is no difference in the accumulated frost among the dry (pristine) samples, differences exist when the samples are pre-wetted. Below, we shed light on this outcome first by visually examining the frosting and refrosting mechanisms of the three materials.

The samples were frosted/defrosted/refrosted in order to compare the frosting mechanisms of dry vs. pre-wetted surfaces. Henceforth, the term pre-wetted implies that a surface has gone through a defrosting stage that generated liquid water on it. The initial tests were carried out on dry samples vertically mounted in the environmental conditions described above for 1 hour, after which the Peltier stage was heated to 2°C until all frost on the samples was melted. After complete defrosting (designated visually), the Peltier was once again cooled to -15°C for 1 hour, and the above cycle was repeated once more. We also measured the water retention of each surface after defrosting. As seen, the water drainage and retention behavior of the three surfaces during the melting cycles is distinctly different. Due to the smoothness and lack of roughness of the MFA samples, the melted frost easily retracted leaving behind water droplets sporadically

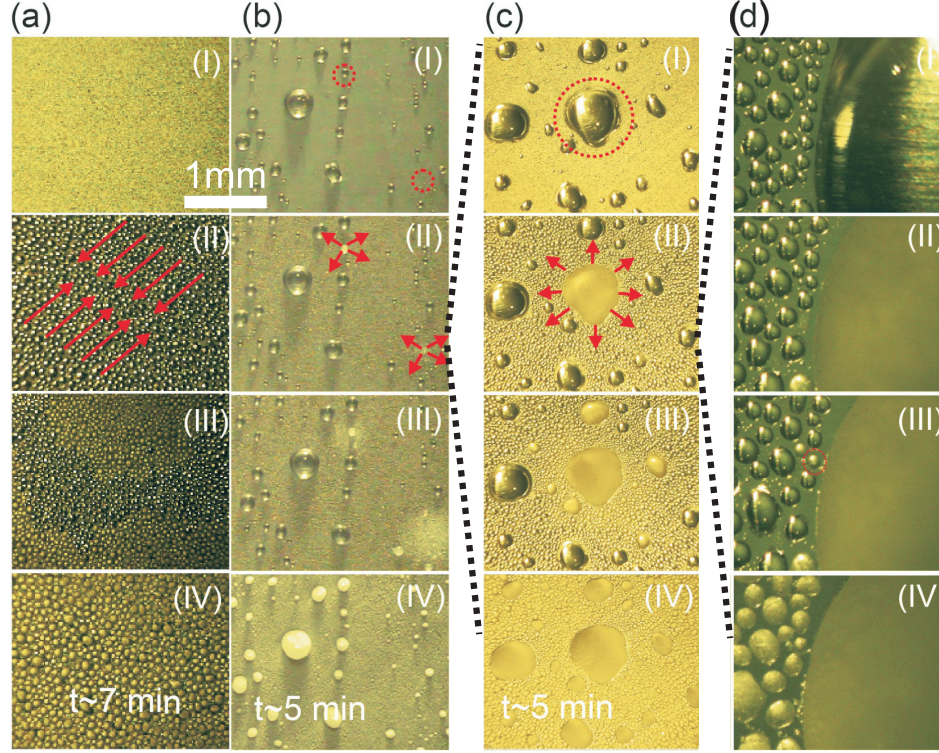


Figure 29. (Color online) Optical images showing condensation/freezing on the MFA (hydrophilic) surface. (a) The propagation of the freezing front on the dry surface is shown with the red arrows in frame (II). In (III) and (IV), already frozen droplets can be seen in yellow. (b) View of the defrosted (pre-wetted) MFA surface: (I) the red spots show where the remnant droplets start to freeze. (II) Red arrows show the initiation of the freezing front, and in (III) the freezing front outward propagation is clearly visible. It took around 5 min to completely freeze the whole pre-wetted surface, which is around 2 min faster than the corresponding dry surface. (c) and (d) Zoomed-in views of the pre-wetted surface.

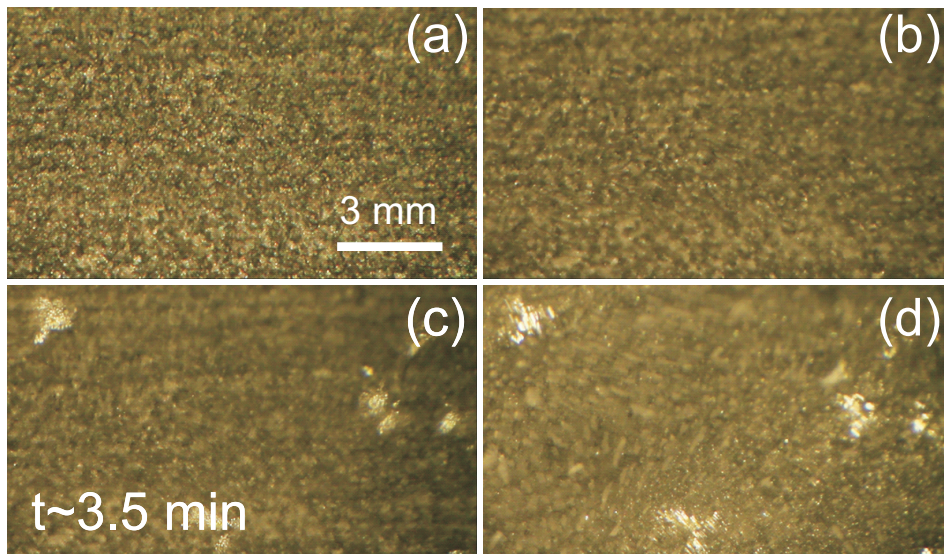


Figure 30. (a) Pristine SPHIL surface placed in frosting conditions. Almost immediately, droplets condense on the surface. Subsequently, they form a barely visible thin liquid layer (b). Once the liquid layer has been formed, it freezes over forming a layer of ice on top of the surface (c). As time progresses, the layer of ice grows (d).

