Doctoral Thesis

Rational Surface Nanoengineering for Phase Change and Separation Applications: From Desublimation Control to Sunlight-driven Antifogging

Author(s):
Walker, Christopher

Publication Date:
2019

Permanent Link:
https://doi.org/10.3929/ethz-b-000359058

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
Rational Surface Nanoengineering for Phase Change and Separation Applications: From Desublimation Control to Sunlight-driven Antifogging

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH Zurich
(Dr. sc. ETH Zurich)

presented by
CHRISTOPHER JOHN WALKER
MSc Mechanical Engineering, ETH Zurich

born 04.07.1988
citizen of
The United Kingdom & The United States of America

accepted on the recommendation of
Prof. Dimos Poulidakos, ETH Zurich
Dr. Thomas Schutzius, ETH Zurich
Prof. Daniel Bonn, University of Amsterdam
Prof. Jan Carmeliet, ETH Zurich

2019
Abstract

As the title suggests, my thesis investigates the use of rationally nanoengineered surfaces to control phase changes and phase separation. More precisely I look at the areas of desublimation frosting, sublimation defrosting, fogging, and oil-water separation. Each of these applications lie within the bounds of technologies that will improve our ability to more efficiently use energy and water, the two most important commodities on earth. Understanding the fundamentals of desublimation frosting is important for many applications, most notably for transportation and environmental building control. Improving the efficiently of defrosting within the sublimation regime adds additional efficiency improvements for such applications. Controlling the formation of condensation can not only be applied in energy generation, but also governs the engineering rules for designing antifogging surfaces, applicable in areas such as eye-wear, windows, and sensing. Oil-water separation has obvious applications in the area of wastewater remediation, such as industrial wastewater treatment or oil-spill cleanup. Each chapter of this thesis is dedicated to research into a novel aspect on one of these respective topics.

In the first chapter, we study the fundamentals of frost formation—both from water condensation (followed by freezing) and in particular from desublimation (direct growth of ice crystals from vapor)—and its implications for designing intrinsically icephobic surfaces. Guided by nucleation physics, we investigate the effect of material composition and surface texturing (atomically smooth to nanorough) on the nucleation and growth mechanism of frost for a range of conditions within the sublimation domain. Surprisingly, we observe that on silicon at very cold temperatures—below the homogeneous ice solidification nucleation limit—desublimation does not become the favorable pathway to frosting. Furthermore, we show that surface nanoroughness makes frost formation more probable, facilitated by capillary condensation, consistent with Kelvin’s equation. The findings show that such nanoscale surface morphology imposed by design to impart desired functionalities—such as superhydrophobicity—or from defects can be highly detrimental for frost icephobicity at low temperatures and water vapor partial pressures.

The second chapter consists of a feasibility study, containing on-going work, in which we introduce a novel phenomenon that can be used to enhance the efficiency of deicing. Here, we observed that ice crystals, upon sublimation, may spontaneously detach from the substrate before they completely sublimate. We present the spontaneous detachment phenomenon and initially examine the conditions at which this happens. This initial analysis provides us with insight allowing us to postulate the mechanism for detachment. We recognize that this phenomenon has obvious applications to enhance ice removal in areas such as transportation and energy generation and its work is therefore planned to continue beyond the scope of this thesis.

In the third chapter we introduce a novel approach for energy sustainable antifogging on transparent surfaces. Going beyond state-of-the-art techniques, such as superhydrophilic
and superhydrophobic coatings, we rationally engineer solar absorbing metasurfaces that maintain transparency to offer an alternative passive antifogging solution. Upon illumination, induced localized heating significantly delays the onset of surface fogging and decreases defogging time. For the same environmental conditions, we demonstrate that our metasurfaces are able to reduce defogging time by up to 4-fold and under supersaturated conditions inhibit the nucleation of condensate, outperforming conventional state-of-the-art approaches in terms of visibility retention. The research here illustrates a durable and environmentally sustainable approach to antifogging and defogging for transparent surfaces, opening up the opportunity for large-scale manufacturing that can be applied to a range of materials, including polymers and other flexible substrates.

In the final chapter, we investigate the implications of surfactants on oil-water membrane separation. Due to the stabilization of the dispersed phase in surfactant-laden emulsions, membrane filtration has become a promising technology to improve separation and flux efficiencies. Here we investigate the fundamental wetting and transport behavior of such surfactant-stabilized droplets and the flow conditions necessary to perform sieving and separation of these stabilized emulsions. We show that, for water-soluble surfactants, such droplets are completely repelled by a range of materials (intrinsically underwater superoleophobic) due to the detergency effect; therefore, there is no need for surface micro-/nanotexturing or chemical treatment to repel the oil and prevent fouling of the filter. With this new understanding, we demonstrate the use of a commercially available filter—without any additional surface engineering or functionalization—to separate oil droplets ($d < 100 \, \mu m$) from a surfactant-stabilized emulsion with a flux of $\sim 11,000 \, L \, m^{-2} \, h^{-1} \, bar^{-1}$.

I believe that the novel ideas and findings that I contributed to will find applications in a variety of areas to contribute to a more sustainable global water and energy future.
Zusammenfassung


Das zweite Kapitel beinhaltet eine Machbarkeitstudie mit aktuell noch laufender Forschung, die eine neue Phänomen der Enteisung vorstellt. Wir beobachten dass Eiskristalle sich während der Sublimation, bevor sie komplett sublimiert sind, spontan von Oberflächen ablösen können. In diesem Kapitel präsentieren wir dieses Phänomen und zeigen die nützigen Ausgangsbedingungen um das Ereignis zu beobachten. Diese erste Analyse bietet uns den nützigen Einblick um einen Ablösungsmechanismus zu postulieren. Wir erkennen, dass dieses Phänomen klare Anwendungen in der Verbesserung der Entfrostungseffizienz in den Bereichen Verkehrswesen und Stromproduktion hat und planen
deshalb, diese Forschung weiterzuführen.


Im letzten Kapitel untersuchen wir die Auswirkungen von Tensiden auf die Öl-Wasser-Membrantrennung. Aufgrund der Stabilisierung der dispersierten Phase in tensidbeladenen Emulsionen ist die Membranfiltration eine vielversprechende Technologie zur Verbesserung der Trenn- und Flusseffizienz. Hier untersuchen wir das grundsätzliche Benetzungs- und Transportverhalten solcher tensidstabilisierter Tröpfchen sowie die Strömungsbedingungen, die für das Sieben und Trennen dieser stabilisierten Emulsionen erforderlich sind. Wir zeigen, dass für wasserlösliche Tenside solche Tröpfchen aufgrund des Reinigungseffektes durch eine Reihe von Materialien (unterwasser-superoleophob) vollständig abgewiesen werden. Daher ist keine Oberflächenmikro-/Nanorauigkeit oder chemische Behandlung erforderlich, um das Öl abzuweisen und ein Verschmutzen des Filters zu verhindern. Mit diesem neuen Verständnis demonstrieren wir die Verwendung eines kommerziell erhältlichen Filters—ohne zusätzliche Oberflächentechnik oder Funktionalisierung—zur Abtrennung von Öltröpfchen ($d < 100 \, \mu m$) aus einer tensidstabilisierten Emulsion mit einem Fluss von $\sim 11,000 \, L \, m^{-2} \, h^{-1} \, bar^{-1}$.

Die neue Ideen und Schlussfolgerungen, die ich in dieser Doktorarbeit präsentiere, erlauben meiner Meinung nach Anwendungen in zahlreichen Bereichen, um zu einer nachhaltigeren globalen Wasser- und Energiezukunft beizutragen.
Acknowledgements

I have a great many people to thank for the success of this thesis. First and foremost, I would like to thank Professor Dimos Poulikakos for providing me the opportunity to do a doctoral thesis under his supervision. His insight, experience, and subject knowledge were crucial to the success of my work and were the most important factors to allow my research to receive the recognition that it did.

Secondly, I have to thank Dr. Thomas Schutzius. I cannot imagine a better supervisor and do not know a better up-and-coming scientist. On a day-to-day level, he was the most important person that contributed to the success of my research. He constantly provided me with valuable advice, ideas, encouragement, knowledge, and energy. He taught me how to think like a scientist and engineer, how to make the improbable seem possible, and what hard work really is.

It is my pleasure to have Professor Daniel Bonn and Professor Jan Carmeliet as external co-examinees. I admire their respective research and extend a great thanks to them for taking the time to critically examine my thesis.

I would like to extend a thank you to all the present and past members of LTNT during my time in the lab. Not only were they helpful and supportive at work, but with many of them I built friendships outside the lab. Additionally, I would like to thank all of the bachelor and master students at LTNT that I worked with, many of which helped to collect data and results that are included in this thesis.

My research would not have been possible without the help of Jovo Vidic, who took care of many aspects concerning electronics, sensing, and data acquisition. We also enjoyed a great many discussions on a variety of topics that helped keep my thesis in perspective during trying times. Peter Feusi helped greatly in the mechanical design and construction of a handful of very integral set-ups that I used in my thesis. His expertise, advise, and know-how were invaluable. Ute Drechsler provided me with invaluable assistance in the BRNC cleanroom. Without her I would have not been able to create the surfaces that were necessary to conduct my research.

Finally, I would like to thank my mother, who provided me with unwavering emotional support throughout the journey. Without her, I would have never been able to make it this far.
## Contents

Abstract ......................................................................... i
Zusammenfassung ............................................................... iii
Acknowledgements .............................................................. v
List of Figures ................................................................... xi
Definition of Variables........................................................... xiii

1 Introduction 1
1.1 The Water-Energy Nexus .................................................. 2
1.2 Multi-phase Water Transport Phenomena .......................... 2
  1.2.1 Fundamentals of Frost Formation ............................... 3
  1.2.2 Challenges in Fogging .............................................. 4
1.3 Oil-Water Separation ...................................................... 6

2 Desublimation Frosting on Nanoengineered Surfaces 9
2.1 Introduction ................................................................ 11
2.2 Theory...................................................................... 13
  2.2.1 Gibbs Free Energy .................................................. 13
  2.2.2 Energetically Favorable Nucleation Pathway ....................... 15
  2.2.3 Heterogeneous Nucleation .......................................... 16
  2.2.4 Nucleation Rate ..................................................... 19
2.3 Methods .................................................................... 23
  2.3.1 Setup ................................................................ 23
  2.3.2 Experimental Protocol .............................................. 24
  2.3.3 Surface Preparation ................................................. 24
  2.3.4 Surface Characterization ............................................ 28
2.4 Results ..................................................................... 29
  2.4.1 Desublimation–Condensation Nucleation Transition ............... 29
# CONTENTS

5.1 Introduction ................................................................ 81  
5.2 Methods .................................................................... 83  
  5.2.1 Materials ............................................................ 83  
  5.2.2 Preparation.......................................................... 83  
  5.2.3 Characterization ...................................................... 84  
  5.2.4 Experimental Protocol .............................................. 85  
5.3 Results and Discussion..................................................... 87  
  5.3.1 Surfactant Influence on Wetting Behavior: The Role of Detergency 87  
  5.3.2 Oil–Water Separation Using Nonfunctionalized Surfaces .......... 92  
  5.3.3 Large-Area Separation Materials ................................. 98  
5.4 Conclusions ................................................................ 101  

6 Conclusion & Outlook .......................................................... 103  
  6.1 Conclusion ................................................................ 103  
  6.2 Outlook .................................................................... 105  
References ....................................................................... 107  
List of Publications .............................................................. 115  
Conference Presentations ....................................................... 115
List of Figures

1.1 The Refrigeration Cycle ............................................... 4

2.1 Gibbs Free Energy ..................................................... 15
2.2 Nucleation Mode as a Function of Temperature and Pressure ...... 16
2.3 Effect of Surface Energy on Gibbs Free Energy ....................... 18
2.4 Effect of Contact Angle on Nucleation ............................... 19
2.5 Nucleation Rate as a Function of Temperature and Pressure ....... 21
2.6 Desublimation Experimental Setup ................................... 23
2.7 Silver Iodide Sample Characterization................................. 25
2.8 AFM of Silicon Samples ............................................... 26
2.9 Boehmite Structure on Aluminum .................................... 27
2.10 Condensation-Desublimation Nucleation Transition of AgI .......... 29
2.11 Effect of Nanotexture on Heterogeneous Nucleation ................. 31
2.12 Experimental Nucleation Conditions for Silicon ....................... 33
2.13 Mechanism for Nucleation on Nanotexture ........................... 35

3.1 Crystal Detachment during Sublimation .............................. 39
3.2 Experimental Protocol for Controlling Sublimation Variables ...... 41
3.3 Detachment Probability for Different Sublimation Cycles ............ 42
3.4 Illustration of Crystal Detachment Progression ....................... 44
3.5 Proposed Mechanism of Crystal Detachment ......................... 45
3.6 ESEM Image Sequence of Sublimating Ice ........................... 46
3.7 Sublimation Process induced by Reduced Vapor Pressure ............ 47

4.1 Nucleation Rate Dependence on Contact Angle ...................... 54
4.2 Effect of Contact Angle on Nucleation Density ....................... 56
4.3 Influence of Temperature on Nucleation Rate ....................... 57
4.4 Working Principle of Metasurface ..................................... 58
4.5 Surface Characteristics of Metasurface ............................... 60
4.6 Contact Angles ........................................................ 63
4.7 Effect of Fogging on Clarity and Distortion ........................... 67
4.8 Optical Characterization of Surfaces .................................. 69
4.9 Temperature Response of Surface Types ............................. 70
4.10 Evaporation of Single Droplet ....................................... 72
4.11 Metasurfaces for Reduced Defogging Time ........................... 73
4.12 Antifogging Performance of Metasurfaces ........................... 75
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Rolling-up Mechanism</td>
<td>82</td>
</tr>
<tr>
<td>5.2</td>
<td>Underwater Contact Angles of Hexadecane</td>
<td>88</td>
</tr>
<tr>
<td>5.3</td>
<td>Surface AFM Scans.</td>
<td>89</td>
</tr>
<tr>
<td>5.4</td>
<td>Oil-Water Interfacial Tension</td>
<td>89</td>
</tr>
<tr>
<td>5.5</td>
<td>Surfactant Concentration on Wetting Behavior</td>
<td>92</td>
</tr>
<tr>
<td>5.6</td>
<td>Demonstrating Emulsion Sieving</td>
<td>93</td>
</tr>
<tr>
<td>5.7</td>
<td>Droplet Distribution with and without Standard Metallic Mesh</td>
<td>95</td>
</tr>
<tr>
<td>5.8</td>
<td>Droplet Entrained in Flow</td>
<td>96</td>
</tr>
<tr>
<td>5.9</td>
<td>Oil-water Separation with Commercially Available Filter</td>
<td>99</td>
</tr>
<tr>
<td>5.10</td>
<td>Dynamics Light Scattering Characterization</td>
<td>99</td>
</tr>
</tbody>
</table>
Definition of Variables and Abbreviations

Desublimation Frosting on Nanoengineered Surfaces

Variables

- $\alpha, \beta, \zeta$: numerical factors for non-spherical embryo shapes
- $\gamma$: interfacial energy
- $\theta$: inherent contact angle
- $\mu$: chemical potential
- $\phi_b$: surface coverage of bumps
- $\phi_p$: surface coverage of pits
- $A$: embryo surface area
- $c$: concentration
- $f$: nucleation geometric factor
- $g_c = (1 + 2mx + x^2)^{1/2}$
- $\Delta G$: change in Gibbs free energy
- $\Delta G^*$: critical change in Gibbs free energy
- $H$: mean curvature
- $J$: pre-exponential nucleation term
- $J_{12}$: nucleation rate
- $J_N$: nucleation rate for nanotextured surface
- $J_S$: nucleation rate for smooth surface
- $k$: Boltzmann constant
- $m$: mass of water molecule
- $n$: number of molecules per unit volume
- $p_0$: ambient pressure
- $p$: environmental water vapor pressure
- $p_n$: saturated vapor pressure over a plane surface of phase $n$
- $r$: embryo radius
- $r^*$: critical embryo radius
- $R$: radius of curvature
- $T$: environment temperature
- $T_\infty$: source cooling block temperature (inside block)
- $T_b$: source cooling block temperature (on block)
- $T_s$: sample temperature
- $v$: embryo volume
- $x = R/r^*$

Acronyms

- 1: parent phase
- 2: daughter phase
- AgI: Silver iodide
- V: vapor phase
- L: liquid phase
- S: solid phase
- TEC: Thermoelectric cooler
Transparent Metasurfaces Counteracting Fogging by Harnessing Sunlight

Variables

\( \alpha, \beta, \lambda \) constants
\( \gamma \) water-air surface energy
\( \delta \) distortion
\( \theta \) macroscopic water contact angle
\( \theta^*_a \) macroscopic advancing contact angle
\( \theta^*_r \) macroscopic receding contact angle
\( \rho_n \) nucleation density
\( A \) absorption
\( C \) clarity
\( d \) dot diameter
\( f \) nucleation geometric factor
\( J \) nucleation rate
\( J_0 \) nucleation constant
\( \Delta G^* \) critical Gibbs Free Energy for condensation
\( I \) mean intensity
\( k \) Boltzmann constant
\( n_L \) molecular volume of water
\( p \) water vapor pressure
\( p_L \) saturated vapor pressure
\( \frac{p}{p_L} \) supersaturation

\( P \) performance factor
\( R \) reflection
\( t \) time
\( t_{df} \) defogging time
\( T \) transmission
\( T_e \) environmental temperature
\( T_s \) sample temperature
\( T_w \) water temperature
\( V_d \) droplet volume

Acronyms

Au gold
iCVD initiated vapor deposition
IR infrared
PFDA perfluorodecyl acrylate
RH relative humidity
RMS root mean square
TBPO tert-butyl peroxide
TCVS trichlorovinylsilane
TiO\(_2\) titania
Detergency and Its Implications for Oil Emulsion Sieving and Separation

Variables

$\gamma$ interfacial energy
$\Delta \gamma = \gamma_{sw} - \gamma_{so}$ surfactant adsorption density
$\theta$ intrinsic contact angle
$\theta^*$ apparent contact angle
$\theta^*_a$ apparent advancing contact angle
$\theta^*_r$ apparent receding contact angle
$\mu$ water viscosity
$\bar{\mu}$ oil viscosity
$\rho$ water density
$\bar{\rho}$ oil density
$d$ droplet diameter
$D$ pipe diameter
$g$ gravity
$N$ number of drops within certain size
$N_0$ total number of drops
$\Delta P$ pressure drop
$R$ pore radius
$L$ pore length

$u$ flow velocity
$v$ kinematic viscosity
$V_z$ sphere velocity
$w$ pore size opening
$Re$ Reynolds Number
$We$ Weber Number

Abbreviations

AFM atomic force microscopy
Al Aluminum
cmc critical micelle concentration
DLC dynamic light scattering
O oil phase
PMMA poly(methyl methacrylate)
PVDF poly(vinylidene fluoride)
S solid phase
SDS sodium dodecyl sulfate
SS stainless steel
W water phase
Introduction
1.1 The Water-Energy Nexus

The concept of the water-energy nexus refers to the interdependence of the world’s two most critical resources: water and energy.\(^1\) It encompasses the relationship between the water used for energy production as well as the energy consumed to extract, purify, treat, transport, heat, cool, or dispose of water.\(^2\) Historically, the motivation to understand this interdependence in great detail has been less relevant, due largely to the relative abundance of both resources.\(^1\) However, recent developments including urbanization, globalization, climate change, as well as population and economic growth have drastically increased the demand for water and energy resources.\(^{1,3}\) For example, approximately three quarters of a billion people world-wide live without access to clean water,\(^4\) while well over a billion people lack access to electricity.\(^5\) Furthermore, climate change—fueled by the ever increasing global energy demand—is causing problems such as forced migration,\(^6\) political tension,\(^7\) and the disruption of important natural habitats.\(^8\)

As these effects are being felt across the globe, both political and scientific efforts are focused on investigating and producing innovative technologies to address the ramifications of the water-energy nexus. Technologies of such include solar water splitting, solar evaporation, fog and dew collection, cloud seeding, membrane water treatment, deicing, radiative cooling, oil-water separation, and solar disinfection.\(^9\) Further improvements in efficiency and performance of these technologies are in many cases fundamentally limited by multi-phase momentum, heat, and mass transport occurring at interfaces. This has lead to an increase in research activity to develop and study rationally engineered surfaces aimed at enhancing these transport phenomena. This thesis adds scientific understanding for three important technological areas addressing the water-energy nexus: oil-water separation, fundamentals of frosting and challenges in fogging.

1.2 Multi-phase Water Transport Phenomena

Understanding multi-phase transport phenomena at interfaces has ubiquitous applications. In particular, understanding and controlling water condensation and freezing at interfaces is paramount to improving the efficiencies of common thermodynamic cycles such as the Rankine cycle for energy generation,\(^{10,11}\) and the refrigeration cycle for building environmental control,\(^12\) whose combined usage account for more than 80% of the total global energy consumption.\(^10\) Additionally, this knowledge is paramount in understanding global climate patterns,\(^13\) clean water harvesting,\(^{14-16}\) and ensuring safe transportation.\(^17\) The second and third chapters of this thesis are dedicated to the study of water condensation and desublimation phase change at interfaces and how one can engineer surfaces to
passively control these phase changes in practical applications. The second chapter investigates the fundamentals of frost formation on surfaces, while the third chapter explores a novel approach to anti-fogging for transparent surfaces.

1.2.1 Fundamentals of Frost Formation

Research into the fundamentals of frost formation typically falls under the larger scope of research aimed to improve icephobicity. Research in icephobicity is primarily concerned with understanding how to engineer surfaces to discourage ice accretion, which has a variety of important industrial applications in areas such as aviation, automotive, and energy generation. Although there are a number of approaches to engineer icephobic surfaces—including surfaces that efficiently remove super-cooled water droplets,18,19 surfaces that repel ice upon freezing,20 or surfaces that exhibit low ice adhesion21—this thesis investigates surfaces that aim to prevent ice nucleation,22,23 in particular from the vapor. Ice nucleation from the vapor is better known as frosting and is one of the most common examples of surface ice accretion. Frosting happens when a critical amount of water vapor in the air is exposed to a surface below the freezing point and proceeds to cover the surface with ice crystals. Although this process is ubiquitous, our fundamental understanding of how it happens is limited. Widening our understanding will inform us on how to improve the efficiency and safety of a variety of applications.

One of the best examples of how a fundamental understanding of frost formation can positively influence global energy efficiency is environmental building control, also known as heating, ventilating, and air conditioning (HVAC). HVAC accounts for between 20–40% of the total energy consumption in developed countries24 and uses the so-called refrigeration cycle, pictured in Figure 1.1. The evaporator is a heat exchanger, whose coils are filled with cold refrigerant used to cool a load (i.e. building environment). The heat extracted from the building environment evaporates the refrigerant to a saturated vapor, which then continues along the cycle. The right side of Figure 1.1 shows a close-up of an evaporator coil. Frost accumulating on the coil—due to even low levels of humidity in the building—will increase the heat transfer resistance ($R$) for the flow of heat from building to the refrigerant ($Q_C$) according to eq 1.1. This will result in a larger temperature difference ($T_i - T_r$) and will thereby reduce the efficiency of the cycle.

$$Q_C = \frac{T_i - T_r}{R}$$ (1.1)

Due to the ubiquity of such a cycle and the global energy consumption used, even incremental changes in the cycle efficiency translate into enormous global energy savings. The work in the second chapter of this thesis aims to better understand how to engineer
4 Introduction

Figure 1.1: Illustration of the refrigeration cycle used for environmental control in buildings. The evaporator is a heat exchanger that typically uses metal pipes filled with a refrigerant used to cool the load (i.e. building). The cold refrigerant removes heat from the building and in the process is evaporated to a saturated vapor. Because the refrigerant is very cold, even low humidity levels in the building can lead to condensate and ice formation on the evaporator pipes. This causes an increase in the resistance ($R$) to the heat flow ($Q_C$) from the load temperature ($T_l$) to the refrigerant temperature ($T_r$), reducing the efficiency of the system.

