Toward Anti-icing and De-icing Surfaces: Effects of Surface Topography and Temperature

GOLROKH HEYDARI

Doctoral Thesis
KTH Royal Institute of Technology
Stockholm 2016
to my Golsa
Abstract

Icing severely affects society, especially in the Nordic countries. Ice accumulation can result in critical performance problems and safety concerns for instance in road, air and sea transportation, transmission lines, marine and offshore structures, wind turbines and heat exchangers. Present active ice-combating approaches possess environmental, efficiency and cost drawbacks. Thus, fabricating icephobic surfaces or coatings impeding ice formation (anti-icing), but facilitating ice removal (de-icing) is desired. However, different conditions in the environment during ice formation and growth add to the complexity of the problem. An icephobic surface that works for a certain application might not be a good candidate for another. These surfaces and the challenges are in focus in this thesis.

Wetting properties are important for ice formation on surfaces from the liquid phase (often supercooled water), where the water repellency of the surfaces could enhance their anti-icing effect. Considering this, different hydrophobic and superhydrophobic surfaces with different chemistry, morphology and roughness scale were prepared. Since any induced wetting state hysteresis on hydrophobic surfaces could influence their performance, the wetting stability was investigated. In particular dynamic wetting studies of the hydrophobic surfaces revealed what surface characteristics benefit a stable wetting performance. Further, the effect of temperature, particularly sub-zero temperatures, on the wetting state of flat and nanostructured hydrophobic surfaces was investigated. This was complemented with studies of the wetting stability of sessile water droplets on flat to micro- and multi-scale (micro-nano) rough hydrophobic samples in a freeze-thaw cycle. To be consistent with most applications, all temperature-controlled experiments were performed in an environmental condition facilitating frost formation. Further, anti-icing properties of hydrophobic surfaces with different topography but similar chemistry were studied by freezing delay measurements.

A dynamic wetting study using hydrophobic samples with similar chemistry but different topography revealed that multi-scale roughness could benefit the wetting stability. However, when these surfaces are utilized at low temperatures the wetting hysteresis observed during a cooling/heating cycle is significant. Such a temperature-induced hysteresis is also significant on superhydrophobic surfaces. I attribute this to condensation followed by frost formation facilitating spreading of
the supercooled water droplet. The freezing delay measurements demonstrate no significant effect of surface topography on anti-icing properties of hydrophobic surfaces, however the flat surfaces showed the longest delay. These findings are in agreement with heterogeneous ice nucleation theory, suggesting preferential ice nucleation in concave sites, provided they are wetted.

In the second part of this thesis, I consider the findings from the previous part illustrating the limitations of (super)hydrophobic surfaces. The de-icing properties of hydrophilic surfaces with a hydration water layer, hypothesized to lubricate the interface with ice, were studied. Here temperature-controlled shear ice adhesion measurements, down to -25 °C, were performed on an adsorbed layer of a polymer, either bottle-brush structured poly(ethylene oxide) or linear poly(ethylene oxide). The ice adhesion strength was reduced significantly on the bottle-brush structured polymer layer, specifically at temperatures above -15 °C, whereas less adhesion reduction was observed on the layer formed by the linear polymer. These findings are consistent with differential scanning calorimetry (DSC) data, demonstrating that the hydration water, bound to the bottle-brush structured polymer, is in the liquid state at the temperatures where de-icing benefit is observed. Further, continuing with the hypothesis of the advantage of surfaces with a natural lubricant layer for de-icing targets, I studied shear ice adhesion on the molecularly flat basal plane of hydrophilic mica down to -35 °C. Interestingly, ultralow ice adhesion strength was measured on this surface. I relate this to the proposed distinct structure of the first ice-like but fluid water layer on mica, with no free OH groups, followed by more bulk liquid-like layers. This combined with the molecularly smooth nature of mica results in a perfect plane for ice sliding.

**Keywords** anti-icing, topography, supercooled water, wetting hysteresis, superhydrophobic, contact angle, nucleation, freezing delay, de-icing, ice adhesion, hydration water, liquid-like layer, smooth, lubrication
Sammanfattning

Isbildning har en stark inverkan på samhället, speciellt i de nordiska länderna. Isuppbyggnad kan resultera i kritiska prestandaproblem och säkerhetsrisker inom t.ex. väg-, luft-, och sjötransport, kraftledningar, marina- och offshorestrukturer, vindkraftverk och värmeväxlande. Nuvarande aktiva isbekämpningsmetoder uppvisar brister i avseende på miljö, effektivitet och kostnad. Det finns därmed ett behov av att framställa ytor eller ytbeläggningar som förhindrar isbildning (anti-isning) eller underlättar borttagandet av redan bildad is (avisning). Dock komplicerar problemet av de många olika förhållanden under vilka is kan bildas. En beläggning som fungerar för en viss tillämpning behöver inte nödvändigtvis vara en bra kandidat för en annan. Dessa ytor och utmaningar relaterade till dem är i fokus i denna avhandling.


De dynamiska vätningsstudierna på hydrofoba ytor med samma kemi men olika topografi avslöjade att en ytråhet på flera längdskalar kan ha en positiv inverkan på vätningsstabiliteten. När dessa ytor är exponerade för låga temperaturer är dock vätningshysteresen under en nedkylnings-/uppvärmnings-cykel significant. Den temperatur-inducerade hysteresen är också betydande för superhydrofoba ytor. Detta tillskrivs jag
kondensation på ytan som följs av frostbildning, vilket i sin tur möjliggör spridning av den underkylda vattendroppen på ytan. Mätning av fördröjningen i frysningsförloppet påvisade ingen betydande effekt av yttopografin för hydrofoba ytor, men släta hydrofoba ytor uppvisade den längsta fördröjningen. Dessa resultat är i överensstämmelse med rådande heterogen iskärnbildningsteori, som visar på fördelaktig iskärnbildning på konkava delar av ytan, förutsatt att dessa väts.


Nyckelord anti-is, topografi, underkylt vatten, vätningshysteres, superhydrofob, kontaktvinkel, kärnbildning, avisning, isadhesion, hydrierat vatten, vätskeliknande skikt, smörjning
List of appended papers

This thesis is based on the following papers referred to in the text by their Roman numbers:

I. **Hydrophobic Surfaces: Topography Effects on Wetting by Supercooled Water and Freezing Delay**  

II. **Wetting Hysteresis Induced by Temperature Changes: Supercooled Water on Hydrophobic Surfaces**  

III. **Hydrophobisation of Wood Surfaces by Combining Liquid Flame Spray (LFS) and Plasma Treatment: Dynamic Wetting Properties**  

IV. **Temperature-Dependent Deicing Properties of Electrostatically Anchored Branched Brush Layers of Poly(Ethylene Oxide)**  

V. **Ultralow Ice Adhesion on Hydrophilic and Molecularly Smooth Mica Surfaces**  
Heydari, G., Tyrode, E., Stenroos C., Koivuluoto H., Tuominen, M., Claesson, P.M., *Submitted.*
The author's contribution to the papers:

I. Major part of planning, experimental work (excluding XPS), evaluation and writing.

II. Major part of planning, experimental work (excluding surface modification of samples and XPS), evaluation and writing.

III. Part of planning, experimental work, evaluation and writing.

IV. Major part of planning, experimental work, evaluation and writing.

V. Major part of planning, experimental work (excluding centrifugal ice adhesion measurements), evaluation and major part of writing.
Summary of papers

Paper I
The wetting properties of (super)hydrophobic surfaces, with similar surface chemistry and different surface topography and different wetting state at room temperature (Cassie-Baxter and Wenzel), are addressed at sub-zero temperatures by determining the temperature-dependent contact angle of microlitre-sized water droplets. A marked decrease in contact angle on the superhydrophobic surface is observed with decreasing temperature, and we attribute this to water vapor condensation and at lower temperatures to frost formation. This reduction, which reveals higher adhesion of the droplet to the surface, is more pronounced for the receding contact angle. In contrast, no significant wetting transition is observed on the smooth hydrophobic surface. The freezing temperature and the freezing delay time were determined for water droplets resting on hydrophobic surfaces of this study. The water freezing delay time is not significantly affected by the surface topography. We discuss this finding within the classical theory of heterogeneous nucleation, where for hydrophobic surfaces only a weak dependence of surface topography on the ice nucleation rate is expected. However, provided water vapor condensation or frost formation allows supercooled water to penetrate concave surface sites, one would expect droplet freezing to occur more readily on a rough surface than on a flat one with similar chemistry. Indeed, the flat surfaces show the longest freezing delay, and no anti-icing benefit of superhydrophobic surfaces is observed.

Paper II
Utilizing hydrophobic or superhydrophobic modified micro-rough wood surfaces, we test the hypothesis that superhydrophobic surfaces also should retard ice formation. In particular, the effect of surface characteristics such as topography and chemistry on wetting hysteresis during freeze-thaw cycle, from room temperature to freezing occurrence at sub-zero temperature and then back to room temperature, and also the freezing delay of supercooled water is explored. Flat surfaces with a similar chemistry are utilized as references. Wetting hysteresis was evaluated using contact angle measurements during the freeze-thaw cycle. A hysteresis in contact angle observed during a cooling-heating cycle that is small on flat hydrophobic surfaces. However, a significant
temperature-induced wetting transition is observed on the rough surfaces, with a higher contact angle observed on cooling compared to during the subsequent heating. Condensation and subsequent frost formation at sub-zero temperatures induce the hysteresis. The freezing delay data show that the flat surface is more efficient in enhancing the freezing delay than the rougher surfaces, which can be rationalized considering heterogeneous nucleation theory. Thus, our data suggests that molecular flat surfaces, rather than rough superhydrophobic surfaces, are beneficial for retarding ice formation under conditions that allow condensation and frost formation to occur.

**Paper III**
Multi-cycle Wilhelmy plate method was utilized for studying dynamic wettability on a superhydrophobic layer on wood surfaces, achieved by combining plasma polymerization and liquid flame spray (LFS). This was performed by measuring the changes of advancing and receding contact angles over repeated cycles. The effects of surface chemistry and surface roughness on the wetting properties were investigated. Multi-scale rough surfaces (micro-nano roughness) showed a high contact angle with relatively low hysteresis, while the surfaces treated only with plasma polymers resulted in lower contact angle with high hysteresis. Thus, the multi-scale roughness increased the hydrophobicity as well as the forced wetting durability compared to micro-scale roughness alone.

**Paper IV**
We explore the idea that presence of hydration water layer on hydrophilic surfaces that remains liquid-like at sub-zero temperatures could possibly reduce ice adhesion, in particular if the liquid-like layer is thicker than or comparable to the surface roughness. For this study a diblock copolymer, having one branched bottle-brush block of poly(ethylene oxide) and one linear cationic block, was electrostatically anchored on flat silica surfaces. The shear ice adhesion strength on such polymer-coated surfaces was investigated down to -25 °C using a homebuilt device. In addition, the temperature-dependence of the ice adhesion on surfaces coated with only the cationic block, only the branched bottle-brush block and with linear poly(ethylene oxide) was investigated. We find that layers formed by the diblock copolymer significantly reduced shear ice adhesion strength compared to bare silica, particularly at temperatures ≥ -10 °C. The
melting point of the hydration water associated with the polymer chain in bulk solution was determined to be \(-18^\circ\text{C}\) using DSC. Thus, we attribute the low ice adhesion and the sliding of the ice cylinder during shearing to the hydration water of the PEO chain that provides a lubricating liquid-like layer at the interface. The linear PEO was found to be less efficient in reducing ice adhesion. This is in qualitative agreement with DSC data where a lower melting point of the hydration water was observed for the bottle-brush architecture.

**Paper V**

Inspired by the slippery surface of ice, we hypothesize that flat hydrophilic surfaces with a hydration layer remaining in the liquid-like state at the solid-ice interface could result in low ice adhesion. Utilizing temperature-controlled ice adhesion measurements on the molecularly smooth basal plane of muscovite mica, we observed the lowest reported ice adhesion on solid surfaces down to temperatures of \(-35^\circ\text{C}\). The ice adhesion is dramatically higher on flat hydrophilic silica surfaces. We relate this to the molecularly smooth nature of the surface and the particular structure of water and ice next to the mica surface as suggested by simulations and scanning probe measurements. This lubricating layer allows the ice to slide across the mica basal plane by application of a low shear force. A significantly higher shear ice adhesion strength on smooth silica surfaces suggests significant differences between mica-ice and silica-ice interactions resulting from the different surface chemistry of these two solid surfaces. This implies that surface modification of (molecularly) smooth surfaces is a possible strategy to reduce ice adhesion.
Nomenclature

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two dimensional</td>
</tr>
<tr>
<td>ACA</td>
<td>Advancing contact angle</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>APTES</td>
<td>3-aminopropyl triethoxysilane</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron spectroscopy for chemical analysis</td>
</tr>
<tr>
<td>Eq</td>
<td>Equation</td>
</tr>
<tr>
<td>HMDSO</td>
<td>Hexamethyldisiloxane</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LFS</td>
<td>Liquid flame spray</td>
</tr>
<tr>
<td>MEMA</td>
<td>Methylether methacrylate</td>
</tr>
<tr>
<td>METAC</td>
<td>Methacryloxyethyl trimethylammonium chloride</td>
</tr>
<tr>
<td>mWP</td>
<td>Multicycle Wilhelmy plate</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PFH</td>
<td>Perfluorohexane</td>
</tr>
<tr>
<td>PFOTES</td>
<td>1H,1H,2H,2H-perfluorooctyltriethoxysilane</td>
</tr>
<tr>
<td>RCA</td>
<td>Receding contact angle</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SFG</td>
<td>Sum frequency generation</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SLIPS</td>
<td>Slippery liquid-infused porous surfaces</td>
</tr>
<tr>
<td>SPFM</td>
<td>Scanning polarization force microscopy</td>
</tr>
<tr>
<td>TM</td>
<td>Tapping mode</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>A</td>
<td>Surface area</td>
</tr>
<tr>
<td>A_c</td>
<td>Cross-sectional area</td>
</tr>
<tr>
<td>A_ij</td>
<td>Interfacial area of phases i and j</td>
</tr>
<tr>
<td>f</td>
<td>Area fraction</td>
</tr>
<tr>
<td>F</td>
<td>Force</td>
</tr>
<tr>
<td>F_w(t)</td>
<td>Force due to wicking and sorption of the liquid at time t</td>
</tr>
<tr>
<td>g</td>
<td>Gravitational constant</td>
</tr>
<tr>
<td>h</td>
<td>Immersion depth</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>$N_{PEO}$</td>
<td>Number of ethylene oxide repeating units</td>
</tr>
<tr>
<td>P</td>
<td>Wetted perimeter</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>ppb</td>
<td>Part per billion</td>
</tr>
<tr>
<td>r</td>
<td>Roughness factor</td>
</tr>
<tr>
<td>r$^*$</td>
<td>Critical radius</td>
</tr>
<tr>
<td>$r_i$</td>
<td>Radius of spherical ice nucleus</td>
</tr>
<tr>
<td>$r_f$</td>
<td>Roughness factor of the wet area</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Arithmetic average roughness</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>VSFS</td>
<td>Vibrational sum frequency spectroscopy</td>
</tr>
<tr>
<td>w</td>
<td>Width</td>
</tr>
<tr>
<td>wt</td>
<td>Weight</td>
</tr>
<tr>
<td>$W_e$</td>
<td>Equilibrium work of adhesion</td>
</tr>
<tr>
<td>$W_p$</td>
<td>Practical work of adhesion</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Minimum angle of tilt</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Free energy</td>
</tr>
<tr>
<td>$\Delta G_{het}$</td>
<td>Energy barrier for heterogeneous ice nucleation</td>
</tr>
<tr>
<td>$\Delta G_{hom}$</td>
<td>Free energy of formation of the critical spherical ice nucleus</td>
</tr>
</tbody>
</table>
<pre><code>                                                             | induced by homogeneous nucleation                     |
</code></pre>
<p>| $\gamma$  | Liquid surface tension                                                   |
| $\gamma_{12}$ | Interfacial energy between two phases                                    |
| $\gamma_i$ | Ice surface energy                                                        |
| $\gamma_{ij}$ | Interfacial energy between phase i and j                                  |
| $\gamma_{iw}$ | Interfacial energy between ice and supercooled water                    |
| $\gamma_{LV}$ | Interfacial tension of liquid-air                                        |
| $\gamma_{SL}$ | Interfacial tension of liquid-solid surface                             |
| $\gamma_{SV}$ | Interfacial tension of solid surface-air                                 |
| $\gamma_w$  | Supercooled water surface energy                                          |
| $\theta$  | Equilibrium contact angle                                                 |
| $\theta^*$ | Apparent contact angle                                                   |
| $\theta_{adv}$  | Advancing contact angle                                                  |
| $\theta_{rec}$  | Receding contact angle                                                    |
| $\theta_w$  | Water contact angle                                                       |
| $\theta_Y$  | Young contact angle                                                       |
| $\rho$    | Density                                                                   |</p>
Table of Contents