located around the surface. For the SPHIL surface, the melted frost wetted the entire surface with a liquid film, which was mostly drained by gravity. The leftover liquid impregnated the texture of the surface, forming a very thin film. Lastly, the drainage of the melted frost on the WPS surface (as reported earlier,^(57; 109) was carried out primarily via the wettable tracks (interdigitated SPHIL domains). Small water droplets remained on the MFA area, while a thin film of water (similar to that on the uniform SPHIL surface) engulfed the SPHIL regions. These defrosting patterns support the respective approach we used earlier to prepare each surface for the pre-wetting experiments (Figure 28c), showing what realistically occurs under such cyclic defrosting situations.

5.4 Discussion: Mechanisms of reduced mass accumulation on superhydrophilic surfaces

The reduced mass accumulation on pre-wetted superhydrophilic surfaces is due to a multitude of factors; all of them stemming from the alteration of the underlying physical mechanisms affecting the freezing and growth of incipient frost layers. We attempt to list and explain all of these factors below.

5.4.1 Condensation

We begin by first looking at the circumstances where we have dry superhydrophilic and hydrophilic surfaces. The first step in the frost formation process is a condensation of liquid droplets on the surface. As already understood in the field, the energy barrier to nucleation is lower on the superhydrophilic than on a hydrophilic surface. After a specific period of time, the superhydrophilic surface forms intermittent thin layers of water, inducing film wise condensation, while the hydrophilic surface carries out dropwise condensation. In the case where both hydrophilic and superhydrophilic surfaces are pre-wetted with an equivalent liquid mass, the droplet condensation behavior on the hydrophilic surface is carried out entirely via dropwise condensation (as before). While for the superhydrophilic surface, condensation is entirely carried out via filmwise condensation (contrary to before where it was first dropwise proceeded by filmwise). Thus, during the condensation stage the hydrophilic surface is accumulating relatively larger mass of liquid when compared to the superhydrophilic surface, due to the different mechanisms of condensation. Now consider the case of a pre-wetted versus dry surface of the same type. For hydrophilic surfaces, the droplet condensation mechanism is almost exactly the same

as before, the only difference being the fact that some of the condensed water has bypassed the condensation phase. In terms of mass accumulation for the pre-wetted case, we should essentially have the same amount of mass accumulated in in the dry case plus the deposited amount of liquid used to pre-wet. In contrast, the superhydrophilic surface is experiencing a different situation, in that the pre-wetting case induces filmwise condensation in the onset, as opposed to dropwise condensation. This will ultimately result in a slight decrease in mass accumulation on the superhydrophilic surface

5.4.2 Freezing

For the dry MFA surface (Figure 29a I), frosting begins with the nucleation of small droplets with relatively uniform size throughout the surface (Figure 29a II). After ≈ 7 min, a freezing wave propagates (Figure 29a III) on the surface, resulting in complete freezing within seconds (Figure 29a IV). In the case of pre-wetted (defrosted) MFA (Figure 29b), freezing is not initiated with a uniform wave that propagates throughout the surface, but rather with sporadic freezing of remnant droplets. As such droplets freeze (Figure 29c), they produce a radial freezing wave that sweeps the surrounding droplets, which in turn freeze their surroundings, and eventually the entire surface. The freezing time decreased from 7 min in the dry MFA case to 5 min in the pre-wetted MFA case. We note that the size of the droplets that freeze first is not extreme (neither largest nor smallest). From previous reports,(113; 114; 115) the freezing time of a droplet is directly dependent on its mass and the contact area. Considering conduction to be the main form of heat transfer away from the droplet, the freezing time (τ_f) of a droplet should scale as $\tau_f \propto mA^{-1}$, where m is the mass of the droplet and A the contact area, or in terms

of the droplet radius r , $\tau_f \propto r^3 A^{-1}$. Smaller droplets require less energy to freeze but also have less contact area than larger droplets. Larger droplets possess more contact area, but also require the largest energy removal to freeze. These two competing mechanisms result in neither the smallest or largest droplets being first to freeze (Figure 29b). The time required for the pre-wetted surface to completely freeze over is decreased because the pre-wetting droplets have bypassed the condensation stage, which releases recalescent heat and delays freezing.

When exposed to the vapor-rich ambient, the dry SPHIL surface (Figure 30) begins with condensate forming via dropwise condensation (DWC), which eventually spreads and forms a thin film, giving rise to filmwise condensation (FWC)(116). This film then freezes producing an ice layer over the entire surface. As seen in Figure 30c, the ice layer forms after only about 3.5 min. This is significantly less than the MFA surface for two reasons; 1) the liquid possesses a higher contact area than on the MFA, thus allowing for faster heat transfer, and 2) FWC occurs at a lower rate than dropwise condensation, implying there is less mass to freeze on the SPHIL surface. In the defrosting/refrosting of the SPHIL surface, a thin liquid film already exists. This film is the remnant water from the melting/draining, and thus induces a direct state of FWC, bypassing the DWC stage that is experienced in the dry SPHIL case. It is interesting to note that the freezing times of dry and pre-wetted SPHIL surfaces are comparable (3.5 min); we'll address this point momentarily.