By examining the fundamentals of the nucleation phenomena that govern desublimation frosting, we not only learn what makes surfaces more resistant to frosting, but also gain general insight into nucleation phenomena, advantageous to a variety of other applications outside of icephobicity governed by nucleation physics, such as biomineralization, crystallization, and surface fouling.

1.2.2 Challenges in Fogging

Not only can the uncontrolled nucleation of water have detrimental effects for power generation, building environment control, and travel, it can also hinder visibility. Visibility hinderance due to fogging is a phenomenon that can be identified in everyday life. Think back to the last time you tried driving a car with fogged windows or stepped out of the...
shower to see your blurred reflection in the mirror. A fogged surface consists of a collection of microdroplets that form on a cool surface when it is exposed to an environment of high humidity. These microdroplets act as tiny lenses, that scatter the incident light, reducing the clarity and increasing the distortion of object viewed through the surface.\textsuperscript{31} Alleviating this visibility hindrance is a requirement for a variety of applications, including eyewear, windows, and sensing, where visibility through a surface is of paramount importance.

Due to its importance, scientists have developed a variety of different approaches to engineer antifogging surfaces, each of which is characterized as either passive or active. A passive approach changes the intrinsic surface properties in order to favorably steer the nucleation behavior in one direction or the other. Active approaches, on the other hand, use an external energy source in an attempt to completely inhibit nucleation on the surface. Superhydrophilicity is one of the most common passive techniques for antifogging.\textsuperscript{32} Condensed water on a superhydrophilic surface results in a continuous film of water instead of individual droplets. The continuous film reduces the light scattering and therefore retains clarity of light transmitted through the transparent surface.\textsuperscript{31} Specially-engineered superhydrophobic surfaces is another passive approach. Successful implementation of superhydrophobicity results in surfaces that can actively shed nucleated drops,\textsuperscript{33–35} using some sort of small and preexisting external force such as wind or gravity. Passive surface engineering techniques such as these are attractive for antifogging because they do not rely on a supplemental external energy source. Nonetheless, these types of surfaces are known to become easily contaminated or damaged over time, resulting in substantial degradation of their antifogging properties.

As previously mentioned, active technologies for antifogging use a supplementary external energy source. Typically this energy is supplied in the form of heat—such as electrically through Joule heating—in order to either evaporate the condensate droplets more quickly or to discourage them from nucleating in the first place.\textsuperscript{36} This is a popular approach, due to the strong dependence of nucleation rate on the surface temperature, whose effect is not stymied by surface contaminants and degradation. Unfortunately, this approach to antifogging relies on a supplementary external energy source, which reduces energy sustainability and in many cases may not be practical. In the third chapter of this thesis, we demonstrate how one can use sunlight as a renewable energy source for surface antifogging. Our approach eliminates the surface degradation and contamination issue of passive solutions, while using an independent and renewable energy source for heating. Using sunlight not only reduces the burden of energy consumption, but also facilitates the implementation of anitfogging for applications where a supplemental on-board energy source may be cumbersome or impossible. This may have important future implications for areas such as instrumentation and sensors for autonomous vehicles.
1.3 Oil-Water Separation

Clean water generation from contaminated water is one of the most important undertakings of the 21st century. Currently it is done mainly using a variety of water purification technologies, such as desalination, de-chlorination, filtering of toxins, bacteria and viruses, and oil-water separation. Particularly relevant to the work presented in the first chapter of this thesis is oil-water separation.

Rapid industrial, economic, and population growth has spurred an increased demand for clean water, while at the same time increasing the production of oily wastewater and pollution. The high energy consumption used to separate oil-polluted water has necessitated the development of innovative technologies that improve the energy efficiency of oil-water separation. Although many conventional methods for the purification of oily wastewater exist, membrane separation processes have proven themselves as an emerging technology in the 21st century. In contrast to conventional technologies, membrane separation promises to be lower cost, have no secondary pollutants, avoid using toxic compounds, have smaller footprints of installation, and can more effectively separate emulsions with oil droplet sizes smaller than 20 \( \mu \text{m} \). Microfiltration membranes (pore sizes of 50-500 nm) and ultrafiltration membranes (pore sizes of 2-50 nm) have already shown high flux and good separation efficiencies when used for oil-water separation.

The main hurdle that remains to wide-spread implementation is maintaining long-term membrane efficiencies. The flux efficiency can be quantified by the overall ability to separate oil and water and the speed at which this can be done for a fixed energy input (e.g. pumping). Additionally, the separation efficiency—or the percentage of oil that is blocked by the membrane—is of obvious importance. One of the largest detriments to flux efficiency is fouling due to surfactant adsorption and/or plugging by oil droplets over time, because it leads to an increased pressure drop across the membrane. Furthermore, the two efficiencies are linked by the pore size of the membrane. Therefore, engineering the pore size with respect to the distribution of oil droplet size is an important aspect to consider when designing the most efficient membranes.

The main approach to mitigating fouling and plugging of the membranes is by altering the wettability of the membrane with respect to water and oil. This is done by imparting both rationalized nano and/or microscopic morphology in combination with selecting the appropriate chemical composition for the membrane surface. Depending on the type of emulsion, two different approaches for the surface wetting behavior have been demonstrated to be effective. Membranes developed to filter water-in-oil emulsions are engineered to enhance superhydrophobicity, while retaining superoleophilicity, allowing oil to easily wick through, while inhibiting the penetration of water droplets. Enhancing the superhydrophobicity of the membrane aids in the removal of filtered water droplets.
and thereby avoiding membrane plugging and reduced flux efficiency. On the other hand, membranes developed to filter oil-in-water emulsions take advantage of membranes that exhibit simultaneous superhydrophilicity and superoleophobicity, allowing water to easily wick through, while inhibiting the penetration of oil droplets. Again, by enhancing the superhyrdophilicity and superoleophobicity, filtered oil droplets are more easily removed from the membrane and allow for flux efficiencies to be maintained over time. Unfortunately, many of the studies have neglected a rigorous investigation and understanding on the effect of surfactants—which are almost always present in such emulsions—and how this influences the membrane effectiveness in separation. Additionally, they often lack any rational engineering explanation of pore size choice, in particular for surfactant-laden emulsions. The first chapter in this thesis addresses these topics and investigates its implications for oil-water separation efficiency. It is the goal of this chapter to enhance our understanding of how to purify water with the minimum energy input.
Desublimation Frosting on Nanoengineered Surfaces

This chapter is reproduced in part with permission from:


Copyright 2018 American Chemical Society.
Abstract

Ice nucleation from vapor presents a variety of challenges across a wide range of industries and applications including refrigeration, transportation, and energy generation. However, a rational comprehensive approach to fabricating intrinsically icephobic surfaces for frost formation—both from water condensation (followed by freezing) and in particular from desublimation (direct growth of ice crystals from vapor)—remains elusive. Here, guided by nucleation physics, we investigate the effect of material composition and surface texturing (atomically smooth to nanorough) on the nucleation and growth mechanism of frost for a range of conditions within the sublimation domain (0 to $-55^\circ$C; partial water vapor pressures 6 to 0.02 mbar). Surprisingly, we observe that on silicon at very cold temperatures—below the homogeneous ice solidification nucleation limit ($<-46^\circ$C)—desublimation does not become the favorable pathway to frosting. Furthermore, we show that surface nanoroughness makes frost formation on silicon more probable. We experimentally demonstrate at temperatures between $-48$ and $-55^\circ$C that nanotexture with radii of curvature within 1 order of magnitude of the critical radius of nucleation favors frost growth, facilitated by capillary condensation, consistent with Kelvin’s equation. Our findings show that such nanoscale surface morphology imposed by design to impart desired functionalities—such as superhydrophobicity—or from defects can be highly detrimental for frost icephobicity at low temperatures and water vapor partial pressures ($< 0.05$ mbar). Our work contributes to the fundamental understanding of phase transitions well within the equilibrium sublimation domain and has implications for applications such as travel, power generation, and refrigeration.
2.1 Introduction

Over the past decade, research in nucleation physics and the rational design of icephobic surfaces has been experiencing rapid growth due to exciting recent findings and the ability to probe and explain previously unexplored phenomena. Examples include distinct frost growth patterns on different chemically treated surfaces that allow easier frost removal or the spontaneous jumping of droplets coalescing on hydrophobic surfaces to prevent freezing of supercooled droplets. Going beyond scientific value, such research is crucial in understanding how to engineer surfaces for commercial usage to benefit practical applications. To this end, industries spanning from road and air transportation, to transmission lines, to energy generation by wind turbines and refrigeration cycles can harvest significant benefit from the development of icephobic surfaces with better performance under temperatures far below the equilibrium freezing point. Icephobicity, at the very fundamental ice formation level, can be characterized as the ability to hinder heterogeneous ice nucleation on the surface. An example of heterogeneous ice nucleation, commonly referred to as frosting, is the formation of ice crystals on a surface at a temperature below the freezing point and exposed to a supersaturated vapor environment. This ice nucleation can follow two pathways: vapor to liquid to solid (condensation-freezing) or vapor to solid (deposition or desublimation). These two pathways, in a variety of forms, have long been an area of interest in the atmospheric sciences due to their importance for understanding how particles in the environment influence the formation of clouds, fog, rain, sleet, and snow. This work has focused on either inorganic crystals or natural particles commonly found in the atmosphere that expedite ice nucleation. Understanding what makes a surface icephobic, however, must involve the intertwined effects of surface material types and properties with respect to counteracting ice nucleation. Furthermore, understanding how these factors affect the mechanism and transition between the two modes of heterogeneous nucleation from vapor is crucial in understanding how to design and tailor icephobic surfaces for different applications.

The effect of surface topography on ice nucleation has been a topic that has received renewed attention in recent years, due to the increased interest in developing inherently icephobic surfaces and the increasing ability to impart topography with desired nanoscale features in a controlled manner. However, due to the number of nucleation modes, there still remain considerable aspects not completely understood, including performance and pathway dependence under a range of environmental conditions. For example, with solidification, studies have concluded that nanotexture, with radii of curvature within 1 order of magnitude of the critical radius, does not facilitate nucleation of supercooled water droplets (heterogeneous nucleation from the melt), although classical nucleation theory would predict it. These results are explained either by the formation of an amorphous quasi-liquid layer at the interface between the nascent ice embryo and the
surface, counteracting the decrease interfacial energy, which should otherwise be provided by the pits, or due to the relatively higher interfacial energy between the liquid and solid in comparison to that of the liquid and vapor, considerably dampening the geometrical effect of the pits to enhance nucleation rate. Evidence that nanotexture and nanoscale surface defects improve crystal nucleation from vapor have been previously shown, such as chemical vapor deposition of diamond as well as the growth of organic crystals. However, despite its importance, the effect of nanotexture on water vapor desublimation, at the intersection of the science bases of ice nucleation and surface nanofabrication, remains largely unexplored.

This chapter begins by introducing the theory behind classical nucleation physics, applied in particular to the sublimation domain of the water equilibrium diagram, and mapping the energetically favorable homogeneous nucleation mode as a function of temperature and supersaturation. We continue by studying heterogeneous nucleation, by examining the influence of a surface on nucleation physics, in particular the its surface energy and topography. We then discuss the nucleation rate and its importance in defining the probability of observing phase change. The results that were gathered, verify our experimental apparatus and methodology by comparing our own findings on silver iodide crystals to those in literature. We use these experiments to begin our discussion on how substrate material affects the barrier to heterogeneous ice nucleation and the heterogeneous condensation–desublimation nucleation transition in practice. We then investigate silicon and aluminum surfaces to elucidate the effect of surface morphology, namely, nanotexturing, on frost nucleation behavior. The chapter ends with a discussion on the basis of our experimental findings. We propose a mechanism for how ice nucleates from vapor under cold (≤−46°C) and dry (< 0.05 mbar) conditions on a host of substrate materials and surface topographies. Based on our findings we suggest rational design rules that must be considered when engineering icephobic surface textures for realistic applications.
2.2 Theory

In order to best advise the design of icephobic surfaces, it is first necessary to understand how a surface can influence icephobicity. The focus here is on desublimation frosting, for which we must begin by digging into the science behind nucleation physics. Although frost nucleation happens heterogeneously in practice—meaning that a foreign surface is present to facilitate the process—we will begin by examining homogeneous nucleation, or phase change in the absence of a foreign surface. We do this because it enables a naturally transition into a discussion and understanding of heterogeneous nucleation and allows us to explore how different surface characteristics, namely surface energy and surface topography, influence the nucleation process. Finally, we will discuss the nucleation rate. As its name implies, this determines the rate of a nucleation event and therefore the likelihood that frost will form on a surface at given environmental conditions and in the presence of a given foreign surface. In summary, this section aims to provide a fundamental discussion that encompasses the basic derivations and theory behind nucleation physics, as it applies to phase change. Here we concentrate in particular on the transition of ice from water vapor in the presence of a foreign surface.

2.2.1 Gibbs Free Energy

The mechanism of nucleation is characterized by the change in Gibbs free energy necessary to transform from a parent phase (1) to a daughter phase (2).\textsuperscript{61,62} In frosting, the parent phase is always water vapor, while the daughter phase can be either liquid water (condensation) or solid ice (desublimation), dependent on the nucleation mode; in the case of liquid formation, this will then solidify. Since our goal is simply to identify the conditions necessary for condensation and desublimation to occur, we have ignored the Gibbs free energy necessary for the liquid to freeze in the ensuing analysis. The critical Gibbs free energy ($\Delta G_{12}^*$) indicates the energy barrier necessary to overcome to begin a spontaneous change from the parent phase (1) to the daughter phase (2) at a specific temperature ($T$) and pressure ($p$) (single component). As previously mentioned, it is instructive to first consider the change in Gibbs free energy ($\Delta G_{12}$) necessary for homogeneous nucleation. We can define the change in Gibbs free energy as

$$\Delta G_{12} = n_2(\mu_2 - \mu_1)v + A\gamma_{12}$$  \hspace{1cm} (2.1)

where $n_2$ is the number of molecules per unit volume of the daughter phase, $\mu_1$ and $\mu_2$ are the chemical potentials of the parent and daughter phases, respectively, $v$ is the nascent embryo volume, $A$ is the nascent embryo surface area, and $\gamma_{12}$ is the interfacial...
energy between the parent and the daughter phase. Furthermore, we can define the difference in chemical potential between the daughter and the parent phase as a function of measurable variables, namely $T$ and $p$,

$$\mu_2 - \mu_1 = -kT \ln \frac{p}{p_2}$$

(2.2)

where $p$ and $p_2$ are the water vapor pressure in the environment and saturated vapor pressure over a plane surface of the daughter phase, respectively, at temperature $T$, and $k$ is the Boltzmann constant. Assuming that $v = \frac{4}{3} \pi r^3 \alpha$ and $A = 4 \pi r^2 \beta$, where $\alpha$ and $\beta$ are numerical factors both greater than unity used to adjust for non-spherical embryo shapes, and $r$ is the embryo radius, we obtain an equation for $\Delta G_{12}$ as a function of $r$,

$$\Delta G_{12} = -\frac{4}{3} \pi r^3 n_2 kT \ln \frac{p}{p_2} + 4 \pi r^2 \beta \gamma_{12}.$$ (2.3)

If we plot eq 2.3 (see Figure 2.1, we see that as $r$ increases, initially so does $\Delta G_{12}$ (ceteris paribus); however, after the embryo has reached a critical size, $r^*$, $\Delta G_{12}$ begins to decrease with a further increasing $r$; therefore, the critical Gibbs free energy ($\Delta G_{12}^*$) has been reached and the growth of a stable nascent embryo is spontaneous. We define $r_{12}^*$ by setting $\frac{\partial \Delta G_{12}}{\partial r} = 0$, which yields

$$r_{12}^* = 2 \gamma_{12}/(n_2 kT \ln \frac{p}{p_2}).$$ (2.4)

Substitution of $r_{12}^*$ for $r$ into eq 2.3 yields an equation for $\Delta G_{12}^*$

$$\Delta G_{12}^* = 16 \pi \gamma_{12}^3 \zeta/(3[n_2 kT \ln \frac{p}{p_2}]^2)$$ (2.5)

where $\zeta = \beta^3/\alpha^2$. 62 Allowing the subscripts V, L, and S to take place of parent phase (1) and daughter phase (2) explicitly as the vapor, phase, liquid phase, and solid phase, respectively, the corresponding critical free energies for condensation and desublimation are

$$\Delta G_{VL}^* = 16 \pi \gamma_{VL}^3 \zeta/(3[n_L kT \ln \frac{p}{p_L}]^2),$$ (2.6)

$$\Delta G_{VS}^* = 16 \pi \gamma_{VS}^3 \zeta/(3[n_S kT \ln \frac{p}{p_S}]^2),$$ (2.7)
respectively.

2.2.2 Energetically Favorable Nucleation Pathway

Figure 2.1: Normalized Gibbs free energy ($\Delta G_{12}/kT$) as a function of the nascent embryo radius ($r$), exemplifying environmental two conditions. (a) $T = 225$ K and $p = 0.3$ mbar, in which case $\Delta G_{VL}^* < \Delta G_{VS}^*$, indicating condensation nucleation is favorable and (b) $T = 225$ K and $p = 0.15$ mbar, in which case $\Delta G_{VL}^* > \Delta G_{VS}^*$, indicating desublimation nucleation is favorable. Dashed lines plot $\Delta G_{VS}/kT$, solid lines plot $\Delta G_{VL}/kT$.

By defining $\Delta G_{VL}^*$ and $\Delta G_{VS}^*$ as a function of $T$ and $p$, we can calculate the most energetically favorable pathway to nucleation for a variety of environmental conditions in order to understand when to expect condensation or desublimation. This is exemplified in Figure 2.1 by plotting eq 2.3 for the case of vapor to liquid and vapor to solid nucleation, respectively. The more energetically favorable nucleation mode for a specific combination of $p$ and $T$ becomes clear by observing the corresponding $\Delta G_{12}$ (the peak of the curve) necessary for nucleation for condensation and desublimation. Figure 2.1 plots the normalized change in free energy for forming liquid ($\Delta G_{VL}/kT$) and solid water embryos ($\Delta G_{VS}/kT$) from vapor vs embryo radius ($r$) for two different environmental conditions according to eq 2.3. It is clear from Figure 2.1 that the relative magnitudes of $\Delta G_{VS}^*$ and $\Delta G_{VL}^*$ can switch based upon differing environmental conditions. For example, in this case, $p$ causes a change in nucleation favorability from condensation (Figure 2.1a) to desublimation (Figure 2.1b).

This methodology can be extended to calculate $(\Delta G_{VL}^* - \Delta G_{VS}^*)/kT$ for many combinations of $p$ and $T$, resulting in a map of the energetically favorable nucleation mode as a function of environmental conditions. The result is shown in Figure 2.2, which plots $\Delta G_{VL}^* - \Delta G_{VS}^*$ as a function of $p$ and $T$ and quantifies the conditions where a liquid or
solid daughter phase is favored. It is clear that at relatively low T and p, the area occupied by \((\Delta G^*_{VL} - \Delta G^*_{VS})/kT > 0\) becomes larger and therefore larger supersaturations favor desublimation nucleation. At higher T and p, condensation nucleation becomes favorable at much smaller supersaturations. Due to the subfreezing temperatures and the corresponding metastable state, some of the condensate will eventually freeze, becoming frost (condensation freezing). We will return to the discussion and implications of the supersaturation soon.

### 2.2.3 Heterogeneous Nucleation

The prior discussion and derivations for homogeneous nucleation allow for an easy transition into heterogeneous nucleation. As mentioned before, heterogeneous nucleation is nucleation in the presence of a foreign substrate. It is ubiquitous in almost all related applications due to the fact that \(\Delta G^*_{T2}\) only becomes small enough when nucleation oc-
Desublimation Frosting on Nanoengineered Surfaces

...heterogeneously. When considering heterogeneous nucleation, \( \Delta G^*_{12} \) is modified by a geometric factor, \( f(\theta_{12}, R) \leq 1 \), which depends on two main properties. The first is the surface energy of the foreign body in the presence of the parent and daughter phases, which can be represented as the inherent contact angle of the daughter phase on the surface in the parent phase (\( \theta_{12} \)). The second property is the topography of the foreign body, which can be represented as the radius of curvature (\( R \)) of the foreign body. Subsequently, we can write the Gibbs free energy barrier to heterogeneous nucleation as: \( f(\theta_{12}, R)\Delta G^*_{12} \). The influence of both of these surface properties will be looked at in closer detail in the following two sections.

**Effect of Surface Energy**

As previously mentioned, the surface energy of the substrate with respect to the daughter and parent can be conveniently represented as the inherent contact angle of the daughter phase on the surface in the parent phase (\( \theta_{12} \)). By only considering the effect of the \( \theta_{12} \), we are assuming that the radius of curvature of the foreign body is infinite (\( R \to \infty \)) and therefore has no influence on \( \Delta G^*_{12} \). Using this assumption the geometric factor loses its dependence on \( R \) and becomes\(^{61,62} \)

\[
f(\theta_{12}) = \frac{1}{4}(2 - 3\cos \theta_{12} + \cos^3 \theta_{12}). \tag{2.8}
\]

A plot of eq 2.8 is shown in Figure 2.3a. One observes that as \( \theta_{12} \) decreases, so too does \( f(\theta_{12}) \), implying that \( f(\theta_{12})\Delta G^*_{12} \) will also decrease for decreasing \( \theta_{12} \). This effect is shown in Figure 2.3b where \( f(\theta_{12})G_{12} \) for four different \( \theta_{12} \) are plotted. The curve with the largest peak corresponds to a \( \theta_{12} = 180^\circ \) (homogeneous nucleation), while the peaks of each curve continually decrease as \( f(\theta_{12}) = 135^\circ = 90^\circ = 45^\circ \), resulting in a decrease in \( f(\theta_{12})\Delta G^*_{12} \).