Abstract...................................................................................................................... v
Sammanfattning ........................................................................................................ vii
List of appended papers ......................................................................................... ix
Summary of papers .................................................................................................. xi
Nomenclature ............................................................................................................ xv
Table of contents ...................................................................................................... xvii
1. Introduction ......................................................................................................... 1
  1.1. Motivation and aims ...................................................................................... 1
1.2. Wetting ............................................................................................................. 2
  1.2.1. Wetting on real surfaces ......................................................................... 2
    Wenzel state ...................................................................................................... 3
    Cassie-Baxter state .......................................................................................... 4
    Validity of Cassie and Wenzel models ........................................................... 4
  1.2.2. Tensile and shear wetting properties ....................................................... 4
  1.2.3. (Super)hydrophobic surfaces ................................................................... 6
  1.2.4. Efficacy of hydrophobic surfaces ............................................................. 7
1.3. Wetting transitions ......................................................................................... 8
  1.3.1. Transitions on rough hydrophobic surfaces ............................................ 8
  1.3.2. Temperature-dependent wetting .............................................................. 9
1.4. Icing ................................................................................................................. 10
  1.4.1. Different types of icing .......................................................................... 11
  1.4.2. Supercooled water .................................................................................. 11
  1.4.3. Homogeneous ice nucleation .................................................................. 12
  1.4.4. Heterogeneous ice nucleation ................................................................. 14
    Supercooled water freezing ............................................................................. 16
1.5. Ice adhesion .................................................................................................... 17
  1.5.1. Ice adhesion measurements ................................................................. 18
  1.5.2. Temperature dependent-ice adhesion ..................................................... 19
1.6. Anti-icing and de-icing .................................................................................. 19
  1.6.1. Anti-icing and de-icing surfaces ............................................................. 20
    Design and fabrication strategies .................................................................... 20
2. Experimental ....................................................................................................... 23
  2.1. Surface preparation ...................................................................................... 23
    2.1.1. Water ..................................................................................................... 24
  2.2. Methods ......................................................................................................... 24
    2.2.1. Wetting properties ............................................................................... 24
      Temperature-controlled contact angle measurements .................................. 24
      Wilhelmy plate method ............................................................................... 25
2.2.2. Freezing of supercooled water............................................................... 26
   *Freeze-thaw wetting properties* .............................................................. 28
2.2.3. Ice adhesion ...................................................................................... 29
2.2.4. Atomic force microscopy .................................................................. 30
2.2.5. X-ray photoelectron spectroscopy .................................................... 31
2.2.6. Differential scanning calorimetry ....................................................... 31

3. Key results and discussion....................................................................... 33

3.1. Wetting transitions on hydrophobic surfaces ..................................... 33
   3.1.1. Dynamic wetting measurements ...................................................... 33
   3.1.2. Temperature effect ......................................................................... 35
   *Wetting transitions over freeze-thaw cycles* ...................................... 38

3.2. Anti-icing properties of hydrophobic surfaces .................................. 41
   3.2.1. Freezing temperature .................................................................... 42
   3.2.2. Freezing delay ................................................................................ 42
   Correlation between the experimental findings and the heterogeneous
   ice nucleation theory .............................................................................. 45
   3.2.3. Superhydrophobics as anti-icing surfaces ...................................... 49

3.3. De-icing properties of hydrophilic surfaces ..................................... 50
   3.3.1. Branched brush layers of poly(ethylene oxide) ............................. 51
   *Study of state of water using differential scanning calorimetry (DSC)* ...... 53
   Temperature-controlled ice adhesion measurements ............................... 55
   3.3.2. Basal plane of mica ....................................................................... 59
   *Shear ice adhesion strength on mica* ................................................. 59
   Superior de-icing properties of mica hypothesized to be due to
   mica-water interactions and the molecular flat nature of the surface........ 61

4. Conclusions .............................................................................................. 63

5. Future work ............................................................................................. 67

6. Acknowledgements .................................................................................. 69

References .................................................................................................... 71
1. Introduction

1.1. Motivation and aims

Icing is a complex issue causing major safety, operation and economic problems in many areas such as road, air and sea transportation, power transmission, telecommunications, offshore, wind turbines and heat exchangers. Active ice-combating methods [1] such as thermal and mechanical methods, or using anti-icing chemicals have the disadvantage of high energy consumption and negative environmental effects. Designing surfaces with high resistance against ice formation (anti-icing surfaces) and ice retention (de-icing surfaces) has attracted lots of attention in recent years [2]. However, ideal icephobic [3], i.e., anti-icing and de-icing, surfaces are not fabricated yet. In addition, there is a debate on what surface characteristics and wetting states result in a promising solution to the problem.

The aim of this thesis is to achieve fundamental understanding of ice accretion and adhesion on surfaces. The specific objective is to correlate the surface chemistry and topography of surfaces to their anti-icing and de-icing performance. This study focuses on ice formation from supercooled water in an environmental condition promoting condensation and frost formation on surfaces that is the most common situation in practical applications. It also investigates how surface morphology is affecting the temperature dependence or stability of the wetting state of surfaces and consequently their anti-icing properties. Finally, the most important goals of this work are to rationalize what surface topography and wetting state is the best for anti-icing purposes, and to suggest what surface topography and chemistry reduces ice adhesion the most.
1.2. Wetting

Wetting is the ability of a liquid to stay in contact with a solid surface and it is defined by the molecular interactions at the contact points. The net force on the molecules in bulk liquid is zero because the neighbor molecules are the same. However, this is not the case for molecules at interfaces with air and the solid surface. The degree of wetting on a surface is usually studied by droplet shape determined by contact angle measurements [4]. The equilibrium contact angle ($\theta$) is related to the balance between the horizontal component of the interfacial tension of liquid-air ($\gamma_{LV}$) (will be noted as liquid surface tension), interfacial tension of liquid-solid surface ($\gamma_{SL}$) and solid surface-air ($\gamma_{SV}$) at the three phase contact line. The relation for an ideal solid surface, that is flat, rigid, chemically homogeneous, and inert, is defined by the Young equation [5] as follows:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

(1-1)

Hydrophilicity, is defined by small contact angles (smaller than 90$^\circ$) when water spreads out on the surface, and low water wettability, i.e., hydrophobicity, is defined by high contact angles (larger than 90$^\circ$) when water beads up on the surface.

1.2.1. Wetting on real surfaces

Real surfaces are rough and/or chemically heterogeneous (non-ideal) thus actual micro-scale contact angles are different from measurable macro-scale contact angles. Thus, in practice utilizing macroscopic optical equipments (enabling to see the apparent solid surface) a range of equilibrium apparent contact angles are measured on surfaces. The difference between the local and apparent contact angle on a rough surface is schematically shown in Figure 1-1.
The largest and the smallest apparent contact angles that could be achieved on a surface by expanding and contracting the liquid are called *advancing* and *receding* contact angles, respectively, that are metastable contact angles [6]. The difference between these two contact angles is called contact angle hysteresis.

**Wenzel state**

For a rough but chemically homogeneous surface where a liquid penetrates in between and completely wets the concave sites (as illustrated in Figure 1-2a), the wetting state is defined by the Wenzel [7] equation (Eq. 1-2). In this equation the apparent contact angle ($\theta^*$) is related to the Young contact angle ($\theta_Y$) as:

$$\cos \theta^* = r \cos \theta_Y$$

(1-2)

where $r$ is the roughness factor, that is the ratio between the actual and the projected surface area. The equation shows that both hydrophilicity and hydrophobicity are enhanced on rough surfaces in the Wenzel state.
Cassie-Baxter state

For a flat but chemically heterogeneous surface (as illustrated in Figure 1-2b), the Young contact angle ($\theta_Y$) is different at different spots on the surface and the apparent contact angle ($\theta^*$) is obtained using the Cassie [8] equation as follows:

$$\cos \theta^* = f_1 \cos \theta_{Y1} + f_2 \cos \theta_{Y2}$$  \hspace{1cm} (1-3)

where $f_1$ and $f_2$ are the area fraction of the parts with chemistry 1 and 2, and $\theta_{Y1}$ and $\theta_{Y2}$ are the Young contact angles on homogeneous surfaces with chemistry 1 and 2, respectively.

Wetting in a Cassie state where air is trapped in the concave sites of a hydrophobic surface (as illustrated in Figure 1-2c) is defined by the Cassie-Baxter equation [9] as:

$$\cos \theta^* = r_f f \cos \theta_Y + f - 1$$  \hspace{1cm} (1-4)

where $r_f$ is the roughness factor of the wet area and $f$ is the fraction of the projected area of the surface that is wet.

Validity of Cassie and Wenzel models

Deviation of some experimental contact angles from the predicted values from Cassie or Wenzel equations [10] resulted in suggestion of certain criteria under which these models could be valid. For instance, it has been suggested that the energy balance at the three-phase contact line is determining the contact angle rather than the balance at the interfacial area within the contact as proposed by Cassie and Wenzel [11-12]. Thus, these equations are valid when the energy balance at the contact area reflects the same states as the contact line. In addition, the drop size should be large in comparison with the scale of surface roughness and chemical heterogeneity [13].

1.2.2. Tensile and shear wetting properties

Tensile wetting properties of surfaces could be related to the free energy associated with the formation and elimination of liquid-solid interface by
tesile forces [14], i.e., the equilibrium work of adhesion \( W_e \) that is given by Young-Dupre equation [15] as:

\[
W_e = \gamma_{LV}(1 + \cos \theta_Y)
\]  

(1-5)

where \( \gamma_{LV} \) is the liquid surface tension, and \( \theta_Y \) is the equilibrium Young contact angle. However, in practices the work demanded for removing a liquid from a surface is governed by the receding contact angle (\( \theta_{rec} \)). Therefore, the practical work of adhesion \( W_p \) [16] has been suggested to be given by [14, 17]:

\[
W_p = \gamma_{LV}(1 + \cos \theta_{rec})
\]  

(1-6)

Thus a higher receding contact angle would result in an easier liquid removal by tensile forces.

On the other hand, shear wetting properties [14] of surfaces can be attributed to spontaneous liquid sliding phenomena at a minimum angle of tilt, \( \alpha \), due to shear forces. For a liquid drop with surface tension \( \gamma_{LV} \), mass \( m \) and width \( w \) (perpendicular to the sliding direction), \( \alpha \) is related to the advancing and receding contact angles according to the Furmidge equation [18] as (see Figure 1-3):

\[
\left(\frac{mg}{w}\right)\sin \alpha = \gamma_{LV}(\cos \theta_{rec} - \cos \theta_{adv})
\]  

(1-7)

where \( g \) is the gravitational constant. Therefore, shear liquid removal is facilitated on surfaces with small contact angle hysteresis.

Figure 1-3: Profile of a liquid droplet with surface tension \( \gamma_{LV} \), mass \( m \), width \( w \) (perpendicular to the sliding direction), advancing and receding contact angles \( \theta_{adv} \) and \( \theta_{rec} \), sliding spontaneously at a tilting angle \( \alpha \).
1.2.3. (Super)hydrophobic surfaces

Design, fabrication, and characterization of (super)hydrophobic surfaces have received enormous attention in the last decades [19-20] due to wide utilization of (super)hydrophobic surfaces in several applications [21-26]. This is related to their wetting properties, high water repellency, moisture barrier and self-cleaning properties, and low surface energy. In particular in connection with this work, (super)hydrophobic surfaces have been suggested for anti-icing and de-icing applications [27] and any relation between water repellency and ice repellency has been discussed in Paper I and II, and will be discussed further in this thesis.

In principle, superhydrophobicity or ultra water repellency is achieved by introducing surface roughness into a flat hydrophobic surface with low surface energy. Inspired by nature superhydrophobic surfaces have been engineered and different wetting states have been suggested for these surfaces [28-29]. However, the extreme states are defined by the Cassie-Baxter and Wenzel models applied on hydrophobic surfaces where the remaining states involve a combination of these.

![Figure 1-4: A liquid droplet in (a) Lotus, and (b) Rose wetting state.](image)

A water drop in the Cassie-Baxter state on a rough hydrophobic surface does not penetrate the micro-structures (concave sites) of the surface that are filled with air, and stays in a suspended state. However, a water drop in the Wenzel state on a rough hydrophobic surface wets the micro-structures (concave sites) of the surface. When appropriate nano-features are added to the micro-structures on a rough hydrophobic surface with wetting properties in the Cassie-Baxter state the wetting state could be enhanced to the *Lotus* state where water-solid contact area is further reduced, and the drop is suspended on the nano-structures [30] (see Figure 1-4a). Similarly, adding proper nano-features to the micro-
structure of a rough hydrophobic surface with Wenzel wetting regime could enhance the water repellency toward the *rose petal* state, where the water-solid contact area is reduced both on the convex sites and concave sites of the surface by limiting the interaction points to the nanostructures [28, 31] (see Figure 1-4b).

Among rough hydrophobic surfaces with similar chemistry, the ones with wetting properties in the Lotus or Cassie-Baxter states, in comparison with the surfaces with the Wenzel or Rose wetting states, present relatively larger or similar advancing contact angles, but smaller contact angle hysteresis. Note that the equilibrium and advancing contact angles are higher in all of these cases in comparison with flat hydrophobic surfaces with similar chemistry. These characteristics would result in different adhesion and water repellency behavior, and this will be discussed in the next section.

There is no well-defined criteria for the value of the advancing and receding contact angles as well as the contact angle hysteresis for different superhydrophobic wetting states. However, it is a common agreement to use the term superhydrophobic for surfaces with equilibrium contact angles $\geq 150^\circ$ [29], though Gao and McCarthy [14] emphasize on criteria of having a contact angle hysteresis $\leq 10^\circ$ as well.

1.2.4. Efficacy of hydrophobic surfaces

For applications where tensile hydrophobicity [14, 17] is required, hydrophobic surfaces with high receding contact angle are preferred. On the other hand in the cases demanding shear-hydrophobicity [14, 17], hydrophobic surfaces with small contact angle hysteresis could be the right choice.

Based on this, rough hydrophobic surfaces with wetting properties in the Lotus and Cassie-Baxter states (non-sticky or *slippy* [32]) surfaces are good candidates as shear hydrophobic surfaces, whereas the *sticky* [32] surfaces with the Rose and Wenzel states are not. In addition, the first group of surfaces (in contrast with the second group) often present high receding contact angles that makes them the right choice as tensile-hydrophobic surfaces as well. It should be noted that shear hydrophobicity could be also achieved utilizing flat hydrophobic surfaces when their smooth topography diminishes the contact angle hysteresis (toward zero in an ideal case), thus eliminating the drop pinning effect. In brief, an ideal superhydrophobic surface should present high advancing
and receding contact angles and low contact angle hysteresis, consequently low tilting angle (that is called rolling angle when all the other criteria are fulfilled so the drop rolls over the surface).

Despite extensive research on (super)hydrophobic surfaces, robustness and wetting-stability of these surfaces is a very important issue, and many challenges exist in this area. An existing debate among researchers on efficiency of (super)hydrophobic surfaces as ice-phobic surfaces is related to these stabilities. In other words, wetting properties of (super)hydrophobic surfaces could alter under certain application-related circumstances or environmental conditions. It will be discussed further in this thesis with a focus on low temperature applications, in particular with respect to supercooled water wetting (see also Paper I, II, III).

1.3. Wetting transitions

1.3.1. Transitions on rough hydrophobic surfaces

Though surface morphology is the key factor determining the wetting states of rough hydrophobic surfaces with a certain chemistry [28, 33-34], depending on the characteristics of water drop formation and deposition different wetting states could be achieved on a certain rough hydrophobic surface [20]. For instance, Quere et al. [32] showed that on a single surface where a deposited drop was suspended in the Cassie-Baxter state, the Wenzel state was observed when a drop was formed by condensation. In this case the contact angle hysteresis was increased from 10°, for the deposited drop, to 110° for the condensation-formed drop. Further, gentle deposition of a sessile drop or dynamic impinging a drop from a height could result in different wetting regimes on a certain surface. In other words, when impinging a drop (compared to the case of a sessile drop, and depending on the impact kinetics [35-38] and surface morphology), an increased wetting (a full or partial transition from the composite states with air gaps) toward the states with complete wetting of the surface micro/nano-structures may be observed.

Depending on surface parameters [39-40], either Cassie-Baxter or Wenzel states could be thermodynamically favorable (reaching the minimum-energy state) [41-42], however in reality not always these states are achieved. In other words, kinetic barriers [20] could result in a drop in the metastable Cassie-Baxter or Wenzel state while the other state
is thermodynamically stable. Therefore, wetting transitions toward both directions could occur. The Cassie-Baxter to Wenzel transition has been reported to be induced by external stimuli [43] in many works, such as by vibration [44] and evaporation [45] of the drops, application of an electrowetting voltage [46-47], changing the surface tension of the liquid [48], putting pressure on the drops [40]. In contrast, few works [41] have discussed the Wenzel state as the metastable phase and the Wenzel to Cassie-Baxter transition [47]. Despite the fact that the latter transition is feasible it appeared to be difficult in practice due to pinning to the surface structures [41].

In most applications demanding a superhydrophobic surface a stable non-sticky state is required, thus the surface morphology and chemistry should be engineered so that the Cassie-Baxter state would be the thermodynamic stable state. In this case, even if any transition occurs it would, in principle, be reversible. However, this is often not accomplished in practice, limiting the advantages of superhydrophobic surfaces.

Wetting transitions on hydrophobic surfaces will be discussed further in the experimental chapter of my thesis (see also Paper I, II and III). Above all, I will describe how the transitions are affected by surface topography and architecture. This is indeed an important issue for designing robust surfaces.

1.3.2. Temperature-dependent wetting

Low temperature wetting is critical when dealing with icephobicity. Thus there is a need to study these wetting characteristics, and any transitions induced by low temperatures.