The dry WPS surface demonstrates an intermediate behavior between its SPHIL and MFA counterparts. For the dry case (Figure 31a), as expected, the MFA regions demonstrate DWC, while the SPHIL regions exhibit FWC(57; 109). The freezing wave propagates outward from

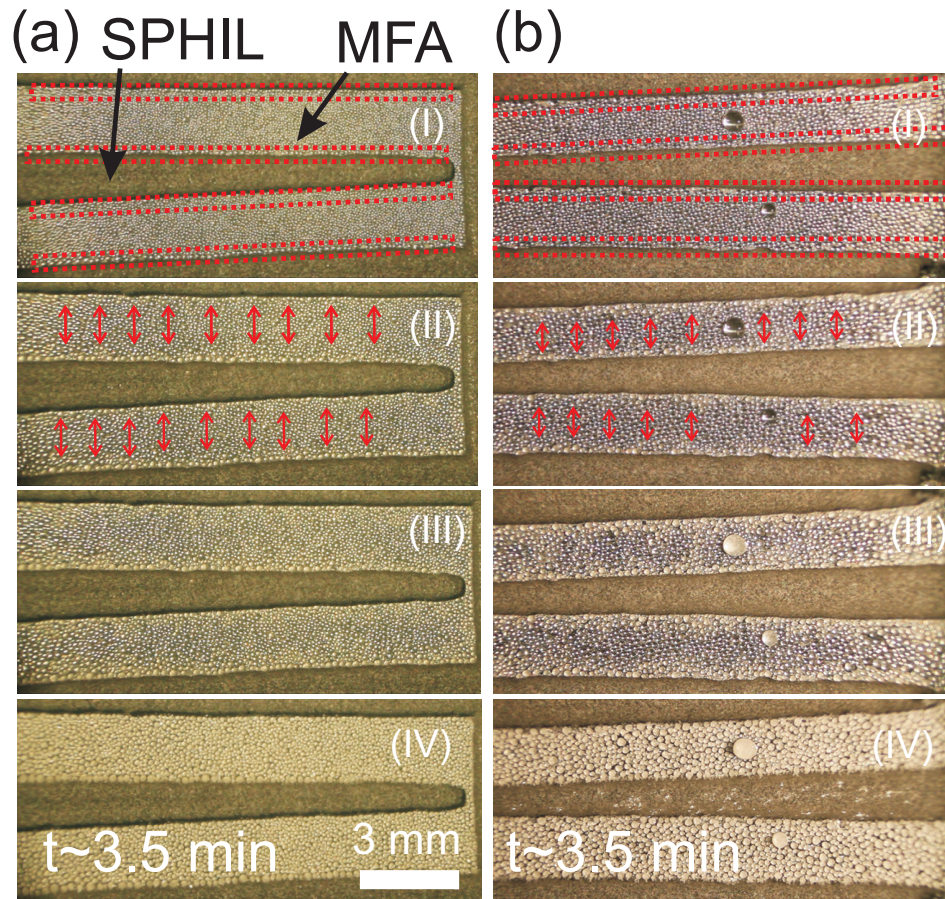


Figure 31. (a) Initially dry, wettability-patterned surface (WPS) with interdigitated domains of hydrophilic MFA and SPHIL aluminum and subjected to frosting conditions (10°C , 75% RH). (I) Frosting begins with dropwise condensation on the MFA region and filmwise condensation on the SPHIL region. Due to the larger liquid/solid contact area on the SPHIL region, the water there freezes earlier than on the MFA regions. (II) Freezing propagates into the MFA region, freezing the droplets in its path (III), until the entire surface has frozen after ≈ 3.5 minutes (IV). (b) In the pre-wetted (defrosted) case, the same exact trend is observed as for the dry case. This is attributed to the fact that the thin film left behind after defrosting resembles the thin film formed immediately by condensation on the SPHIL surface. Scale bar applies to both image sequences.

Material	Dry (min)	Pre-wetted (min)
MFA	7	5
SPHIL	3.5	3.5
WPS	3.5	3.5

TABLE IV

FREEZING TIME OF THE ALUMINUM SURFACES TESTED UNDER DRY AND
PRE-WETTED CONDITIONS.

the SPHIL region, as freezing occurs there first, and then into the MFA domains where droplets are abundant. The freezing time for the WPS surface is of the same scale as that of a uniform SPHIL surface (≈ 3.4 min). This can be explained by the fact that the SPHIL regions of the WPS surface freeze first, with the front propagating into the MFA areas, eventually resulting in complete freezing of the surface. In the pre-wetted WPS case (Figure 31b), the same behavior is observed as when dry, even on the same time scale. The freezing occurs from within the SPHIL region, and spreads into the MFA area, eventually freezing the remnant water droplets; freezing is completed in 3.5 minutes. For a complete summary of the observed freezing times, see 5.4.2.

5.4.3 Frost Layer Growth

Once condensation and freezing has taken place the final phase of frost layer growth and development occurs. It is during this phase, that the most significant influences related to the differences of the dry vs. pre-wetting occur. Each of these factors are outlined below and analyzed.