**Effect of Surface Topography**

The geometric factor \( f \) becomes considerably more complicated when also taking into consideration the surface topography, namely the radius of curvature of the surface (\( R \)). Surface topography can be broken into two types: (1) the radius of curvature is concave, such as a nanopit and (2) the radius of curvature is convex, such as a nanobump. When considering concave radii of curvature (negative) we obtain\(^{75} \)
Figure 2.3: The inherent contact angle of the daughter phase on the surface in a parent phase ($\theta_{12}$) effects the critical Gibbs free energy necessary to be overcome for the nucleation of a stable embryo. (a) Plot of eq 2.8 indicating the dependence of $f(\theta_{12})$ on $\theta_{12}$. (b) Plot of $f(\theta_{12}, R)\Delta G_{12}/kT$ vs $r$ for four different $\theta_{12}$ illustrating the decrease in $\Delta G_{12}^*$ for decreasing $\theta_{12}$. Black curve represents $\theta_{12} = 180^\circ$, dark gray curve represents $\theta_{12} = 135^\circ$, light gray curve represents $\theta_{12} = 90^\circ$, and lightest gray curve represents $\theta_{12} = 45^\circ$. Each shade of gray is plotted as a point on the plot in (a) to correspond to the matching $\theta_{12}$.

$$f(m, R) = \frac{1}{2} \left[ 1 - \left( \frac{1 + mx}{g_c} \right)^3 - x^3 \left[ 2 - 3\left( \frac{x + m}{g_c} \right) + \left( \frac{x + m}{g_c} \right)^3 \right] + 3mx^2 \left( \frac{x + m}{g_c} - 1 \right) \right]$$

where $m = \cos \theta_{12}$, $g_c = (1 + 2mx + x^2)^{1/2}$, and $x = R/r_{12}^*$. For convex radii of curvature (positive) we obtain

$$f(m, R) = \frac{1}{2} \left[ 1 + \left( \frac{1 - mx}{g_c} \right)^3 + x^3 \left[ 2 - 3\left( \frac{x - m}{g_c} \right) + \left( \frac{x - m}{g_c} \right)^3 \right] + 3mx^2 \left( \frac{x - m}{g_c} - 1 \right) \right]$$

where $m = \cos \theta_{12}$, $g_c = (1 - 2mx + x^2)^{1/2}$, and $x = R/r_{12}^*$. Figure 2.4 shows the theoretical influence that nanotexture has on $f(\theta_{12}, R)$ for a variety of plausible $\theta_{12}$.
Figure 2.4: Nanotexture can theoretically change the heterogeneous nucleation barrier to a varying degree dependent on $\theta_{12}$ and $r_{VS}^*$. The change in $f(\theta_{12}, R)$ for both (a) bumps and (b) pits under conditions $T_\infty = -47.9$ to $-55.2^\circ C$ (corresponding to $p/p_S = 1.45$) for three plausible $\theta_{12}$. Transparent gray areas indicate $R < 10r_{12}^*$ indicating the necessary surface curvature to influence nucleation.

values and within the experimental range of $p$ and surface temperatures ($T_s$) that were investigated in the ensuing sections. Examining Figure 2.4 it is clear that, independent of $\theta_{12}$, smaller $R$ values have a larger influence on $f(\theta_{12}, R)$. To be precise, the analysis indicates that roughness, whose radius of curvature $R$ is up to 1 order of magnitude above the minimal radius of curvature of stable nuclei ($r_{12}^*$), should affect the nucleation energy barrier of the daughter phase at the same conditions as a surface with no roughness. On the one hand, small convex (positive) values of $R$ (<25 nm) leads to an increase in $f(\theta_{12}, R)$, and therefore an increase in $f(\theta_{12}, R)\Delta G_{12}^*$. However, the small concave (negative) values of $R$ (<25 nm) have the opposite effect happens, namely $f(\theta_{12}, R)\Delta G_{12}^*$ decreases. Figure 2.4 provides evidence that sufficiently nanotextured surfaces are capable of drastically changing $f(\theta_{12}, R)$ and therefore $f(\theta_{12}, R)\Delta G_{12}^*$.

### 2.2.4 Nucleation Rate

Comparing the magnitude of $\Delta G_{VL}^*$ and $\Delta G_{VS}^*$ will inform us of the favorable pathway to ice nucleation at any given $T$ and $p$, however it does not directly inform us about the likelihood of the nucleation event to actually happen. The parameter to study here, dependent on $\Delta G_{12}^*$, is the nucleation rate of the daughter phase ($J_{12}$), which indicates the time and space scale necessary for nucleation to occur. The rate at which nucleation
of the daughter (2) in parent (1) phase occurs is calculated using an Arrhenius equation,

\[ J_{12} = J \exp \left( -\frac{\Delta G_{12}^*}{kT} \right), \quad (2.11) \]

where \( J \) is a pre-exponential factor, which depends on the rate at which vapor molecules strike a unit area of the embryo. This rate is given from kinetic gas theory as \( p/(2\pi mkT)^{1/2} \), where \( m \) is the mass of a water molecule. Therefore in a unit volume of vapor, the rate of formation of the daughter embryos that can grow spontaneously is given as

\[ J_{12} = \frac{p4\pi r_{12}^* \beta n_1}{(2\pi mkT)^{1/2}} \exp \left( -\frac{\Delta G_{12}^*}{kT} \right). \quad (2.12) \]

To compare the rate of stable embryo formation for condensation and desublimation, we can first study the pre-exponential term in equation 2.12. For condensation and desublimation, the pre-exponential terms only differ by a factor of \( \beta \) and in this case are equal to within a factor of two as the other variables do not change. Therefore it is commonly assumed that the pre-exponential term for condensation and desublimation are the same and given as \( J = 1 \times 10^{29} \text{ m}^{-3}\text{s}^{-1} \). This allows the nucleation rates for condensation and desublimation to be given as

\[ J_{VL} = J \exp \left( -\frac{\Delta G_{VL}^*}{kT} \right), \quad (2.13) \]

\[ J_{VS} = J \exp \left( -\frac{\Delta G_{VS}^*}{kT} \right), \quad (2.14) \]

respectively. Consequently, if \( \Delta G_{VS}^* < \Delta G_{VL}^* \), the nucleation rate of solid ice crystals will dominate the nucleation rate of liquid droplets \( (J_{VS} > J_{VL}) \), however, it is advisable to calculate \( J_{12} \) in order to understand whether nucleation will happen on a reasonable time and space scale.

### Effect of Surface Energy

As we saw earlier, \( \theta_{12} \) can have a significant influence on \( \Delta G_{12}^* \). Referring to eq 2.12 it becomes clear that \( \theta_{12} \) should also influences \( J_{12} \). To underpin the effect of \( \theta_{12} \) on \( J_{12} \), Figure 2.5 compares nucleation rates by plotting \( J_{12} \) as a function of \( p \) and \( T \) using eqs 2.13 and 2.14. For consistency, this is done for the same range of \( T \) and \( p \) chosen in
Figure 2.2. Figure 2.5a,b show the case of a homogeneous nucleation ($\theta_{VL} = \theta_{VS} = 180^\circ$) and heterogeneous nucleation case ($\theta_{VL} = \theta_{VL} = 50^\circ$), respectively. It was assumed that $R = \infty$ in order to solely illustrate the influence of surface energy. Eq 2.14 is used when desublimation nucleation is favorable (between the solid gray and black lines) and eq 2.13 is used when condensation nucleation is favorable (left of solid gray line). The orange line represents $J_{12} = 1$ embryo $\text{cm}^{-2} \text{s}^{-1}$ and is considered a lower limit of an appreciable nucleation rate. Here, we clearly see that the nucleation rate for the homogeneous case is too insignificant at the $p$ and $T$ values that we chose in Figure 2.1a,b. However, in the presence of a surface with $\theta_{VL} = \theta_{VL} = 50^\circ$, for the same environmental conditions, the nucleation rate becomes appreciable and frost formation would be expected.

Figure 2.5: Surface plots comparing homogeneous and heterogeneous nucleation rates ($J_{12}$) vs $p$ vs $T$. The effect of surface energy on nucleation is illustrated by plotting (a) homogeneous nucleation ($\theta_{VL} = \theta_{VS} = 180^\circ$), and (b) heterogeneous nucleation on a surface ($\theta_{VL} = \theta_{VS} = 50^\circ$ and $R \to \infty$). The green shaded area indicates that $J_{12}$ is large enough to observe nucleation on a reasonable time and area scale ($J_{12} > 1$ embryo $\text{cm}^{-2} \text{s}^{-1}$) and the red area indicates that $J_{12}$ is too small to result in observed nucleation on a reasonable time and area scale ($J_{12} < 1$ embryo $\text{cm}^{-2} \text{s}^{-1}$). Solid gray line indicates $(\Delta G_{VL}^{*} - \Delta G_{VS}^{*})/kT = 0$. The solid black line indicates the equilibrium transition from vapor to solid. Orange line indicates $J_{12} = 1$ embryo $\text{cm}^{-2} \text{s}^{-1}$. The red and blue circles indicate conditions illustrated in Figure 2.1a, $T = 225$ K, $p = 0.3$ mbar and Figure 2.1b, $T = 225$ K, $p = 0.15$ mbar, respectively.
Effect of Surface Topology

It should be clear that both surface curvatures are inherently created when fabricating roughness—where we have seen that bumps and pits inhibit or promote nucleation, respectively. Unclear, at first glance, remains what the effect will be on the nucleation rate for the combination of both. In order to elucidate this we begin by quantifying the heterogeneous nucleation rate for a smooth surface ($J_S$) by adapting eq 2.12,

$$J_S = J \exp \left( \frac{-f(\theta_{12}) \Delta G_{12}^*}{kT} \right)$$

(2.15)

to include the heterogeneous function, $f(\theta_{12})$, for $R \to \infty$. In order to quantify $J_{12}$ for a nanotextured surface we make the assumption that all pits and bumps have the same $R$ and that there is an even distribution of pits and bumps across the whole surface. In other words the surface coverage of bumps ($\phi_b$) and pits ($\phi_p$) are both 0.5. This allows us quantify the heterogeneous nucleation rate for our idealized nanotextured surface ($J_N$) by taking a weighted average of the respective $J_{12}$ for bumps and pits,

$$J_N = J \left[ \phi_b \exp \left( \frac{(-f_b(\theta_{12}, R) \Delta G_{12}^*)}{kT} \right) ight. + \phi_p \exp \left( \frac{(-f_p(\theta_{12}, R) \Delta G_{12}^*)}{kT} \right) \]$$

(2.16)

where $f_b(\theta_{12}, R)$ and $f_p(\theta_{12}, R)$ are homogeneous modifying functions for bumps and pits of $R$, respectively. Figure 2.4 indicates that $f(\theta_{12}, R)$ can change substantially when nanotexture is present. Due to the exponential dependence of $J$ on $f(\theta_{12}, R)$, a change in $R$ leads to an order of magnitude larger change in $J$. Although, $f_b(\theta_{12}, R)$ and $f_p(\theta_{12}, R)$ increase and decrease, respectively, the exponential increase of the first term, corresponding to the pits, vastly outweighs the second term, corresponding to the bumps, resulting in $J_N >> J_S$. This analytical comparison of $J_{12}$ for a smooth surface and nanotextured surface allows shows that a nanotextured surface greatly increases $J_{12}$, due to the dominance of the pits.

In summary, a surface therefore can change the condensation-desublimation nucleation transition dependent on the surface properties, namely the intrinsic contact angle of water ($\theta_{VL}$), the intrinsic contact angle of ice ($\theta_{VS}$), and $R$, but also considerably lowers the magnitude of $\Delta G_{12}^*$, resulting in a drastic increase $J_{12}$. 
2.3 Methods

2.3.1 Setup

Figure 2.6: The experimental setup consists of experimental chamber with connections to vacuum, water vapor inlet, and sample and source cooling blocks; imaging system with LED warm white light source, (1) focusing objective, (2) collimating lens, (3) focusing lens, (4) beam splitter, (5) mirror, and (6) CMOS camera; computer with data acquisition system to record sample temperature \( T_s \), ambient chamber pressure \( p_0 \), source cooling block temperature \( T_b \) and inside \( T_\infty \) block, and camera image, and PID control of both thermoelectric coolers (TECs); and liquid nitrogen dewar.

We performed all of the experiments using the experimental setup illustrated in Figure 2.6, featuring a gas-tight chamber, capable of reaching absolute pressures \( p_0 < 0.2 \) mbar through the use of a roughing vacuum pump (Vacuubrand GmbH, RE 2.5 rotary vane pump). During the experiments it was imperative to obtain the highest possible accuracy of \( p \), due to its high influence on \( \Delta G_{12}^* \) and ultimately \( J_{12} \). We were able to most accurately measure and precisely control \( p \) by altering the temperature of the source cooling block \( T_\infty \), on which a thin layer of source ice was grown. We calculated the environmental water vapor pressure \( p \) knowing the temperature of the thin ice layer on the block (assumed to be the same as the copper block). Furthermore, the source cooling block was designed to be 100 times the area of the sample cooling block area in order to maintain constant \( p \) during nucleation and growth of the ice on the sample. We
assumed that the \( p \) in the chamber had reached equilibrium when the difference between \( T_\infty \) and \( T_b \) became constant (\( \approx 0.5^\circ \text{C} \)), indicating no further change in heat flux through the source cooling block.

We controlled the sample temperature (\( T_s \)) by regulating the temperature of the sample cooling block. \( T_s \) and \( T_\infty \) could be independently regulated using the combination of the appropriate cold nitrogen vapor line and thermoelectric cooler (TEC). We measured all temperatures using resistance temperature detectors (IST AG, Pt1000, \( \pm 0.15^\circ \text{C} \)) located inside of each copper block, approximately 1 mm behind the exposed surface. A viewing window at the bottom of the chamber enabled the observation of the sample during the nucleation process using a home-built inverted microscope (objects 1-6 in Figure 2.6). We synchronized the recorded images from a CMOS USB camera (Thorlabs, DCC1645C) with the temperature and pressure measurements (Pfeiffer Vacuum, CMR 363) using a data acquisition system (Beckhoff, Ethercat EK1100) and signal processing software (National Instruments, Labview 2015) for later analysis.

### 2.3.2 Experimental Protocol

At the beginning of each set of experiments, the chamber was pumped down and held at \( p_0 < 0.2 \text{ mbar} \) until the desired \( T_\infty \) was reached. To set \( p \), we evaporated water into the chamber by opening a valve exposing the chamber to a vile of deionized water,\(^1\) during which we observed an isothermal temperature response of \( T_\infty \), indicating the formation of ice on the source copper block. At this point we slowly decreased \( T_s \) at a rate of \( 0.1^\circ \text{C/s} \). At some \( T_s < T_\infty \) we observed nucleation. We calculated the supersaturation (\( p/p_S \)) at the onset of nucleation by calculating \( p_S \) from the recorded value of \( T_s \) as nucleation occurred.

### 2.3.3 Surface Preparation

We used the following cleaning protocol at different stages of surface fabrication: 4 min ultrasonication in baths of acetone, isopropanol, and water followed by a 2 min 600 W oxygen plasma (PVA TePla, GIGAbatch 210M).

---

\(^1\)For the silicon experiments, the difficulty in maintaining a gas-tight seal of the chamber at low temperatures forced us to introduce water into the chamber by opening the vacuum release valve and exposing the chamber to atmospheric lab conditions.
**Silver Iodide**

We fabricated the silver iodide (AgI) samples on 175 µm, one-inch diameter glass cover slides. We initially cleaned the glass slides using the aforementioned cleaning protocol and then coated them with a 2 nm layer of evaporated titanium (to improve silver adhesion) followed by a 10 nm layer of evaporated silver (Evatec, BAK501). We proceeded to place the glass slides in an airtight environment for 60 s containing a beaker of a 2% vol. iodine (Sigma-Aldrich, >99.99% trace metals basis) in deionized water solution heated to 60°C. The iodide vapor reacted with the silver to form AgI crystals, confirmed by the change in sample color and SEM micrographs as illustrated in Figure 2.7.

![Figure 2.7](image-url)

**Silicon**

We fabricated the silicon samples from four-inch, 100 µm thick, double-side polished, p-doped, ⟨100⟩ crystal orientation silicon wafers. We diced the wafers into 1 x 1 cm chips and cleaned them using the aforementioned cleaning protocol. After cleaning, the smooth silicon samples were used as is. We fabricated the nanotextured silicon samples by first sputtering a 2 nm layer of gold onto the silicon chips (VON ARDENNE GmbH, Cluster System CS3205), which resulted in a nanoscale in homogeneous gold layer that was suitable to use as a hard mask. We then exposed the gold coated silicon chips to a 50 W reactive ion etch using 100 sccm flow rate of sulfur hexafluoride, 40 sccm flow rate of oxygen at 20°C sample temperature and 40 mTorr chamber pressure for 2 min (Oxford Instruments, Plasmalab 80 Plus).
Figure 2.8: (a,b) AFM micrographs (AFM tip radius 2 nm) of smooth silicon (RMS roughness = 0.94 nm) and nanotextured silicon surface (RMS roughness = 61.8 nm), respectively, used in experiments to determine the role of nanoroughness on desublimation nucleation; the mean curvature ($H$) is overlaid on the height profile as a surface plot. (c,d) Histograms showing the surface area fraction as a percentage of the total surface occupied by different magnitudes of $R$. The solid red line indicates $R = 10r_{12}^*$. The smooth silicon surfaces (c) contain no $R \leq 10r_{12}^*$, while the nanotexture silicon (d) has 18% surface coverage of $R \leq 10r_{12}^*$ illustrated by the transparent gray area.
Figure 2.8a and b show micrographs obtained with atomic form microscopy using a 2 nm extra sharp tip, overlaid with a surface plot of mean curvature ($H = 1/R$) for our smooth (untreated wafers, RMS roughness = 0.94 nm) and nanotextured silicon (RMS roughness = 61.8 nm) samples, respectively. The histograms shown in Figure 2.8c,d indicate the percent area fraction of the surface covered by concave pits of radius $R$ (negative values) for our smooth and nanotextured silicon samples, respectively. Comparing the smooth and nanotextured silicon surfaces, we observed that the nanotextured surface has 18% of its area—a significant fraction—covered with nanopits with $R \leq 10r_{12}^*$, while the smooth silicon has effectively none of its area covered with nanopits with $R \leq 10r_{12}^*$.

**Aluminum**

We fabricated the aluminum samples by initially cleaning 100 µm thick aluminum sheets (Korff AG, Switzerland) with the aforementioned cleaning protocol followed by a 10 min immersion in boiling deionized water. During the immersion of the aluminum in the boiling water, the native oxide layer on the surface reacts and becomes hydrolyzed and undergoes a chemical and morphological change leading to the formation of boehmite nanostructures, which can be observed in Figure 2.9.

Figure 2.9: The immersion of aluminum in boiling water, causes the native oxide layer on the surface to become hydrolyzed and undergo a morphological change, known as the boehmitage process, resulting to grass-like nanostructures. Scale bar: 1 µm
2.3.4 Surface Characterization

We characterized the AgI and aluminium samples using scanning electron microscopy (Hitachi SU8000). We characterized the smooth and nanotextured silicon samples using atomic force microscopy (Bruker, Dimension FastScan) in tapping mode using 2 nm sharp tips.
2.4 Results

2.4.1 Desublimation–Condensation Nucleation Transition

In order to investigate the heterogeneous condensation–desublimation nucleation transition, we examined condensation and desublimation behavior on silver iodide coated surfaces (AgI), a well-known ice nucleation agent.79

Figure 2.10: Experimental condensation–desublimation nucleation transition. The heterogeneous transition can be experimentally observed by plotting $T_s$ vs $p/p_s$ at the onset of nucleation for a given surface and observing the nucleation mode. (a) Experimentally observed results for AgI (purple data points) correspond well to experiments done on AgI by Bryant63 (dark gray data points) and Schaller65 (light gray data points). Here, desublimation is observed (filled purple data points) when $p/p_s < p_L/p_s$ (green dashed line) and $p/p_s > 1$ (black solid line). Condensation is observed (unfilled purple data points) when $p/p_s > p_L/p_s$. AgI exhibits a condensation–desublimation nucleation transition at approximately $T_s = -12^\circ$ C. Optical micrographs show examples of (b) condensation and (c) desublimation on AgI; circled data points in (a) correspond to condensation (red) and desublimation (blue). Scale bars: 200 µm

Figure 2.10a shows a plot of $p/p_s$ vs $T_s$ vs nucleation mode on AgI; we denote two
regions: \( p > p_L \) (refers to region of \( p/p_S > p_L/p_S \)) and \( p < p_L \) (refers to a region of \( p/p_S < p_L/p_S \)). When \( p > p_L \), the vapor is saturated with respect to a flat liquid surface. When \( p > p_S \) (\( p > p_S \)), the vapor is supersaturated with respect to a flat solid surface. Due to the limitations set by the size of \( r^* \) (of the order of nm) it is impossible to observe the nascent embryo at the onset of nucleation in our experimental setup; therefore, we attributed a condensed nucleating phase for \( p < p_L \) and \( p > p_S \) to desublimation. This is further strongly supported by observing that the growing ice crystal is a polyhedron; cf. Figure 2.10c. We observed that for relatively higher values of \( T_s \) (\( > -12^\circ \text{C} \)), \( p > p_L \) when we observe nucleation and the nucleate consists of metastable liquid water, which given sufficient time freezes, Figure 2.10b (condensation regime). When \( T_s < -12^\circ \text{C} \), the onset of nucleation takes place when \( p < p_L \) and \( p/p_S > 1 \), and we observe the growth of an ice crystal with 6-fold symmetry, Figure 2.10c. Additionally, Figure 2.10c compares our results with those obtained in previous studies.\(^{63,65}\) Their good agreement in heterogeneous condensation–desublimation nucleation transition \( T_s \) and value of \( p/p_S \) in the desublimation regime is used to confidently confirm the accuracy of our experimental apparatus and methods.

### 2.4.2 Role of Nanoroughness on Desublimation Nucleation

Due to its high affinity to ice, AgI proved to be a good substrate to examine the role that material property plays in altering \( \Delta G^*_V \) and \( \Delta G^*_S \) at relatively high \( T_s \) (\( > -20^\circ \text{C} \)). However, the inherent inhomogeneous surface texture created when fabricating the AgI samples, seen in Figure 2.7b, made it a poor candidate to decouple the effects of \( \theta_{12} \) and \( R \) in order to study the effect of nanotexture on the nucleation behavior from vapor. We chose silicon as a representative substrate to fundamentally investigate the effect of surface roughness on desublimation nucleation due to its ability to be engineered to specific values of \( R \) and the existence of reliable methodologies to impart corresponding desired surface textures.

We tested the effect of nanotexture on the nucleation mechanism by conducting experiments on smooth silicon and nanotextured silicon (details in Section 2.3.3) at four values of \( p \) using the experimental protocol described earlier (Section 2.3.2). Figure 2.11a shows a box plot of supersaturation, \( p/p_S \) at the moment when nucleation was observed, vs \( p \) for smooth and nanotextured silicon samples; each box includes a total of nine experiments on each sample type using three different samples of each type. The values \( p \) of 0.05, 0.04, 0.03, and 0.02 mbar used in the experiments correspond to equilibrium vapor pressures over flat ice at temperatures (\( T_{\infty} \)) of -47.9, -49.7, -52.0, and -55.2\(^{\circ} \text{C} \), respectively. Examining the plot it is clear that \( p/p_S \) is considerably lower for the nanotextured samples, implying that \( J_{12} \) has been considerably increased. In order to further confirm the influence of nanotexture on nucleation rate, and its importance in technical
Figure 2.11: Experimentally measured effect of nanotexture on heterogeneous nucleation. Box plot showing the experimentally measured $p/p_S$ at the first observation of nucleation on smooth silicon (blue), nanotextured silicon (green), and nanotextured aluminum (red) vs $p$ corresponding to limit of the experimental chamber ($T_{\infty}=-47.9\text{ to }-55.2^\circ\text{C}$). Each box represents the experimental spread for nine individual experiments ($n=9$). The nine experiments were done on three different samples of each sample type. The results indicate that it is statistically more likely for nucleation to occur on nanotextured surfaces. Crystal growth observed on (b) smooth silicon and (c) nanotextured silicon at $p=0.04\text{ mbar}$ 30 s after first observed nucleation. (b,c) Scale bar: 200 µm

applications, we conducted experiments on three nanotextured aluminum samples as a $p$ value of 0.05 mbar (9 total experiments). Similar to nanotextured silicon, we observed that these surfaces resulted in an increased $J_{12}$ at reduced $p/p_S$ and therefore an earlier onset of nucleation, seen by the red box in Figure 2.11a. This provides stronger evidence for the effect of nanotexture across a range of materials to increase $J_{12}$.