Both water wettability and surface wetting properties could vary at low temperatures. As reported in the work by Floriano et al. [49] water surface tension increases from 72 mNm$^{-1}$ at 25 °C to about 79.8 mNm$^{-1}$ when the temperature is reduced to about -27 °C. This would result in first, an increase in the practical work of adhesion (given by Eq. 1-6) that has been observed to directly correlate with the de-icing properties of surfaces [16], and second, an increase in the tilting angle (given by Eq. 1-7) at lower temperatures. In Paper I and II, and also in the experimental chapter of this thesis I discuss how the temperature dependent-water surface tension would affect the work of adhesion on hydrophobic surfaces.
A number of works have explored wetting stability of a range of hydrophobic surfaces (with different chemistry and morphology) subjected to low temperatures down to sub-zero utilizing sessile [50-54] (Paper I and II of this work) or impinging [55-57] water droplets. However, contradictory results are obtained on correlation between i) surface parameters, such as topography and ii) the initial wetting state, and the final wetting state at low temperatures. I will discuss this further in the experimental chapter of this thesis (see also Paper II) where our findings are compared to the reported results, and it has been attempted to understand the disagreement among researchers. In brief, I attribute this to the difference between environmental conditions, where in humid conditions with a temperature gradient between the surface and ambient, growth of condensation and frost induce a transition in wetting states of rough hydrophobic surfaces toward lower hydrophobicity. However, the transition could be absent in dry conditions, that ambient air is unsaturated with water vapor. I note that the humid condition is more relevant for most practical situations, thus this situation was utilized in my work (see Paper I and II). In the experimental chapter I also discuss how surface characteristics could enhance or diminish the transition.

Further, reversibility and recovery of the wetting transition is another important issue for surfaces subjected to cyclic icing/de-icing or freeze-thaw. The robustness of the wetting state on superhydrophobic surfaces during cooling-heating cycles has been reported in few works [58-59]. In this thesis we address this issue on hydrophobic surfaces with a focus on the effect of roughness (see Paper II).

1.4. Icing

Ice build-up on surfaces causes major safety problems, reduces productivity and damages function of various sectors in cold regions. Icing results in delay, safety problems and also injuries in air, sea, rail and road transportation. In the case of wind turbines and hydroelectric power plants it lowers efficiency, also ice throwing from wind turbines puts lives at risk. Ice accretion dramatically affects the performance of heat exchangers and pumps. Large amount of money and energy is spent for combating ice in telecommunications, offshore and marine platforms and structures [27, 60-67].
1.4.1. Different types of icing

Icing could be divided in two main categories. First, solid ice accretion from liquid water at or below 0 °C, and second frost formation from water vapor at supersaturated condition through desublimation or condensation followed by freezing [68]. Further, atmospheric icing [69-70] is a general term referring to precipitation icing, in-cloud icing and frost formation. Depending on metrological parameters such as temperature and wind speed, precipitation could result in freezing drizzle, rain, wet snow or dry snow. Precipitation icing occurs when rain or snow impinge a surface at freezing temperatures. Whereas, in-cloud icing refers to icing from small (micron-sized [71]) droplets that are in supercooled state (≤0 °C, this state of water will be described further), colliding with a surface at freezing temperatures. It should be noted that the droplet size distribution and relative humidity are among important parameters determining the type of atmospheric icing [71]. For example, according to Fortin et al. [72] rime ice is formed at temperatures far from 0 °C, lower relative humidity, and from smaller water droplets. However, glaze ice is formed at temperatures closer to 0 °C, higher relative humidity, and from larger droplets. The white or milky opaque appearance of rime ice deposit results from trapped air [65]. In contrast, freezing of a water film on surfaces would result in a transparent glaze ice coating that is denser and harder.

1.4.2. Supercooled water

Liquid water can be supercooled to below zero degrees Celsius without changing to solid. In other words, liquid water could stay in a metastable supercooled state [73] down to the homogeneous nucleation temperature at about -41 °C [74]. At sub-zero temperatures solid ice is the thermodynamically stable phase when considering the volume free energy of the system. However, formation of ice nuclei during the nucleation phase of crystallization induces a kinetic barrier for liquid to solid phase change. In this case, the total free energy of the system is affected by an increase in surface free energy due to formation of an ice nuclei-water interface. Consequently, water could stay in the metastable supercooled state until the size of the ice nuclei reaches a critical value at which the energy barrier is overcome and the thermodynamically stable phase, i.e., ice, is formed.
1.4.3. Homogeneous ice nucleation

Phase transition (crystallization) of pure water, in absence of any foreign body, from metastable supercooled liquid or supersaturated vapor phase to solid phase is induced by homogeneous nucleation (see schematic drawing in Figure 1-5).

![Figure 1-5: Schematic illustration of homogeneous and heterogeneous nucleation of an ice embryo from supercooled liquid water parent phase.](image)

When the embryo, ice nucleus, is nucleated from the metastable parent phase, the interfacial energy between the nucleus (phase 2) and the parent phase (phase 1), i.e., \( \gamma_{12} \), adds a positive term to the total free energy of the system (\( \Delta G \)) given by:

\[
\Delta G = V \Delta G_V + A_{12} \gamma_{12}
\]  

(1-8)

where \( V \) and \( A_{12} \) are the volume and the surface area of the nucleus in the parent phase, respectively, and \( \Delta G_V \) is the volume free energy difference between the nucleus and the parent phase. The general trend for variation in the total free energy of the system (\( \Delta G \)) versus radius of spherical ice nucleus (\( r_i \)) is plotted in Figure 1-6. As seen in this figure, the volume energy and surface energy components correlate with the volume (\( 4/3 \pi r_i^3 \)) and the surface area (\( 4\pi r_i^2 \)) of the spherical ice nucleus, respectively. The surface energy component destabilizes the nucleus formation at small radii. Adding more molecules to the ice nucleus
resulting in larger radii would increase the total energy of the system until a critical radius \( r^* \) \(^{[75]} \) is reached. From this point the volume energy dominates. Thus, the total energy is lowered and the nucleus becomes thermodynamically stable. The critical radius of spherical ice nucleus \( r^* \) is calculated by setting the derivative of \( \Delta G \) from Eq. 1-8 with respect to \( r_i \) to zero, thus \( r^* \) is given by:

\[
r^* = -\frac{2\gamma_{12}}{\Delta G_V}
\]

(1-9)

Figure 1-6: Change in surface energy (top curve), total free energy - \( \Delta G \) (middle curve), and volume energy (bottom curve) of the system during ice nucleation versus radius of spherical ice nucleus \( r_i \).

The free energy of formation of the critical spherical ice nucleus induced by homogeneous nucleation \( (\Delta G_{hom}^* \) ), the energy barrier \(^{[76]} \) in Figure 1-6, is obtained by substituting the calculated \( r^* \) from Eq. 1-9 in Eq. 1-8:

\[
\Delta G_{hom}^* = \frac{16\pi\gamma_{12}^3}{3\Delta G_V^2}
\]

(1-10)

It should be noted that \( \gamma_{12} \) and \( \Delta G_V \) are temperature dependent, and for the case of ice nucleus formation from supercooled water as the parent phase, could be calculated with the equations provided in the Supplementary material of Paper I. These equations and Eq. 1-9 and 1-10 show that \( r^* \) and \( \Delta G_{hom}^* \) are smaller at higher degree of supercooling (lower temperatures) \(^{[77]} \).

Spontaneous freezing of supercooled water drops by homogeneous nucleation has been seen to be volume dependent. For example homogeneous nucleation of 233 K and 238 K has been reported for single
droplets with a diameter of 1 and 100 µm, respectively [78]. In principle the smaller the volume of drops would result in lower probability of formation of the critical ice nucleus.

1.4.4. Heterogeneous ice nucleation

Water crystallization induced by a foreign body such as a nucleation particle or a surface initiates through heterogeneous nucleation (see schematic drawing in Figure 1-5). This is the most common ice nucleation mechanism in nature. Computer simulations and nucleation rate calculations by Sanz et al. [77] show that at temperatures higher than 20 K below melting, homogeneous ice nucleation is practically not feasible. This thesis focuses on ice nucleation and formation, in particular freezing, i.e., supercooled water to ice transition, on surfaces (see Paper I and II). Therefore, theories of heterogeneous ice nucleation will be discussed further.

![Figure 1-7: Difference in the energy barrier of homogeneous and heterogeneous ice nucleation based on the classical nucleation model.](image)

Based on the classical nucleation theory [79], the energy barrier for heterogeneous ice nucleation ($\Delta G_{het}^*$) tends to be lower in comparison with that for homogeneous ice nucleation (see illustration in Figure 1-7) [80]. At a certain temperature, the barrier reduction is a function of surface morphology, geometry of the nucleation sites on the surface (surface features), and surface chemistry.

Reriting equation 1-8 for the case of heterogeneous ice nucleation, considering parent phase (supercooled water in this thesis) as phase 1, ice nucleus as phase 2 and the nucleation site as phase 3 would result in equation 1-11.
\[ \Delta G = V \Delta G_V + A_{12} \gamma_{12} + A_{23} \gamma_{23} - A_{23} \gamma_{13} \]  

(1-11)

where \( \gamma_{ij} \) is the interfacial energy between phase \( i \) and \( j \), and \( A_{ij} \) is the interfacial area of phases \( i \) and \( j \). It should be noted that several interfacial energies are involved in this equation. Moreover, Eq. 1-11 could be implied to different geometries [79-81].

![Schematic illustration of a critical ice nucleus with a spherical cap geometry, radius \( r^* \) and contact angle \( \Theta \), nucleated on a spherical nucleation site with radius \( r \), from a parent phase.](image)

Using Eq. 1-11 for a certain geometry when the critical ice nucleus (with a spherical cap geometry) forms on a spherical nucleation site (with radius \( r \)), schematically shown in Figure 1-8, and doing similar calculations used for \( \Delta G_{hom} \) determination, Fletcher [75] suggested the following equation for \( \Delta G_{het} \):

\[ \Delta G_{het}^* = \left( \frac{8 \pi \gamma_{12}^3}{3 \Delta G_V^2} \right) f(m, x) \]  

(1-12)

where \( f(m, x) \) is a function of the wetting characteristics, contact angle of the ice nucleus on the nucleation site in the supercooled water parent phase (\( \theta \) in Figure 1-8) as given by Eq. 1-13 [82], and curvature characteristics, radius of convex (\( r \) in Figure 1-8) and concave curvature as given by Eq. 1-14, of the nucleation sites [75, 80].

\[ m = \cos \theta = \frac{(\gamma_i - \gamma_{lw})}{\gamma_{lw}} \cos \theta_w \]  

(1-13)
where $\gamma_i$ is the ice surface energy (often reported to be 109 mJ/m$^2$, however Makkonen [83] suggests a value of 73 mJ/m$^2$), $\gamma_w$ is the supercooled water surface energy that is temperature-dependent [49], $\gamma_{iw}$ is the interfacial energy between ice and supercooled water (suggested [80] to be calculated with Eq. 1 in the Supplementary material of Paper I), and $\theta_w$ is the water contact angle on the nucleation site in air, assumed to be equal to the ice nucleus contact angle in air [82].

$$x = \frac{r}{r^*}$$

(1-14)

Detailed discussions and equations for $f(m,x)$ in the case of different nucleation site geometries are presented in section 1.1 in Paper I. In general $0 \leq f \leq 2$, thus the ice nucleation in presence of a surface tends to be facilitated ($\Delta G_{het}^* \leq \Delta G_{hom}^*$) and the rate depends on the nucleation site curvature and wetting. Calculating $\Delta G_{het}^*$, from Eq. 1-12, at $f=2$ (when $x=0$ or $\theta = 180^\circ$ [75]) would give the same energy barrier as homogeneous nucleation ($\Delta G_{hom}^*$, see Eq. 1-10). It should be noted that theoretically ice nucleation occurs most easily on hydrophilic and concave sites (i.e., in surface depressions).

Applying the classical nucleation theory for studying kinetics of heterogeneous ice formation on macroscopic surfaces [55, 82, 84-87] is challenging. There is a remaining debate on correlating the surface characteristics such as topography and wetting to the theoretical parameters. I note that real surfaces have a distribution of curvatures and the ice nucleation probability correlates with the nanoscale local surface characteristics. These important issues will be discussed in detail in the experimental chapter of this thesis (see also Paper I and II).

**Supercooled water freezing**

Freezing (crystallization) of supercooled water on surfaces is initiated by heterogeneous ice nucleation followed by ice crystal growth. Crossing the nucleation barrier energy is the rate-limiting step (see the Eq. 14 for nucleation rate in Paper I). In principle, for anti-icing purposes demanding longer freezing delay time, the nucleation should be retarded. Once the nucleation initiates the growth occurs with a rate that depends on removal of the released latent heat of fusion [86] (see also Paper II). Once the critical radius has been reached, freezing starts, and the latent heat of fusion is released causing the temperature of water to rise. This
step will be referred to as *freezing onset* in this work. Next, ice crystals are formed isothermally [88]. In this thesis (also Paper I and II), I focus on investigating the time to freezing onset at different temperatures and surface characteristics such as wetting properties and morphology. This is done in connection with theoretical studies where the experimental finding are compared with the predictions based on the heterogeneous ice nucleation model suggested by Fletcher [75].

### 1.5. Ice adhesion

Work of adhesion of water at room temperature (given by Eq. 1-5) has been correlated to ice adhesion strength. In particular, ice adhesion strength measured by applying a shear force showed a strong correlation with the practical work of adhesion, given by Eq. 1-6 [16]. Ice surface tension and ice-solid surface interfacial tension are assumed to be equivalent to those of water in this correlation. In addition as I will discuss in the experimental chapter of this thesis, the surface tension and the contact angle of supercooled water at the desired sub-zero temperature (thus any possible wetting transitions) should be considered in these equations. Makkonen [89] discusses that the experimental work of adhesion of ice (determined from the force required to remove ice from a surface divided by the surface area) may deviate from the theoretical equilibrium work of adhesion of water due to additional work spent for solid surface/ice deformation (for example on a non-rigid solid surface or for ductile ice at lower degree of supercooling) or due to complexity of the ice-solid surface contact. He discusses the effect of surface roughness and mechanical interlocking of ice on rough wetted surfaces, resulting in a mixed adhesive-cohesive failure when removing ice. Further he adds, the size and orientation of ice crystals at the interface, that are a function of the solid surface as well as the accretion method, have been proposed to affect the ice adhesion strength. The temperature could also affect the experimental ice adhesion strength, as discussed in the next section. With respect to the mentioned correlation between ice adhesion and work of adhesion it may be concluded that hydrophobic surfaces are always preferred over hydrophilic surfaces where lower ice adhesion is desired. However, I have shown that ice adhesion can be small on hydrophilic surfaces with certain characteristics. This will be discussed in this thesis (see also Paper IV and V).
1.5.1. Ice adhesion measurements

Ice adhesion strength can be measured in different ways. It could be determined by dividing the normal force required to pull ice off from the surface to the ice-solid surface contact area [90-91], see Figure 1-9a. In another common method utilizing a centrifuge ice adhesion test device, the centrifugal force demanded for detaching ice (built up with a certain thickness (about 10 mm) often in a climate chamber or a wind tunnel (see Paper V)) on special sample holders is measured. Here shear ice adhesion strength (shear stress) is calculated by dividing the obtained centrifugal force to the area of detached ice [92-93], see Figure 1-9b. Alternatively, shear ice adhesion strength could be determined by dividing the maximum shear force demanded for sliding ice on the surface to the ice-solid surface interfacial area [16], see Figure 1-9c. The two last methods have been utilized in this thesis where more details will be presented in the experimental chapter (see also Paper IV and V).

Figure 1-9: Schematic illustration of devices for measuring ice adhesion strength on surfaces utilizing (a) normal, (b) centrifugal, and (c) shear forces. In my thesis work I utilized shear and centrifugal forces.

Due to differences in the ice types formed, depending on the accretion method and the environmental conditions, and measurement method it is often difficult to quantitatively compare results from different devices.
1.5.2. Temperature dependent-ice adhesion

Temperature-induced wetting transitions, mentioned in the section 1.3.2, could result in a temperature dependence of ice adhesion strength. I note that this is another motivation for studying the effect of sub-zero temperatures on the wetting properties of surfaces. For example, the ice adhesion strength measured on a hydrophobic surface, that shows transition toward the hydrophilic regime when utilized at sub-zero temperatures, would be different from (potentially higher than) what is expected by only considering wetting properties at room temperature. In addition, physical-mechanical properties of the desired solid surface, such as modulus, might change with temperature, affecting the measured ice adhesion. I note that this could be more sensitive to the surface (in particular at the interface with ice) properties. Further as mentioned earlier, ice behavior changes from ductile at higher temperatures (close to 0 °C) to rigid at lower temperatures (far from 0 °C) that could reduce the measured ice adhesion at lower temperatures, in particular on rigid surfaces [89]. Temperature might also affect the measured ice adhesion strength by inducing varying amount of stress at the ice-solid interface due to the different thermal contraction of ice and solid surface on cooling [89]. Moreover, temperature-dependent existence of a liquid-like layer and its thickness on surfaces could influence the ice adhesion strength. This will be discussed in section 1.6.1 and further in the experimental part of this thesis (see also Paper IV and V).

With these I conclude that ice adhesion on surfaces is a complex issue, and in order to achieve a better understanding temperature controlled studies in a wide range of temperatures is demanded. In the current thesis I will discuss this topic (see also Paper IV and V).

1.6. Anti-icing and de-icing

The purpose of anti-icing techniques [67] is to keep the surfaces free from ice. This is achieve through active methods such as applying heat [89] for example by electrothermal, ultrasonic and infrared heating systems. However, this approach is very expensive and requires a lot of energy [94]. Utilizing freezing point depressant chemicals in the form of organic fluids [95] or salts is another anti-icing approach, however it has a limited-time effect and environmental concerns. De-icing techniques deals with removing accreted ice from surfaces. Thus, thermal and
chemical methods could be utilized to melt the ice. De-icing could also be performed by applying mechanical forces [92]. However, the accessibility is a limitation with this method, and it could result in stress-caused failure in certain applications such as power networks. There are other specific anti/de-icing approaches [27], however energy-demand and cost stays high, while efficiency is not satisfactory and environmental problems remain.