5.4.3.1 Molecular Diffusion

Frost layer growth occurs via two mechanisms, frost layer thickness growth and molecular diffusion. In the case of frost layer thickness growth, water vapor is directly transported to the top of the frost layer and allowing it to grow in thickness. In the case of molecular diffusion, water vapor diffuses through the frost layer and settles. Depending on whether surfaces are dry/pre-wet and hydrophilic/superhydrophilic, the effect of molecular diffusion is significantly altered. Consider the case of a dry hydrophilic surface, droplets condense, freeze and grow. Due to sporadic nature of droplet condensation, this growth results in a porous network of ice/frost which water vapor is able to diffuse into. In the case of a pre-wetted hydrophilic surface, nothing is changed, the droplets are dispersed on the surface as if they formed in the conventional manner (condensation). The same type of porous ice/frost network is formed and there is no expected change. For the case of a superhydrophilic surface, the molecular diffusion is affected. A pre-wetted superhydrophilic surface is inundated with a thin layer of liquid. This layer of liquid freezes and expands, forming a solid ice/frost structure. Thus the porous structure that would previously exist in the dry superhydrophilic circumstance is no longer present. This significantly impedes, possibly eliminating, the molecular diffusion component contributing to frost development on the surface.

5.4.3.2 Frost Thickness

The height to which a frost layer develops (thickness) is limited by thermodynamic considerations. As the frost layer becomes thicker and thicker, its temperature decreases due to its increasing distance from the cold substrate. It is important to understand that a frost layer

has an initial rapid growth period that eventually tails off. While at the same time, the mass continues to increase. The mass increase is due to the fact that in later time periods, the main mechanism that induces mass accumulation is not frost layer thickness growth but rather densification vs molecular diffusion. Water vapour is transported into the porous network, where it freezes, releasing latent heat that melts the surrounding ice, which congeals and freezes, causing the ice layer to densify. In light of this mechanism, it is important to look back once again on the pre-wetted/dry surfaces. For the hydrophilic sample, there is really no change in the thickness growth rate for the pre-wet vs dry case. While in the pre-wetted superhydrophilic case, there is an early freezing ice layer forming. This ice layer originally expands and forms a thick layer. Thus from the onset, a closer value to the thermodynamic limit is achieved. We see that there exists a dependence on the thickness of the existing frost layer. Thus, as the thickness increases, the mass contribution due to frost layer thickness decreases. The initially increased thickness ultimately results in less overall mass accumulation in a pre-wetted superhydrophilic surface.

5.4.3.3 Density

As seen above, the pre-wetting of a superhydrophilic surface results in changes in both the molecular diffusion and frost thickness formation on the surface. A final physical component that is altered, and coupled to the above, is the frost density. The main mechanism responsible for the densification of frost, as stated before, is molecular diffusion. With molecular diffusion being reduced due to the pre-wetting effects, the subsequent frost is less dense. The lower density results in lower thermal conductivity, which ultimately results in less mass accumulation.

CHAPTER 6

CONCLUSIONS AND RESEARCH OUTLOOK

6.1 Thesis conclusion

6.1.1 Droplet Control on Superhydrophobic Paper Surfaces

We presented a low-cost, facile method to produce superhydrophobic paper by coating common sandpaper with a commercially available fluoroacrylic copolymer (PMC). The underlying roughness of the sandpaper combined with the natural hydrophobic state of PMC resulted in advancing, receding, and sliding angles of $156^{\circ}\pm4.5^{\circ}$, $130^{\circ}\pm6.3^{\circ}$, and $13^{\circ}\pm2.4^{\circ}$, respectively. The superhydrophobic substrates were patterned with a common household inkjet printer to produce wettable domains. Varying intensities of black ink (up to 0.5 g m^{-2} add-on rate) were patterned onto the substrates, which were dried and tested for water droplet wettability and mobility. As the amount of ink deposited increased, the wettability of the surface improved and the droplet mobility decreased (surface became sticky). There was little to no quantitative difference in modifying wettability among the different ink colors. At 50 % ink deposition (0.25 g m^{-2}), droplet mobility was entirely impeded for all ink colors. Line tracks with 50 mm length and width varying from 0.1 mm to 2 mm were created by depositing 47 % cyan ink. Using the aforementioned lines, the tests revealed good control and tuning of droplet sliding from mobile (0.1 mm track) to immobile (2 mm track). A theoretical model accurately predicted the droplet release inclination angle for printed lines of known width and wettability. Specially printed areas

exemplified the construction of low-cost microfluidic devices capable of splitting, storing, and analyzing water droplets of a given size. The present technique holds promise for expanding the utility of superhydrophobic paper substrates into the regime of point-of-care diagnostics.

6.1.2 Droplet Impact on Non-Uniform Wettability Surfaces

We studied droplet impact on axially-symmetric, non-uniform wettability surfaces. We expanded upon previously presented models for uniform-wettability surfaces, and predicted the maximum spreading diameter of droplets impacting on symmetric patterns on varying wettability surfaces. The present model was expanded to account for n annular regions of different wettabilities, and calculated the corresponding maximum spreading diameters. In addition, within our model we explore the concept of a wettability contrast barrier that must be overcome by the impacting droplets in order to continue their spreading phase. We show under which conditions a droplet can successfully overcome this barrier, and under which conditions it cannot. It is shown that impact consisting of transition from a hydrophilic to hydrophobic region is independent of the inner philic region. While impact consisting of transition from the hydrophobic to hydrophilic domain is dependent on the hydrophilic inner domain. The model put forth makes strong use of the previously-reported droplet impact model of Passandideh-Fard et al. It also draws upon geometric assumptions, such as cylindrical shape for the expanding liquid and spherical cap for the impacting droplet.