It is also interesting to observe the shape of the ice growing on the silicon surface. Figure 2.11b,c show images of ice growing on smooth and nanotextured silicon, respectively. It is clear that the ice growing on both surfaces is not symmetric like it was on the AgI coated surfaces (Figure 2.10a), although the cold temperature and dry environment would lead one to expect to be in a desublimation regime.
2.5 Discussion

We interpret our experimental results to indicate that $R$ of the order of magnitude of $r_{12}^*$ does indeed improve the favorability of ice growth in our experimental range. However, it is unclear that desublimation nucleation is causing ice formation here. As can be seen in Figure 2.12a, no clear condensation–desublimation nucleation transition—as we were able to obtain for AgI coated surfaces (Figure 2.10)—was attained on smooth silicon for the temperature ranges that we studied. Furthermore, the macroscopic shape of the ice crystals provides insight into the microscopic crystal configuration upon nucleation and therefore evidence for the interface at which growth began, whether it be solid–vapor or solid–liquid. The basal face of ice 1h crystals observed on the AgI samples (Figure 2.10c) is consistent with growth beginning from the solid–vapor interface, while the secondary prism face of ice 1h crystals observed on the silicon samples (Figure 2.10b) is indicative of growth from the solid–liquid interface, providing further evidence that condensation followed by freezing is the energetically favorable pathway for frost formation for the range of $T_s$ used in our experiments. Nevertheless, our observations show that nanotexture does influence nucleation and catalyzes the formation of ice. We offer two feasible explanations that we see for this behavior: (1) The nanoroughness radius of curvature $R$ of the scale of $r_{VS}^*$ is able to significantly reduce $f(\theta_{VS}, R)$ (as described in Section 2.2.3) and ice desublimation is thermodynamically more favorable at lower $p/p_S$; or (2) the extreme temperatures in these experiments ($< -48^\circ C$) makes it likely for a minuscule volume of metastable liquid formed in the nanotexture through capillary condensation to freeze, enabling the pathway to frost nucleation at lower $p/p_S$.

Due to the crystalline structure of ice, it is expected that adding curvature at such as small scale will disrupt the lattice near the substrate surface, resulting in an amorphous phase known as a quasiliquid layer, whose thickness increases with decreasing pit radius, contradicting our first explanation. The thickness or actual existence of the quasiliquid layer may be dependent on substrate type, including crystallographic match with respect to bulk ice and strength of the water–surface interaction. The idea that ice crystal growth can be enhanced by surface defects as a two-step process involving a liquid intermediary, however, has been proposed earlier and has been experimentally demonstrated for a variety of organic liquids. The proposed mechanism for the enhanced growth of ice crystals from vapor involves an intermediary liquid phase caused by capillary condensation. The phenomenon of capillary condensation can be described by the Kelvin equation

$$\ln \left( \frac{p}{p_L} \right) = \frac{-4\gamma_{VL} \cos \theta_{VL}}{n_L dkT} \quad (2.17)$$

where $d$ is the diameter of the cavity. Equation 2.17 illustrates that if $\theta_{VL} < 90^\circ$, then the equilibrium vapor pressure over the interface $(p)$ can be smaller than that of the bulk.
Figure 2.12: The heterogeneous condensation–desublimation nucleation transition for silicon could not be experimentally observed for $0^\circ < T_s < -65^\circ$C. (a) Experimentally observed results for silicon (gray data points) all fall above $p/p_s > p_L/p_s$ (green dashed line). Even at extremely cold $T_s (< -60^\circ$C) there was no clear evidence for a transition to a desublimation regime similar to what was observed on AgI, providing evidence that condensation followed by freezing remains the energetically favorable pathway to frost for all $T_s$ used in this study. (b) Optical micrograph shows example of frost crystals grown at $T_s = -56.7^\circ$C. Unlike the crystal shape observed in the desublimation region for AgI, characteristic of the basal face of ice 1h, the crystal shape is characteristic of the secondary prism face of ice 1h, providing further evidence of growth from the liquid-solid interface. Scale bar: 200 µm.
equilibrium vapor pressure ($p_L$) and result in stable condensate that forms at undersaturated vapor pressures. Even if the $\theta_{VL} > 90^\circ$, capillary condensation can take place at considerably smaller $p$ than in the absence of nanotexture. Although, minuscule values of condensate can form inside these cavities, emergence in not thermodynamically favorable for the liquid condensate at under-saturated vapor pressure with respect to liquid water, which limits any macroscopic growth of the condensate until the appropriate supersaturated conditions have been reached.\textsuperscript{74} However, very low temperatures considerably increase the ice embryo nucleation rate, rendering it still sufficient for nucleation events to occur in a reasonable time, even in the minuscule liquid volumes associated with capillary condensate in our nanotexture. In contrast to the metastable liquid condensate, the now-nucleated ice crystals are able to grow out of the nanotexture due to the supersaturation above the thermodynamically stable ice crystals.\textsuperscript{88}

This explanation also warrants a discussion on the effect of freezing point depression (Gibbs–Thompson Effect) on the nucleation of ice embryos in the nanotexture. It has been show that water inside nanopores with $d < 12$ nm leads to lower equilibrium solidification temperatures and complete suppression of solidification for radii under 2.8 nm.\textsuperscript{82,89,90} This effect, akin to the formation of quasiliquid layers at locations of high $R$,\textsuperscript{69,82} should, in theory, only suppress ice nucleation at the very bottom of the nanopits where the pit diameter is of the correct scale. The nanotexture on the tested surfaces are characterized by an RMS roughness of 61.8 nm and have peak-to-peak distances on the order of 100 nm, implying that if the capillary condensate is able to fill the nanopits, then the ice nucleation should still be able to nucleate homogeneously inside the condensate, at the side-wall surface interface, or at the three-phase line. It is also worth mentioning that the effect of the low $p$ used in our experiments may have an influence on the adsorption of water molecules on the surface and thereby may influence the surface energies of liquid–vapor and solid–vapor;\textsuperscript{91} however, the situation is complicated by the presence of other adsorbates such as volatile organic compounds, which previously has been shown to increase surface hydrophobicity.\textsuperscript{92}

Upon the basis of this discussion and our experimental results, we conclude that metastable capillary condensate forming within cavities created by the nanotexture and its subsequent freezing at low temperatures allows ice crystals to form and grow at lower $p/p_S$ than on the smooth silicon samples, due to the lack of "seed" condensate on smooth samples. An analysis of this discussion and comparison between the nanotexture and smooth surfaces is illustrated in Figure 2.13. In this frost formation pathway we note that the capillary condensate only plays a role in initiating frost growth, when significantly low $T_s$ are present to enable a substantial nucleation rate of ice for the small capillary condensate volumes. At higher $T_s$ the capillary condensate should also be present, but does not have the chance to propagate out of the nanotexture, due to the resulting low $J_{LS}$.\textsuperscript{93}
Figure 2.13: Mechanism to explain the earlier observed nucleation on nanotexture. At \( p/p_s = 1.4 \), metastable liquid can nucleate on the nanotextured silicon due to the Kelvin effect, while metastable vapor is still present above the smooth silicon. Due to the considerable supercooling (below the homogeneous nucleation limit), the small volume of metastable liquid freezes in the pores and is able to grow to be macroscopically visible, while the vapor over the smooth silicon remains metastable. At \( p/p_s = 3.0 \), metastable liquid can finally nucleate on the smooth silicon and due to the considerable supercooling, freezes.
2.6 Conclusions

In this chapter we revisit the analysis of the heterogeneous condensation–desublimation nucleation transition. Our motivation is to understand it in the context of surface icephobicity in order to advise the engineering of rationally designed icephobic surfaces under low water vapor pressure and temperature conditions. After rigorously defining and experimentally validating the regions of nucleation behavior as condensation or desublimation based upon $T_s$ and $p$ for a well-known ice nucleation agent, we study a nanotextured substrate to quantitatively define the effect of surface nanotopography on the barrier to frost nucleation and define a mechanism for nucleation behavior at low temperatures.

Our results are significant as they build on our understanding of the nucleation process of ice crystals from vapor. We observe that true desublimation can indeed occur on specific materials, whose solid-substrate interfacial energy is equal to or less than its liquid-substrate interfacial energy. Although these materials may be of high interest in the atmospheric sciences, their use in design of icephobic surfaces is less obvious. On surfaces relevant for icephobicity, we surprisingly found that the nucleation mode at low temperatures on sufficiently nanotextured surfaces ($R < 25$ nm, 1 order of magnitude above the minimal radius of curvature of stable ice nuclei, $r_{12}^*$) differs from the expected desublimation mode. The substantially lower temperatures necessary to achieve desublimation nucleation on such surfaces, enable surface topography of the right scale to trigger a different pathway to crystal growth, namely freezing of metastable capillary condensate, resulting in macroscopic crystal growth at lower supersaturation.

To this end, we conclude that the design of icephobic surfaces for very low-temperature applications place a significant amount of effort to use surfaces with as few nanoscale defects as possible to avoid ice crystal growth through freezing of capillary condensate. Nonetheless, it has been recently reported that nanotexture and roughness decreases frost adhesion, rendering the question of whether or not nanoengineered sample texture should be used, highly dependent on the area of application.

In summary, we find that smoother surfaces outperform nanotextured surfaces under low temperature and vapor pressure conditions. We conclude that most engineering relevant surfaces (silicon, metal, plastic) will exhibit this behavior, as long as their lattice spacing and chemical composition do not render it a strong ice nucleator (such as AgI), which has very important implications for applications such as air travel, power generation, and condenser technology.
Feasibility Study: Sublimation-driven Ice Crystal Detachment

This chapter contains preliminary results with the intent of subsequent publication:

Walker, C.; Schutzius, T.M.; Poulikakos, D. Sublimation-driven Ice Crystal Detachment for Enhanced Surface Deicing. (under preparation)
Abstract

This chapter consists of a feasibility study, containing on-going work, closely related to the previous chapter on desublimation. Here, we observed that ice crystals, upon sublimation, may spontaneously detach from the substrate before they completely sublime. In this chapter we present the spontaneous detachment phenomenon and initially examine the conditions at which this happens. This initial analysis provides us with insight, allowing us to postulate the mechanism for detachment. Because the sublimation is set in motion by heating the substrate, we postulate that the heat flux supplied at the substrate-ice interface causes a temperature gradient along the c-axis of the ice crystal. This temperature gradient must lead to equilibrium vapor pressure gradients and therefore heterogeneous sublimation rates across the surface area of the crystal. The heterogeneous sublimation rates lead to a receding geometry at the substrate-ice interface, that we term undermining, causing the detachment of the crystal from the surface. We recognize that this phenomenon has obvious applications to enhance ice removal in areas such as transportation and energy generation and its work is therefore planned to be continue beyond the scope of this thesis.
3.1 Introduction

Controlling surface ice accretion has a variety of important implications in industries such as power generation, refrigeration and transportation. Ice accretion on heat exchanger coils during power generation and refrigeration cycles creates larger temperature gradients and reduced heat transfer, resulting in reduced cycle efficiencies. In transportation, undesired build-up of ice is detrimental to safety, creating slippery roads, disrupting flight aerodynamics, and causing catastrophic sensor malfunctions. A number of different approaches exist aimed at mitigating the effect of surface ice build-up. If the approach utilizes intrinsic surface features such as chemistry or nano and microstructures they are referred to as icephobic surfaces. Icephobic surfaces can be broken up into different groups depending on how they combat the build-up of ice. For example, some surfaces aim to inhibit ice nucleation while others aim to demonstrate low ice adhesion. Recently, another approach to icephobicity has been studied, namely surfaces that spontaneously shed ice during the freezing phase transition. In this work, we present and study a similar phenomenon that harness sublimation phase transition to spontaneously shed ice crystals.

Figure 3.1: Two examples of an ice crystal spontaneously detach from the surface during the sublimation process. Scale bars: 300 µm

Figure 3.1 illustrates two examples of ice crystals that spontaneously detach from a substrate during sublimation. It is the goal of this work to investigate and explain the phenomena at work causing this spontaneous detachment. After understanding the detachment process, we aim to engineer surfaces that demonstrate enhanced sublimation-driven ice crystal detachment. We envision these surfaces to be useful in a host of applications where enhanced ice removal speed and efficiency is of importance, such as in power generation and transportation.
3.2 Methods

3.2.1 Surface Preparation

The samples used in this study consisted of silver iodide (AgI) coated glass cover slips fabricated with the process explained in section 2.3.3: The glass cover slips (175 µm thick) were initially cleaned by four-minute ultrasonication in individual baths of acetone, isoproponal, and water followed by a two-minute 600W oxygen plasma (PVA TePla, GIGAbatch, 210M). The slides were then coated using an evaporation process with a 2 nm layer of evaporated titanium (to improve silver adhesion) followed by a 10 nm layer of evaporated silver (Evatec, BAK501). We proceeded to place the coated glass slides in an airtight environment for between 30–60 s. The environment contained a beaker of a 2% vol. iodine (Sigma-Aldrich, >99.99% trace metals basis) in deionized water solution heated to 60°C. The iodide vapor reacted with the silver to form AgI crystals, confirmed by the change in sample color and SEM micrographs.

3.2.2 Experimental Protocol

We used the setup introduced in section 2.3.1 (see Figure 2.6; herewithin refered to as the environmental chamber) as well as an environmental scanning electron microscope (ESEM; FEI Quanta 650) to conduct experiments. Figure 3.2 illustrates the protocol used to conduct the ice crystal desublimation and subsequent sublimation used for the experiments in the environmental chamber. To begin we put the chamber under light vacuum by reducing the pressure of the chamber to approximately 0.2 mbar, while holding the source cooling block temperature ($T_b$) at a constant $-15°C$ (see dashed line in Figure 3.2). We then evaporated water vapor into the chamber to form ice on the source cooling block. By forming ice on the source cooling block at a known temperature we could very accurately measure the water vapor pressure inside the chamber. After establishing a constant water vapor inside the chamber, we desublimated crystals onto the AgI samples by decreasing the temperature of the sample below the temperature of the source cooling block. After some time the sample temperature was increased above the temperature of the source cooling block and the sublimation process began. A similar process was used for the ESEM, however the vapor pressure was controlled using a mass flow controller instead of the source cooling block.
Feasibility Study: Sublimation-driven Ice Crystal Detachment

Figure 3.2: By controlling the desublimation and sublimation rate and time of the ice crystals during the experiments we could investigate the effect of three variables on the detachment process. Controlling \((dT/dt)_d\) allowed us to set the nucleation rate \((\rho_n)\). Controlling \(-\int T dt\) allowed us to alter the initial crystal size before sublimation. Controlling \((dT/dt)_s\) allowed us to study the affect of sublimation rate on the detachment probability.

Controlling the Variables

In order to understand the mechanism for detachment we controlled for three different variables that we believed could effect the sublimation detachment process. The way we controlled these is illustrated in Figure 3.2. By adjusting the speed of desublimation \((dT/dt)_d\) we were able to control the nucleation density \((\rho_n)\) in order to observe whether the overlapping of crystals as they grew to larger sizes had an effect. Additionally we controlled the size of the crystal before they began to sublimate. This was done by controlling the combination of the time and degree of supersaturation during the desublimation process, represented by the shaded area \((-\int T dt)\). This allowed us to understand if the initial crystal size influenced the detachment process. Finally, we also varied the sublimation rate \((dT/dt)_s\) in order to investigate its influence on the detachment process.

Quantifying the Detachment Probability

To investigate the effect of each of the aforementioned variables on detachment, we quantified the probability that any observed desublimation nucleation site, resulting in a crystal, would then detach during the sublimation process by calculating the ratio of observed nucleation sites to the number of detached crystals \((\sigma_d)\). This was done by recording videos of the process and later using image analysis software to count the nucleation sites and subsequently the number of crystals that completely detached and
fell of the surface.

3.3 Results and Discussion

3.3.1 Results

For the first set of experiments we set a constant \((\frac{dT}{dt})_d\), which resulted in a fixed nucleation density \((\rho_n = 50 \pm 7)\). We then conducted experiments varying the size of the crystals and the subsequent sublimation rate by changing the variables \(-\int T dt\) and \((\frac{dT}{dt})_s\), respectively. The results, summarized in Figure 3.3 by the filled data points, demonstrate a direct correspondence between the detachment probability \((\sigma_d)\) and \(-\int T dt\). Reducing the crystal size \((-\int T dt)\), produced, without fail, a corresponding reduction in \(\sigma_d\). Although there are only four sets of experiments, these result still provides a strong indication that the size of the crystal, before sublimation begins, is an important factor in predicting \(\sigma_d\)—the larger the initial crystals size, the higher \(\sigma_d\) becomes.

Figure 3.3: Results of six sets of experiments done using different desublimation/sublimation cycles. Four sets of experiments were done holding the nucleation density constant at \(\rho_n = 50 \pm 7\) (filled data points) and two sets of experiments were done holding the nucleation density constant at \(\rho_n = 12 \pm 5\) (unfilled data points). (a) Graphical representation of experimental conditions to illustrate the relative magnitudes of \(-\int T dt\) and \((\frac{dT}{dt})_s\). Experiments were done with large crystals at a slow sublimation rate (■), large crystals at a high sublimation rate (●, ◦), slightly smaller crystals as a low sublimation rate (▲), and small crystals at a high sublimation rate (▼, ▽). (b) Quantification of detachment probability \((\sigma_d)\) using a box plot for each of the experimental sets. One observes that \(\sigma_d\) decreases with the crystal size \((-\int T dt)\) independent of \(\rho_n\).
The same set of experiments (filled data points) also shows that it is unlikely that the sublimation rate has any influence on the likelihood of detachment. The filled black circle represents the case of a high sublimation rate. It's detachment probability is both less than and greater than the detachment probabilities of two sets of experiments conducted at low sublimation rates (filled square and triangle, respectively). Whether the detachment probability of the high sublimation rate crystals is less than or greater than the that of the low sublimation rate crystals depends on the initial size of the crystals, not on the sublimation rate.

During the experiments done with $\rho_n = 50 \pm 7$ (filled data points), crystals began to overlap before sublimation began. In order to test whether the overlapping of crystals was a factor influencing $\sigma_d$, we conducted similar experiments by reducing $(\frac{dT}{dt})_d$ and thereby the nucleation density to a lower value ($\rho_n = 12 \pm 5$). Again, we observed detachment and saw that it again decreases as a function of crystal size. Based upon these results one could perhaps infer that overlapping is detrimental to $\sigma_d$, by comparing the filled triangle and unfilled circle, both of which have similar initial crystal sizes, but result in different $\rho_n$. The overlapping crystals ($\rho_n = 50 \pm 7$) show a reduced $\sigma_d$ compared to the non-overlapping crystals ($\rho_n = 12 \pm 5$).

### 3.3.2 Discussion

The experiments we conducted provided evidence that the probability of detachment is correlated to the crystal size before sublimation commences. Additionally, over the course of the experiments, we often observed a consistent change in the crystal contrast at its edges during the sublimation process prior to detachment. This can be seen in Figure 3.1a and is illustrated indepth in Figure 3.4.

Often, the ice crystals would begin to develop regions of high contrast at the edges that increased in size, the longer the sublimation proceeded. This phenomenon is indicated by the red arrows in Figure 3.4. We postulate that this change in contrast is caused by a changing crystal geometry during sublimation and evidence that the crystal is detaching from the substrate through what we term an undermining process. Initially, the crystal is in contact with the substrate and the interface of the crystal is parallel to the substrate. This allows light to be transmitted to and reflected from the substrate without being scattered, resulting in a clear image of the substrate below the ice crystal. As the crystal begins to detach from the substrate at its edges its surface becomes non-parallel to the substrate (see Figure 3.5), which scatters both the incoming and reflected light, resulting in dark areas in the image.

In addition to the contrast change at the edges, we occasionally observe a hole form at the center of the crystal. In Figure 3.4 the center of the ice crystal completely sublimates,
Figure 3.4: Image sequence of a crystal sublimating and subsequently detaching from the surface. At $t = 0$ s the crystal is completely transparent. As sublimation proceeds the edges begin to darken towards the center of the crystal (indicated by the red arrows). We postulate that this is due to the light being diffracted by the non-parallel interface of the ice crystal as it detaches from the surface. In the second before detachment we additionally observe that the center part of the crystal completely sublimates (indicated by the beige arrows) forming a hole. At this point the crystal detaches completely from the surface. Scale bar: 200 µm.

Creating a hole, right before detachment (indicated by the beige colored arrows). This is in contrast to Figure 3.1a where the detachment of the crystal happens without the observation of a central hole. Based on these observations we postulate a physical mechanism to explain the occurrence of the detachment process, summarized in Figure 3.5. Because we induce the sublimation process in these experiments by holding the vapor pressure constant and increasing the surface temperature, a temperature gradient along the c-axis of the ice crystal is created due to the relatively low thermal conductivity of ice ($2.2 \text{ W m}^{-1} \text{ K}^{-1}$). We estimate the temperature gradient by performing a number of calculations. We begin by estimating the average sublimation rate, $J$, by

$$J = \frac{\Delta a}{\Delta t} \rho_S$$

(3.1)

where $\Delta a$ is the change in the edge length of the crystal, $\Delta t$ is the change in time, and $\rho_S$ is the density of ice. The heat flux, $\dot{Q}''$, can then be calculated by

$$\dot{Q}'' = \Delta H_{\text{sub}}(J)$$

(3.2)

where $\Delta H_{\text{sub}}$ is the heat of sublimation. Assuming a ratio of 0.8 for the crystal height to
Figure 3.5: We propose that mechanism for detachment is an undermining process. The undermining is a result of the heat flux ($\dot{Q}''$) being localized at the surface-crystal interface. This creates a temperature gradient along the c-axis of the crystal—the bottom of the crystal being warmer than the top. The temperature gradient induces an equilibrium vapor pressure gradient along the c-axis of the crystal at the prism faces—the bottom of the crystal having the highest vapor pressure due to its relatively cooler temperature. This vapor pressure difference causes a faster sublimation rate at the bottom than the top. Simultaneously, the increased mass loss at the base induces another temperature gradient from the middle to the outside of the crystal along the basal face. By the same reasoning the middle of the crystal sublimates faster than the outside causing the sometimes observable central hole before detachment.

the edge length$^{62}$ and using 1D Fourier’s Law of conduction we calculate a difference in temperature of across the crystal of 0.1 K, meaning that $T_{\text{top}}$ is 0.1 K cooler than $T_{\text{bottom}}$. For our experiments at approximately $T = -15^\circ\text{C}$ this translates to a difference in vapor pressure of approximately 0.02 mbar. Based upon this difference in vapor pressure from top to bottom of the crystal we expect a difference in sublimation rate along the crystal’s c-axis. Using Langmuir’s theory on the rate of sublimation$^{97}$ we calculated a 7% greater sublimation rate at the bottom of the crystal than at the top. Because the crystal is losing mass at differing rates along the c-axis we expect that the geometry of the crystal to then change as illustrated by the schematic under the middle image of Figure 3.5. We postulate that the change in crystal geometry will have two consequences. Firstly, it will act to magnify the difference in sublimation rate along the c-axis, due to the added length necessary for the heat to travel to reach the top outside area of the crystal. Related to the first, it will also cause the temperature of the middle of the crystal to be greater than at the outside ($T_{\text{middle}} > T_{\text{out}}$). Again, by the same reasoning, this will create a gradient in sublimation rate from the center to the edges of the crystal. This is how we explain the common observance of the hole created at the center of the crystals.