1.6.1. Anti-icing and de-icing surfaces

Due to the problems and limitations accompanied with active anti/de-icing methods, incorporating the anti/de-icing characteristics in target surfaces, that are supposed to be ice-free, seems fascinating. In other words, the target surfaces could be modified or coated with the aim to involve anti/de-icing properties. This passive approach includes design and fabrication of i) anti-icing surfaces (see Paper I and II) so that ice formation is ideally prevented or effectively delayed, and/or ii) de-icing surfaces (see Paper IV and V) where the ice adhesion to the substrate is lowered, or ideally ice would release with natural forces such as gravity or wind. Different proposed mechanisms of action of these surfaces [96], that are the subject of this thesis, will be mentioned. Lv et al. [27] report that existing commercial icephobic coatings, having ice adhesion higher than 230 kPa, are far from being efficient. Makkonen [89] calculates that the ice adhesion to a vertically mounted surface should be at about 0.44 kPa to release a 5 cm thick layer of ice. In other words, for a surface with an ice adhesion of about 100 kPa (the threshold suggested by Hejazi et al. [3] for icephobic surfaces) a 10 m thick ice layer [89] is released due to gravity. The discussion suggests that the anti/de-icing surfaces (passive methods) should be combined with active methods to increase the efficiency and reduce the energy consumption.

Design and fabrication strategies

Since ice is solid water the most natural approach is to investigate utilization of hydrophobic and in particular superhydrophobic surfaces as icephobic surfaces. However, the reports are contradictory in this area. Many researchers report anti-icing properties of hydrophobic and in particular superhydrophobic surfaces [50, 55, 84-86, 97-103], however, no or limited benefits of such surfaces have been reported in other studies.
Surprisingly, hydrophilic surfaces have been reported to enhance anti-icing properties in comparison with hydrophobic surfaces in some cases [82, 105-106]. Further, though de-icing properties of (super)hydrophobic surfaces have been widely suggested [16, 55, 90-91, 93, 97, 107-114], their efficacy for practical purposes have been doubted in some reports [3, 68, 115-117] (Paper I, II). In certain cases ice formation is prevented [55] on superhydrophobic surfaces under a kinetic regime, where water is repelled from the surface before undergoing freezing.

In principle limited water wetting of these surfaces, attributed to their low surface energy combined with topography effect (in the case of rough surfaces), as well as their low molecular interactions (such as absence of electrostatic and hydrogen bonding) with water and ice, expedite their anti-icing and de-icing properties. Further, on superhydrophobic surfaces (in the composite state with air gaps within surface features, i.e., Lotus or Cassie-Baxter state), the smaller ice-solid contact area would facilitate the ice removal from the surface (de-icing). However, the correlation between hydrophobicity and icephobicity is relevant when the surface wetting state remains stable at sub-zero temperatures [68, 118-120] (Paper I). In addition, the surfaces should be mechanically robust while subjected to icing/deicing cycles, where no wetting transition would be observed due to changes in the surface morphology [54, 93]. In this thesis I will discuss this approach and its limitations further. In particular, I attempt to study the feasibility of utilizing superhydrophobic surfaces as icephobic surfaces and understand the inconsistency among findings in this area. Environmental conditions inducing growth of condensation and frost on the surface, i.e., humid condition (see Paper II), that is relevant for most practical situations would be emphasized in this work.

In recent years another approach has been proposed for making de-icing surfaces, inspired by the insect-eating pitcher plant Nepenthes, where ice adhesion is reduced on slippery liquid-infused porous surfaces (SLIPS) [121-124] through fluids, such as perfluorinated liquids, infused in porous materials generating a continuous lubrication film on the surface. Modification of SLIPS are ongoing regarding for example the chemical composition of the fluid, that should wet the substrate but be immiscible with water, and the limited durability of the lubricant due to leaking or evaporation [125].
An aqueous quasi liquid layer, with different properties from both bulk water and solid ice, is proposed to cover the surface of ice and the interface between a solid and ice [126-129]. However, measuring the properties and the temperature-dependence for this layer at the ice-solid interface is challenging [129] but it is suggested to exist at the interface [89, 130-132]. For instance, the increase in ice adhesion strength with decreasing temperature has been attributed to the decrease in the thickness of this layer [133]. Further, the nature of solid surfaces [133] as well as surface attached ionic groups and their counterions [131, 134-135] are proposed to affect the measured ice adhesion strength due to their influence on the liquid-like layer. In addition, de-icing properties of a coating fabricated by grafting cross-linked poly(acrylic acid) hydrogels inside micro-pores of silica surfaces have been attributed to the lubrication effect of a liquid water layer [136]. The de-icing benefit of surfaces due to the lubrication effect of the liquid-like layer at the interfaces with ice could be studied further, utilizing surfaces promoting this lubricating layer. This approach will be discussed further in the experimental chapter of this thesis (see also Paper IV and V).

Further, utilizing elastomeric coatings with low modulus has been suggested to provide de-icing properties [135, 137]. There are also other anti/de-icing strategies [27, 89], in most cases inspired by nature, that could be implied for designing icephobic surfaces. However, most of them are still far from being suitable for practical applications.
2. Experimental

2.1. Surface preparation

Silica having a topographically flat surface (roughness < 0.5 nm) was employed as one substrate in this thesis work. It was modified utilizing different methods, mentioned in Table 2-1 and described in detail in the Papers I to IV.

Table 2-1: Description of modified silica samples used in this study.

<table>
<thead>
<tr>
<th>substrate</th>
<th>sample notation</th>
<th>fabrication method</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>flat silica</td>
<td>smooth hydrophobic</td>
<td>silanization with PFOTES</td>
<td></td>
</tr>
<tr>
<td>(silicon wafer)</td>
<td>Wenzel hydrophobic-60nm</td>
<td>APTES silanization + 60 nm-nanoparticles deposition + sintering at 800 °C + silanization with PFOTES</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td>Wenzel hydrophobic-800nm</td>
<td>APTES silanization + 800 nm-nanoparticles deposition + sintering at 800 °C + silanization with PFOTES</td>
<td></td>
</tr>
<tr>
<td></td>
<td>superhydrophobic</td>
<td>dip-coat (silica nanoparticles dispersion in fluoro-polymer solution) + calcination at 500 °C + silanization with PFOTES</td>
<td></td>
</tr>
<tr>
<td>Si-HMDSO</td>
<td>coat with plasma polymerized-HMDSO</td>
<td></td>
<td>II &amp; III</td>
</tr>
<tr>
<td>Si-PFH</td>
<td>coat with plasma polymerized-PFH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>flat silica</td>
<td>cationic polymer</td>
<td>adsorption of (METAC)$_m$</td>
<td>IV</td>
</tr>
<tr>
<td>(fused-silica windows)</td>
<td>bottle-brush polymer</td>
<td>adsorption of (PEO$_m$MEMA)$_n$,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>diblock copolymer</td>
<td>adsorption of (METAC)$_m$-$b$-(PEO$_m$MEMA)$_n$,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>linear PEO</td>
<td>adsorption of linear PEO</td>
<td></td>
</tr>
</tbody>
</table>

PFOTES: 1H,1H,2H,2H-perfluorooctyltriethoxysilane, APTES: 3-aminopropyl triethoxysilane, HMDSO: hexamethyldisiloxane, PFH: perfluorohexane, METAC: methacryloxyethyl trimethylammonium chloride, PEO$_m$MEMA: poly(ethylene oxide)methylether methacrylate, PEO: poly(ethylene oxide)

In addition, I used wood as a rough substrate with micro-scale surface roughness for preparing the samples mentioned in Table 2-2 where the details could be found in the Papers II and III. Finally, mica was utilized as a molecularly smooth surface (Paper V).
Table 2-2: Description of modified wood samples used in this study.

<table>
<thead>
<tr>
<th>substrate</th>
<th>sample notation</th>
<th>fabrication method</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>rough wood</td>
<td>wood-PFH</td>
<td>coat with plasma polymerized-PFH</td>
<td>II &amp; III</td>
</tr>
<tr>
<td></td>
<td>wood-HMDSO</td>
<td>coat with plasma polymerized-HMDSO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>wood-TiO₂-PFH</td>
<td>LFS-deposition of TiO₂ nanoparticles + coat with plasma polymerized-PFH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>wood-TiO₂-HMDSO</td>
<td>LFS-deposition of TiO₂ nanoparticles + coat with plasma polymerized-HMDSO</td>
<td></td>
</tr>
</tbody>
</table>

PFH: perfluorohexane, HMDSO: hexamethyldisiloxane, LFS: liquid flame spray

2.1.1. Water

In all experimental parts of this thesis water refers to "Milli-Q water" that was water purified utilizing a Milli-ROP1s unit connected to a Milli-Q plus 185 system, and filtered through a 0.2 μm Millipak filter. Milli-Q water has resistivity of 18.2 MΩcm and organic content of less than 3 ppb.

2.2. Methods

2.2.1. Wetting properties

*Temperature-controlled contact angle measurements*

Temperature-dependent wetting properties could be determined using contact angle measurements at temperatures of interest. The sessile drop method is commonly utilized for measuring the static contact angle of liquids on surfaces where a microlitre-sized [138] drop of the liquid is placed on the surface and the two-dimensional profile of the drop is imaged using a high speed camera. Advancing (ACA) and receding (RCA) contact angles of the sessile drops of liquids are determined by tilting the sample. The contact angle of the advancing and receding side of the drop profile right before sliding over the surface is the ACA and RCA, respectively. Alternatively, the ACA and RCA are measured by keeping the dispensing needle inside the drop and continuously but slowly [139] increasing and decreasing the volume of the drop until the base line moves.

In this study, contact angle of 4 µL sized-water drops on the sample surfaces was measured using an optical goniometer (DataPhysics OCA40micro instrument (DataPhysics GmbH, Germany) equipped with a high speed CCD camera (maximum 2200 images s⁻¹) with 20 times
magnification, a computer programmable droplet-dispensing unit and a tilting base unit. SCA 20 (DataPhysics) software (the tangent method) was used for image analysis. The Peltier cooling stage of the instrument was utilized for temperature-controlled measurements where the drop was dispensed on the surface, subsequently the sample was cooled from room temperature (23-25 °C) down to the desired sub-zero surface temperature. A schematic drawing of the system is presented in Figure 2-1. In Paper I and II, the temperature of the drop and the sample surface was monitored and recorded using fast response temperature sensors connected to a high-resolution temperature logger (TC-08, Pico Technology, UK). In Paper II, I also used an IR camera (Optris PI230, Optris, Germany) for monitoring the temperature of the water droplet and the sample surface. The contact angle measurements were performed in a climate control room with relative humidity of about 40% at room temperature (~23-25 °C). Furthermore, in order to minimize frost formation, dry N₂ atmosphere was used for temperature-controlled ACA and RCA study in Paper I where the sessile drop was placed on the surface after the surface temperature reached the desired temperature.

![Diagram](Image)

Figure 2-1: Schematic illustration of the device used for temperature-controlled contact angle measurements. The surface temperature is controlled with a Peltier element in a room with temperature ~23-25 °C and humidity RH~40%. Thus, there is a temperature-gradient between the surface and the environment.

**Wilhelmy plate method**

The Wilhelmy plate method [140] is a technique for studying wetting properties of surfaces by indirect measurement of contact angle. In principle a sample plate is immersed in a probe liquid and a balance detects a force, acting on the plate, referred to as $F$. This force is a combination of the wetting force and the buoyancy force.
\[ F(h) = P\gamma \cos \theta - \rho A_c h g \]  

(2-1)

where \( F \) is the detected force, \( P \) the wetted perimeter of the plate, \( \gamma \) the probe liquid surface tension, \( \theta \) the liquid-solid-air contact angle, \( \rho \) the probe liquid density, \( A_c \) the cross-sectional area of the plate, \( h \) the immersion depth, and \( g \) the acceleration of gravity. Knowing the liquid surface tension and the plate perimeter the static contact angle could be determined. However, for porous and hygroscopic samples the plate perimeter and the contact angle are not constant during measurements. In addition, the liquid wicking and sorption would change the plate weight. Therefore for such samples, Eq. 2-1 is modified by adding a time-dependent force term \[141\] as follows:

\[ F(h, t) = P\gamma \cos \theta + F_w(t) - \rho A_c h g \]  

(2-2)

where \( F_w(t) \) is the force due to wicking and sorption of the liquid at time \( t \). By plotting the force \( F \) versus immersion depth \( (h) \), the contact angle could be calculated and the dynamic sorption and penetration of the probe liquid could be evaluated.

Advancing and receding contact angles could be determined by linear regression of the immersion and withdrawal curves to zero depth \((h=0)\) \[142\].

A Sigma 70 tensiometer from KSV Instruments was utilized for wettability studies with the Wilhelmy plate method in this thesis work (Paper III) where multicycle Wilhelmy plate measurements (with 20 cycles) \[142\] were performed. In this mode a plate is immersed into and withdrawn from the probe liquid repeatedly for several cycles and advancing and receding contact angle are determined at the end of each cycle.

2.2.2. Freezing of supercooled water

Freezing of water drops on surfaces was studied in terms of 1) degree of water supercooling, i.e., freezing temperature, and 2) time delay in freezing of (supercooled) water drops, i.e., freezing delay. In other words, freezing temperature is considered as a temperature \((\leq 0^\circ C)\) at which a sessile drop resting on a surface undergoes freezing, and freezing delay at a certain temperature is considered as the delay in freezing after a sessile drop on a surface reaches the target temperature. Initiation of the
freezing of the sessile drop, i.e., freezing onset is the moment when the formed ice nuclei start to grow, it could be visualized by high speed imaging of the profile of the drops and monitoring the change in optical appearance of the drops where the white part in the middle of the images of the drops in the liquid state (see Figure 2-2-a), due to light reflection, disappears at the freezing onset as the drops becomes cloudy (see Figure 2-2-b). Complete freezing of the drops is realized by the appearance of a small protrusion on the top of the frozen drops in the solid state (see Figure 2-2-c). Alternatively, the freezing onset is determined by accurate reading of the drop temperature. At the freezing onset a sudden increase in the drop temperature (monitored by a fast response temperature sensor or an IR camera) is observed due to release of the latent heat of fusion.

![Figure 2-2: An example of high speed imaging of the freezing process of sessile water droplets on a surface.](image)

For freezing studies (Paper I and II), the same DataPhysics OCA40micro instrument system used for temperature-controlled contact angle measurements was utilized combined with the Peltier cooling stage, the fast response temperature sensors and the high-resolution temperature logger. The measurements were performed in a climate control room with relative humidity of about 40% at room temperature (~23-25 °C). Room temperature 5 µL sized-water drops were placed on the surface of the samples and subsequently cooled either to the temperature where freezing was initiated (for freezing temperature studies) or to the desired sub-zero temperature (for freezing delay studies). Details of freezing measurements performed in this thesis are summarized in Table 2-3.
Table 2-3: Summary of evaluated characteristics and utilized methods for freezing studies.

<table>
<thead>
<tr>
<th>Paper</th>
<th>studied freezing characteristics</th>
<th>freezing onset exploring method</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>freezing temperature</td>
<td>high speed camera</td>
</tr>
<tr>
<td></td>
<td>freezing delay</td>
<td>temperature sensor</td>
</tr>
<tr>
<td>II</td>
<td>freezing delay</td>
<td>high speed camera</td>
</tr>
<tr>
<td></td>
<td>*IR camera</td>
<td></td>
</tr>
</tbody>
</table>

* the same IR camera described in the section 2.2.1

A typical IR camera-temperature versus time curve, illustrating the freezing event of a sessile drop on one of the samples of my work (wood-TiO2-PFH sample used in Paper II and III), is presented in Figure 2-3. As seen in this figure, at the freezing onset the drop temperature increases suddenly to 0 °C (see point II in the Figure 2-3), where the imaged profile of the drop at this moment is changing from dark with a white spot (see point I (considered a few seconds before the freezing onset) in the Figure 2-3) to cloudy with no white spot. After the complete freezing the drop temperature goes down to sub-zero temperatures (see point III in the Figure 2-3).

![Figure 2-3: Freezing of sessile drops monitored by IR camera, the drop profiles are added from CCD camera imaging as a guide.](image)

Freeze-thaw wetting properties

Stability of wetting properties of surfaces during freeze-thaw cycles could be investigated by contact angle measurements within these cycles. A smaller freeze-thaw contact angle hysteresis (gradient between contact angles before and after a cycle) on a surface presents the higher stability of the wetting state of the surface during the cycle. The same equipment
system utilized for freezing measurements were utilized in these measurements. Room temperature (about 23-25 °C) 5 µL sized-water drops were placed on the surface of the samples and then cooled at a certain rate to a chosen sub-zero temperature. After reaching the target temperature the temperature of the Peltier was not changed until the drop was frozen. This first stage of the cycle is referred to as "freeze". Next, the Peltier temperature was increased back to room temperature where the drop was melted and its temperature continued to increase to room temperature. This second stage of the cycle is referred to as "thaw". Contact angle of the drops was plotted versus temperature during the freeze and thaw stages of the cycle using the high speed captured images of the drops combined with the recorded temperatures for those frames.