6.1.3 Electrically Conductive Superhydrophobic Coatings

We presented an investigation of electrically-conducting superhydrophobic and slippery lubricant impregnated coatings for active defrosting over periods of several hours. Even though

these types of surfaces fail to passively combat frost formation over prolonged time periods, their conductive property facilitates the implementation of active defrosting techniques that can keep the surface frost-free. We studied the role of the impregnating lubricant in effecting heat transfer across the interface, and showed that the thermal properties of the lubricant play little to no importance once a thick layer of frost has formed. This behavior is ascribed to the dominant thermal resistance of the thick (mm) frost layer. Building upon this understanding, we presented an active technique that thermally pulsed the sample in order to melt nascent frost layers that developed over periods of 30 mins. This allows us to eliminate the dominance of the thermal resistance of the thick frost layers that develop over prolonged periods, and take advantage of the higher thermal conductivities of the impregnating lubricants. The cyclic heating approach showed 35% energy savings over the method where the frost deposited over long periods was melted in one cycle. The present approach provides guidance for practical technologies in cold climates where frosting must be averted over periods of days or even longer.

6.1.4 Frosting and Icing of Pre-Wetted Surfaces

We have studied the frost formation mechanisms of both dry and pre-wetted hydrophilic, superhydrophilic, and wettability-patterned aluminum surfaces (interdigitated patterns). We showed that the frosting mechanisms for both circumstances are different for hydrophilic surfaces, while similar behaviors are seen for superhydrophilic and wettability-patterned surfaces. In addition, among the practically-relevant (Al) materials studied, superhydrophilic and WPS surfaces demonstrate slightly superior performance in terms of frost-combating capabilities under pre-wetted conditions.

6.2 Research Contribution

6.2.1 Droplet Control on Superhydrophobic Paper Surfaces

- Demonstration of a low-cost technique for the fabrication of superhydrophobic paper using a fluoroacrylic copolymer and commercially available sandpaper
- Easy-to-use method for the design and implementation of wettability-patterned surfaces using aforesaid superhydrophobic paper and common household printer and ink
- Control of sliding droplets was achieved through specially utilized design wettability-patterned tracks on superhydrophobic paper
- A model was put forth to accurately predict the sliding angle of droplets on non-uniform wettability surfaces
- A proof-of-concept Point-of-Care diagnostic device capable of splitting and analyzing liquid droplets was designed, and tested, using the aforementioned materials and techniques

6.2.2 Droplet Impact on Non-Uniform Wettability Surfaces

- First analytical model to address axisymmetric impact of droplets on non-uniform wettability surfaces
- Proposal, and confirmation, of the existence of a cross-over energy caused by the increased energy requirement to transition from a wettable to a non-wettable domain
- Demonstration of droplet spreading on multi-region surfaces being independent of the wettability of the inner-most region

6.2.3 Electrically-Conductive Superhydrophobic Coatings

- A superhydrophobic, electrically conductive, spray coating capable of Joule heating was designed and fabricated
- Surfaces of varying wettability were subjected to low-temperature high-humidity environmental conditions in order to induce prolonged periods of frosting. Demonstrated that prolonged frosting is independent of surface wettability
- Joule heating was used to return a surface to a frost-free state. Helping maintain frost-free state over prolonged periods of time
- A unique pulsed heating approach was demonstrated in order reduce the energy consumption of Joule-heated surfaces. Resulting in a 35% decrease in energy required to keep surface frost free
- A heat transfer model was presented to effectively predict and model the role of impregnating fluids in textured materials

6.2.4 Frosting and Icing of Pre-Wetted Surfaces

- Surfaces of varying wettability are pre-wetted with a known mass of liquid and subjected to frosting conditions. Simulating the frosting of surfaces under pre-wetted conditions.
- Pre-wetted surfaces containing segments with superhydrophilic properties result in less frost accumulation than hydrophilic surfaces
- A model is put forth to demonstrate that less frost accumulation on superhydrophilic surfaces is due to a reduction in molecular diffusion of water

6.3 Recommendations for Future Research

6.3.1 Droplet Control on Superhydrophobic Paper Surfaces

This work allows for the possibility of low-cost, easy-to-use POC diagnostic devices. The devices would be paper based, and produced via common household printers, thus lending themselves to implementation in developing regions where access to sophisticated instrumentation is limited. The need for the determination of what type of POC diagnostic would be designed is necessary. In addition, the droplet sliding model presented needs to be expanded for more complex shapes and geometries.

6.3.2 Droplet Impact on Non-Uniform Wettability Surfaces

The model put forth addressed droplet impact on axisymmetric non-uniform surfaces. The issue of non-symmetric impact on non-uniform surfaces has yet to be addressed in the community. The symmetry of conventional problems is often used in order to simplify the energy equations as well as the momentum transfer analysis. Non-symmetric impact is far more difficult to physically understand and analytically interpret.

6.3.3 Electrically-Conductive Superhydrophobic Coatings

Airplanes and turbine blades are examples of critical mechanical systems that are subjected to prolonged periods of frosting, and must be maintained in a relatively clean state. Use of the presented coatings would allow these surfaces to be maintained ice/frost free and operational. These coatings need to be tested under real-world environmental conditions. In addition, pulsing parameters need to be optimized in order to ensure that energy expenditure is minimized.

6.3.4 Frosting and Icing of Pre-Wetted Surfaces

Only pre-wetted surfaces consisting of hydrophilic and superhydrophilic wettabilities were tested. Other types of surfaces, such as hydrophobic, superhydrophobic, and lubricant-impregnated surfaces, need to be pre-wetted and tested. In addition, surfaces were always pre-wetted with similar masses of liquid. Studies need to be performed where surfaces are pre-wetted with varying liquid masses in order to test pre-wetting effects.