In order to corroborate our postulated detachment mechanism it was our goal to visualize the undermining process by collecting ESEM micrographs. Unfortunately, we have not yet
Figure 3.6: ESEM images sequence of sublimating ice. Here, the sublimation process is induced in the same manner as in the environmental chamber—the vapor pressure is held constant and the temperature of the surface is increased. (a) The ice starts as a non-symmetric ice block. (b) As sublimation begins we observe faster sublimation near the center of the ice block, indicated by the orange arrows. (c) This preferential sublimation results in the formation of a hole at the center of the ice block. Soon after the hole has been formed, we observe movement of the ice indicated by the red arrow and the subsequent change in position in (d). Similar movement is observable again near the end of the sublimation process indicated by the red arrow in (e) and the subsequent change in position of the ice in (f). This movement indicates partial detachment from the surface. Scale bar: 100 µm.
Figure 3.7: Image sequence of the sublimation process induced by reducing the vapor pressure inside the chamber and holding the surface temperature constant. Here we do not observe the same change compared to when the vapor pressure is held constant and the surface temperature is increased. This indicates that the crystal geometry during the sublimation process differs depending on the method used to induce sublimation. Scale bar: 200 µm

been able to have precise control over the desublimation and sublimation process inside the ESEM due to an exposed surface colder than our sample. Nonetheless, we have been able to still obtain preliminary micrographs that confirm the formation of a hole at the center of the sublimating crystal and also indicate partial detachment of the ice crystals. These two observations are shown in Figure 3.6. In Figure 3.6b we begin to observe the increased rate of sublimation at the center of the ice block indicated by the orange arrows. This results in a hole at the center of the ice first observable in c. Additionally, we observe the partial movement of two parts of the ice block as sublimation continues. Soon after the hole has been made, we observe movement of the ice indicated by the red arrow in c and the subsequent change in position in d. Another example of this is observable again near the end of the sublimation indicated by the red arrow in e and the subsequent change in position in f. We observed similar behavior in the environmental chamber for crystals that did not completely detach and fall from the surface due to gravity.

The final experiment we conducted thus far to support our current theory is using the environmental chamber to induce sublimation by a different mean. Here we reduce the vapor pressure at a constant surface temperature. The result of this is shown in Figure 3.7. This process did not result in any observable crystals detachment or movement. Additionally, we did not observe the same change in contrast along the ice crystal edges, rather a more homogeneous distribution across the basal face of the crystal. These experiments provide strong evidence that the detachment process is dependent on the sublimation being induced by an increase in the substrate temperature.

### 3.4 Outlook

Although we have shown an interesting new phenomenon relevant for enhanced ice removal, there still remains a large portion of work that is still to be completed. Until this
point we have experimentally demonstrated that the spontaneous detachment of sublimating ice crystals depends largely on their initial size. Using bright field microscopy, we observed a contrast change during the sublimation process, providing a strong indication that the crystals geometry deforms during sublimation. We postulated that this is evidence of an undermining process, which acts to detach the crystal from the substrate and also causes preferable sublimation at the center of the crystal. In some cases the formation of a hole at the center of the crystal before it detaches from the surface is evident, which we were able to partially corroborate with preliminary ESEM micrographs.

Based upon these preliminary observations, we have offered the proposed undermining process as the mechanism for detachment. This is strengthened by the fact that we do not observe detachment or similar contrast changes when the sublimation process is done by reducing the chamber water vapor pressure instead of increasing the substrate temperature. Although it seems likely that the proposed mechanism could be responsible for the detachment process it is imperative to provide stronger evidence of the undermining mechanism. Our goal is to perform the same set of experiments that we have conducted in the environmental chamber in the ESEM. Tilting the ESEM stage should provide irrefutable visual evidence of the undermining process we are in search of, if it is in fact the responsible mechanism for detachment.

After we establish the detachment mechanism with more convincing evidence, it is our goal as engineers to then design, fabricate, and demonstrate surfaces that enhance this phenomenon in order to aid in the faster and more efficient removal of ice accretion from exposed surfaces. There are most likely a variety of different ways to go about this. One such idea would be to encourage the ice to grow in an ice-equivalent Cassie-Baxter state by coating only the tops of a large array of micro-pillars with an ice nucleating agent, such as silver iodide. Rationally, one would believe that if the crystals grow only in contact with the tops of the pillars, the reduced ice-substrate contact would expedite the undermining process and crystal detachment would happen quicker achieving the goal of enhanced deicing.
Transparent Metasurfaces Counteracting Fogging by Harnessing Sunlight

This chapter is reproduced in part with permission from:


Copyright 2019 American Chemical Society.
Abstract

Surface fogging is a common phenomenon that can have significant and detrimental effects on surface transparency and visibility. It affects the performance in a wide range of applications including windows, windshields, electronic displays, cameras, mirrors, and eyewear. A host of ongoing research is aimed at combating this problem by understanding and developing stable and effective antifogging coatings that are capable of handling a wide range of environmental challenges passively without the consumption of electrical energy. Here we introduce an alternative approach employing sunlight to go beyond state-of-the-art techniques, such as superhydrophilic and superhydrophobic coatings, by rationally engineering solar absorbing metasurfaces that maintain transparency, while upon illumination induce localized heating to significantly delay the onset of surface fogging or decrease defogging time. For the same environmental conditions, we demonstrate that our metasurfaces are able to reduce defogging time by up to 4-fold and under supersaturated conditions inhibit the nucleation of condensate outperforming conventional state-of-the-art approaches in terms of visibility retention. Our research illustrates a durable and environmentally sustainable approach to passive antifogging and defogging for transparent surfaces. This work opens up the opportunity for large-scale manufacturing that can be applied to a range of materials, including polymers and other flexible substrates.
4.1 Introduction

The loss of visibility due to surface fogging is a common phenomenon, which presents itself in a variety of daily situations, affecting both transparent and reflective surfaces, such as windows, windshields, electronic displays, cameras, mirrors, and eyewear including eyeglasses, safety glasses, ski and scuba goggles, and face masks. This visibility loss is a result of microsized water droplets that nucleate and grow on the surface due to either a sudden increase in relative humidity or a sudden drop in surface temperature. These water droplets disperse and reflect the incident light, severely affecting optical clarity.

A number of concepts have been studied and implemented to suppress this undesirable phenomenon. Temporary passive solutions include surfactants or superhydrophilic coatings, both of which increase the relative energy of the surface and shift the equilibrium from a plethora of tiny individual droplets to a very thin and continuous layer. In contrast to individual droplets, this thin and continuous water layer does not scatter the incident light and therefore does not interfere as much with the transparent clarity of the surface. Although improvements have been made to render superhydrophilic coatings more robust, these coatings are more susceptible to contamination due to their increased surface energy and are prone to water inundation, which can reduce visibility. Research aimed at addressing this concern has concentrated on developing zwitter-wettable surfaces, which exhibit either hydrophobic or hydrophilic properties dependent on the water droplet residence time on the surface. Permanent passive solutions typically take the approach of implementing superhydrophobic self-cleaning surfaces to remove condensed water droplets from the surface. Intricately engineered superhydrophobicity is necessary here to alleviate nanoscale condensate that nucleates within the textures and destroys the stability of the Cassie-Baxter state and therefore their hydrophobicity in environments of high relative humidity. Both growing condensate droplets as well as new macroscale droplets that come into contact with the surface will be forced into the Wenzel state, producing pinned droplets, destroying the desirable superhydrophobic characteristics, and thus rendering the surface even more adhesive than an otherwise flat surface of the same chemical composition. There have also been approaches to mitigate the loss of hydrophobicity resulting from surface condensate, and therefore render such sustainable hydrophobic surfaces effective for antifogging. Many of these approaches, inspired by surface features observed on insect eyes and plant leaves, include creating textured surfaces whose size and rationalized geometry allow condensate to grow in the Cassie-Baxter state. Because the Cassie-Baxter state preserves droplet mobility, these droplets can be easily removed by small external forces such as wind or gravity. An additional and extensively investigated approach is to use the excess energy of coalescing droplets, resulting from the reduction in free surface area, to propel themselves off the surface. While both of these approaches enhance the antifogging performance, they do not reduce the likelihood of the formation of the undesired condensate in the first place, which, in
particular over time, can have a detrimental effect for certain applications.

To address this challenging problem, we propose a different approach. As in recent path-breaking studies revolving around harnessing light and sunlight for new applications,\textsuperscript{114–117} including catalysis, materials synthesis, and desalination,\textsuperscript{118–121} we utilize a sustainable solution by means of rationally designed transparent natural sunlight absorbing surfaces,\textsuperscript{122,123} hereafter termed as metasurfaces, designed to inhibit the heterogeneous nucleation of condensate and also exhibit superior antifogging performance, while maintaining optical transparency. We begin by showing qualitatively and quantitatively the shortcomings of three different kinds of wetting behavior on a plain glass substrate, ranging from superhydrophilic to hydrophobic. Additionally, we show that the light-absorbing metasurfaces of the present work enhance evaporation rates of already accumulated condensate. To this end, we analyze, both experimentally and theoretically, the condensation and evaporation behavior of a single droplet on control surfaces and our metasurfaces. This fundamental analysis and discussion provide the motivation to subsequently consider condensation and evaporation of multiple droplets. For our metasurfaces, we observe significant reduction in condensate nucleation rate and an increased evaporation rate. We believe that this research, as a stand-alone technology, as well as in combination with the previously described state-of-art research, will lead to more robust and enhanced passive antifogging and defogging surfaces.
4.2 Theory

This section provides an explanation of important theory necessary to gain a deeper understanding and appreciation of the research presented in this chapter. We examine the influence of surface wettability and surface temperature on the nucleation rate and what their respective implications are for developing antifogging surfaces. Additionally, we briefly introduce the heat generation process resulting as a consequence of electromagnetic waves interacting with the metasurface.

4.2.1 Effect of Surface Wettability on Nucleation Rate

Surface condensate occurs when the environmental conditions are present that are required to overcome the energy barrier to nucleation barrier of liquid to vapor. This energy barrier to nucleation changes with surface wettability. Here we will show how the nucleation rate depends on the surface wettability and relative humidity (i.e. vapor pressure) at a given temperature.

Borrowing the equations derived in sections 2.2.1 and 2.2.3, the critical Gibbs free energy necessary for heterogeneous nucleation of condensate from water vapor ($\Delta G^*$) can be written as a function of surface-water contact angle ($\theta$).

$$\Delta G^* = f(\theta) \frac{16\pi \gamma^3}{(3[n_L kT_s \ln(p/p_L)]^2)}$$

(4.1)

where $\gamma$ is the surface tension of water in air, $n_L$ is the number of water molecules per unit volume, $k$ is Boltzmann’s constant, for a surface temperature $T_s$ and supersaturation $p/p_L$, where $p$ is the water vapor pressure of the environment and $p_L$ is the saturated vapor pressure over a plane surface of water at $T_s$. The function $f(\theta)$ illustrates the effect of surface chemistry and can be expressed as:

$$f(\theta) = \frac{1}{4} (2 - 3 \cos \theta + \cos^3 \theta)$$

(4.2)

where $0 < f(\theta) < 1$; a larger $\theta$ results in a larger $f(\theta)$ (refer to section 2.2.3 for a more detailed discussion). According to eq. 4.1 a larger $\theta$ results in a larger $\Delta G^*$. Borrowing eq 2.11 from section 2.2.4, we know that the nucleation rate has an inversely exponential dependency on $\Delta G^*$. 

Figure 4.1: Dependence of the heterogeneous nucleation rate ($J$) on both vapor supersaturation and water contact angle. Due to the increased surface area of higher contact angle droplets the energy barrier for heterogeneous nucleation ($\Delta G^*$) increases with contact angle. The exponential dependence of $\Delta G^*$ on $J$ is illustrated by showing $J$ for a substrate with $\theta = 125^\circ$ is > 30 orders of magnitude lower, as compared to the $p/p_L$ where $J = 1 \text{ mm}^{-2} \text{ s}^{-1}$ for a substrate with $\theta = 80^\circ$. The black dashed line corresponds to $J = 1 \text{ mm}^{-2} \text{ s}^{-1}$.

\[ J = J_0 \exp \left( -\frac{\Delta G^*}{kT} \right), \]

(4.3)

Therefore we can deduce that a larger $\theta$ results in a larger $\Delta G^*$ and therefore an exponentially smaller $J$. One can confirm this quantitatively by combining eqs. 4.1, 4.2, and 4.3 to plot the dependence of $J$ on $p/p_L$ for two $\theta$ (Figure 4.1). We observe that the difference in $\theta$ of $55^\circ$ changes $J$ by many orders of magnitude. For example, at $p/p_L \approx 2.25$, a surface with $\theta = 80^\circ$ would result in $J = 1 \text{ mm}^{-2} \text{ s}^{-1}$, while a surface with $\theta = 125^\circ$ at the same $p/p_L$ would result in $J \approx 10^{-35} \text{ mm}^{-2} \text{ s}^{-1}$, or for all intents and purposes absolutely no observation of nucleation on a reasonable time scale. Furthermore, $p/p_L$ would have to be $\approx 3.5$ before a surface with $\theta = 125^\circ$ would result in a substantial nucleation rate of $J = 1 \text{ mm}^{-2} \text{ s}^{-1}$.

Theoretically one could then engineer a enhanced fog-resistant surface by simply coating the surface with a low surface energy chemistry. In reality this is unfortunately not the case. Although it has been demonstrated that biphilic surfaces (surfaces with alternating hydrophobic and hydrophilic areas) favor nucleation on the hydrophilic areas, we found that solely hydrophobic surface chemistry does not exhibit the nucleation resistance.
that would theoretically be expected. We found that although the hydrophobic surfaces reduced the number of nucleation sites, they were not able to withstand higher supersaturations than neutrally wetting surfaces. Figure 4.2a,b show a control glass surface and a hydrophobic surface, respectively, that have been exposed to slightly supersaturated ($p/p_L \approx 1.02$) conditions for 60 seconds and Figure 4.2c quantifies the nucleation rate ($J_{VL}$). Based upon Figure 4.1, we would expect practically no nucleation on either surface, however experimentally we still observe nucleation on both surfaces. The discrepancy has been explained by the presence of randomly distributed, high-surface-energy nucleation sites on the surface.\textsuperscript{124,125} More of which must be present on the neutrally wetting surface.

Due to their reduced nucleation rate, hydrophobic surfaces are able to reduce the total amount of condensate coverage on the surface when compared to a higher energy surface. We calculated the volume of water on the surface of a hydrophobic sample and an untreated sample by measuring the droplet sizes, assuming an advancing contact angle, and using a spherical cap approximation. We calculated a reduction of approximately 10% in water volume for the hydrophobic surface, compared to the untreated one, after 60 s of exposure to supersaturated conditions. Although hydrophobic coatings may reduce the nucleation rate, they unfortunately do not solve the problem of retaining visibility of transparent surfaces at supersaturated conditions.

4.2.2 Effect of Temperature on Nucleation Rate

As with surface wettability, we can do a similar analysis on the influence of surface temperature on nucleation rate. We begin by quantifying the dependence of the water vapor saturation pressure ($p_L$) on $T_s$, given by the August-Roche-Magnus formula

$$p_L(T_s) = \alpha \exp \left( \frac{\beta T_s}{\lambda + T_s} \right)$$

(4.4)

where $\alpha = 6.1$, $\beta = 17.6$, and $\lambda = 243$ are constants. Eq 4.4 introduces a first exponential dependence of $p_L$ on $T_s$. Eq 4.1 indicates that the larger $p_L$ becomes, the larger $\Delta G^*$ becomes. Furthermore $J$ has an inverse exponential dependence on $\Delta G^*$ (eq 4.3). The linear dependence of $T_s$ in eqs 4.1 and 4.3 makes it difficult to outright claim a double exponential dependence of $T_s$ on $J$. Figure 4.3 plots the dependence of $J$ on $T_s$ by combining 4.1, 4.3, and eqs 4.4, showing that there is a strong exponential dependence of $J$ on $T_s$. A temperature increase of only 1°C reduces the nucleation rate by approximately four orders of magnitude. Therefore, even small temperature increases can have a very significant effect on reducing the chance for nucleation. This is important in light of the ensuing analysis on the effectiveness of our metasurfaces.
Figure 4.2: Effect of the water contact angle on condensation nucleation density. We compared the nucleation density of a neutrally wetting glass ($\theta^*_{\text{a}} = 87 \pm 3.0^\circ$ and $\theta^*_{\text{r}} = 68.7 \pm 5.5^\circ$) to a hydrophobic glass (pPFDA-coated, $\theta^*_{\text{a}} = 128.5 \pm 6.2^\circ$ and $\theta^*_{\text{r}} = 93.3 \pm 13.3^\circ$). The micrographs in (a) and (b) were taken 60 seconds after the onset of nucleation on (a) neutrally wetting glass and (b) pPFDA-coated glass to visually show the difference in nucleation density. The nucleation is observed to happen at the same supersaturation for both surfaces (just above supersaturation). Using computer-aided image analysis, the (c) nucleation rate ($\dot{J}$) on each substrate was quantified for seven experiments ($n = 7$). The nucleation rate has an influence on the condensate coverage after exposure to a supersaturation of 1.3 for 10 min as illustrated for the (d) control sample and (e) pPFDA-coated glass. Using computer-aided image analysis, the (f) water surface coverage ($\kappa$) on each substrate was quantified for seven experiments ($n = 7$). The pPFDA-glass has approximately 10% less water on its surface, as compared to the control sample. Scale bars: (a–b), 50 $\mu$m; (d–e), 500 $\mu$m.
4.2.3 Light Induced Surface Plasmon Resonance

Light induced plasmonic resonance is a tool used for this study and is certainly not the focus of the work in this chapter. Nonetheless, this section would not be complete without a brief overview of the physics behind the heating process utilized by the metasurface. The metasurface refers to a thin coating made of a dielectric embedded with nanometer sized noble metal particles (a detailed explanation will be introduced in section 4.3.1). Although the particles are orders of magnitude smaller than the wavelengths of the electromagnetic radiation produced by the sun, the corresponding electromagnetic fields can nevertheless excites free charges in noble metal particles. Due to the oscillation of the electromagnetic field the free charges also begin to oscillate from side-to-side in the particle. These collective oscillations are called plasmons. Analogous to a mass-spring-damper system, specific frequencies can cause the oscillations of the free charge to begin to resonate. The excitement frequency that causes this resonance depends on the material, size and shape of these particles, as well as the proximity to other nanoparticles. There is a large amount of research that is being conducted to investigate the dependence of these parameters, providing scientists the knowledge to engineer coatings that exhibit this effect at desired electromagnetic wavelengths. Here we created a metasurface that broadly absorbs across the whole electromagnetic spectrum produced by the sun (400–2500 nm).

The captured energy of these electromagnetic waves using the plasmonic resonance phenomenon described can be used to generate very confined heat by collective motion energy to be dissipated through ohmic losses. The heat generated by a nanoparticle is known to be proportional to the intensity of the illuminating light where the proportionality constant is the absorption efficiency of the particle. The absorption efficiency is defined as the absorption cross-section normalized by the geometrical cross-sectional area of the
Figure 4.4: Illustration of a simplified working principle of the metasurface. On the right the metasurface is depicted as a thin coating consisting of nanoparticles embedded in a dielectric bulk. Depending on the frequency of the electromagnetic field, the material, size, and spacing of the nanoparticles the electron cloud of the atoms in the nanoparticle can be excited to resonance by the electromagnetic field as shown on the top left. This energy generates confined heat through ohmic losses. credit: Efstratios Mitridis.

particle under illumination. Due to the plasmonic resonance it turns out that the absorption cross-section is larger than the geometrical cross-section and therefore the heating effect is magnified. This is important because a greater heating effect results in better antifogging and de-fogging.

4.3 Methods

4.3.1 Surface Preparation

We used double side polished, 4 in, 500 μm thick wafers (UniversityWafer, Inc.) made of fused silica. We cut the wafers into 5 × 5 mm square specimen. Prior to cutting, a 3.3 μm polymer top-layer was applied to protect the glass surface. After the cutting process, the protective layer was removed by sonication in acetone for 2 min, followed by an equal-time sonication in isopropyl alcohol and water. We also treated each specimen with oxygen plasma (Oxford Instruments, Plasmalab 80 Plus) for 7 min. Shortly after, we prepared seven different sample types, explained here in the following sections in detail.
Untreated Control

We stored freshly diced and cleaned glass wafer pieces in a dust-free environment, under ambient temperature ($\approx 23^\circ$C) and relative humidity (RH = 40–60%), for several days (> 5 d), which was enough time for the adsorbed hydrocarbon layer to approach equilibrium with the surfaces (therefore providing stable advancing and receding contact angles).

Hydrophilic Control

We immediately (< 1 h) used the plasma-treated glass specimen.

Untreated Metasurface

We used sputter deposition (Von Ardenne CS 320 C) to fabricate the light-absorbing metasurface on top of the fused silica substrates, in line with previous research.\textsuperscript{126} This is a coating technique that has demonstrated its flexibility in a roll-to-roll multilayer process for depositing transparent conducting oxides on windows at large-area.\textsuperscript{127} Also, its applications extend to highly controllable metallization\textsuperscript{128} and deposition of tiny amounts of noble metals with subsequent cost reduction.\textsuperscript{129} Two component materials were used, gold nanoparticles (Au) and titanium dioxide (TiO$_2$), with the following deposition parameters: 50 W dc field, 6 $\mu$bar pressure, 3 s duration, and 600 W RF field, 6 $\mu$bar pressure, 43 s duration, respectively. We fabricated a structure of eight alternating Au and TiO$_2$ layers in total with the first layer being TiO$_2$. The metasurface was finalized with an extra TiO$_2$ top layer (deposition time of 72 s). The thickness of the metasurface has been estimated $\approx 60$ nm with a mean absorption of 37\% and transmission of 36\% (see also Figure 4.5b) in the wavelength range of 400–750 nm.

Figure 4.5a shows a schematic illustration of the different layers constituting the metasurfaces. They consist of repeated ultrathin bilayers of Au nanoparticles and TiO$_2$ There is also an additional protective TiO$_2$ top-layer. Our metasurfaces have k + 1 bilayers in total and a thickness of $\approx 60$ nm. The internal structure of the metasurfaces is revealed in the scanning electron micrograph, which shows that the layers of Au nanoparticles are embedded in, and spaced apart by, the TiO$_2$ layers. For improved image quality and to emphasize the flexibility of the multilayer design, here we show a micrograph of the metasurface consisting of 22 bilayers. In Figure 4.5a, bottom-row, the atomic force micrograph of our metasurface indicates that the surface is very smooth with RMS roughness < 1 nm.
Figure 4.5: Surface characterization of the metasurface. (Top Left) Schematic representation of the multilayer structure of Au nanoparticles and TiO$_2$, which make up the metasurface. (Top Right) Scanning electron micrograph of the metasurface cross-section, acquired with secondary electrons, where the bright circular spots are the Au nanoparticles. (Bottom) Atomic force micrograph of the metasurface. Scale bar: 50 nm
Silane-Treated Control

For the single droplet evaporation experiments, we used a home-built vacuum chamber for chemical vapor deposition of trichlorovinylsilane (TCVS; 97%, Sigma-Aldrich) on our glass substrates. For this purpose, we first transferred 1 mL of TCVS into a glass container under nitrogen atmosphere. With the container connected to the chamber and its valve closed, we then evacuated the chamber until a stable pressure of 100 µbar was reached at which moment the valve was opened, while the chamber was also isolated from the vacuum pump. The deposition time was 20 min at a temperature of ≈ 23°C. In the end, we removed the excess TCVS with a prolonged evacuation and purging cycle.

Silane-Treated Metasurface

We followed the same process as in for the Silane-Treated Control to deposit TCVS on our metasurface coated glass samples.

Hydrophobic Control

We utilized initiated chemical vapor deposition (iCVD; iLab Coating System, GVD Corporation) to deposit ultrathin conformal films of poly(perfluorodecyl acrylate) (pPFDA) on clean glass substrates in order to render them hydrophobic. The advantage of pPFDA over other fluoropolymers lies on its low surface energy (9.3 mN/m), which is half of the surface energy of the widely used poly(tetrafluoroethylene) (18 mN/m). Silane-treatment of the substrates precedes the iCVD process. The covalently bound surface vinyl groups in TCVS react with the vinyl groups in perfluorodecyl acrylate monomers and bind them chemically to the substrate. For the iCVD deposition we used 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA; 97%, with tert-butylcatechol as inhibitor, Sigma-Aldrich) and tert-butyl peroxide (TBPO; 98%, Sigma-Aldrich) as monomer and initiator, respectively. The main deposition parameters are reported here: the TBPO flow rate was 2.6 sccm, the PFDA flow rate was 1.0 sccm, the substrate temperature was ≈ 20°C, the filament temperature was ≈ 300°C, the PFDA container temperature was 80°C, the process pressure was ≈ 100 mTorr, and the deposition time was 15 min. We stabilized all temperatures for 5 min prior to each deposition. We also purged the vacuum chamber with nitrogen for 10 min after deposition.
Hydrophobic Metasurface

We followed the same procedure as mentioned for the Untreated Metasurface to deposit pPFDA on our glass, metasurface-coated specimen.