2.2.3. Ice adhesion

In this thesis the shear strength of the ice/solid interface is referred to as ice adhesion. The ice adhesion was measured using an in-house designed and built device [129] here its schematic illustration is shown in Figure 2-4. The device has a temperature controlled stainless steel chamber that is insulated using a 2 cm thick cork frame. Temperature-control is provided by a refrigerated/heating circulator (Julabo FP50-ME, Germany) down to subzero temperatures of -35 °C with a precision better than 0.1 °C. The samples of interest were positioned in the chamber where Teflon cylinders with an internal diameter of 10 mm were placed on top of the samples. The cylinders were subsequently filled with 1 hr deaerated (using a water jet pump) Milli-Q water. To freeze water inside the Teflon cylinders the chamber was cooled to -25 °C. The Teflon cylinder with frozen water is referred to as "ice cylinder". Next, the chamber temperature was changed to the temperature of interest for ice adhesion measurements, and the measurements were performed 15 minutes after reaching the desired temperature. The temperature close to the surface of the samples was recorded using a fast response sensor. The shear force required to remove the ice cylinder from the sample was applied and measured using a pneumatic piston (CDQSB25-30D, SMC, China) in combination with a force sensor (LCMFD, Omegadyne Inc, USA) that was connected to a pushing rod (diameter and length of 6 mm and 7 cm, respectively). Compressed air at a pressure of 2.8 bar with an air flow rate of 10 mLmin⁻¹ was driving the pneumatic piston. The pushing rod was positioned about 2 mm above the surface with its tip close to the ice
cylinder. Afterwards, the piston was pressurized when a pneumatic valve was actuated and resulted in slow movement of the rod toward the ice cylinder. A custom made Labview program was used for recording the force versus time data and the chamber temperature. The shear ice adhesion strength was obtained by dividing the maximum of the recorded force by the area of the ice cylinder.

![Figure 2-4: Schematic illustration of the temperature-controlled shear ice adhesion strength measurements. Ice cube is formed in a cylinder inside a temperature-controlled box. The shear force, measured with a force sensor, is applied by a pneumatic piston.](image)

Further, in one study (see also Paper V) ice cubes, with area of 30×30 mm² and a height of about 10 mm, were accreted on surfaces in an icing wind tunnel located at Tampere University of Technology, with T = -10 °C, air-flow = 25 m/s, relative humidity = 76%, and average droplet diameter = 30 µm. After 16 hours at -10 °C, the surfaces were moved to a centrifugal ice adhesion test device [143].

2.2.4. Atomic force microscopy

Atomic force microscopy (AFM) is widely used for high resolution (nanometer scale) imaging of the surface topography. The sample is positioned on the top of a scanner that moves the sample in X, Y and Z direction. A probe attached to a cantilever scans across the surface. A laser focused on the backside of the cantilever is reflected onto a mirror and then into a photodetector. The probe/surface interactions affect the position of the laser spot in the photodetector, which is corrected to its initial position by a feedback loop. In my work surface images were captured utilizing an AFM Nanoscope Multimode V (Bruker, USA) (used in Paper I) and an AFM Dimension Icon (Bruker, USA) (used in Paper II and III) both operated in Tapping® mode (TM) in air. NanoScope analysis
software (Bruker) was used for image analysis. Intermittent contact of the tip and the sample in TM avoids lateral forces that could damage both tip and the sample (specially soft samples) but still giving high image resolution. In TM the cantilever is oscillated at or near its resonant frequency. The feedback loop keeps the oscillation amplitude of the cantilever constant by adjusting the relative position of the cantilever with respect to the sample in Z direction. With this height images of the surfaces are achieved. In addition variation in energy dissipation during tapping affected by material properties such as tip-sample adhesion, surface viscoelasticity and stiffness results in a shift in phase angle for the cantilever oscillation. Phase images are obtained using these shifts in oscillation phase. TM imaging has also been used in this thesis work for measuring the thickness of the plasma polymer coatings (used for surface modifications) in Paper II and III, and for determining size distribution of LFS-generated nanoparticles in Paper II.

2.2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS), also referred to as electron spectroscopy for chemical analysis (ESCA), is a highly surface sensitive analytical method with an analysis depth of approximately 2-10 nm for quantitative chemical characterization of surfaces. In XPS the sample is irradiated with X-rays generated by excitation sources under high vacuum conditions. The photons interact with surface atoms, resulting in emission of photoelectrons with characteristic energies for each element. From the number and kinetic energy of the emitted photoelectrons the binding energies and intensity of photoelectron peaks can be determined, that is also affected by the chemical state of the atom. Therefore, XPS spectra provide quantitative information about surface elements and their chemical state.

Surface chemical composition of our samples in Paper I, II and III were characterized quantitatively utilizing a Kratos AXIS Ultra\textsuperscript{DLD} X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) and a monochromatic Al K\textsubscript{x} X-ray source operated at 150 W.

2.2.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique that measures changes in enthalpy of a sample due to changes in physical
and chemical properties as a function of time or temperature. These changes are monitored by cooling or heating the sample and an inert reference at a constant rate and measuring the difference between heat flow rate to the sample and to the reference. Due to phase transitions or chemical reactions a sample could absorb or release heat in endothermic or exothermic processes, respectively.

In this thesis a Mettler Toledo DSC 1 STAR® System was utilized to study the state of water in aqueous solutions of the polymers used for fabricating modified silica samples in Paper IV. Empty DSC aluminum sample pans (capacity 40 µL) were used as reference. The samples were initially cooled at a rate of 10 °C/min from 25 °C to 2 °C followed by cooling to -80 °C at a rate of 2 °C/min. After a 10 min isotherm session at -80 °C, the samples were heated at a rate of 1 °C/min to 30 °C. Phase transitions were studied during these cooling and heating sessions.
3. Key results and discussion

In this chapter I first discuss the stability of the wetting properties of hydrophobic surfaces as a crucial factor for their applications, in particular for anti/de-icing purposes. This is done in relation to Papers I-III where the effect of surface characteristics such as surface topography and chemistry, and environmental conditions such as temperature, on the wetting transitions are studied. The next section presents the results from evaluation of the anti-icing properties of hydrophobic surfaces, in relation to Paper I and II, where a conclusion will be made on the feasibility of these surfaces as icephobic surfaces. This is followed by the findings from investigating de-icing properties of hydrophilic surfaces with particular characteristics, in connection with Paper IV and V.

3.1. Wetting transitions on hydrophobic surfaces

3.1.1. Dynamic wetting measurements

Hydrophobic and superhydrophobic surfaces that are durable when subjected to several wetting cycles could be beneficial for different applications. In this section the Multicycle Wilhelmy plate (mWP) method [142] is utilized for describing the dynamic wetting properties of these surfaces where advancing and receding contact angles could be determined during repeated wetting cycles in water. Smaller changes in contact angle during several cycles are characteristic of samples with higher wetting durability. This method is even more advantageous for chemically and/or topographically heterogeneous surfaces where average contact angles over an area of interest are achieved. Since stochastically rough surfaces are more relevant for practical situations, wood surfaces with micro-rough structures were modified and utilized in this work (wood-HMDSO, wood-PFH, wood-TiO$_2$-HMDSO and wood TiO$_2$-PFH, see Table 2-1). Flat silica surfaces coated with the same plasma polymers where utilized as topography reference samples presenting similar chemistry (Si-HMDSO and Si-PFH, see Table 2-1). Detailed characterizations of these surfaces are reported in Paper II and III.
Analysis of the AFM height images of the Si-HMDSO and Si-PFH samples illustrate that flat silica surface (see Figure 3-1a), with RMS roughness of $0.2\pm0.02$ nm, remains smooth after being coated with plasma polymerized HMDSO (see Figure 3-1b) and PFH where their RMS roughness is below 1 nm. These surfaces are thus suitable flat reference samples. The wood surfaces (see Figure 3-1c) have micro-sized roughness features, in order of 100 µm determined with scanning electron microscope (SEM) imaging (see Figure 3 of Paper III). When modified, local nano-scale structures could be observed in the AFM images that are more pronounced on TiO$_2$-LFS-coated surfaces (compare Figure 3-1e with 3-1d), resulting in multi-scale roughness.

Advancing (ACA) and receding (RCA) contact angles and contact angle hysteresis measured at room temperature at the first and 20$^{th}$ wetting cycles for selected surfaces of this work are summarized in Table 3-1 (see also Paper III). As seen in Table 3-1, the TiO$_2$-LFS-coated surfaces with multi-scale roughness present smaller hysteresis while having higher ACA and RCA when compared with the hydrophobized micro-rough wood surfaces. Further, the multi-scale roughness also enhanced the durability of the hydrophobic wood surfaces during 20 wetting cycles, as demonstrated by a smaller change in the wetting parameters reported in
Table 3-1. It should be noted that PFH treated surfaces show slightly higher hydrophobicity than HMDSO treated ones, which is related to higher hydrophobicity of fluorocarbon in comparison with siloxane. The data on flat Si-HMDSO and Si-PFH samples show that the hydrophobicity of the plasma polymer coating is lower than observed on pure fluorocarbon and siloxane surfaces (see Paper II for more discussions).

<table>
<thead>
<tr>
<th>surface</th>
<th>ACA</th>
<th>RCA</th>
<th>Hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cycle 1</td>
<td>cycle 20</td>
<td>cycle 1</td>
</tr>
<tr>
<td>Si-HMDSO</td>
<td>106±1</td>
<td>104±1</td>
<td>90±0</td>
</tr>
<tr>
<td>wood-HMDSO</td>
<td>145±5</td>
<td>141±4</td>
<td>88±5</td>
</tr>
<tr>
<td>wood-TiO₂-HMDSO</td>
<td>160±6</td>
<td>161±7</td>
<td>128±18</td>
</tr>
<tr>
<td>Si-PFH</td>
<td>112±1</td>
<td>111±1</td>
<td>99±1</td>
</tr>
<tr>
<td>wood-PFH</td>
<td>144±10</td>
<td>136±5</td>
<td>80±8</td>
</tr>
<tr>
<td>wood-TiO₂-PFH</td>
<td>159±9</td>
<td>159±10</td>
<td>134±10</td>
</tr>
</tbody>
</table>

3.1.2. Temperature effect

In this section the effect of temperature on wetting transitions is first explored utilizing two different surfaces (modified silica surfaces noted as smooth hydrophobic and superhydrophobic, presented in Table 2-1) from those utilized in the previous section. Further study of the temperature dependence of wetting transitions is performed utilizing HMDSO-treated surfaces used in section 3.1.1, during freeze-thaw cycles. XPS broad binding range (0-1400 eV) and high-resolution carbon 1s data reveal a similar chemistry of smooth hydrophobic and superhydrophobic surfaces that all were hydrophobized with the same fluorosilane (see Table 3-2).

<table>
<thead>
<tr>
<th>surface</th>
<th>C/F</th>
<th>CF₂/CF₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>smooth hydrophobic</td>
<td>0.6±0.1</td>
<td>4.3±0.3</td>
</tr>
<tr>
<td>superhydrophobic</td>
<td>0.6±0.1</td>
<td>5.1±0.3</td>
</tr>
<tr>
<td>Wenzel hydrophobic-60nm</td>
<td>0.6±0.1</td>
<td>4.4±0.2</td>
</tr>
<tr>
<td>Wenzel hydrophobic-800nm</td>
<td>0.6±0.1</td>
<td>5.2±0.4</td>
</tr>
</tbody>
</table>

From the roughness analysis of the AFM topographical images (see Figure 2 of Paper I), the RMS roughness of the superhydrophobic sample is 160 nm over a 10×10 μm² area, while it is about 1 nm for the smooth
hydrophobic sample. Mean values of 5 contact angle measurements at room temperature, reported in Table 3-3, demonstrate that the water wetting state is very different on these surfaces with different topographical characteristics but similar chemistry. The superhydrophobic surface has high water contact angle with almost no contact angle hysteresis, demonstrating the Cassie-Baxter state.

Table 3-3: Wetting characteristics at room temperature (23-25 °C).

<table>
<thead>
<tr>
<th>surface</th>
<th>static CA</th>
<th>ACA</th>
<th>RCA</th>
<th>hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>smooth hydrophobic</td>
<td>100±2</td>
<td>107±2</td>
<td>94±2</td>
<td>13±4</td>
</tr>
<tr>
<td>superhydrophobic</td>
<td>161±2</td>
<td>161±2</td>
<td>161±2</td>
<td>0±4</td>
</tr>
<tr>
<td>Wenzel hydrophobic-60nm</td>
<td>133±2</td>
<td>137±2</td>
<td>83±4</td>
<td>54±6</td>
</tr>
<tr>
<td>Wenzel hydrophobic-800nm</td>
<td>126±4</td>
<td>130±2</td>
<td>92±2</td>
<td>38±4</td>
</tr>
</tbody>
</table>

Temperature-controlled static equilibrium contact angle measurements on the smooth hydrophobic and superhydrophobic samples at surface temperatures ranging from 23-25 °C down to -13 °C, presented in Figure 3-2, reveal an influence of temperature on the wetting state of the superhydrophobic sample. The data in this figure show that the contact angle decreases at temperatures below 15 °C. I relate this to condensation and, when temperature is lowered below 0 °C, frost formation facilitating partial spreading. In contrast, the static contact angles on the smooth hydrophobic sample are almost unaffected.

Figure 3-2: Static contact angles on smooth hydrophobic and superhydrophobic surfaces as a function of temperature. The static contact angle was determined in ambient air with about 40% relative humidity at 23 °C.
At some selected temperatures, advancing and receding contact angles were also studied as presented in Figure 3-3a. These measurements were performed in a close to dry atmosphere in order to minimize frost formation, consequently not directly comparable to the data reported in Figure 3-2. The receding contact angle decreases significantly on the superhydrophobic surface at temperatures below 0 °C, i.e. in the case of supercooled water droplets. However, on the smooth hydrophobic surface it decreases marginally when temperature is reduced. On contrary, the temperature dependence of the advancing contact angles on both surfaces is weak. At room temperature the water droplet on the superhydrophobic surface is placed on a composite surface of solid and air. During cooling, evaporated water from the droplet condenses in the air pockets beneath the droplet and when the temperature decreases further it undergoes freezing. This results in a wetting transition from the Cassie-Baxter towards the Wenzel state with reduced receding contact angle and increased contact angle hysteresis.

The practical work of adhesion (Eq. 1-6) is plotted in Figure 3-3b, using the temperature dependent-water surface tension values from the literature [49]. The data in this figure demonstrate an increase in the work of adhesion of water with decreasing temperature, partly as a result of the increasing surface tension of water (lines in Figure 3-3b), and
partly due to decreasing receding contact angles that is attributed to the wetting state transitions induced by condensation followed by frost formation. The temperature effect on the wetting transition and consequently on the work of adhesion is much larger for the superhydrophobic surface in comparison with the smooth hydrophobic surface.

**Wetting transitions over freeze-thaw cycles**

This section is motivated by the fact that the robustness of the wetting states on hydrophobic and superhydrophobic surfaces during cooling-heating cycles is critical for the anti-icing and de-icing implications. Only few works [58-59] dealt with this, and the role of surface roughness on the wetting reversibility during temperature cycles was not clear. In this thesis work I emphasize freeze-thaw cycles resembling environmental conditions inducing condensation and frost formation. In order to illustrate the topography effect, flat hydrophobized silica surface (Si-HMDSO) as well as random rough hydrophobic (wood-HMDSO) and multi-scale rough superhydrophobic (wood-TiO₂-HMDSO) wood surfaces, that are relevant for practical applications, were utilized. It note that, as mentioned in section 3.1.1, RMS roughness of Si-HMDSO is below 1 nm, thus this surface is suitable as flat reference sample.

High resolution-XPS spectra, summarized in Table 3-4, reveals similar chemistry of wood-TiO₂-HMDSO and Si-HMDSO.

<table>
<thead>
<tr>
<th>surface</th>
<th>sample 1</th>
<th>sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare wood</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Si-HMDSO</td>
<td>0.25</td>
<td>0.28</td>
</tr>
<tr>
<td>wood-TiO₂-HMDSO</td>
<td>0.29</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Static water contact angles on modified silica and wood surfaces, coated with plasma polymerized HMDSO, measured during a freeze-thaw cycle are presented in Figure 3-4. I note that temperature cycle-wetting properties of surfaces coated with plasma polymerized PFH are in qualitative agreement with the ones with plasma polymerized HMDSO (see Paper II for the discussions on theses samples).

The cycle started with a liquid droplet held at room temperature that was subsequently cooled down to -7 °C. The droplet remained in the
liquid state also below 0 °C (it was supercooled). The temperature was maintained at -7 °C until the droplet underwent freezing where the last data point on the cooling session on each plot is for solid ice. Next, during heating to room temperature the frozen droplet melts at 0 °C. The contact angle of solid ice is, of course, not changing until reaching the melting point.

Figure 3-4: Static contact angles measured during a freeze-thaw cycle on (a) Si-HMDSO, (b) wood-HMDSO, and (c) wood-TiO₂-HMDSO. The measurements were done in contact with ambient air with about 40% relative humidity at 23°C and the error bars correspond to the standard deviation of at least 3 measurements.

Table 3-5: Effect of temperature on dynamic wetting parameters.

<table>
<thead>
<tr>
<th>measured parameter</th>
<th>surface</th>
<th>wood-TiO₂-HMDSO</th>
<th>wood-TiO₂-PFH</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACA</td>
<td>wetting cycle-1</td>
<td>160±6</td>
<td>159±9</td>
</tr>
<tr>
<td></td>
<td>wetting cycle-20</td>
<td>161±7</td>
<td>159±10</td>
</tr>
<tr>
<td></td>
<td>Freeze/thaw cycle-initial</td>
<td>162±3</td>
<td>157±2</td>
</tr>
<tr>
<td></td>
<td>Freeze/thaw cycle-end</td>
<td>107±4</td>
<td>113±4</td>
</tr>
<tr>
<td>RCA</td>
<td>wetting cycle-1</td>
<td>128±18</td>
<td>134±10</td>
</tr>
<tr>
<td></td>
<td>wetting cycle-20</td>
<td>127±19</td>
<td>127±8</td>
</tr>
<tr>
<td></td>
<td>Freeze/thaw cycle-initial</td>
<td>116±5</td>
<td>114±5</td>
</tr>
<tr>
<td></td>
<td>Freeze/thaw cycle-end</td>
<td>94±5</td>
<td>92±2</td>
</tr>
</tbody>
</table>

During the freeze-thaw cycles on the modified silica surfaces, higher contact angles were observed on cooling than on the subsequent heating. The contact angle decreases slightly with decreasing temperature resulting in a small but noticeable wetting hysteresis. However, comparing the initial and final contact angles measured on the rough wood surfaces in the beginning and at the end of the freeze-thaw cycles demonstrates a significant wetting hysteresis. For comparison, advancing and receding contact angles measured in the beginning and at the end of
the freeze-thaw cycle (see Paper II) and during the first and 20th wetting cycles at room temperature (data reported in Table 3-1, see Paper III) are presented in Table 3-5.