APPENDICES

Appendix A

SUPPORTING INFORMATION: INKJET (CHAPTER 2)

A.1 Derivation

We modify Extrand and Gent's(49) analysis to accommodate a droplet moving on a spatially non-uniform surface. We consider a droplet centered over an ink-coated (wetable) track of known fixed width (w); the track is surrounded by the superhydrophobic paper. The advancing and receding contact angles on the ink track are $\theta_{\text{a}_{\text{ink}}}$, and $\theta_{\text{r}_{\text{ink}}}$, respectively. The corresponding values for the superhydrophobic paper are $\theta_{\text{a}_{\text{paper}}}$, and $\theta_{\text{r}_{\text{paper}}}$. This configuration is shown in (Figure A1), which also defines the azimuthal angle $\phi_1 = \sin^{-1} \left(\frac{w}{2R} \right)$ on the contact line where the philic line track meets the phobic domain. For the droplet domain that is in contact with the philic track (subscript 1), we consider a linear variation of $\cos \theta$ from $\cos \theta_{\text{r}_{\text{ink}}}$ at $\phi = 0$, to $\cos \theta_{\text{r}_{\text{paper}}}$ at ϕ_1 . Thus

$$\cos \theta_1 = \frac{\phi}{\phi_1} \cos \theta_{\text{r}_{\text{paper}}} + \left(1 - \frac{\phi}{\phi_1} \right) \cos \theta_{\text{r}_{\text{ink}}} \quad (\text{A.1})$$

The same approach is applied to the domain where the droplet is in contact with the superhydrophobic paper (subscript 2). We consider a linear variation of $\cos \theta$ from $\cos \theta_{\text{r}_{\text{paper}}}$ at ϕ_1 , to $\cos \theta_{\text{a}_{\text{paper}}}$ at $\phi = \pi/2$. Thus

$$\cos \theta_2 = \left(\frac{\phi - \phi_1}{\frac{\pi}{2} - \phi_1} \right) \cos \theta_{\text{a}_{\text{paper}}} + \left(\frac{\frac{\pi}{2} - \phi}{\frac{\pi}{2} - \phi_1} \right) \cos \theta_{\text{r}_{\text{paper}}} \quad (\text{A.2})$$

Appendix A (Continued)

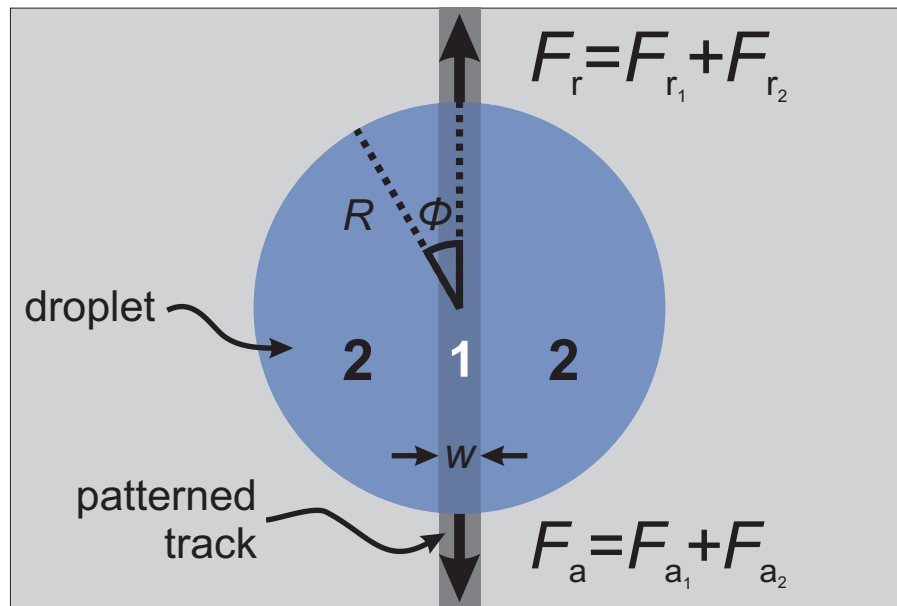


Figure A1. Top view schematic of a water droplet (radius R) sliding on a wettability patterned track (width w). F_a and F_r are the forces due to surface tension in the region of an advancing and receding contact line, respectively. ϕ is the azimuthal angle. 1 and 2 represent two distinct solid-liquid contact regions: 1) hydrophilic track; 2) superhydrophobic coated paper.

Appendix B

SUPPORTING INFORMATION: DROPLET IMPACT (CHAPTER 3)

B.0.1 Applicability to Other Theories

The present theoretical framework accounts for the role of the underlying surface wettability in the energy equation, and the cross-over energy that must be overcome when the fluid encounters a less wettable region. The study does not attempt to provide an exact theoretical framework to predict the maximum spreading diameter of impacting droplets, but rather explain the fundamental behavior expected when impact occurs on some ideal surfaces (wettability changes radially but not angularly). The equations used have an inherent overestimation or underestimation in their predictions. Thus, when they are modified to explain the phenomena we are presenting, the predicted values also suffer from the same shortcomings. Nonetheless, there is value in the present ideal system, which provides clues and a foundation for droplet impact on more complex wettability surfaces.