4.3.2 Surface Characterization

We imaged the cross section of the metasurface with a Hitachi SU8230 scanning electron microscope. We characterized the surface topography of the samples with a Brooker Dimension Fastscan atomic force microscope. We characterized the spectral properties of the metasurface, tinted laminate (LLumar Esprit Series ATC 35 CH SR HPR), and control samples for the 400–1650 nm wavelength range using a home-built spectroscopic system. We measured the advancing and receding contact angles of each sample type using a DataPhysics OCA 35 goniometer, by the inflation/deflation method (droplet volume of 2–3 \( \mu \)L). The observations of the condensing droplets under the microscope were performed using an upright microscope (Olympus BX60), with a 5× objective (Olympus MPlan 5×/0.10 BD JAPAN) and a 20× objective (LMPLanFI 20×/0.40 BD JAPAN) in a bright-field configuration.

Contact Angle Measurements

Both the advancing (\( \theta^*_a \)) and receding (\( \theta^*_r \)) contact angles for each of the tested surfaces used in this study are an integral part that we use to explain the phenomena that we observed. We measured and summarized both \( \theta^*_a \) and \( \theta^*_r \) in Figure 4.6 for all of the surfaces used in this study, using 3 different samples of each kind and 2-3 measurements for each sample, for a total of 7 measurements (\( n = 7 \)). Figure 4.6a,b show the spread across the measurements for each sample type using box and whisker plots. For our study it is important that \( \theta^*_a \) and \( \theta^*_r \) are comparable between the same sample types of control and metasurface (i.e. the silane-treated control and metasurface must have similar contact angles). This is important in order to rule out any sort of effect on antifogging or defogging that is not due to the sunlight absorbing properties of the metasurfaces.

Inspecting Figure 4.6, one observes that, in spite of the fact that surface chemistry is expected to be identical between metasurfaces and control samples of the same type, \( \theta^*_a \) is slightly larger and \( \theta^*_r \) is slightly smaller for the metasurfaces. This increase in the contact angle hysteresis is a typical signature for increased surface roughness, assuming that the droplets sit in the Wenzel state.
4.3.3 Experimental Protocol

We carried out the clarity and distortion measurement experiments using an upright microscope (Olympus BX60) and a 5x objective (Olympus MPlan 5x/0.10 BD JAPAN) in a dark-field configuration. We placed the matrix of dots, which served to quantify the clarity and distortion, on top of a Peltier element to cool. We then placed the sample on top of the dotted matrix and blew a steady stream of nitrogen onto the sample while cooling it down to 6°C in order to create a locally dry environment and to prevent premature condensate formation on the sample. After the temperature had stabilized, we stopped the nitrogen stream, exposing the sample to 40% relative humidity at 24°C ($p/p_L = 1.28$), at time $t = 0$ s. We then recorded the fogging process on the sample exposed to the above-mentioned supersaturated conditions for a duration of 10 min.

Single Droplet Evaporation

We conducted the single droplet evaporation experiments using the setup depicted in Figure 4.10. Using two lenses, we collimated and focused a broadband (sun-mimicking) halogen light source (Schöll’s Fiberoptic GmbH, Flexilux 600 longlife 1.25 A) onto each test sample at a power density of 4000 W m$^{-2}$ (corresponding to 4 suns). In order to get the most representative results for the aforementioned applications, it was important...
that the surface of each sample was fully irradiated by the focused light source and that as little contact with the holder as possible was made in order to limit heat diffusion from the metasurface to the surrounding media. Our focused light had a diameter of \( \approx 7 \text{ mm} \) and we used \( 5 \times 5 \text{mm} \) samples. We irradiated the sample with light until its temperature reached steady state (see Supporting Information, Infrared thermography and temperature response measurements). We recorded the temperature of the sample using an infrared (IR) camera (FLIR SC7500, spectral range of 1.5–5.1 \( \mu \text{m} \)) before the droplet was placed on the sample \( (t < 0 \text{ s}) \) as well as after placing the droplet and throughout its complete evaporation period. After placing a 1 \( \mu \text{L} \) droplet on the sample, we also imaged the droplet with a CMOS camera from a side-view perspective. In order to allow each droplet to reach a constant receding contact angle, and therefore give comparable data between sample types, \( t = 0 \text{ s} \) corresponds to the moment when each droplet reached a volume of 0.6 \( \mu \text{L} \). Starting at \( t = 0 \text{ s} \), we computed the contact angle and volume of the droplet until it had completely evaporated. For both sample types (untreated control and untreated metasurface), we carried out three experiments on different samples. We carried out all the experiments in an environment with RH = 64\%, at 21.8° C. We also acquired the transient thermal response of an untreated control and an untreated metasurface in response to illumination using the infrared camera, with a 50 mm F/2 lens at a frame rate of 10 fps for two different power densities (1 sun and 4 suns). We kept the optical axis of the camera tilted at an 85° angle with respect to the horizontal plane of each surface in order to alleviate the Narcissus effect.

**Multidroplet Defogging**

For the multidroplet defogging experiments, we used the same setup as depicted in Figure 4.11, mounting a Canon 5D Mark III DSLR camera at an angle of approximately 45°. We placed a fishbone pattern on the holder below the sample in order to improve contrast and illustrate the sample transparency. We fogged each sample by cooling it down to 0°C for 5 min in an environment with a relative humidity of 60% at 23.0°C (\( p/p_L = 2.75 \)). We proceeded to take the sample off the Peltier element and transferred it to the holder, which was then irradiated with light at a power density of 1000 W m\(^{-2}\) (approximately 1 sun) in an environment with a relative humidity of 60% at 23.0°C. We measured the time and visually recorded the samples using the camera until the condensate had completely evaporated. We conducted seven experiments on different samples for each sample type (control untreated, control hydrophobic, metasurface untreated, metasurface hydrophobic). We tested each sample population for a standard normal distribution using the Kolmogorov-Smirnov test and validated the improvement in defogging time using the two-sample t test.
Antifogging

We carried out the antifogging experiments using the setup depicted in Figure 4.12. We placed a small printed illustration (edelweiss flower) below the sample holder, to give an enhanced impression of visibility retention. The illustration was sprayed with a passive antifogging agent (Aqualung Anti Fog Spray) to reduce condensation on the flower (not completely effective as condensate is slightly visible for \( t = 30–60 \) s in Figure 4.12, behind the otherwise fog-free metasurface). The experiments were conducted by setting the temperature of the water bath \( (T_w) \) and measuring the environmental air temperature inside the chamber \( (T_e) \). We also measured the sample temperature \( (T_s) \) to determine \( p/p_L \). We used the fan in order to get a homogeneous distribution of \( p/p_L \) throughout the chamber. When \( T_w \) reached \( 65^\circ \)C, we turned the fan on and the experiments began, corresponding to \( t = 0 \) s. We recorded the process for 60 s. In order to determine the supersaturation of the vapor in the chamber with respect to the sample, we ran three individual experiments both for the metasurface and control samples. For the metasurface we obtained an average environmental temperature across the three experiments of \( 35.9 \pm 0.3^\circ \)C and an average surface temperature of \( 35.8 \pm 0.4^\circ \)C. These three experiments resulted in an average supersaturation above the metasurface of \( 1.01 \pm 0.01 \). For the glass surface, we obtained an average environmental temperature across the three experiments of \( 37.3 \pm 0.5^\circ \)C (the increase in environmental temperature was due to the slow warming of the chamber after repeated experiments) and an average surface temperature of \( 33.7 \pm 0.6^\circ \)C. These three experiments resulted in an average supersaturation above the glass surface of \( 1.22 \pm 0.01 \).
4.4 Results and Discussion

In order to understand and put into perspective the inherently intertwined phenomena of visibility diminution and surface fogging for transparent and reflective media, we began by investigating the behavior of superhydrophilic (the most common state-of-the-art technique to retain visibility), hydrophobic, and untreated glass with intermediate wetting behavior ($\theta^* \approx 90^\circ$), under exposure to a supersaturated water vapor environment.

Figure 4.7a–c shows superhydrophilic, untreated, and hydrophobic glass samples, respectively. The samples were placed on a background consisting of an array of dots before ($t = 0$ s) and after exposure for 10 min ($t = 600$ s) to an environment of supersaturated water vapor (supersaturation ($p/p_L$) equal to 1.3 where $p$ and $p_L$ are the partial and saturation pressure of water vapor, respectively). We used the array of dots as a reference to both qualitatively and quantitatively observe the clarity and distortion caused by condensate on the samples upon exposure to supersaturated vapor conditions.

Figure 4.7a compares a superhydrophilic glass surface before being exposed to supersaturated vapor ($t = 0$ s) and after exposure for 10 min ($t = 600$ s). Comparing this to the same conditions for untreated and hydrophobic samples in Figure 4.7b,c respectively, we clearly observe that the superhydrophilic glass retains similar clarity as before exposure to supersaturated conditions, while the array of dots under the untreated and hydrophobic substrates suffers from significant blurriness due to the microdroplets scattering incident light. This supports the motivation for using superhydrophilic surfaces where maintaining transparency is important even when exposed to supersaturated vapor environments. Although the superhydrophilic glass sample retains the highest clarity among the three types of glass, it appears to suffer from distortion, apparent by the asymmetry of the array of dots at $t = 600$ s. In contrast, this asymmetry is not observable when inspecting the untreated and hydrophobic samples in Figure 4.7b,c.

To quantify our visual observations, we determined the parameters clarity, $C$, and distortion, $\delta$ (see also illustration in Figure 4.7d). We quantified $C$ by measuring the mean intensity of each dot, $I$ ($N = 25$ dots in total per sample), and normalizing it to the respective mean background intensity, $I_b$, at $t = 0$ and $t = 600$ s (subscripts 0 and $t$ denote time zero and $t$, respectively). We measured the respective intensities by taking the mean gray scale value of the pixels in either the dot or the background. We calculated $C$ per each dot at time $t$ by

$$C = 1 - \log_{10} \left[ \left( \frac{I_t}{I_{b,t}} \right) / \left( \frac{I_0}{I_{b,0}} \right) \right]$$

(4.5)
Figure 4.7: Effect of fogging on the clarity and distortion for differing wetting behavior of transparent surfaces. We characterized both the clarity and distortion of transparent glass surfaces by using a dot array placed under the surfaces. (a–c) Darkfield micrographs of the surfaces and the dot array were taken before \((t = 0\ s)\) and 10 min after \((t = 600\ s)\) the samples were exposed to supersaturated vapor conditions. The before and after images of the (a) superhydrophilic, (b) untreated (neutrally wetting), and (c) hydrophobic glass are shown. We quantified the clarity and distortion by analyzing the dot array for each sample type as illustrated in (d) using eqs 4.5 and 4.6. The quantified effect of fogging on (e) clarity, \(C\), and (f) distortion, \(\delta\), on each of the three surfaces is illustrated as box plots, where each type of surface was tested using six different samples \((n = 6)\). We also estimated the visibility retention through the three surfaces by introducing a performance factor, \(P\), and compared them to a sunlight absorbing metasurface \((P = 1)\), as shown in boxplot (g). Scale bar (a–c): 100 \(\mu\)m.
We quantified \( \delta \) by measuring the position of each dot, \((x_{i,0}, y_{i,0})\) at \( t = 0 \) s and \((x_{i,t}, y_{i,t})\) at \( t = 600 \) s, and used this to calculate the distance that each of the dots moves. Normalizing this distance with the diameter of the dots, \( d \), yields

\[
\delta = \frac{\Delta s}{d} = \frac{1}{d} \sqrt{(x_{i,t} - x_{i,0})^2 + (y_{i,t} - y_{i,0})^2}
\]

\(C\) and \(\gamma\) are reported in Figure 4.7e,f, respectively, as box plots, where the values of each box and whisker are made up of six experiments \((n = 6)\) and \(N = 25\) dots per experiment for a total of 150 measurements. As expected, Figure 1e confirms that the clarity of the untreated and hydrophobic glass surfaces is significantly reduced when compared to that of the superhydrophilic glass. We attribute the slightly better performance of the hydrophobic glass compared to the untreated glass to the reduction in nucleation density of water on the hydrophobic glass and therefore the reduction in the number of drops that scatter the light. Furthermore, Figure 4.7f confirms that the distortion in the case of the superhydrophilic sample is considerable, especially when compared to the untreated and hydrophobic samples. An ideal superhydrophilic surface should produce a perfectly continuous water film across the entire sample; however, this is not what we observed. We attribute this to the high surface energy of the treated glass, making it more susceptible to contamination\(^{134}\) that creates pinning points, acts to break up the continuous film, and results in the observable distortion. Even if the surface remained completely clean, additional pinning points from the edges would also create a curved water interface at the edges and also result in distortion. In order to quantify and compare the overall visibility retention of the three surfaces (superhydrophilic, untreated and hydrophobic glass), we introduced a performance factor, \(P = (1 - \delta)C\), that combines the values of both clarity and distortion. The higher the performance factor the better the visibility retention through the sample. We furthered our comparison to also consider the performance of our metasurface, assuming it remains condensate free (which we demonstrate later). Figure 4.7g shows that the untreated glass is the worst performer, followed by the hydrophobic surface and the superhydrophilic surface. Finally, the metasurface achieves maximum performance (100%). It is important to understand that \(C\) does not take total light transmission through the surface into consideration; therefore, although our metasurface has a visible light transmission of 36% compared to the glass transmission of \(\approx 87\)%, this does not affect \(P\). We chose not to incorporate transmission into \(P\) because for many applications, a reduction in visible light transmission is a desirable property to optimize user visibility comfort and performance. Applications such as car windows, building windows, and sun-protective eyewear utilize transmission ranging from 15–50\%,\(^{135,136}\) 2–70\%,\(^{137}\) and 15–25\%,\(^{138,139}\) respectively. Advantageously, we designed the metasurfaces studied in this work to harvest both visible and near-infrared light in order to obtain the most efficient antifogging performance. What is important here is that although the metasurface reduces the sample transmittance, the maximum clarity and lowest distortion are achieved due to the deeply subwavelength gold nanoparticles.
In order for the metasurfaces to achieve best performance in a supersaturated vapor environment, they must inhibit the formation of condensation on the surface. To this end, we studied the efficacy of our metasurfaces to use naturally occurring sunlight to generate plasmonic surface heating in order to aid in defogging and antifogging of surfaces exposed to supersaturated vapor environments to maintain clarity and limit distortion. We began by comparing the spectral properties of our metasurface to those of plain glass and a sample with a commercially available tinted laminate having a similar level of transmission in the visible spectrum.

Comparing the spectral properties of our metasurface to those of a commercially available tinted laminate having a similar level of transmission in the visible spectrum (Figure 4.8a,b) shows the reflection ($R$), transmission ($T$), and calculated absorption ($A = 1 - T - R$) of both samples in the 400-1650 nm wavelength range. For comparison, Figure 4.8c shows the spectra for uncoated glass. The visible light transmission (400-750 nm) for the metasurface and tinted laminate was 36% and 33%, respectively. Figure 4.8a shows that the metasurface has a relatively constant broadband absorption in the measured wavelengths. On the other hand, 4.8b shows that the commercially available tinted laminate has high absorption in the visible wavelengths (400-750 nm); however, in the near-infrared range (750-1650 nm) its absorption drastically decreases. The broadband absorption of the metasurface is advantageous because it allows for increased absorption of sunlight in the near-infrared and therefore a higher temperature response to inhibit fogging or encourage evaporation (see Figure 4.8c for the spectral properties of the control used to create the metasurface.
Figure 4.9: Comparison of light-induced heating characterization of the metasurface, commercially available tinted surface, and uncoated glass surface. (a) Experimental setup showing how the temperature increase of the samples upon illumination was measured. (b) Sample temperature increase, $\Delta T$, over time, $t$, for the metasurface, tinted laminate, and uncoated glass samples. Sample thickness was $\approx 4\text{ mm}$.

With the knowledge of the spectra for each sample, we measured the temperature response and time until steady state for each of the three sample materials. Figure 4.9a shows a schematic of the experimental setup, and the spectral irradiance data of the light source, that we used to illuminate the samples and measure their temperature. Figure 4.9b shows a plot of sample temperature above ambient, $\Delta T = \bar{T}_s(t) - \bar{T}_s,0$, versus time, $t$, upon illumination, for the metasurface and the commercially available tinted laminate, where $\bar{T}_s(t)$ and $\bar{T}_s,0$ are the average sample temperatures at time $t$ and $t = 0$, respectively. The steady-state value of $\Delta T$ for the metasurface was 130% higher than that of the commercially available tinted laminate.

In the rest of this work we compared the efficacy of our metasurfaces to untreated glass (hereafter referred to as control) for defogging and antifogging applications. Figure 4.10a illustrates the setup that we employed. It consisted of a sun-mimicking light source and a lens to focus the light onto the sample plane (the metasurface was facing upward) with a spot diameter of 7 mm that fully illuminated our $5 \times 5\text{ mm}$ samples at a power density of 4 suns. We mounted two cameras to extract data in order to quantify the experiments; a tilted-view CMOS camera to observe the droplet’s apparent contact angle and a top-view infrared (IR) camera to construct the temperature profile of the sample and droplet. It is well-known that the contact angle progression of an evaporating droplet
can have a significant effect on the evaporation time\textsuperscript{140–142}, therefore in order to isolate the effect of the illuminated metasurface we treated both surfaces with a vapor-deposited trichlorovinylsilane (TCVS). This resulted in a consistent receding contact angle of approximately $50^\circ$, allowing consistent measurements between surfaces, beginning when the droplets reached the receding angle and then continued evaporation in the constant contact angle mode. Figure 4.10b quantifies the contact angle progression of the evaporating droplets as a function of time for both the control and metasurface samples. We observed that the receding angle for both samples is the same and the constant contact angle mode becomes the mode of evaporation for the duration of the experiments. By establishing the same contact angle progression during evaporation for both surfaces, we show in Figure 4.10c that the metasurface increases the droplet evaporation rate by approximately 4-fold for a droplet that is of the same order of magnitude compared to the sample size. This is caused by the considerable light absorption and heating of our metasurface, which is observable by examining Figure 4.10d,e. Here we show synchronized side-view (visible) and top-view (IR) image sequences of illuminated droplets on a control and metasurface sample, respectively, before and for the duration of evaporation. The leftmost IR images ($t < 0$ s) show the surfaces at steady state under illumination before a droplet is placed on the surface. While the control sample in Figure 3d remains very close to room temperature, the metasurface takes advantage of light-induced localized surface plasmon oscillations on the nanometer-scale gold particles, resulting in heating of the surface by $> 10^\circ$C. When placing a droplet on the surface, we observed a reduction in the temperature of the surface, shown in the IR images ($t = 0$ s) of Figure 4.10d,e. This can be explained by the effect of evaporative cooling, which causes the droplet, and subsequently the surface it is in contact with, to cool due to the energy required by water molecules to overcome the latent heat of evaporation and change from liquid into vapor. Advantageous to the evaporation, the metasurface is able to transfer more heat into the droplet, while the droplet maintains a temperature lower than the surface temperature. Near the end of evaporation, the metasurface returns to its steady-state temperature, as in the case without the droplet and so does the control, which is observable at $t = 200$ and 800 s in the IR images of Figure 4.10d,e, respectively.

Using the ability of our metasurfaces to effectively harness sunlight energy over a broad spectrum and turn it into heat, we showed that we could reduce the drying time of single droplets. We proceeded to focus on the drying of fogged surfaces, as such an investigation is more relevant for surface defogging and antifogging. One would expect the enhanced evaporation rate in the case of the metasurface to also be present for multiple droplets, albeit to an extent that remains to be shown. We investigated this by conducting defogging experiments on four different samples. As before, the control surface was plain untreated glass (untreated control), which we initially compared to plain glass coated with poly(perfluorodecyl acrylate) (pPFDA; hydrophobic control) to render it hydrophobic. The third and fourth samples consisted of an untreated metasurface and a metasurface treated with pPFDA (hydrophobic metasurface) to render it hydrophobic.
Figure 4.10: Sunlight absorbing metasurfaces drastically reduce evaporation time of a single droplet. (a) Experimental setup consisting of a sun-mimicking light source and a lens system to focus the light on the sample with a power density of 4000 W m$^{-2}$. We used a CMOS camera to observe the contact angle progression of the droplets and an IR camera to record the sample and droplet temperature profiles. (b) Plot of contact angle, $\theta^*$, versus time, $t$, for control samples (red curves) and metasurfaces (blue curves). The evaporation rate of the metasurfaces was approximately four times higher than the control, as seen in plot (c), droplet volume, $V_d$, versus $t$. (d,e) Side view and infrared top view image sequence of a single droplet evaporating on a (d) control surface and (e) metasurface. Scale bars (d,e): 1 mm.
Figure 4.11: Using metasurfaces to enhance visibility restoration by reduced defogging time. Using metasurfaces that efficiently turn the absorbed light into heat, we were able to reduce the defogging time compared to a control surface. The transparency vs $t$ is shown for an (a) untreated glass surface (untreated control) and an (b) untreated glass metasurface (untreated metasurface) illuminated by a lamp with a power density of 1 sun. Statistically, the metasurfaces reduced the defogging time ($t_{df}$) by approximately 25% as shown in (c). We tested both the control and metasurface samples against their hydrophobic counterparts to see if hydrophobicity also has an effect on $t_{df}$. For both pairs of samples we obtained two sample t test $p$ values $< 0.05$ to prove this was the case. Significance bars in (c) are represented by * for $p < 0.05$ and *** for $p < 0.001$. Scale bars (a,b): 2 mm.

We initially exposed each surface to supersaturated conditions by cooling the surface. This caused a layer of condensate to form. The samples were then transferred to the experimental setup depicted in Figure 4.10a. To better mimic real-world conditions, we changed the power density to 1 sun (1000 W m$^{-2}$). We then measured the evaporation time for seven different samples of each type. We found that both the untreated and hydrophobic metasurfaces outperformed the untreated and hydrophobic control samples by reducing the time necessary for complete surface defogging.

Figure 4.11a,b shows image sequences of the untreated control and the untreated metasurface, respectively. Qualitatively, one observes that the condensate surface coverage remains similar for the first 70 s, followed by a faster reduction of condensate surface coverage on the untreated metasurface, and hence a reduced defogging time. Figure 4.11c shows a box plot of the defogging time ($t_{df}$) for seven individual runs on the two sample types depicted in Figure 4.11a,b. Figure 4.11ac additionally shows $t_{df}$ for the hydrophobic control and metasurface. As expected, the quantitative analysis indicates that there is
a clear improvement in $t_{df}$ for the metasurfaces when compared to the plain glass, illustrated by a two sample t test $p$ value $< 0.001$, indicating that the difference between the two population means is statistically significant. Here we note that the untreated metasurfaces have a slightly lower receding contact angle, by approximately 10°, than the untreated control surfaces (see Figure 4.6). However, the significant reduction of $t_{df}$ should not be attributed to this small difference in wettability and can only be due to the metasurface heating and corresponding evaporation enhancement by increasing the saturation vapor pressure above the droplets.