The small wetting hysteresis detected during dynamic wetting measurements at room temperature on these surfaces (see Paper III), is not comparable to the large hysteresis observed during the cooling-heating cycle. I relate this to the temperature cycling and particularly condensation and frost formation. Since the outer HMDSO plasma polymer layer has very similar chemistry on the rough modified wood and the flat modified silica surfaces, the larger temperature-induced wetting transitions for the rough surfaces is clearly due to the larger roughness of the wood samples. Further due to this roughness effect, initial contact angles measured at the beginning of the cycle at room temperature are also higher on the rough wood surfaces. The multi-scale roughness introduced by the TiO\textsubscript{2}-LFS coating increases the contact angle further. These are indeed in agreement with the findings reported in section 3.1.1. For the rough modified wood surfaces the contact angle starts decreasing at a temperature of about 10 °C. This is due to water vapor condensation and, at subzero temperatures, frost formation on the surfaces. When the ice melts at 0 °C, the contact angle on the modified rough wood surfaces decreases significantly (see Figure 3-4b and c) due to the presence of water in surface depressions leading to a transition in the wetting state. A smaller hysteresis during freeze-thaw cycles for the wood-TiO\textsubscript{2}-HMDSO surface compared to the wood-HMDSO surface is also attributed to the multi-scale roughness introduced by the LFS treatment. Consequently, rough hydrophobic surfaces with characteristics resulting in a higher wetting stability during dynamic measurements at room temperature could diminish the effect of temperature upon cooling-heating cycles, resulting in higher temperature stability of the wetting properties.

Discussions on how the wetting hysteresis is not related to any orientation of the surface chemical groups, the droplet evaporation or droplet or surface contamination can be found in Paper II. In order to investigate the robustness of the modifications during freeze-thaw cycles, the contact angle measurement was performed on a droplet placed on a carefully dried spot on the samples that underwent a freeze-thaw cycle. A representative graph for the wood-TiO\textsubscript{2}-PFH sample is presented in Figure 3-5. After 10 freeze-thaw cycles, the contact angles were found to
be very similar to the contact angles on the initial cycle, demonstrating the robustness of the coatings.

![Graph showing static contact angle measurements during consecutive freeze-thaw cycles](image)

**Figure 3-5:** Static contact angle measurements during consecutive freeze-thaw cycles for evaluation of the robustness of the coating on wood-TiO$_2$-PFH. The measurements were done in ambient air with about 40% relative humidity at 23 °C and the error bars correspond to the standard deviation of at least 3 measurements. The solid and dotted lines present data during the first and subsequent freeze-thaw cycles, respectively.

### 3.2. Anti-icing properties of hydrophobic surfaces

In this section, I attempt to correlate the hydrophobic surface parameters governing their wetting properties with the anti-icing characteristics. Anti-icing is evaluated in terms of temperature and time delay for freezing of supercooled water droplets on different surfaces fabricated for this study, presenting desired morphology and chemistry. The aim is to understand what surface parameters could result in the lower freezing temperature or longer freezing delay at certain sub-zero temperature, and this is done in connection with the findings from the previous section. In particular, the focus is on how surface topography of hydrophobic surfaces is involved in the anti-icing performances, and whether superhydrophobic surfaces favor anti-icing under realistic conditions allowing frost formation to occur. This important issue is reported in few recent works, however the findings are contradictory and there is certain need for elucidation (see Paper I and II for detailed discussions on theses contradictions).
3.2.1. Freezing temperature

Freezing temperature of supercooled water droplets on both smooth hydrophobic and superhydrophobic surfaces utilized in section 3.1.2, having similar chemistry (see Table 3-1 and 3-2 for chemistry and wetting characterizations, respectively), were found to fall in the temperature range between -14 and -22 °C. As reported in Table 2-3, the freezing onset was monitored utilizing the high speed camera and fast temperature sensors monitoring the temperature of the water droplet and the surface. The water and surface temperatures decrease at the same rate until a sudden increase is observed in the water temperature once the freezing starts, at the freezing onset where the droplet becomes hazy. This temperature jump is related to the release of the latent heat of fusion at this point (see Figure 5 and 6 of Paper I).

The relatively large spread in freezing temperatures, i.e., -14 to -22 °C, demonstrates the stochastic nature of the heterogeneous ice nucleation process. Thus, no significant effects of superhydrophobic surfaces on lowering the freezing temperature (in comparison with smooth but hydrophobic surfaces with similar chemistry) could be seen in this experiment.

However, freezing delay studies at certain (preferably higher) temperatures (next section) could be more informative.

3.2.2. Freezing delay

In the first part of this study, rather than surfaces used in previous section (3.2.1), two additional rough hydrophobic surfaces are utilized, i.e., Wenzel hydrophobic-60nm and Wenzel hydrophobic-800nm. These surfaces (presented in Table 2-1) were fabricated with surface modification of the same flat silica substrates utilized for smooth hydrophobic and superhydrophobic surfaces. It should be noted that two different sized nanoparticles were deposited during fabrication of these surfaces with the aim to provide two different roughness scales. Indeed, this is achieved and concluded from analysis of their height AFM images presented in Figure 3-6, where Wenzel hydrophobic-60nm has a much smaller RMS roughness of 9 nm in comparison with Wenzel hydrophobic-800nm with RMS roughness of 250 nm as well as the superhydrophobic surface with RMS roughness of 160 nm. Further, height profiles of these samples (see Figure 3-6) reveal a well-packed
monolayer of the deposited 60 nm particles for Wenzel hydrophobic-60nm surface. In contrast, the 800 nm particles form a patchy layer with particle clusters separated by surface areas with no particles.

As reported in Table 3-1 these surfaces have similar chemistry, which is also similar to smooth hydrophobic and superhydrophobic surfaces utilized in section 3.1.2. Different roughness scale results in difference in their wetting properties, see Table 3-2. The large contact angle hysteresis of these nano-structured rough hydrophobic surfaces, combined with the reported advancing and receding contact angles, suggest a Wenzel wetting state for the water droplets on these surfaces. Consequently these model hydrophobic surfaces with tuned and different surface topography but similar chemistry present different wetting states, from Wenzel to Cassie-Baxter. This enabled me to systematically study the effect of surface roughness on the freezing of supercooled water droplets.

The delay time for freezing of supercooled water droplets cooled from room temperature at a rate of 12-14 °C/min down to either -5 °C or -10 °C, and then held at these temperatures until reaching the freezing onset is reported in Figure 3-7. The error bar corresponds to the standard deviation from 5 different measurements. Since the heterogeneous ice nucleation rate is faster at lower temperatures (see Eq. 14 of Paper I), the freezing delay time is significantly longer at -5 °C on all surfaces. However, at a given temperature, -5 °C or -10 °C, the difference in
freezing delay on these hydrophobic surfaces, with completely different topography and wetting properties is not significant. I note that it could be expected that local small nano-sized features on the smooth hydrophobic surface, observed in the AFM images (see discussions on Figure 2a of Paper I), and the nanoparticles aggregation on the Wenzel state surfaces (see Figure 3-6) lower the energy barrier for ice nucleation and thus reduce the freezing delay time on these surfaces. However, the superhydrophobic surface does not provide any benefit for retarding freezing when compared with the other surfaces. Rather, the freezing of supercooled water droplets appears to be somewhat longer on the smooth hydrophobic and Wenzel hydrophobic-60nm but the difference is small.

The small difference in surface chemistry (reported in Table 3-2) cannot counteract the large difference in surface topography of the surfaces utilized in this study. I conclude that the water freezing on hydrophobic surfaces under static conditions that allow frost formation to occur is not significantly affected by the surface topography. Thus, no benefit from a superhydrophobic surface is observed.

Figure 3-7: Delay in freezing of 5 µL sized supercooled water droplets measured at temperatures of -5 °C and -10 °C for the four model hydrophobic surfaces with similar surface chemistry but different wetting and topography characteristics. The error bar corresponds to the standard deviation.
Correlation between the experimental findings and the heterogeneous ice nucleation theory

Plotting $f(m, x)$ (presented in section 1.4.4, and given by Eq. 7 and 11 of Paper I for convex and concave surface features, respectively) variation with $x$ (by Eq. 1-14, see section 1.4.4) presented in Figure 3-8, demonstrates how the energy barrier of homogeneous ice nucleation at a certain supercooling temperature (given by Eq. 1-10) is affected by the local surface topography of the hydrophobic surfaces used in this study. I note that the lower the value of $f(m, x)$ corresponds to the lower energy barrier for ice nucleation. Using Eq. 1-9, the value of the critical ice nucleus radius ($r^*$) can be calculated to be only 9.1 and 4.5 nm at -5 °C and -10 °C, respectively. Thus, it is the surface energy of a small surface area, in contact with this nano-sized critical ice nucleus, that matters for ice nucleation. Consequently the local contact angle, not the macroscopic contact angle, should be used in Eq. 1-13 for calculating the value of the interfacial energy parameter, i.e., $m$, that enters the function $f(m, x)$. Since the surfaces of this study with different topography scale have comparable surface chemistries, the value of $m$ is similar in all cases. Using the receding contact angle of water of about 94° (from RCA on smooth hydrophobic sample), and an ice surface energy of 106 mJm⁻², $m$ is calculated to be -0.08.

Figure 3-8: The function $f(m, x)$ for convex (black curve) and concave (red curve) surface features vs. the roughness parameter $x$ plotted for contact angles of 94° ($m = -0.08$). The scheme in the figure illustrates the small $x$ (where the critical radius of ice nucleus is comparable to the size of the surface features) toward large $x$ (where the critical radius of ice nucleus is much smaller than the size of the surfaces features).
It should be noted that \( f(m,x) \) for any value of \( x \), reduces with decreasing contact angle of the ice nucleus, thus the hydrophobic surfaces are expected to be preferred over hydrophilic ones for anti-icing purposes (See discussions on Figure 8 of Paper I).

The schematic drawing in Figure 3-8 shows that \( f(m,x) \) tends to be smaller on flat areas than on highly convex areas. However, the dependence of \( f(x,m) \) on \( x \) for hydrophobic surfaces is rather small. This translates to a weak dependence on surface topography. In practice, any real rough surface has a distribution of curvatures with both convex and concave surface features explaining why it should be avoided to use a single roughness parameter such as RMS or \( R_a \) (arithmetic average roughness) to define the surface topography. Indeed, the probability of the ice nucleation, defined by \( f(m,x) \), is controlled by the local nanoscale surface energy and surface curvature. Further, provided the supercooled water could penetrate into the concave surface features, for instance enhanced by vapour condensation or frost formation, ice nucleation occurs more readily in these sites than on planar surfaces, as shown in Figure 3-8. The experimental findings presented in Figure 3-7, demonstrating insignificance of surface topography influence on the freezing delay time data, is predicted from the theory providing the small concave sites are not accessible for supercooled water.

In the second part of the freezing delay study on hydrophobic surfaces in this thesis work, with the aim to illustrate the effect of surface roughness, the rough hydrophobic wood samples used in the temperature-constant and temperature-cycling wetting transition studies (see section 3.1), in particular the ones with different morphology but similar chemistry, i.e., wood-HMDSO (micro-rough) and wood-TiO\(_2\)-HMDSO (multi-scale rough), are utilized. I note their larger roughness scale in comparison with the nano-structured hydrophobic surfaces utilized in the first part of this section, and recall their temperature-induced wetting hysteresis upon a freeze-thaw cycle, reported and discussed in section 3.1.2. I attempt to illustrate whether there is any relation between significant temperature-related wetting state transitions and the rate of heterogeneous ice nucleation on these rough hydrophobic surfaces. Similar to the wetting transitions study, flat hydrophobized silica surface with a similar chemistry, i.e., Si-HMDSO, is utilized as a reference illustrating the effect of surface topography.
The freezing process was monitored utilizing the IR camera (see section 2.2.2) in combination with the high speed CCD camera. Upon cooling to the freezing onset, IR camera observation demonstrates a similar rate for the change in temperature of the surface of the samples and water droplet. The freezing onset in these measurements was determined from the moment that a jump was observed in the temperature of water measured by the IR camera, that corresponds to the change in the optical appearance of the droplet observed in the CCD frames (see discussions on Figure 6-7 in Paper II for the ice nucleation and freezing kinetics).

Figure 3-9: Freezing time characteristics for 5 µL sized supercooled water droplets measured on flat modified silica (Si-HMDSO), multi-scale rough modified wood (wood-TiO₂-HMDSO) and rough modified wood (wood-HMDSO) surfaces with similar chemistry. The filled bars represent the freezing delay (the error bars correspond to the standard deviation), and the striped bars represent the cooling time from 0 °C to the desired temperature. The complete bars represent the overall time the droplet is below 0 °C in the supercooled state prior to freezing.

Freezing time characteristics, presenting the cooling time from 0 °C to the target temperature (-4 °C or -7 °C), shown with the striped bars, added to the freezing delay at the target temperature, shown with the filled bars, on the samples of this work are reported in Figure 3-9 (see Paper II for the data and discussions on the modified wood samples coated with plasma polymerized PFH). The error bar corresponds to the
standard deviation from 10 different measurements. It should be noted that the cooling rate was 4.5 ± 1 and 12.1 ± 2.4 °C/min for the wood and silica samples, respectively. This is related to the higher thermal conductivity and lower thickness of silica in comparison with the wood surfaces. Consequently, the cooling time (the striped bars) is longer for wood samples than for silica. The effect of different cooling rate thus different cooling time, for the modified silica and modified wood samples, on the freezing delay results will be discussed.

The critical ice nucleus radius ($r^*$) could be calculated to be 11.3 nm at -4 °C and decreases (according to Eq. 1-9) to 6.4 nm at the higher degree of supercooling at -7 °C. The activation energy that needs to be overcome to reach the critical nucleation size also decreases with the increase in the degree of supercooling (see Eq. 1-10). This predicts the shorter freezing delay time at -7 °C compared to -4 °C as seen in Figure 3-9. This is in agreement with the freezing delay data on model nanostructured surfaces used in the freezing study.

Based on the theoretical discussions, the local nanoscale energy and topography of surfaces are controlling the heterogeneous ice nucleation rate. Since the local chemistry of the surfaces used for the data in Figure 3-9 is similar, according to the discussion in relation to Figure 3-8 ice nucleation is expected to occur less readily on the most flat surfaces. Indeed, the longest freezing delay data (filled bars) in Figure 3-9 is related to the flat modified silica surface both at -4 and -7 °C that lacks concave sites. I note that, despite the higher cooling rates for the flat modified silica samples, resulting in shorter cooling time to reach the target subzero temperature on these samples, in comparison with the rough modified wood samples the largest freezing time characteristics data (the complete bars in Figure 3-9) are observed on the flat silica surfaces.

When comparing the freezing characteristics of the rough modified wood surfaces, the one with multi-scale roughness, i.e., wood-TiO$_2$-HMDSO provides a small benefit at -4 °C, whereas no significant effect is observed at -7 °C (Figure 3-9). Based on the discussions on Figure 3-8, ice nucleation is predicted to be most enhanced on the concave sites with the smallest radius, providing water can penetrate these sites. Similarity in the freezing delay time at -7 °C for these two modified wood surfaces, despite their different topography, suggests that significant frost formation at this temperature facilitates entering of supercooled water
into the surface depressions to a similar extent on these surfaces. However, the enhanced hydrophobicity and the smaller wetting hysteresis for the wood-TiO$_2$-HMDSO surface in comparison with wood-HMDSO surface, discussed in section 3.1.2 (see Table 3.1 and Figure 3-4), still promote the freezing delay at the supercooling temperature of -4 °C. I attribute this to less frost formation during the time scale of our measurement ($\approx 640 \pm 360$ s below 0°C) at this temperature.

3.2.3. Superhydrophobics as anti-icing surfaces

This thesis work demonstrate no anti-icing benefit of superhydrophobic surfaces in comparison with flat surfaces with a similar chemistry. I relate this to the wetting transitions on superhydrophobic surfaces at sub-zero temperatures. However, there are contradictory reports in the literatures on temperature-stability of the wetting state on superhydrophobic surfaces [50-57, 104, 144] (see also Paper I and II). Consequently, there is no agreement in the literature about icephobic properties of these surfaces. In particular, where there are reports proposing efficiency [55, 86] of these surfaces for anti-icing purposes, other literature debate their benefit or report no benefit in agreement with our findings in this thesis [82, 104] (see also Paper I and II). In addition, superhydrophobic surfaces have been reported to provide icephobicity under dynamic conditions when an impinging droplet bounces off the surface prior to freezing [55, 84, 104, 145]. I believe the experimental and environmental conditions utilized in different studies are affecting the conclusions. In addition, proposing the anti-icing benefit of a superhydrophobic surface is relevant providing the freezing delay time is compared to a flat reference sample with the same chemistry as performed in our work.