B.0.2 Describing Wettability by Contact Angles

Surface wettability can be described in terms of equilibrium (sessile) contact angle, or when the contact line is moving, in terms of advancing and receding contact angle. The contact angles reported in this work were measured as follows. A droplet with diameter 2.1 mm was deposited on a uniform-wettability surface and allowed to come to equilibrium. Subsequently, the volume of this droplet was increased at a steady rate so that the contact line advanced steadily. The

Appendix B (Continued)

contact angle formed by the droplet in this configuration is the advancing contact angle and was used to characterize the wettability of the different domains in this study. In the opposite situation where liquid is removed from the droplet, the contact line recedes, and the contact angle is known as the receding contact angle. In general, the two values (advancing and receding) of the contact angle are not similar, and their difference designates the mobility of the liquid on the surface. If this difference (known as contact angle hysteresis) is small, the liquid mobility is high (defining a self-cleaning surface). When the hysteresis is large, the liquid mobility is low, designating a sticky surface(117). The static/equilibrium contact angles are not referred in the main body of manuscript. They are mentioned in for completeness only. It is important to understand, that there are two types of advancing angles, static advancing angle (described above) and dynamic advancing angle (oftentimes referred to as the dynamic angle). In the case of a liquid droplet impacting a solid surface, where the advancing rim makes a contact angle with the surface as the rim advances. Depending on the impacting velocity of the droplet, this angle changes. This is what we refer to as the dynamic advancing angle.

B.0.2.1 Constancy of the Advancing Contact Angle

The dynamic advancing contact angle varies with Capillary number ($Ca = \frac{\mu U_o}{\sigma}$), but remains constant above a specific velocity. The capillary number is dependent on the contact-line velocity, which is of the order of the droplet impact velocity(118). Hoffman's law(119) relates the static angle to the dynamic advancing angle via use of the Capillary number, and is widely used in analytical formulations. Our experimental results confirmed a constant dynamic advancing angle for the range of Weber number studied, see Figure A2. This applied to the glass

Appendix B (Continued)

and coated domains. Thus, rather than incorporating the Hoffman law in order to predict the dynamic advancing angle, we averaged all the experimentally-observed values and used the average of $\theta = 115^\circ \pm 0.4^\circ$ for the glass domain and $\theta = 147^\circ \pm 0.9^\circ$ for the coated domain.

B.0.2.2 Validity of using the advancing angle in the energy equation

In the analytical portion of this work, we substituted the advancing angle into equations that are generally used in conjunction with the static/equilibrium contact angle. There is an ongoing discussion on the validity of this substitution. Certain authors(67) have noted this type of substitution to be invalid, while others found it valid(66; 68). Relying on our own experimental measurements, we maintain that the use of the advancing angle is physically valid and consistent for the situations examined herein.

B.0.2.3 Contact Angle Values

Contact angles of water droplets were measured using an in-house goniometer. The coated domain exhibited a static contact angle of $138^\circ \pm 0.9^\circ$, advancing contact angle $143.4^\circ \pm 1.6^\circ$, and receding contact angle of $135^\circ \pm 0.5^\circ$. The glass domains exhibited a static contact angle of $33^\circ \pm 1.0^\circ$, advancing contact angle $45.2^\circ \pm 1.7^\circ$, and receding contact angle of $\approx 0^\circ$.

Appendix B (Continued)

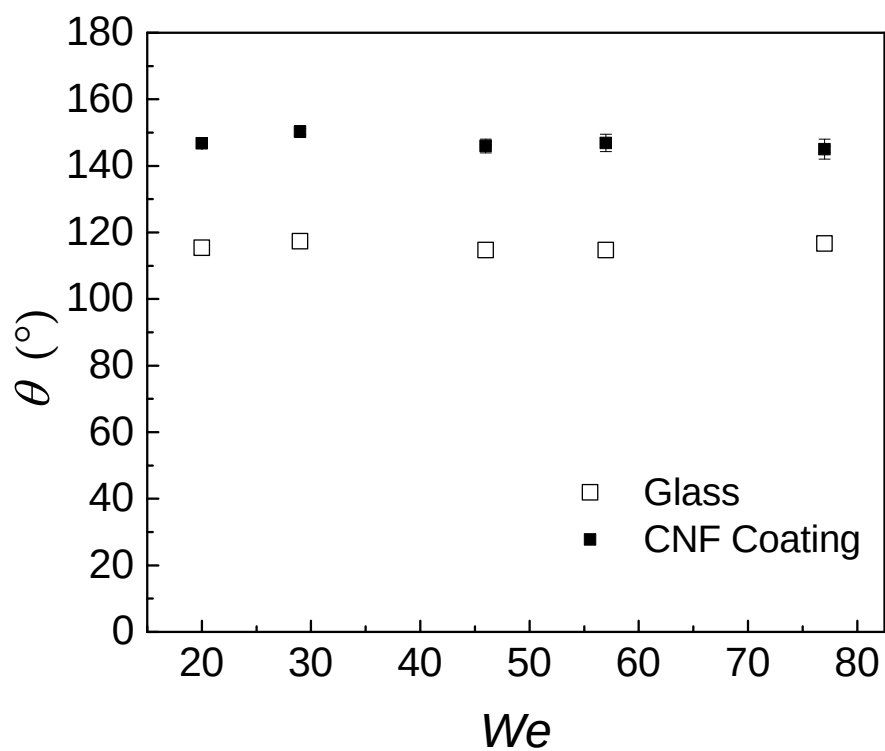


Figure A2. Experimentally-measured values of the dynamic advancing angles of droplets impacting on two types of surfaces utilized, glass (open squares) and coated glass (black squares). As seen from this graph, the angle remains relatively constant. The error bars are smaller than the symbol size. Error bars represent the standard statistical error of the measurements taken.