Additionally, our results in Figure 4.11c show that the hydrophobic surfaces have better performance in comparison to their respective untreated samples, both of which have a two sample t test $p$ value $< 0.05$. On the one hand this seems surprising because it is well-known that droplets on a surface with a larger receding angle have a slower evaporation rate than neutrally wetting or hydrophilic droplets, at least in the microliter volume range. On such scales, it is probable that, independent of the macroscopic receding angle, the droplets evaporate with a constant contact radius (see Figure 4.10b, the tail end of contact angle progression; see also ref 141). On the other hand, we observed that the volume of liquid on the surface in the form of condensate droplets is approximately 10% less for hydrophobic glass than for the control glass. This means that there is simply less water on the surface to vaporize and offers the most rational explanation as to why we observed a decrease in $t_{df}$ for the hydrophobic samples.

As mentioned, the ability to inhibit fogging is an important quality of our metasurfaces and could be used to an advantage in many applications, particularly for specialized outdoor eyewear, which can suffer from visibility loss from fogging even during sunny weather. We tested the efficacy of our metasurfaces by comparing them to control samples, both untreated and superhydrophilic, exposing each sample to the same supersaturated conditions. We created a supersaturated environment by modifying our experimental setup, illustrated in Figure 4.12a, to include a chamber housing the sample and including a water bath and a small fan. Additionally, the camera was tilted at a shallow angle with respect to the sample plane in order to avoid direct light exposure to the sensor.

The fogged surfaces appear brighter due to light scattering by the droplets, to which the slightly tilted camera with respect to the incident light is sensitive. Figure 4.12b–d shows image sequences of the fogging behavior of the untreated control, superhydrophilic state-of-the-art, and untreated metasurface samples, respectively, under supersaturated conditions. The first and perhaps most important observation is that the metasurface remains for the most part condensate free. Although one observes slight condensate bursts on parts of the surface, it quickly evaporates again, and at steady state the metasurface remains condensate free. In contrast to the metasurface, the untreated control and superhydrophilic surfaces in Figure 4.12b,c show immediate condensate formation. On the one hand, the condensate on the untreated control takes the form of many droplets that scatter the light and almost completely eradicate the visibility of the background.
Figure 4.12: Antifogging performance enhancement by efficient sunlight absorbing metasurfaces. We tested the antifogging performance of our metasurfaces and compared it to the performance of untreated control and superhydrophilic state-of-the-art samples, using the setup illustrated in (a). We enhanced the setup with the inclusion of a simple environmental chamber in which we placed a bath of warm water at a temperature \((T_w)\) while also measuring the environmental temperature \((T_e)\) and the sample temperature \((T_s)\) in order to achieve a supersaturated environment. We used a fan to ensure that the water vapor inside the chamber was well mixed. The results for 60 s of supersaturation are shown in the image sequences for the (b) untreated control, (c) superhydrophilic state-of-the-art, and (d) untreated metasurface samples. In order to better demonstrate the distortion effect of the superhydrophilic sample, we slightly increased the distance between the surface and the flower illustration. Scale bar (b–d): 2 mm.
On the other hand, the condensate on the superhydrophilic state-of-the-art surface results in a film of water that distorts the background. Both of these surfaces significantly reduce the visibility of the background in comparison to the metasurface. Remarkably, the metasurface remains condensate free. This is because it is able to more efficiently turn the broadband illumination into heat and to significantly raise the temperature of the surface in comparison to the control samples. The approximately 3°C temperature increase due to the heat response of the metasurface combined with the convective heating inside the chamber produces a $p/p_L$ of approximately unity ($1.01 \pm 0.01$) for the aforementioned experimental conditions. The control sample also profits from the convective heating inside the chamber, however the heat response from the light irradiance is considerably less, resulting in a $p/p_L$ of $1.22 \pm 0.01$ and the necessary conditions for fogging to occur.
4.5 Conclusions

Surface fogging is a common hindrance, especially when considering the clarity and distortion of light traveling through transparent or back from reflective surfaces. Because of the importance of the phenomenon there are a variety of existing approaches to mitigate this loss in optical efficiency, however we demonstrated that the most widely used solution, superhydrophilic surfaces, does not retain all optical efficiency aspects, resulting in significant image distortion, while untreated and hydrophobic surfaces result in significant loss of clarity. Both of these methods change the inherent surface energy of the substrate, which continues to prove to be a difficult characteristic to maintain for long periods. We demonstrated a novel approach by employing plasmonic metasurfaces harnessing the broadband spectrum of the sun, to efficiently heat up a surface, thereby significantly improving defogging and antifogging properties, without a marked loss of transparency. For applications that require reduction of light transmission, the broadband absorption of our metasurfaces offers a favorable property compared to commercially available products used for reducing light transmission, such as tinted laminates. This approach would result in considerable performance gains for applications such as windows, windshields, electronic displays, cameras, mirrors, and eyewear. The variety of substrates, including polymers and flexible surfaces, which can be coated with our metasurfaces as well as the potential manufacturing scalability of the metasurface coating process make this technology a viable solution for antifogging and defogging in commercial applications.
Detergency and Its Implications for Oil Emulsion Sieving and Separation

This chapter is reproduced in part with permission from:


Copyright 2017 American Chemical Society.
Abstract

Separating petroleum hydrocarbons from water is an important problem to address in order to mitigate the disastrous effects of hydrocarbons on aquatic ecosystems. A rational approach to address the problem of marine oil–water separation is to disperse the oil with the aid of surfactants in order to minimize the formation of large slicks at the water surface and to maximize the oil–water interfacial area. Here we investigate the fundamental wetting and transport behavior of such surfactant-stabilized droplets and the flow conditions necessary to perform sieving and separation of these stabilized emulsions. We show that, for water-soluble surfactants, such droplets are completely repelled by a range of materials (intrinsically underwater superoleophobic) due to the detergency effect; therefore, there is no need for surface micro-/nanotexturing or chemical treatment to repel the oil and prevent fouling of the filter. We then simulate and experimentally investigate the effect of emulsion flow rate on the transport and impact behavior of such droplets on rigid meshes to identify the minimum pore opening ($w$) necessary to filter a droplet with a given diameter ($d$) in order to minimize the pressure drop across the mesh—and therefore maximize the filtering efficiency, which is strongly dependent on $w$. We define a range of flow conditions and droplet sizes where minimum droplet deformation is to be expected and therefore find that the condition of $w \approx d$ is sufficient for efficient separation. With this new understanding, we demonstrate the use of a commercially available filter—without any additional surface engineering or functionalization—to separate oil droplets ($d < 100 \mu m$) from a surfactant-stabilized emulsion with a flux of $\sim 11,000 \text{ L m}^{-2} \text{ h}^{-1} \text{bar}^{-1}$. We believe these findings can inform the design of future oil separation materials.
5.1 Introduction

Separating petroleum hydrocarbons from water is an important problem to address in order to mitigate the disastrous effects of their release into marine ecosystems from industrial accidents or oil tanker sinking.\textsuperscript{144,145} Strategies to mitigate the adverse effects of such events vary depending on circumstances (e.g., biodegradation, skimming, controlled burns, and siphoning, etc.), but the goal is the same—complete removal of hydrocarbons. Reduction of oil substances dispersed in water is a challenging problem, in part due to the number of different ways the system can manifest itself—separate phase, two-phase emulsion, or solubilized.\textsuperscript{146} A rational approach to address the problem of marine oil-water separation is to disperse the oil with the aid of surfactants in order to minimize the formation of large slicks at the water surface and to maximize the oil-water interfacial area. In the Deep Water Horizon spill, one of the strategies was to inject dispersant (COREXIT 9500) at the wellhead that was 1500 m below water in order to disperse the oil at-depth and prevent large slicks.\textsuperscript{144} Such an approach naturally produces a two-phase emulsion. While smaller oil droplets are neutrally buoyant, larger ones will eventually migrate to the surface of the water and, if collected, will need to be separated.

Previous work on oil-water emulsion separation has emphasized the role of filters for promoting coalescence,\textsuperscript{147} while more recent work, mostly grounded in wettability engineering research, has emphasized surface micro-/nano-engineering to impart filters with underwater superoleophobicity to prevent fouling in filtration ranging from micro- to ultrafiltration.\textsuperscript{40,42} While such approaches are logical for simple oil-water mixtures, it is not obvious that such surface engineering is necessary for surfactant-stabilized oil-in-water emulsions. Taking inspiration from a classic experiment done in 1930s by Adam,\textsuperscript{148} whereby the so-called "rolling-up" mechanism was identified,\textsuperscript{149} we investigate this phenomenon and test its implications for separation in microfiltration, whose findings, we believe, will help govern nano- and ultrafiltration design.

The rolling-up mechanism, illustrated in Figure 5.1, shows the wetting behavior of hexadecane to a standard fluoropolymer (poly(vinylidene fluoride)) without and with the presence of a surfactant, namely, sodium dodecyl sulfate (SDS). In the former case, the receding contact angle ($\theta^*$) is $\approx 0^\circ$—practically superoleophilic—while in the latter case it is $>150^\circ$, practically superoleophilic. It should be noted that this extreme nonwetting state is achieved in the absence of any surface micro-/nanotexturing, which is usually required to observe such behavior.\textsuperscript{150} While oil-solid interactions in micellar solutions are well-documented,\textsuperscript{148,151–155} such knowledge has yet to be applied to the design of meshes for separation of surfactant-stabilized oil-water emulsions.\textsuperscript{42,44,150,156,157} Therefore, while previous work has been done on the effect of pore size on pressure drop and separation,\textsuperscript{147,158} the focus of this work is to understand this surfactant-induced antiwetting mechanism, which is referred to here as detergency—the process whereby soils, liquid
or solid, are removed from a substrate material\textsuperscript{151}—and to see its implications for oil separation from surfactant-stabilized emulsions by studying droplet-mesh interactions at the single droplet level.

![Image of receding contact angle measurement](image.png)

**Figure 5.1:** Surfactants (detergents) can switch the wettability of a surface. Image sequences showing an underwater receding contact angle measurement (withdrawal method) of hexadecane on a poly(vinylidene fluoride) coated substrate (a) without and (b) with surfactant in the water (0.03 mol L\textsuperscript{-1}). Arrows indicate the direction of acceleration due to gravity (\(g\)). Due to the buoyancy of hexadecane in water, the image in panel (b) is inverted to enhance clarity.
5.2 Methods

5.2.1 Materials

We used the following chemicals and substrates in our study on wettability under the influence of micellar solutions and our study on separation:

<table>
<thead>
<tr>
<th>Chemical or Material</th>
<th>Supplier</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wettability Study</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(vinylidene fluoride)</td>
<td>Sigma-Aldrich</td>
<td>$M_w = 180,000$ by GPC</td>
</tr>
<tr>
<td>poly(methyl methacrylate)</td>
<td>EVONIK</td>
<td>high-gloss graphical quality</td>
</tr>
<tr>
<td>borosilicate glass</td>
<td>Menzel-Gläser</td>
<td>D263 M</td>
</tr>
<tr>
<td>aluminum</td>
<td>Metall Service Menziken</td>
<td>EN AW-1085 (AI99.9), highly polished</td>
</tr>
<tr>
<td>stainless steel</td>
<td>Metall Service Menziken</td>
<td>304/1.4301, N4 finish</td>
</tr>
<tr>
<td>sodium dodecyl sulfate</td>
<td>Sigma-Aldrich</td>
<td>micellar average molecular weight is 18,000</td>
</tr>
<tr>
<td>Triton X-100 solution</td>
<td>Sigma-Aldrich</td>
<td>laboratory grade</td>
</tr>
<tr>
<td>Fluorinert FC-770 oil</td>
<td>Sigma-Aldrich</td>
<td></td>
</tr>
<tr>
<td>hexadecane</td>
<td>Sigma-Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>deionized water</td>
<td>Millipore</td>
<td>Direct-Q 3 System</td>
</tr>
<tr>
<td><strong>Separation Study</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4404 stainless steel mesh</td>
<td>TWP Inc.</td>
<td>wire dia. $= 0.02$ mm, opening $(w) = 0.02$ mm</td>
</tr>
<tr>
<td>syringe filter</td>
<td>Acrodisc</td>
<td>glass 1 µm fiber prefILTER, 0.45 µm polypropylene filter</td>
</tr>
<tr>
<td>fluorescent dye</td>
<td>Radiant Color N.V.</td>
<td>RADGLO CFS-0-06 Yellow</td>
</tr>
<tr>
<td>sodium dodecyl sulfate</td>
<td>Sigma-Aldrich</td>
<td>micellar average molecular weight is 18,000</td>
</tr>
<tr>
<td>hexadecane</td>
<td>Sigma-Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>deionized water</td>
<td>Millipore</td>
<td>Direct-Q 3 System</td>
</tr>
</tbody>
</table>

5.2.2 Preparation

Prior to all measurements and experiments, we cleaned all substrates by sonication in a deionized water bath, isopropanol bath, and an acetone bath each for 5 minute time intervals (excluding the PMMA in acetone, due to its solubility) followed by 3
minutes of oxygen plasma ashing at 100 W (Diener electronic GmbH Type FEMTO PCCE). The PVDF surface was spun-coat onto the clean glass after cleaning and directly used for testing afterward. We prepared a stock solution of SDS (0.03 mol L\(^{-1}\)) in deionized water for facile experimental repeatability with the micellar environment. Prior to the separation experiments, we cleaned the stainless steel mesh by soaking in a deionized water bath, isopropanol bath, and acetone bath. The syringe filters were used as received.

### 5.2.3 Characterization

#### Contact Angle Measurements

We conducted contact angle measurements using a commercially available goniometer (DataPhysics, OCA 35). For the contact angles of hexadecane shown in Figure 5.2, we conducted at least 10 contact angle measurements for each surface and in each environment. Due to the lower density of hexadecane with respect to water, we built an inverted PMMA housing to simplify the underwater contact angle measurements. We initially filled the housing with either deionized water or the stock solution of 0.03 mol L\(^{-1}\) SDS in water and then carefully set the sample in the liquid environment using clean tweezers. We then introduced a hexadecane drop onto the surface through the dispensing needle to measure the advancing contact angle. We then removed the oil from the surface through the needle to measure the receding contact angle. In order to measure the angles, we used image analysis software provided with the goniometer from the recorded videos of the inflation and deflation process, done 10 different times on different locations for each sample.

#### Interfacial Tension Measurements

We used the pendant drop method, with a commercially available droplet shape analyzer (DataPhysics, OCA 35),\(^{159}\) to calculate the interfacial tension of hexadecane in water and SDS micellar solutions with varying concentration. A transparent plastic bath was initially filled with hexadecane and a water droplet with different concentrations of SDS (ranging from 0 to 0.03 mol L\(^{-1}\) in water) was introduced through the dispensing needle into the hexadecane environment. We used a pristine
plastic housing and needle for interfacial tension surface measurements without surfactant and between each trial of varying surfactant concentration, we thoroughly cleaned the plastic housing and replaced the needle, beginning with measurements of low concentration and proceeding to higher values. We recorded the droplet shape and analysis was done using computer software. Five to ten measurements for each concentration were performed.

5.2.4 Experimental Protocol

Oil-Water Separation Using Nonfunctionalized Surfaces

We tested the separation characteristics of a stainless steel mesh by analyzing droplet distributions of a surfactant-stabilized oil-in-water emulsion with and without the presence of the stainless steel mesh (1.4401 stainless steel, wire diameter = 0.02 mm, wire opening = 0.02 mm). The emulsion had a concentration of $\sim 4$ wt % hexadecane, and its flow rate was $382 \mu$L min$^{-1}$ in a pipe diameter $D = 4.8$ mm; therefore, the mean flow velocity was $u = -0.35$ mm s$^{-1}$. The emulsions were generated by mechanically mixing hexadecane and a micellar solution (SDS, 0.03 mol L$^{-1}$ in water) at room temperature. In order to perform sieving experiments, we wanted to be able to reproducibly produce a significant number of oil droplets with diameters ($d$) larger than the mesh pore sizes ($d > w$). To achieve this, we always used the same emulsion mass (10 g), oil concentration (4 wt % oil), temperature, mixing speed (1500 s$^{-1}$), and mixing time (25 min). Furthermore, for sieving experiments, the emulsion was added to the experimental setup immediately after mixing ceased—to minimize the effect of coalescence—and the emulsion flow rate was kept constant.

The experimental setup consisted of a home-built inverted bright field laser microscope with a water-immersed objective. We used a high-speed camera (Photron FASTCAM SA1.1) to record the separation for later analysis and made a PMMA housing in order to facilitate observations. The housing consisted of a hollow column that was mounted into a recessed hole in a PMMA block which could be fitted with an objective from below in order to observe droplets on the plane immediately below the mesh. Initially, we observed the droplet size distribution of an SDS-stabilized oil-in-water emulsion without the use of any mesh. We initially filled the column with the emulsion and used the syringe pump to control the flow rate. We made five separate recordings to analyze the size and count of oil droplets that we
observed using a self-developed Matlab image recognition code. These data acted as the control data for the size distribution of the emulsion. We then inserted and sealed the stainless steel mesh between the column and the block and we made five further recordings of the same emulsion at the same flow rate. We did not observe any effect of the fluorescent dye on the underwater wetting behavior of hexadecane on the mesh. Again, we analyzed the size and count of these droplets using the same Matlab code.

Large-Area Separation Materials

The separation ability of large-area, commercially available material was investigated using a syringe filter. We filled a syringe with an emulsion consisting of a 5 wt% hexadecane in a 0.03 mol L$^{-1}$ SDS-water environment. The syringe filter was connected to the syringe, and the emulsion was pushed through the filter into an empty glass vile. In order to characterize the oil separation ability of this filter, we analyzed the emulsion before and after separation with dynamic light scattering (DLS; Malvern DLS Zetasizer Nano ZS). Specifically, we were interested in characterizing droplets with sub-micrometer diameters, which we achieved by allowing the emulsion to settle for $>1$ hour.
5.3 Results and Discussion

5.3.1 Surfactant Influence on Wetting Behavior: The Role of Detergency

To better understand the effect of substrate material on surfactant-induced underwater oleophobicity, we began by observing the influence of an anionic surfactant, sodium dodecyl sulfate (SDS), on the wetting behavior of an oil (hexadecane) droplet on a variety of substrates in an aqueous medium. We conducted two sets of contact angle measurements, one set in pure water and the second set in an SDS micellar solution sufficiently above the critical micelle concentration (cmc; 0.03 mol L\(^{-1}\)). Each set consisted of both receding (\(\theta^*_r\)) and advancing (\(\theta^*_a\)) contact angles measurements on a variety of clean surfaces made of or coated with different materials.

Figure 5.2a shows a plot of \(\theta^*_a\) and \(\theta^*_r\) for hexadecane underwater vs surface composition, and it is clear that these values depend greatly on the surface composition. For the sake of discussion, we will concentrate on the two tested surfaces that have the most oleophobic and oleophilic wetting properties, which are borosilicate glass (further referred to as glass) and poly(vinylidene fluoride) (PVDF), respectively. Due to the chemical nature of oxygen-plasma treated glass, its surface has a strong affinity for water; therefore, it is expected to exhibit underwater oleophobicity. PVDF, on the other hand, is hydrophobic, so here one would expect that, in a water environment, PVDF would exhibit oleophilic behavior. This is confirmed by Figure 5.2a. All of the other surfaces tested here exhibit \(\theta^*_a\) and values that fall between those measured for PVDF and glass, with their values of \(\theta^*_r\) being low enough to consider them oleophilic (<90°). The high contact angle hysteresis can be explained by the fact that the surfaces all have some degree of roughness as shown in Figure 5.3.

Figure 5.2b shows the effect on \(\theta^*_a\) and \(\theta^*_r\) of the addition of SDS surfactant to the aqueous environment for each of the surfaces. In all cases, after the addition of surfactant, the surfaces became underwater superoleophobic. To understand the wetting behavior of hexadecane on glass and PVDF, where glass stayed superoleophobic and PVDF underwent an oleophilic to superoleophobic wetting transition, it is instructive to refer to the Young-Dupre equation. Here, the equation is applied to an oil droplet in a water environment in contact with a solid surface.
Figure 5.2: Detergents alter the underwater wetting behavior of oils to a range of materials. Underwater advancing (dark gray bars, $\theta^*_a$) and receding (light gray bars, $\theta^*_r$) contact angle measurements with hexadecane on a range of substrate materials (a) without and (b) with the presence of a surfactant (sodium dodecyl sulfate, 0.03 mol L$^{-1}$). Acronyms: Al, aluminum; SS, stainless steel; PMMA, poly(methyl methacrylate); PVDF, pol(vinylidene fluoride).

\[
\cos \theta = \frac{\gamma_{sw} - \gamma_{so}}{\gamma_{ow}}
\]  

(5.1)

where $\theta$ is the intrinsic contact angle of an oil droplet on the surface and $\gamma_{sw}$, $\gamma_{so}$, and $\gamma_{ow}$ are the solid-water, solid-oil, and oil-water interfacial energies, respectively. The nature of surfactants is to positively adsorb at the interface between polar and nonpolar materials causing the associated $\gamma$ to decrease. Based upon the nature of the interfaces, we can reason as to whether or not the surfactant molecules positively adsorb there and ultimately whether or not the respective $\gamma$ should be affected.\textsuperscript{148} For the present system (oil-water-solid), a reduction in $\gamma_{ow}$ is expected due to the nonpolar and polar nature of oil and water, respectively; here, SDS...
Figure 5.3: Micrographs obtained with atomic force microscopy (AFM) of surfaces used for contact angle measurements. The surfaces depicted in the micrographs are (a) aluminum, (b) stainless steel, (c) PVDF, (d) PMMA, and (e) glass.

Figure 5.4: The effect of surfactant concentration in water (c) on the interfacial tension between oil and water (γ_{ow}). We made the following water-oil-surfactant mixtures: water-hexadecane, water-FC 770, water-hexadecane-Triton X-100, water-FC 770-Triton X-100, and water-hexadecane-sodium dodecyl sulfate.
migrates from the bulk water phase to the interface. Experimentally, we observed a significant reduction of $\gamma_{ow}$ with the addition of surfactant. This effect is shown in Figure 5.4, for which we tested the combination of two oils (hexadecane and FC-770) with two surfactants (SDS and Triton-X 100). For example, when going from 0 to 0.03 mol L^{-1} SDS in water, $\gamma_{ow}$ for a water-hexadecane interface reduced by 60%. To understand the impact of the presence of surfactant on $\gamma_{sw}$ and $\gamma_{so}$, it is instructive to refer to the Gibbs adsorption equation, which relates the change in surface energy with the chemical potential of a single surfactant component and a surfactant adsorption density ($\Gamma$), combined with Equation 5.1 to yield

$$\frac{d(\gamma_{so} - \gamma_{sw})}{d\gamma_{ow}} = \frac{\Gamma_{so} - \Gamma_{sw}}{\Gamma_{ow}} \tag{5.2}$$

In the case of a glass surface, previous work for a system with a high-surface-energy solid, an oil, and an anionic surfactant has shown that $\Gamma_{so} > \Gamma_{sw}$, therefore, with the addition of surfactant, $\gamma_{so}$ is expected to decrease relative to $\gamma_{sw}$. From eq 5.1 we see that, in order to maintain underwater superoleophobicity, the right-hand side of the equation should remain constant, which is possible if $\gamma_{sw}$ is sufficiently small relative to $\gamma_{so}$ prior to the addition of surfactant so that it remains smaller after the addition ($\Delta \gamma = \gamma_{sw} - \gamma_{so} < 0$). Also required is that $\gamma_{ow}$ experiences a proportional decrease compared with $\gamma_{so}$. Due to the polar nature of both glass and water, it is conceivable that $\gamma_{sw}$ is relatively small, even with respect to $\gamma_{so}$ after surfactant adsorption. As for the simultaneous decrease of $\gamma_{ow}$ and $\gamma_{so}$ with surfactant adsorption, we expect $\gamma_{so}$ to decrease ($\Gamma_{so} > \Gamma_{sw}$), and from experiments we know that $\gamma_{ow}$ for water–hexadecane interface is reduced (see Figure 5.4). Together, this is our interpretation of how a polar material (glass) can maintain underwater superoleophobicity after exposure to a surfactant.