Among reported works that have utilized sessile water droplets (similar to this thesis), a considerable freezing delay times up to several hours has been reported [50, 98] on superhydrophobic surfaces at temperatures down to -20 °C in thermally homogeneous environment utilizing a chamber, where the ambient air never reached supersaturation. I note that in these cases, in absence of a temperature gradient between the surface and the environment promoting water vapour condensation and frost formation, no wetting transition was observed [50, 58] facilitating the anti-icing benefit of superhydrophobic surfaces. However, studying the effect of temperature on the wetting state at a relative humidity of 30% (related to the temperature 23 °C) in a
cooling-heating cycle from about 23 °C to -6 °C and back to about 23 °C by Furuta et al. [59] demonstrated a decrease in the contact angle on both smooth and rough hydrophobic surfaces with decreasing temperature, that was recovered during heating of smooth surfaces whereas wetting hysteresis was observed on rough surfaces. This is in qualitative agreement with our observations. Similar wetting transition was observed by Yeong et al. [58] at high humidity, despite utilizing the thermally homogeneous environment.

Among dynamic (utilizing impinging water droplets) studies, the ones that worked at a dry condition with a controlled low humidity (2-5%) environment [55, 86] report a significant anti-icing benefit of superhydrophobic surfaces in comparison with less hydrophobic surfaces with similar chemistry. Since the Cassie-Baxter wetting state is maintained on the hydrophobic surfaces at low temperatures under low humidity, the droplets could bounce off the surface before they freeze. In addition, reduced heat transfer from the droplet to the surface on superhydrophobic surfaces with air gaps has been proposed to reduce the nucleation rate (by prolonging the time between point II to point III in Figure 2-3) on these surfaces [86]. However, in qualitative agreement with our findings, superhydrophobic surfaces with anti-icing benefit in dry condition studies eventually provided no benefit when utilized at sub-zero temperatures below the dew point, where the condition is changing from dry to humid allowing frost formation [86]. In addition, Jung et al. [82] utilizing droplets impinged on a range of different surface chemistries and topographies report shorter droplet freezing delay time on a superhydrophobic surface in comparison with surfaces with higher wettability.

In conclusion, the anti-icing properties of superhydrophobic surfaces are limited by the wetting transitions toward less hydrophobicity that is dominant in most practical humid environmental conditions, enhancing the effect of concave sites on reducing the energy barrier of heterogeneous ice nucleation, as discussed in section 3.2.2.

3.3. De-icing properties of hydrophilic surfaces

Rather than the limited or non-existent benefit of superhydrophobic surfaces for anti-icing purposes, discussed in the previous section, the findings on de-icing properties of these surfaces are inconsistent as well
The implication of these surfaces for practical de-icing purposes has been reported to be limited due to the wetting transitions induced by temperature changes under humid conditions (in agreement with our findings, reported in section 3.2.3), as well as failing to stay mechanically durable during icing/deicing cycles [54, 93]. This necessitates considering other approaches for design and fabrication of de-icing surfaces. As briefly mentioned in the introduction chapter of this thesis (see section 1.6.1), an approach to enhance the proposed positive effect of the liquid-like layer, at interface of a solid with ice, on reducing the ice adhesion strength is regarded in this study.

I start this section by exploring the de-icing properties of certain hydrophilic surfaces (their characteristics will be described and choosing these surfaces will be motivated) in relation to the state of water interacting with them. In particular, the effect of temperature on the shear ice adhesion strength (see section 1.5.1) on these surfaces is studied. The goal is to illustrate what surface chemistry and characteristics could promote formation of hydration water remaining in the liquid state at well below 0 °C, facilitating ice removal by shear forces due to a lubrication effect. Further, utilizing temperature-controlled measurements down to -25 °C, described in section 2.2.3, it is attempted to understand whether and how temperature influences ice adhesion strength and ice removal responses. I continue this section by studying the de-icing properties of molecularly smooth hydrophilic mica surfaces hypothesized to induce a lubricating layer at the interface towards ice at temperatures below 0 °C, resembling the quasi-liquid layer providing the slippery nature of the ice surface [96]. The findings from temperature controlled-shear and centrifuge (see section 1.5.1) ice adhesion measurements on the basal plane of mica will be discussed in connection with the reported mica-water and mica-ice interactions (see also Paper V).

3.3.1. Branched brush layers of poly(ethylene oxide)

Two bound states have been proposed for the water associating to hydrophilic polymers chains: non-freezable (with no first order thermal transition down to -100 °C [146-148]), and freezable bound water. Though the association of the freezable bound water, that will be referred to as "hydration water" in this thesis, is weaker in comparison with the
first state type, its melting temperature is reduced below 0 °C due to the presence of the polymer. In this work I study how the adsorbed layer of polymers with poly(ethylene oxide), abbreviated as PEO, chemistry with different structures could promote the formation of the associated hydration water, with melting point well below 0 °C, facilitating the ice removal from the surface at relevant temperatures. Choosing PEO chemistry for this study is motivated by its large implication in active anti-icing materials [149] as well as proposing anti-fouling, -protein, -cell and -bacteria properties attributed to their hydration [150-151] and steric [152-154] effects. In particular it is reported that each ethylene oxide group is hydrated [155-156] by 2-4 water molecules [150-151, 157] through hydrogen bonding of the water molecules with the ether oxygen [151, 158].

For this study I utilized flat fused silica substrates (with roughness ($R_a$) of less than 0.5 nm) modified with the adsorbed polymer layers listed in Table 2-1 (see also Paper IV). The polymer referred to as “diblock copolymer” is a diblock copolymer, (METAC)$_m$-b-(PEO$_{45}$MEMA)$_n$, with a linear cationic block, (METAC)$_m$, and an uncharged bottle-brush block with PEO side chains (PEO$_{45}$MEMA)$_n$. The molecular structures of this polymer and the corresponding two homopolymers are presented in Figure 3-10.

![Figure 3-10: Molecular structure of (a) (METAC)$_m$, (b) (PEO$_{45}$MEMA)$_n$, and (METAC)$_m$-b-(PEO$_{45}$MEMA)$_n$.](image)

The number average molecular weight ($M_n$) and the number of ethylene oxide repeating units ($N_{PEO}$) for these polymers are reported in Table 3-6. As studied thoroughly elsewhere [159-161], this diblock copolymer with strong electrostatic anchoring combined to a branched bottle-brush structure provides a water rich (> 90 wt%) thick layer (> 45 nm) on silica benefiting lubrication in water. This prompts utilization of
this sample for our study. The ice adhesion strength as a function of temperature was studied on the layer formed by this diblock copolymer, as well as on layers formed by its two blocks separately, using the two other samples referred to as "cationic polymer" and "bottle-brush polymer" in Table 2-1. In addition, a linear polymer PEO (with a molecular weight resulting in similar number of ethylene oxide repeating units ($N_{EO}$) to the other polymers with PEO chemistry, see Table 3-6) was also utilized for exploring the effect of polymer architecture on ice adhesion.

Table 3-6: Number average molecular weight ($M_n$) and number of ethylene oxide repeating units ($N_{EO}$) of the cationic polymer (METAC)$_m$, the non-ionic bottle brush polymer (PEO$_{45}$MEMA)$_n$, the diblock copolymer (METAC)$_m$-b-(PEO$_{45}$MEMA)$_n$ and the linear PEO.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_n \times 10^{-3}$</th>
<th>$N_{EO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>* (METAC)$_m$</td>
<td>22.1</td>
<td>0</td>
</tr>
<tr>
<td>* (PEO$_{45}$MEMA)$_n$</td>
<td>257</td>
<td>5600</td>
</tr>
<tr>
<td>* (METAC)$<em>m$-b-(PEO$</em>{45}$MEMA)$_n$</td>
<td>235</td>
<td>4600</td>
</tr>
<tr>
<td>** linear PEO</td>
<td>200</td>
<td>4540</td>
</tr>
</tbody>
</table>

*characterized by size exclusion chromatography (SEC)
**reported by the manufacturer

*Study of state of water using differential scanning calorimetry (DSC)*

The state of water in solutions containing the polymers used for surface modification of the samples used in the ice adhesion studies was investigated utilizing differential scanning calorimetry (DSC), see also Paper IV. DSC cooling and heating thermograms for aqueous solutions of the polymers were obtained by cooling the hermetically sealed sample pans from 25 °C to 2 °C, and then further to -80 °C at a rate of 10 °C min$^{-1}$ and 2 °C min$^{-1}$, respectively. The samples were allowed to stay at -80 °C for 10 min, followed by heating to 30 °C at a rate of 1 °C min$^{-1}$. During cooling, a sharp exothermic peak is observed in the temperature range -18 ± 3 °C for all polymer solutions, where the position of this peak was scattered for the replicates of each polymer solution. This peak is attributed to crystallization of supercooled free water in the polymer solution that explains the variation in the peak position due to the stochastic nature of ice nucleation. No exothermic peak is observed for the freezing of hydration water in agreement with literature data reporting the low rate of freezing for this type of water [150, 157, 162]. On the other hand, the
heating thermograms of the frozen solutions demonstrate two endothermic peaks, referred to as "Peak H1" and "Peak H2" in Figure 3-11. This is in agreement with previous reports [150, 157, 162-164] on freezing of aqueous solutions of linear polymer PEO using DSC. Melting of frozen hydration water results in Peak H1 at temperatures well below 0 °C, where melting of ice results in Peak H2 at about 0 °C. Only one peak (Peak H2) is observed for the (METAC)_m polymer solution, demonstrating the absence of significant amount of the hydration water bound to the polymer. Similar appearance of Peak H1 at about -18 °C for solutions of (PEO_{45}MEMA)_n and (METAC)_m-b-(PEO_{45}MEMA)_n reveals the role of the non-ionic block of the copolymer, in particular the hydrophilic PEO side chains, on promoting the formation of hydration water. However, the hydration water associated with linear PEO melts at a significantly higher temperature (at about -10 °C, and similar to the literature data [157, 163]) in comparison with the polymers with the bottle-brush structure of PEO. This proposes different organization of the hydration water next to the linear and branched bottle-brush PEO polymer, hypothetically due to the high density of PEO chains in the branched bottle-brush structure.

\[ \text{Figure 3-11: A representative DSC-heating curves of aqueous solutions of (METAC)_m, (PEO}_{45}\text{MEMA})_n, (METAC)_m-b-(PEO}_{45}\text{MEMA})_n, \text{and linear PEO.} \]
**Temperature-controlled ice adhesion measurements**

When detaching ice from a surface the actual break may be observed at the ice-solid interface, i.e., adhesive failure, or within the ice, i.e., cohesive failure. At a certain temperature the failure will be adhesive provided the ice-sample adhesion strength is lower than the ice cohesive strength. The cohesive strength of ice is reported [133, 165-166] to be between 1000 kPa to 3500 kPa in the temperature range of -5 to -25 °C.

Figure 3-12 illustrates three types of responses observed during shear ice adhesion measurements. Moving the ice cylinder along the surface under a relatively low force is referred to as "sliding" response, where adhesive failure was observed (see the red curve in Figure 3-12). I note that this response was detected at temperatures closer to 0 °C. "Sudden break", the black curve in Figure 3-12, is referring a response where the ice cylinder remained fixed on the surface until suddenly breaking at a certain applied force. This response was favored at lower temperatures. The third response (see the blue curve in Figure 3-12), i.e., "intermediate", was detected at the temperature border between the other two responses, referring to the case that the cylinder was found to slide for a certain distance followed by suddenly breaking off from the surface. The failure could be either adhesive or cohesive for the sudden break or intermediate responses.

![Figure 3-12: Three different ice detachment responses observed during shear ice adhesion measurements.](image-url)
The measured shear ice adhesion strength on flat silica substrate \((R_a < 0.5 \, \text{nm})\) with an adsorbed \((\text{METAC})_m-\text{b-(PEO}_{45}\text{MEMA})_n\) layer, is presented in Table 3-7. Measurements noted as "2\(^{nd}\)" were performed directly after the first measurements, noted as "1\(^{st}\)", on the same spot on each sample. The data for the bare silica sample are reported from the work by Tyrode and coworkers [129], where exactly the same type of silica substrate was studied using the same procedure and device utilized in this thesis.

Table 3-7: Shear ice adhesion strength as a function of temperature for diblock copolymer sample (silica coated with an adsorbed layer of the diblock copolymer). Two consecutive measurements on each sample are noted as 1\(^{st}\) and 2\(^{nd}\). The mean values and the standard deviations are determined from at least 5 measurements on each type of sample at each temperature.

<table>
<thead>
<tr>
<th>temperature (^{\circ}\text{C})</th>
<th>shear ice adhesion strength (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>diblock copolymer (1(^{st}) measurement)</td>
</tr>
<tr>
<td>-5</td>
<td>10±5</td>
</tr>
<tr>
<td>-10</td>
<td>80±50</td>
</tr>
<tr>
<td>-15</td>
<td>290±60</td>
</tr>
<tr>
<td>-20</td>
<td>370±70</td>
</tr>
<tr>
<td>-25</td>
<td>580±170</td>
</tr>
</tbody>
</table>

* data from ref [129]

As shown in Table 3-7, the ice adhesion on bare silica is significantly reduced in the presence of the diblock copolymer layer. Sliding response (see Figure 3-12) and adhesive failure were observed at temperatures \(\geq -10\) \(^{\circ}\text{C}\). At lower temperature of -15 \(^{\circ}\text{C}\) and -20 \(^{\circ}\text{C}\) the shear ice adhesion strength increased to about 300 and 400 kPa, respectively, where the intermediate response was observed (see Figure 3-12). At -25 \(^{\circ}\text{C}\) the shear ice adhesion strength increased further, and the ice cylinder was detached from the surface with a sudden break response, and the failure was cohesive leaving remnant of ice on the surface.

The 2\(^{nd}\) measurements on the same spots at temperatures of -5 \(^{\circ}\text{C}\) and -10 \(^{\circ}\text{C}\) are consistent with the findings from the 1\(^{st}\) measurements though slightly higher values were obtained. However, the results significantly deviate from the 1\(^{st}\) measurements when the temperature is decreased further. I attribute this to partial removal of the adsorbed polymer layer from the substrates resulting from the applied shear forces (increasing with decreasing temperature) during the 1\(^{st}\) measurements. It should be
noted that for the bare silica reference surfaces cohesive failure was always observed at \( \leq -20 \, ^\circ\text{C} \).

The findings from the DSC study (see Figure 3-11) demonstrating the presence of hydration water with melting point at about \(-18 \, ^\circ\text{C}\) for bulk polymer solutions, could explain the low shear ice adhesion strength on the hydrophilic \((\text{METAC})_m\text{-b-(PEO}_{45}\text{MEMA})_n\) layer (see illustration in Figure 3-13). Presence of a thin liquid-like layer is proposed for explaining some benefits also at even lower temperatures.

![Figure 3-13: Schematic illustration of the lubrication effect of hydration water, bound to the thin polymer layer of branched bottle-brush structured PEO, at the interface of ice with a flat surface.](image)

Table 3-8: Shear ice adhesion strength at \(-10 \, ^\circ\text{C}\) on adsorbed layers of the cationic, linear PEO, bottle brush polymer and the diblock copolymer on silica substrates. Data for diblock copolymer sample and bare silica are reproduced from Table 3-7 for comparison. Two consecutive measurements performed on each sample are noted as 1\(^{st}\) and 2\(^{nd}\). The mean values and the standard deviations are determined from at least 5 measurements on each type of sample.

<table>
<thead>
<tr>
<th>surface</th>
<th>shear ice adhesion strength (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1(^{st}) measurement</td>
</tr>
<tr>
<td>cationic polymer</td>
<td>270(\pm)90</td>
</tr>
<tr>
<td>linear PEO</td>
<td>340(\pm)30</td>
</tr>
<tr>
<td>bottle-brush polymer</td>
<td>100(\pm)30</td>
</tr>
<tr>
<td>diblock copolymer</td>
<td>80(\pm)50</td>
</tr>
<tr>
<td>bare silica</td>
<td>450(\pm)100</td>
</tr>
</tbody>
</table>

I continue this section by describing the results of ice adhesion measurements on surfaces with adsorbed layer of the two polymer blocks of \((\text{METAC})_m\text{-b-(PEO}_{45}\text{MEMA})_n\), in order to illustrate the role of these homopolymers on the de-icing properties of the diblock copolymer layer.
Further, the ice adhesion results on the adsorbed layer of linear polymer PEO will be reported to get across the effect of the polymer architecture. I note that the previous studies [160], demonstrated lower adsorbed amount and water content of the layers formed with homopolymers compared to the diblock copolymer layer (see Paper IV for more discussions). The results for two consequent measurements, i.e., 1\textsuperscript{st} and 2\textsuperscript{nd}, at a temperature of -10 °C are reported in Table 3-8.

The bottle-brush homopolymer layer presents similar response as well as low shear ice adhesion strength, about 100 kPa, to the diblock copolymer during the 1\textsuperscript{st} measurements. I note that also at -5 °C and -15 °C similar results for these two polymers were obtained (see Figure 6 in Paper IV). This correlates well with the DSC data (see discussions for Figure 3-11) revealing a similar thermal transition for the hydration water associated with the bottle-brush polymer to that associated with the diblock copolymer. However, the significant increase in shear ice adhesion strength to about 300 kPa during the 2\textsuperscript{nd} measurements, suggests that the adsorbed polymer layer is significantly removed from the substrate during the 1\textsuperscript{st} measurement. This is explained by the weak non-electrostatic affinity of this non-ionic polymer to the silica substrate. Consequently, the effect of these two polymers on the shear ice adhesion strength, related to their hydrated water-thermal transition, is similar providing the polymer layer covers the surface. The data in Table 3-8 for the adsorbed layer of the linear-PEO illustrates the significantly higher shear ice adhesion strength, about 340 kPa, already during the 1\textsuperscript{st} measurement. This is supported by the lower adsorbed mass reported for this polymer elsewhere [167] (see also Paper IV), lower surface affinity [168] in comparison with (PEO\textsubscript{45-MEMA})\textsubscript{n} with bottle-brush architecture, as well as higher melting point of the hydration water (see Figure 3-11). In the case of the adsorbed layer of the cationic polymer, (METAC)\textsubscript{m}, a high shear ice adhesion strength was measured with the intermediate response (see Figure 3-12). This high adhesion is also suggested by the DSC findings, detecting no hydration water. The similar ice adhesion values on the first and second measurements for linear PEO is explained by its initial low adsorption, consequently absence of a full coverage on the surface, resulting in the high ice adhesion already during the first measurement. However, I relate the increase in the measured shear ice adhesion strength at the 2\textsuperscript{nd} measurements for the other samples, as seen
in Table 3-8, to partial removal of the adsorbed polymer layers from the substrates during the 1st measurements.