Appendix C

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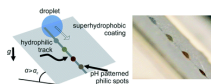
Inkjet patterned superhydrophobic paper for open-air surface microfluidic devices

Muhammad Elshewey,* Thomas M. Schutzu[†] and Christopher M. Mayfield^{*,†}

Author affiliations

Abstract

We present a facile approach for the fabrication of low-cost surface biomicrofluidic devices on superhydrophobic paper created by drop-casting a fluorocyclic copolymer onto microtextured paper. Wettability patterning is performed with a common household printer, which produces regions of varying wettability by simply controlling the intensity of ink deposited over prespecified domains. The procedure produces surfaces that are capable of selective droplet sliding and adhesion, when inclined. Using this methodology, we demonstrate the ability to tune the sliding angles of 10 μ L water droplets in the range from 13° to 40° by printing lines of constant ink intensity and varied width from 0.1 mm to 2 mm. We also formulate a simple model to predict the onset of droplet sliding on printed lines of known width and wettability. Experiments demonstrate open-air surface microfluidic devices that are capable of pumpless transport, mixing and rapid droplet sampling (~0.6 μ L at 50 Hz). Lastly, post treatment of printed areas with pH indicator solutions exemplifies the utility of these substrates in point-of-care diagnostics, which are needed at geographical locations where access to sophisticated testing equipment is limited or non-existent.



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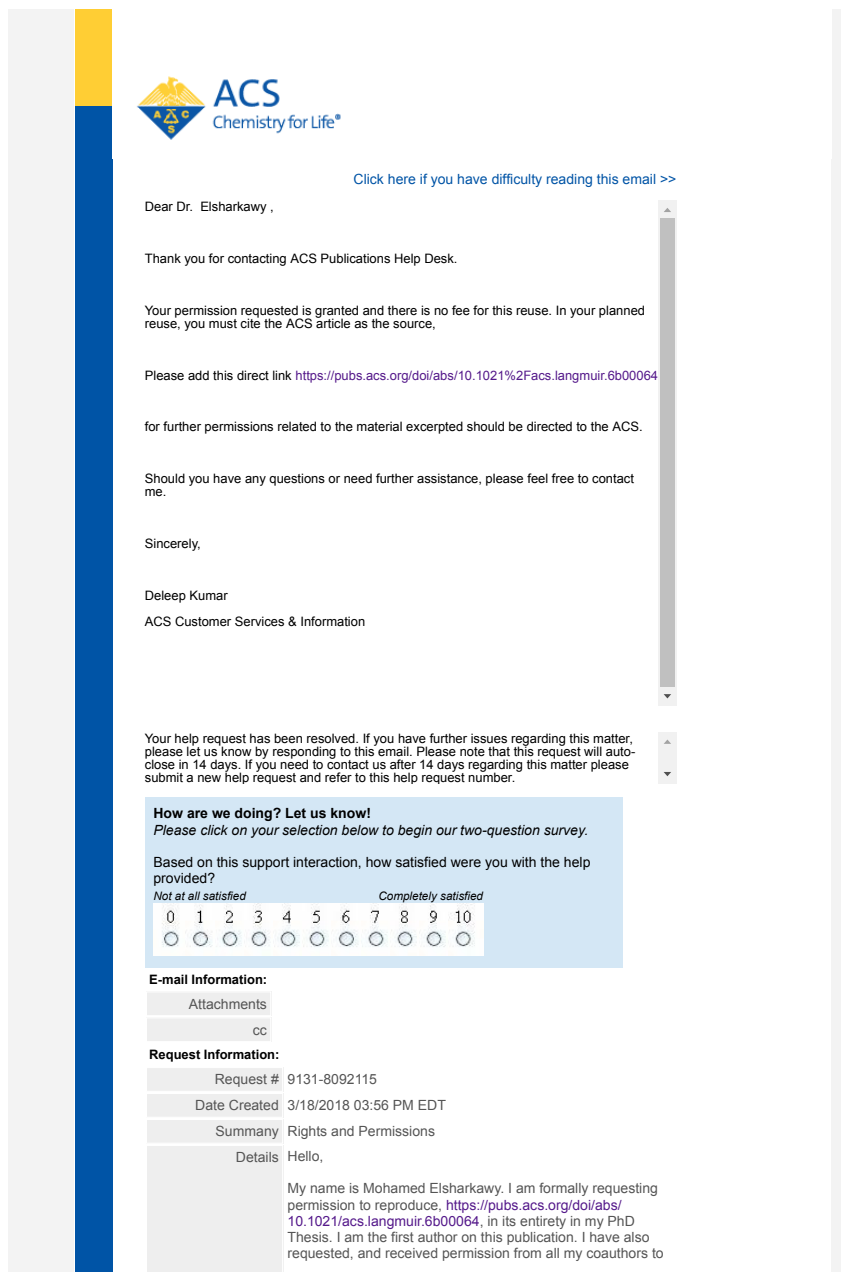
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Appendix C (Continued)



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HONORS

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PUBLICATIONS

- 1) T. M. Schutzius, M. Elsharkawy, M. K. Tiwari, C. M. Megaridis, "Surface Tension Confined (STC) Tracks for Capillary-Driven Transport of Low Surface Tension Liquids," *Lab on a Chip*, 2012, 12, 5237-5242
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