The PVDF substrate represents a different case. In Figure 5.2b we observe that the wettability switches from underwater oleophilic to underwater superoleophobic. Again, based upon our experimental result, we know that $\gamma_{ow}$ is significantly reduced. If this wetting transition were to simply be due to a reduction in $\gamma_{ow}$, then one would expect $\theta^*$ to decrease, which goes against our experimental findings; therefore, another phenomenon must be at work. From eq 5.1 we see that, for $\theta$ to go from $< 90^\circ$ to $> 90^\circ$, then $\Delta \gamma = \gamma_{sw} - \gamma_{so}$ should go from $\Delta \gamma > 0$ to $\Delta \gamma < 0$. The presence of surfactants at the solid–water interface causes a reduction in $\gamma_{sw}$ with respect to $\gamma_{so}$. Previous work on the underwater wetting of oil on low-energy
solids has shown that, for water-soluble surfactants, $\Gamma_{so} > \Gamma_{sw}$.\textsuperscript{164} therefore, one would expect $\gamma_{sw}$ to decrease with respect to $\gamma_{so}$. and for a sufficient decrease, $\Delta \gamma$ should go from positive to negative. In addition to this mechanism, which explains the switch in wettability after the addition of surfactant, the small degree of surface roughness as seen in Figure 5.3c may also enhance the oleophobicity by allowing small pockets of water to remain entrapped between the oil droplet and the surface resulting in the droplet contacting a composite water–solid interface.\textsuperscript{165}

It is useful to discuss detergency and its related antiwetting mechanisms with respect to oil already in contact with a solid. Several mechanisms relevant to the present investigation for oil removal and repellency through the aid of surfactants have been suggested based upon macroscopic experimental observations.\textsuperscript{148,149,166} The so-called rolling-up mechanism (detergency), first proposed by Adam,\textsuperscript{148} states that the three-phase contact line spontaneously shrinks due to surfactant adsorption at selected interfaces (oil–water and water–solid), resulting in an increase in contact angle and ultimately oil separation from the surface. It occurs when the following condition is satisfied: $\gamma_{so} + \gamma_{ow} \cos \theta - \gamma_{sw} > 0$.\textsuperscript{149} The ability of the surfactant to infiltrate between the oil and surface and separate the two phases is described by the diffusional mechanism, which has been demonstrated by experiment\textsuperscript{149} and with simulations\textsuperscript{167,168} on glass surfaces. Simulations have indicated that, after covering the water-oil interface, the excess surfactants interact with the oil molecules on the oil-substrate interface. This hydrophobic interaction of surfactant tails with the oil molecules provide the driving force for the "rolling up" effect and ultimately detachment.\textsuperscript{168} It appears that this mechanism probably does not necessarily rely on the alteration of substrate–water interfacial energy. Rather, the gradual increase in the contact angle of the oil droplet can be attributed to the invasion of surfactant molecules to the oil-water interface as surfactant-laden water is able to penetrate between the oil and solid phase and ultimately provides an intermediary layer of surfactant molecules between the oil drop and the substrate.\textsuperscript{149,167,169} Alternatively, depending on substrate characteristics, the surfactant may be adsorbed at the water-substrate interface and ultimately affect the water-substrate interfacial tension. The adsorption of surfactants at solid–liquid interfaces is however much more complex than surfactant adsorption at air–liquid or liquid–liquid interfaces due to the wider range of molecular interactions that can occur between solid and surfactant molecules.\textsuperscript{170} In the case of ionic surfactants, which is of pertinence to SDS (due to the anionic nature of its hydrophobic head), the interactions that govern the adsorption process are not only determined by the hydrophilic/phobic nature of the substrate, but also determined by possible electrostatic forces between the surfactant and the substrate.
What is relevant to the present study is that, at equilibrium in a surfactant-laden water environment, the hexadecane droplet resides in a nonwetting state with respect to the solid PVDF surface, due to a reduction in $\gamma_{sw}$—switching the wetting ability of the surface. Interestingly, due to the variety and number of mechanisms available for surfactants to adsorb at a variety of interfaces and inherently change the interfacial properties of the three-phase system, it seems that a wide range of substrates can benefit from this detergency mechanism, supported by the consistently high underwater hexadecane contact angles on all the surfaces that we investigated. Ultimately, the presence of surfactant rendered all of our studied surfaces underwater superoleophobic without requiring micro or nanotexturing or chemical treatment. We found that for one to observe underwater superoleophobic behavior for hexadecane, the surfactant concentration should exceed the cmc value, as demonstrated in Figure 5.5. The observation of this phenomenon across the complete range of substrates shows the versatility and facility of this detergency mechanism and opens up the choice, without restriction, of the substrate materials for facile oil separation.

5.3.2 Oil–Water Separation Using Nonfunctionalized Surfaces

Our observations of the intrinsic underwater superoleophobic behavior of a range of surface types in a surfactant environment led us to investigate this phenomenon.
and its implications for the efficacy of oil–water separation through filtering, aiming at surface simplicity, durability, and robustness, which, in different combinations, are limiting factors of micro and nanotextured surface technologies (i.e., coating degradation).

The efficacy of a separation medium for oil–water emulsion separation can be determined by its separation efficiency. Separation efficiency for a fixed energy input (e.g. pumping) can be quantified by the overall ability to separate oil and water and the speed at which this can be done. These two quantities end up being intimately related. On the one hand, the ability to completely separate oil and water depends on the smallest oil droplets that can be blocked from passing through the separation medium. Understandably, smaller pore radii, \( R \), are able to block smaller oil droplets, ultimately leading to better separation ability for the finest emulsions. The pore radii, however, also exhibit a strong relationship to the pressure drop across the separation medium, where the pressure drop per unit length of the pore, \( \Delta P/L \), is proportional to \( R^{-4} \), which is an important factor affecting the energy input and separation speed. In short, the smaller the pore size, the slower the allowable flow rate will be for the same pressure drop. Due to mechanical strength limitations of filter media and concerns of oil droplet breakthrough forces, it is advisable to keep the pressure drop across the separation
media as low as possible. To this end, we conducted experiments that quantified the optimal pore size in relation to complete separation ability, by quantifying the smallest droplets that can be filtered with a given pore size through the so-called "size sieving" effect, or separation based upon drop size.\(^{42}\)

Figure 5.6a illustrates the setup used to conduct these experiments, which consists of (1) an oil (hexadecane)-in-water surfactant (SDS, \(0.03 \text{ mol L}^{-1}\) in water) stabilized emulsion flowing due to gravity against (2) a simple stainless steel mesh; the interaction between oil droplets and mesh is visualized with (3) an inverted home-built fluorescence bright field laser microscope with a water-immersed objective. Note that the surface of the wires in the mesh is not textured; instead, the interaction with the oil is purely regulated by the presence of the surfactant in the mixture. The flow is regulated with (4) a syringe pump. Figure 5.6b shows a micrograph of one of the as-purchased woven stainless steel meshes that was used in this study, which has repeated square pores. Figure 5.6c shows a micrograph of a single pore indicating the pore width, \(w = 20\mu m\); the mesh is false-colored yellow to improve clarity. Figure 5.6d,e show image sequences obtained with fluorescence bright field microscopy, where fluorescent emulsified oil droplets are flowing toward a square pore of width 20 \(\mu m\)—in the case of the large droplet, the droplet is blocked, while the small droplet passes through. In the case where the droplet is blocked, we observed that the entire droplet retains a spherical shape during impact with the mesh, indicating that the mesh is completely nonwetting with respect to the droplet even at the microscale. To better understand the minimum value of \(d\) that can be blocked by a pore of width \(w\), it is instructive to expose the mesh to an emulsion with a distribution of droplets with diameter values in the range of \(w\); thus we performed droplet sieving experiments. We did not study the sieving behavior of oil-in-water emulsions with no surfactant present. If there is no presence of surfactant, then creating a large number of very small oil droplets, which are difficult to separate, is energetically unfavorable. Therefore, the droplets will migrate to the surface of the water relatively quickly, due to the buoyancy forces, where they will pool. At this point, the oil can be skimmed.

Figure 5.7 shows the results of these sieving experiments. For a control experiment, the size distribution of the surfactant-stabilized oil droplets in the flowing emulsion was measured without any separation medium (hatched bars). Here, we can see the relative frequency of an oil droplet, \(N/N_0\), vs \(d\). As expected, no droplets with \(d > 45 \mu m\) are observed. Figure 5.7 also shows the distribution of oil droplets that have passed through the mesh with \(w = 20 \mu m\) (gray bars), and it is clear that there is a strong sieving effect at \(d \approx w\). That is, droplets with \(d < w\) pass through
Figure 5.7: Standard metallic meshes are capable of sieving emulsions without fouling. Plot of the relative frequency of a droplet in a surfactant-stabilized oil-in-water emulsion \((N/N_0)\) vs oil droplet diameter \((d)\) with (filled gray bar) and without (hatched bar) the presence of a mesh. The two vertical lines represent the wire spacing of the mesh (20 \(\mu\text{m}\)) and the value of \(d\) where the oil droplet is zero. Also shown are the regions where the droplets are smaller \((d < w)\) and larger \((d > w)\) than the wire spacing and the corresponding behavior of the droplet, i.e., passing \((d < w)\) and blocking \((d > w)\).
Figure 5.8: Effect of liquid flow velocity on the critical diameter of an oil droplet that is entrained. (a) Rigid sphere of diameter \( d \) in a fluid with a uniform velocity, \( u \). When \( u < 0 \) and the sphere is less dense than the surrounding fluid, the resulting drag force acts against the buoyant force. Uniform flow velocity, \( u \), vs hexadecane droplet diameter, \( d \), vs (b) hexadecane droplet velocity, \( V_z \), (c) Reynolds number, \( Re = \rho (V_z - u) d / \mu \), of the flow around the droplet, and (d) Weber number, \( We = \rho V_z^2 d / \gamma \), of the droplet. Dashed line in panel b indicates \( V_z = 0 \). Panels c and d are only shown for \( V_z \leq 0 \) (i.e. droplets entrained in the surrounding flow).

the mesh while, for \( d > w \), the droplets are blocked. It should be noted that during these experiments we observed minor choking of the mesh due to blocked droplets that did not immediately coalesce; however no fouling due to oil wetting the mesh was observed. We expect that, in the actual separation process, blocked droplets will eventually coalesce,\(^\text{172} \) growing larger and increasing their buoyancy force allowing them to overcome drag and capillary forces, which will limit choking of the pores. This drop coalescence rate, however, remained outside of the scope of this study.

To better understand why \( d \approx w \) is a sufficient condition for droplet separation, it is instructive to consider the flow behavior of a single emulsified droplet. Figure 5.8a shows the flow conditions around a rigid sphere when \( Re = \rho (V_z - u) d / \mu \ll 1 \), where \( V_z \) is the sphere velocity, \( u \) is the uniform flow velocity far from the sphere, and \( \mu \) is the viscosity of the surrounding fluid.

Here, the sphere experiences a drag force (Stokes') which is equal to \( 3 \pi d \mu (u - V_z) \) and a buoyant force which is equal to \( \pi d^3 (\bar{\rho} - \rho) g / 6 \), where \( g \) is the acceleration due to gravity and the forces act in opposite directions. Therefore, when the forces are in balance, the sphere has a terminal velocity. In the present work, the sphere is
a viscous liquid, whose terminal velocity assuming it is moving freely under gravity through an immiscible fluid can be modelled as\(^{171}\)

\[
V = \frac{1}{3} \left( \frac{d}{2} \right)^2 \left[ \frac{\bar{\rho}}{\rho} - 1 \right] \frac{\mu + \bar{\mu}}{\mu + (3/2)\bar{\mu}} g \left( \frac{\bar{\rho}}{\rho} - 1 \right) \frac{\mu + \bar{\mu}}{\mu + (3/2)\bar{\mu}} + v
\]

where \(v = \mu/\rho\) is the kinematic viscosity of the surrounding fluid and \(g = g\hat{z}\) is the acceleration due to gravity. If the surrounding fluid is flowing with a uniform velocity, \(u = u\hat{z}\), then the above equation can be adjusted to

\[
V_z = \frac{1}{3} \left( \frac{d}{2} \right)^2 \left[ \frac{\bar{\rho}}{\rho} - 1 \right] \frac{\mu + \bar{\mu}}{\mu + (3/2)\bar{\mu}} + u
\]

where \(V_z = \mathbf{V}\hat{z}\) and \(u - V_z\) is the flow velocity relative to the object. To understand how the surrounding flow affects the sphere velocity, Figure 5.8b shows a contour plot of \(d\) vs \(u\) vs \(V_z\) calculated from eq 5.4 where the surrounding fluid and liquid sphere are water and hexadecane, respectively. It is clear that there is a range of values for \(d\) and \(u\) where \(V_z < 0\) and the hexadecane droplets are therefore entrained in the flow. To see if the Stokes’ estimate of the drag force is valid in Figure 5.8b when \(V_z < 0\), Figure 5.8c plots \(d\) vs \(u\) vs \(Re\). It is clear that, for the experimental conditions in Figure 5.6 and Figure 5.7 (\(-\mu = 0.35\) mm s\(^{-1}\) and \(d \sim 5 - 40\) µm), \(Re = 2.1 \times 10^{-5}\) to 0.01 and the condition for Stokes’ flow (\(Re \ll 1\)) is satisfied.

With \(V_z\), we can now estimate the dynamic pressure (driving sphere deformation) and its relative importance with respect to Laplace pressure (resisting sphere deformation) for a low-viscosity sphere (\(\bar{\mu}(V_z - u)/\gamma_{ow} \ll 1\)), which is represented by the Weber number (\(We = \bar{\rho}V_z^2 d/\gamma_{ow}\)). Large and small values of \(We\) indicate that large and small droplet deformations are to be expected, respectively. Figure 5.8d plots \(d\) vs \(u\) vs \(We\) for \(V_z < 0\). Although the surfactant lowers the interfacial tension between the oil and water phases, the small \(d\) still causes \(We\) to be extremely small at the chosen flow rate and significant droplet deformation is energetically unfavorable. Therefore, the capillary forces are expected to dominate the inertial forces during the separation process, which is confirmed by the sieving experiments in Figure 5.6. Since the droplet sizes that were observed in the presence of the mesh were almost all smaller than the pore size of the mesh, we can assume that very minimal deformation of the droplet due to inertia to squeeze
the drop through any of the pores took place. We conclude that, to be most efficient in separation, one should choose a value of $w$ that is just slightly smaller than the smallest droplet diameter that is desired to be filtered. After the droplets are blocked by the mesh by the optimal pore size, we expect that the oil droplets would coalesce via Ostwald ripening, producing larger droplets that have a buoyant force sufficient to overcome the drag force of the entraining water flow and would move toward the top of the emulsion, separating the oil from the water phase. Due to the low values of $We$, it is expected that the separation flux could be greatly increased without emulsion droplets passing through the mesh. If we impose the conditions $Re < 1$ and $We < 1$, to be consistent with the model, the we see from Figure 5.8c,d that the maximum value of $-u$ is 4.9 mm s$^{-1}$, which corresponds to an emulsion flux rate of 17,640 L m$^{-2}$ h$^{-1}$.

5.3.3 Large-Area Separation Materials

Up until this point we have created a science base to support the development of new scalable technology, based on commercially available materials to separate surfactant-stabilized oil-in-water emulsions, that is potentially applicable in an industrial setting. The science base is grounded in two areas: thermodynamics (the equilibrium wetting nature of different materials in different environments) and fluidics (the balance between pore size and separation efficiency). Based upon our thermodynamic observations and analysis, we have learned that the detergency effect is applicable to a wide range of materials, allowing a practically unconstrained choice of material for the filter medium. Based upon our fluidic observations and analysis, we have learned about the relationship between pore size of the filter medium to the smallest allowable emulsion droplet size to achieve separation. Using this information we selected nonwoven glass/polypropylene syringe filters—with effective commercially available solution to efficiently filter emulsions with minimum droplet diameters in the microscale. To demonstrate this, Figure 5.9a show gravity-driven emulsion separation with such a nonwoven material. In this demonstration, the emulsion flux is $\sim 11,000$ L m$^{-2}$ h$^{-1}$ bar$^{-1}$.

Figure 5.10b shows a plot of intensity vs effective particle diameter for the oil-in-water emulsion before and after filtering (Acrodisc, glass 1 µm fiber prefilter, 0.45 µm polypropylene filter), and it is clear that before filtering, there are particles with sub-micrometer diameters and that after filtering, all particles with $d > 0.45$ µm are separated. To confirm that the signal is attributed to oil droplets, we ran a
Figure 5.9: Demonstrating complete separation of oil from water with commercially available materials. Surfactant-stabilized (SDS) oil (hexadecane)-in-water emulsion (0.03 mol L\(^{-1}\) SDS in water, \(\sim 5\) wt \% hexadecane) being filtered with a commercially available filter. Here, the flow rate of the water and emulsion is controlled with a syringe pump and the separation flux is \(\sim 11,000\) L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). (a) Time series of separation. (b) Cross-section of filter showing three individual layers. (c,d) Prefilter layers (glass) and (e) polypropylene. Scale bar: panels a and c–e, 100 \(\mu\)m.

Figure 5.10: Dynamic light scattering characterization of surfactant stabilized oil-in-water emulsions before and after filtering (sub-micron pore size). (a) Intensity vs. effective diameter for surfactant stabilized (SDS 0.03 mol L\(^{-1}\) oil-in-water emulsions (5 wt. \% hexadecane) before (black solid line) and after (red dashed line) filtering with a sub-micron filter (pore size 450nm, illustrated in Figure 5.9). (b) Control experiment: Intensity vs. effective diameter for an aqueous surfactant solution (SDS 0.03 mol L\(^{-1}\)) before (black solid line) and after (red dashed line) filtering with the same filter.
control experiment where we analyzed the aqueous surfactant solution before and after filtering, and it is clear that in both cases, the signal intensity is well-below that observed for the unfiltered oil-in-water emulsion.
5.4 Conclusions

This chapter investigated the fundamentals of filtering emulsions that are stabilized in a surfactant-laden water environment. We found that surfactants exhibit a detergency effect beyond a certain concentration (critical micellar concentration), causing oil droplets—at both micro and macroscale—to be in a superoleophobic state with respect to a range of solid materials without the need for surface chemical functionalization or surface micro or nanotexturing—a wettability design rule. With this new understanding with respect to wettability, we identify the pore size of a woven mesh necessary to filter an emulsion droplet with a prescribed diameter, with the goal being to minimize the pressure drop across the mesh. Due to the small scale of the droplets, we found that capillary forces dominated, and droplet deformation was energetically unfavorable during filtering. Therefore, to filter a droplet with a given diameter, the pore opening should be just slightly smaller—a fluidic design rule. Once the droplets are blocked by the mesh, we expect that coalescence of droplets will occur and, once the droplets are large enough, that they move upward due to buoyancy to populate the region of oil at the top of the emulsion where they can be skimmed. Due to the detergent-driven nonwetting nature of the meshes, we were able to demonstrate the ability to filter droplets on the basis of size, with the mesh filtering droplets above a selected diameter (emulsion sieving). We then demonstrated complete separation of a surfactant-stabilized emulsion with a commercially available nonwoven material (as purchased, no functionalization) with an emulsion flux of $\sim 11,000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ demonstrating the capabilities of this approach.
6.1 Conclusion

This thesis has contributed to developing a deeper understanding of interfacial phenomena and nucleation physics for nanotechnologies aimed at solving challenges at the water-energy nexus.

The second and third chapters of the thesis delved into the fundamentals of phase change well into the sublimation regime of the water phase diagram. We began by studying nucleation physics and demonstrated its significance to further develop our understanding behind the fundamentals of frosting. The second chapter investigated the pathways of frost formation, namely condensation-freezing and desublimation. Here we derived the environmental conditions and surface chemistry that define the regions of condensation-freezing and desublimation. We were able to show the transition between condensation-freezing and desublimation nucleation for a well known ice-nucleating agent, silver iodide. Upon studying more relevant engineering materials such as silicon and aluminum we found that the transition to desublimation nucleation does not take place above a temperature of approximately $-60^\circ\text{C}$. Nonetheless, we found that at temperatures around $-50^\circ\text{C}$ nanotexture—a typical characteristic of superhydrophobic surfaces—enhance the nucleation rate at lower supersaturations leading to enhanced frosting. These results are relevant for engineers when designing icephobic surfaces for such applications as airplane wings or evaporator coils in refrigeration cycles.

In the third chapter we introduced a phenomenon that could be used to more efficiently remove ice during the sublimation process. Under certain conditions we observed that the removal of ice from a substrate through sublimation could be enhanced through a detachment process—at some point during the sublimation of...
the ice crystal we observed an abrupt and spontaneous detachment of it from the substrate. By characterizing the conditions at which this happened and visually studying the process, we came up with a preliminary hypothesis of the mechanism responsible for the behavior. As this work is at present a feasibility study, our goal is confirm the mechanism of detachment and engineer surfaces to improve this effect in order to enhance surface deicing.

In the four chapter we returned to the fundamentals of nucleation physics paired with experimentation to demonstrate robust antifogging surfaces. Although we theoretically showed that altering either the surface wettability or temperature can be used to design more efficient antifogging surfaces, we experimentally demonstrated the pitfalls of solely using surface wettability to mitigate the effects of fogging for transparent surfaces. We showed that, although altering the surface wettability can work temporarily, the surfaces are susceptible to contamination or isolated defects that render the antifogging coatings useless. We overcame this drawback by introducing a temperature increase, mimicking the approach of surface heating used by most active antifogging surfaces. However, instead of relying on a supplementary and integrated energy source, we illustrated the use sunlight—a renewable and independent energy source—to achieve the same surface heating effect. This demonstration paves the way in developing durable antifogging surfaces that do not require a supplementary and integrated energy source.

The final chapter addressed the problem of water contamination and its remediation. One of the most important areas here is the efficient separation of oil and water emulsions using micro and nanofiltration membranes. Although much groundbreaking research in this field has been produced over the last decade it has neglected two important aspects relevant to the fundamental understanding of how to engineer more efficient separation membranes. We have attempted to fill the gap in understanding by more closely investigating the effect of surfactants in oil-water emulsion separation, in particular how surfactants change the interfacial energies present in the three-phase system and the effect this has on the wetting properties of the membrane with respect to oil and water. We further characterized and quantified the most efficient pore size distribution for surfactant-laden emulsions. In summary, the first chapter sheds new light on the oil-water membrane separation process by investigating previously neglected, but important aspects of the process.
6.2 Outlook

There are countless new directions to take the research areas of using interfaces to control phase change and oil-water separation. For example, research can be done to improve on the proof-of-concept provided by fundamental discoveries. In this thesis, it would be very valuable to further improve the selective absorption of the antifogging metasurface by exploring new materials. Tuning the light absorption to be selectively and of greater magnitude in the infrared spectrum of the sun would open up the range of applications for the technology to include products such as eyeglasses and fully transparent windows.

On the other hand, there is plenty of space for fundamental research to explore previously unobserved phenomena. The research area of icephobicity lends itself well to this, because of its broad scope (preventing nucleation, reducing ice adhesion, repelling super-cooled water droplets, and developing ice-shedding surfaces) and because many aspects of each area are not very well understood. An example of a further research endeavour, demonstrating current and ongoing research in ice-phobicity, is the sublimation-driven ice crystal detachment, that has been included as a feasibility study in this thesis.
References


References


List of Publications


Conference Presentations