In summary, the hydration water of the PEO chain can lubricate the interface of a hydrophilic flat surface with ice. This effect is attributed to the presence of a liquid-like layer, and it is relevant down to the temperatures where the liquid-like state remains. Further, the PEO chain structure was found to affect the temperature-dependent association of water and consequently the de-icing properties, where the bottle-brush structure is suggested to be beneficial in comparison with the linear structure.

3.3.2. Basal plane of mica

In this section I continue by exploring the hypothesis, inspired by the natural lubrication of the quasi-liquid layer on the ice surface, that a hydrophilic surface with a hydration layer in the liquid-like state at sub-zero temperatures is desired for de-icing. This study is further motivated by the findings from the previous section (3.3.1) demonstrating the positive effect of the hydration layer.

Hydrophilic muscovite mica, a layered aluminosilicate mineral [169-170] (see Paper V for details), cleaved to expose a molecularly smooth surface [171-172] that will be referred to as mica in this thesis, was utilized for the study presented in this section. Though the water contact angle of close to zero degrees on mica suggests a high ice adhesion strength [16], using mica in this study is encouraged by first, the interesting findings in the area of mica-water and mica-ice interactions, and second the molecularly flat surface of mica. These matters and their consequences on ice adhesion will be discussed further in connection with the experimental results.

Shear ice adhesion strength on mica

Figure 3-14 presents the values for shear ice adhesion strength measured on mica at temperatures ranging from -10 °C to -35 °C utilizing the same device [129] used in previous section (3.3.1). The data for bare silica surfaces (with \( R_a \) below 0.5 nm) [129] are reproduced from Table 3-7 for comparison. As illustrated in Figure 3-14, the ice adhesion strength shows a weak tendency to increase as the temperature decreases down to -35 °C, where even at this temperature the average ice adhesion strength remains
below 30 kPa. I note that the sliding response (see Figure 3-12) with adhesive failure was observed in the whole temperature range studied, where the ice slides across the surface by applying a very small force (see Figure 1 in Paper V). In contrast, the ice adhesion strength on the silica surfaces was found to be drastically larger, where the adhesion increases with decreasing temperature. Further, as mentioned in section 3.3.1 and described in detail by Tyrode and coworkers [129], in the case of flat silica the ice removal is altering from a sliding response with adhesive failure at -15 °C to sudden break response (see Figure 3-12) with cohesive failure at temperatures below -20 °C.

I note that by performing the centrifugal ice adhesion test (see section 2.2.3) on ice cubes formed in a wind tunnel (see section 2.2.3) on mica surfaces at -10 °C, with the aim to study the possible effects of the ice accretion method on the ice adhesion strength [89], I also found similar values as reported in Figure 3-14, about 34±10 kPa.
Superior de-icing properties of mica hypothesized to be due to mica-water interactions and the molecular flat nature of the surface

An ordered hydration layer on mica has been demonstrated by extensive theoretical and experimental studies on interactions of mica with water [171, 173-178] (see Paper V for more details). Sum-frequency-generation (SFG) vibrational spectroscopy study at room temperature and relative humidity of about 90%, suggested a strongly hydrogen bonded water layer on mica [179], confirmed by molecular dynamics simulations [180]. In particular, a 2D ice-like epitaxial water monolayer, where all water molecules are hydrogen bonded to another or to mica, thus no free OH-groups, has been proposed. In particular, scanning polarization force microscopy (SPFM) and AFM studies demonstrated a thin solid ice layer (about 0.3-0.7 nm thick) on mica covered with continuous supercooled liquid-like layer in the temperature range -20 °C to -10 °C, changing to supercooled water droplets at temperatures below -30 °C [181]. No growth of supercooled water droplets was noted unless cooling further to -45 °C to provide strong supersaturation. The thin first ice layer was related [181] to the 2D ice-like water layer with no free OH group suggested by the SFG study on mica at room temperature [179]. Meanwhile, the presence of the liquid-like layer and supercooled droplets observed by SPFM at well below 0 °C [181] was proposed to be related to the about 10% mismatch between the mica and ice lattice structures [173] which counteracted further ice growth.

The ultralow ice adhesion strength on mica is proposed to be related to the lubrication effect of the liquid-like layer on top of the first thin ice-like layer, with no free OH groups, on the basal plane of mica, demonstrated down to below -30 °C [181]. I note that the molecularly flat surface of mica, with sub-nm scale roughness, could enhance the lubrication effect of this nm thin layer.

On the other hand, the presence of a liquid-like layer also on silica is proposed by the combined spectroscopic and ice adhesion studies on silica [129], giving rise to the sliding behavior at -10 °C. Though silica surface \( (R_a < 0.5 \text{ nm}) \) is rougher than the basal plane of mica (rms roughness 0.025 nm) [182], explaining their largely different ice adhesion strength based on their surface roughness difference is implausible. Consequently I suggest that the ultralow ice adhesion could be achieved on a very smooth surface, providing the structure and interaction across
the liquid-like layer at the interface with ice could induce the sliding with limited energy dissipation.

Figure 3-15: Schematic illustration of the proposed effect of the interactions of molecularly smooth mica (the left scheme) and nm smooth silica (the right scheme) with ice, on the required shear force for de-icing.

In conclusion, a plane for easy ice sliding on mica is suggested to be provided by the distinct different structure of the first ice-like layer (with no site for further hydrogen bonding), and the subsequent liquid-like layers. In contrast, a high density of surface silanol groups on silica surface [183] promote the hydrogen bonding with ice, reported to increase the ice adhesion strength [184]. The proposed effect of the surface chemistry and structure of these smooth hydrophilic surfaces, i.e., mica and silica, on the interactions with water molecules, and thus the ice adhesion strength is illustrated in Figure 3-15.
4. Conclusions

The aim of this thesis is to understand how surface characteristics, such as chemistry, topography, morphology, surface curvature and structure, in particular in local nano-scale, could influence the water wetting properties and stability, specifically at sub-zero temperatures, as well as ice formation and adhesion on the surface. This understanding is very important for designing surfaces that resist or retard ice formation (anti-icing), and/or reduce ice adhesion (de-icing).

In the first part of this thesis (section 3.1) the role of surface morphology of hydrophobic surfaces, having different wetting states, on the stability of their wetting properties at room temperature, and also when subjected to low sub-zero temperatures, as well as, in a freeze-thaw cycle was investigated through temperature controlled water contact angle measurements. It was demonstrated that surface multi-scale (micro-nano) roughness, positively affected superhydrophobicity, indeed results in significantly enhanced dynamic wetting stability in comparison with micro-scale rough surfaces with a similar chemistry at room temperature. However, this effect is much diminished in a freeze-thaw cycle that facilitates condensation and frost formation on the surface. Further, in a similar environmental condition, a wetting transition toward lower hydrophobicity and sticky states was observed on the nanostructured superhydrophobic surfaces at low temperatures when water is supercooled. This suggests limited efficiency of superhydrophobic surfaces for anti-icing purposes, unless condensation and at sub-zero temperatures frost formation are avoided by controlling the environmental conditions. In summary, flat hydrophobic surfaces show the highest wetting stability when subjected to low temperatures.

In the second part of this work (section 3.2), I explored the anti-icing properties of the hydrophobic surfaces, with different topography, and studied the freezing delay. The freezing delay measurements on supercooled sessile water droplets on the nanostructured surfaces reveal no benefit of superhydrophobic surfaces. However, the flat surfaces show
a tendency to prolong the freezing delay in comparison with superhydrophobic surfaces or rough hydrophobic surfaces with a similar chemistry. These findings are in agreement with the classical heterogeneous ice nucleation theory, suggesting that the energy barrier of ice nucleation is lowest on concave sites. Based on the theory the size of the critical ice nucleus is calculated to be few nm, thus I suggest that the local nano-scale surface energy and curvature of the surfaces are involved in ice nucleation and should be considered. Further, the negative effect of the surface concave sites on freezing delay was more pronounced in the case of micro-rough hydrophobic surfaces in comparison with nanostructured hydrophobic surfaces, suggesting facilitated penetration of supercooled water in the surface concave sites in the case of micro-rough surfaces. However, in agreement with the study on nanostructured surfaces, flat hydrophobic surfaces with a similar chemistry to the micro-rough surfaces proposed the longest freezing delay. Finally based on the findings from this study and the previous part, flat hydrophobic surfaces are proposed to enhance anti-icing properties in practical situations inducing condensation and frost formation, however superhydrophobic surfaces could still be beneficial in the cases that the droplet rolls off or bounces off the surface prior to freezing.

The third part of this thesis (section 3.3) focuses on an approach for designing de-icing surfaces, inspired by the slippery surface of ice related to a quasi-liquid layer existing naturally on the ice surface. For this purpose, temperature controlled-shear ice adhesion strength measurements were performed on flat hydrophilic surfaces covered with nm thin polymer layers incorporating poly(ethylene oxide) chemistry, demonstrated to promote formation of a hydration layer that remains in the liquid state down to -18 °C (for bulk solution of a polymer with bottle-brush structured poly(ethylene oxide)). Indeed, a significant ice adhesion reduction was observed on these surfaces in a temperature range that the formation of a liquid-like layer is promoted by the hydration water. This illustrates the lubrication effect of the liquid-like layer induced by poly(ethylene oxide) chemistry. However, a linear structured poly(ethylene oxide) was less efficient in ice adhesion reduction in agreement with findings on the sub-zero temperature state of water interacting this polymer. Motivated by these findings the de-icing advantages of the molecularly flat basal plane of hydrophilic mica was studied. Though the ice adhesion strength is expected to be large on mica
with almost zero contact angle, I found ultralow adhesion on this surface down to -35 °C. It is explained by the proposed distinct structure of the first ice-like layer on mica [181], with no free OH groups for further hydrogen bonding, followed by liquid-like layers on top that provide a plane for sliding of ice by very small forces. The effect of this lubrication layer is suggested to be enhanced by the molecularly flat surface of mica. However, no such benefit was observed for smooth silica surfaces with a demonstrated liquid-like layer at the interface with ice [129]. Thus, it is speculated that the structure and interactions across this layer is the key parameter promoting the ice sliding with limited energy dissipation.
5. Future work

In this thesis I explored the effect of topography on the anti-icing properties of surfaces, and reached the conclusion that in an environmental condition where frost could form on surfaces, freezing of supercooled water droplets are delayed most significantly on hydrophobic surfaces that are flat. This could be further studied utilizing flat hydrophobic surfaces with a chemistry promoting the hydrophobicity and with smaller local nano-scale surface features than those used in this thesis work, resulting in even higher contact angle for the ice nucleus on the surface. This kind of flat hydrophobic surface is expected to present the largest freezing delay. Further, the effect of surface topography on the kinetics of ice nucleation from supercooled water as the parent phase, investigated in this thesis work, could be expanded with the aim to understand the effect of topography on the ice nucleation from the vapor phase. Such a study could be performed utilizing non-contact microscopy, such as scanning polarization force microscopy (SPFM), to image the growth of ice from the saturated environment with respect to water vapor.

In my thesis I report the effect of temperature on wetting transitions of hydrophobic surfaces by contact angle measurements. These wetting transitions could be imaged using sessile water droplets on model hydrophobic and superhydrophobic surfaces with tuned structural dimensions using techniques such as X-ray computed tomography at sub-zero temperatures. This would directly demonstrate the wetting transitions. A similar study could be conducted to illustrate the wetting transitions with respect to the relative humidity close to the surface when there is a gradient between the surface and the ambient.

Further, the results presented in this thesis propose a de-icing benefit of flat hydrophilic surfaces with a hydration layer. Better understanding of the effect of the hydration layer on the ice adhesion strength can be achieved utilizing surface chemistries promoting this layer. I note that utilizing surface sensitive techniques to study the interactions of these
surfaces with water at room temperature as well as with ice below 0°C would provide a deeper understanding. In particular and related to this thesis work, vibrational sum frequency spectroscopy (VSFS) on mica surfaces at different relative humidity at sub-zero temperatures could provide additional understanding. In addition, digging into structure and dynamic of water and ice at the interface with a solid surface will enhance our insight on the ice adhesion strength on different types of surfaces.

It would also be motivated to explore other approaches for designing ice-phobic surfaces, such as utilizing flat hydrophobic surfaces with low elastic surface modulus, which could enhance the de-icing properties. This is promoted by a mismatch in strain for ice and the solid surface when a force is applied to remove ice. This approach could be evaluated in the case of hybrid materials where the outermost layer of a hydrophobic elastomeric material is modified with a hydrophilic chemistry whereby promoting the hydration layer effect. In this case the effect of surface modulus is expected to be combined with the lubrication layer effect. Further, the idea of slippery liquid-infused porous surfaces (SLIPS) could be promoted by encapsulation systems, where the lubrication fluid is released from the bulk of the material to the surface providing the ice-release.
6. Acknowledgements

I am really thankful to have many great people around, supporting me during these PhD years. First, I would like to thank my main supervisor, Prof. Per Claesson. Thanks for giving me the opportunity to work these years under your supervision. I could not ask for a better supervisor, I am so proud of working with such a smart, curious and scientific person who is amazing personally as well. You kept me motivated and relaxed all through these years with your unique smile. I still wonder how you comment wisely on a subject that you hear for the first time! I am really grateful for having you as my supervisor! My co-supervisor, Assoc. Prof. Eric Tyrode, your valuable scientific inputs are the first to be thankful. I also appreciate your criticism and guides. My co-supervisors in the beginning of this journey, Assoc. Prof. Esben Thormann, Assoc. Prof. Andra Dedinaite, thank you so much for all your support and great discussions at meetings, down in the labs and your life lessons. I really learned from those meetings with a big supervisory team though sometimes nobody agreed to the other! Prof. Agne Swerin, thank you very much for involving me in this beautiful and challenging project. I learned a lot from TopNANO project that you led. I should also thank Top-level Research Initiative and Nordic Innovation for financial support within the TopNANO project. As well as all representatives from academic and industrial partners within Nordic countries for their valuable inputs.

I would like to thank all co-authors, Dr. Maziar Sedighi, Dr. Mikko Tuominen, Dr. Matthew Fielden, Janne Haapanen, Prof. Jyrki Mäkelä, Prof. Magnus Wålinder, Prof. Ricardas Makuska, Dr. Ceslav Visnevskij, Christian Stenroos, Dr. Helē Koivuluoto for your scientific collaboration. Dr. Mikael Järn, you were not only a co-author, you were a consultant and a good friend to me in these years. I always had something to ask you and you always got back to me with a proper answer. Thank you so much!

I would like to thank all my colleagues and seniors at division of surface and corrosion science for making 8 hours of my everyday life happier during these years. All my office mates, Gunnar, Hiro, Xin, Chao,
Dr. Peter Szakalos, Saman, Sulena, Nicklas, all beautiful girls of surfcorr., especially Zahra, Neda, Eleonora, Akanksha, Sara, Deborah and Shadi, thanks to you I did love my second home. Shadi, I trusted your long list of motivation to do PhD in this division and now I believe you were right. Thanks for your support during the first year. I would like to dedicate a special thanks to colleagues at KTH and SP who kindly helped me during this research, Kenth Johansson, Rodrigo Robinson, Xiaoyan Liu, Lukas Boge, Marie Erntsson, Petra Mille, Johan Andersson, Asaf Oko, Lisa Skedung, Lina Ejenstam, Annika Dahlman, Karin Hallstensson. Jonathan Liljeblad, thanks for your support in ice adhesion study. Mikael Sundin, thank you very much for your creative mind helping me in practical problems, always!

I would like to express my deepest gratitude to my family. My lovely dad you have always been my mentor in life. I have never seen a person like you, living without judging anybody and just seeing the good part of people. You always wanted me to be a good human before anything else, I hope I have not disappointed you. My amazing, energetic mum, you always encouraged me to fly to my dreamland and expressed your deepest love on my way. I love both of you and try to follow you and keep smiling, no matter where, no matter when! My sweet sister, Ghazal, I am really blessed to have you and your happy hubby, Yousef-Dariush. So glad that we are so close in heart, and thanks for being here and supporting me from time zero of this journey. Cannot wait to HUG your little one soon!

My love, Maziar, you have been best of everything to me. Best classmate, best friend, best colleague and best husband. We made several difficult decisions together and ended up in being proud. I cannot imagine how else you could support me during these years, even before I ask! Thank you!

My life, Golsa, when you laugh "nothing else matters". I could not believe a little kid can be such wise. You understood me better than me, I think our heart is really connected. You make me proud when you walk happily and count how many people you love in the world. This is all I want for you, to love and to be loved. Mummy promises the funniest plays, soon!
References


149. Itagaki, K., Polyethylene Glycol as an Ice Control Coating. 1984: US Army Corps of Engineers, Cold Regions Research & Engineering Laboratory.


156. Tyrode, E., et al., Hydration state of nonionic surfactant monolayers at the liquid/vapor interface: structure determination by vibrational sum


