On the Physics of Icing and the Rational Design of Surfaces with Extraordinary Icephobicity

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ABSTRACT

Icing of surfaces is commonplace in nature and technology, affecting everyday life and sometimes causing catastrophic events. Fundamental understanding and handling of surface icing are very challenging problems which require interdisciplinary knowledge from diverse scientific fields, such as: nucleation thermodynamics and heat transfer; fluid dynamics; surface chemistry and surface nanoengineering. Here we discuss key aspects and findings related to the physics of ice formation on surfaces and show how such knowledge could be employed to rationally develop surfaces with extreme resistance to icing (extraordinary icephobicity). While superhydrophobic surfaces with micro-, nano-, or (often biomimetic) hierarchical roughnesses have shown in laboratory settings under certain conditions excellent repellency and low-adhesion to water down to temperatures near or below the freezing point, extreme icephobicity necessitates additional important functionalities. Other approaches, such as impregnated ultra-smooth hydrophobic surfaces, exhibit both advantages and serious limitations with respect to icing. In all, a clear path toward passive surfaces with extreme resistance to ice formation remains a challenge, but it is one well worth undertaking. Equally important to potential applications is scalable surface manufacturing and the ability of icephobic surfaces to perform reliably and sustainably outside the laboratory and under adverse conditions. These include hostile environments in terms of the surface mechanical, chemical, and thermal resilience. Such issues and related research directions are also addressed in this article.

1. Introduction

Due to its ubiquitous nature, and the serious safety, production, and performance issues it poses, ice formation is a research topic that has received considerable attention. In recent years, as a result of the emergence of methods of surface nanoengineering and the (related) vivid interest of the research community on the topic of superhydrophobicity, the goal of development of surfaces with *extraordinary resistance to ice formation and retention* is taking center stage in the activities of many researchers, bringing with it a host of additional challenges. One could loosely use the term *supericephobicity* for such surfaces, but with the qualifier that no consensus for a quantifiable definition of this term exists in the literature so far.

Many aspects of icing remain poorly understood—and are therefore difficult to predict—due to the relative complexity of the problem. It is a multiphase process, which is highly sensitive to environmental conditions, and it is based on water, which has unique physical properties and complex behavior. This is an important point, since any serious attempt at generating an icephobic (ice repellent) surface is based on the premise that a good understanding of its underlying mechanisms is in place, or needs to be attained first. Thermodynamically, there are three pathways to ice formation: 1) metastable vapor-stable solid; 2) metastable vapor-metastable liquid-stable solid; 3) metastable liquid-stable solid. Each of these phase change processes requires a different type of surface characteristics in order to repel ice. Hence, from an engineering perspective, if one poses the broad question: *What constitutes a truly icephobic surface?* One must often respond: *It depends,* as the environmental and operating conditions affect ice formation greatly.

With these perspectives in mind, the following article provides an overview and vision of how the authors—and other researchers working on similar topics—rationalize their approach to icephobicity. From a knowledge dissemination perspective, icephobicity is becoming a research topic with rapidly increasing presence and impact annually—as defined by citations (see **Figure 1**)—and has broad commercial appeal; however, its success from an application perspective has been limited. Due to its relevance for industrial/commercial applications, this article mainly discusses the following pathways to ice formation: liquid-solid transition and vapor-liquid-solid transition, which are of great importance for icing in nature and many engineering applications. For these transition types, we considered studies in which different environmental conditions, surface geometry, and surface wettability (intrinsic) were investigated, in order to elucidate the nuances of the icing process, and therefore guide the design of high-performance supericephobic surfaces. This approach necessitates a fusion of fluid mechanics (droplet transport and related droplet/surface interactions) and thermodynamics (nucleation theory and heat transfer) in order to rationalize surface engineering. Since there are already some reviews on anti-icing surfaces,[1,2] it is necessary to place this one into context: While previous reviews emphasized biology as a guiding principle for surface construction,[1] or focused solely on the capabilities of superhydrophobic surfaces as a strategy,[2] this review aims to outline a series of works utilizing design principles based upon thermodynamics and fluid mechanics which focused on eliminating the formation of ice on a surface under atmospheric conditions; this stands in contrast to works which emphasize reducing ice adhesion once it has formed. We begin by considering aspects of nucleation theory and heat transfer, and then we move onto transport of droplets in a metastable liquid phase (supercooled). We subsequently combine and utilize these two perspectives to rationalize the construction of engineered icephobic surfaces. We give due consideration to the need for long-term performance (also under adverse conditions) and the scalability of a given fabrication process, since industrial implementation is generally the final, long-term goal of these efforts. With all of this, we give some final thoughts on where we think the research is headed and what the big problems to surmount are.

2. Ice Nucleation Considerations: Towards Rational Icephobic Surface Design

A rational surface design and engineering techniques to control icephobicity presuppose a substantial understanding of ice nucleation as the origin of phase transformation in nature and technology. To facilitate the discussion, **Figure 2** shows a schematic representation of the relevant effects and parameters for describing the ice nucleation physics. **Figure 2a** shows the condition required for homogeneous nucleation to proceed, which is depicted in the classic plot of the change in Gibbs free energy (ΔG) vs. ice embryo radius (r). **Figure 2b** shows spatially where nucleation can occur within a liquid droplet: at the free interface (homogeneous nucleation) or at the solid interface (heterogeneous). **Figure 2c-d** show how surface curvature can affect the formation of a critical ice embryo (increasing ice-water contact angle or inhibiting adsorption of water molecules to the embryo interface).

Strategies to prevent ice formation—and therefore ice nucleation—on surface structures have been studied intensively since the 1950's.[3] If we look to nature for inspiration, biological organisms have adopted a number of strategies to survive cold climatic conditions, including the so-called *antifreeze protein* (AFP).[4] AFPs in fish living in polar climates can depress body fluid freezing down to -2°C, and AFPs in insects can prevent freezing down to temperatures as low as -10°C.[4] The anti-freezing character of AFPs is explained by several factors: 1) their high affinity to adsorb (migrate) to the water ice front (liquid-solid interface); 2) their excellent structural match to the ice crystal, which inhibits the growth of the ice front (adsorption inhibitor), as illustrated in **Figure 2d**.[5] As a result of the adsorbed AFP's a curved water ice front is formed and locally the melting point is depressed, an effect closely related to the one of surface curvature on nucleation, discussed in the coming subsection.

From a thermodynamic perspective, the precise understanding of the mechanism for ice nucleation, *i.e.*, the process initiating ice crystallization and frost formation, is of fundamental importance for the development of effective and sustainable icephobic concepts, and this is still an open topic. Since two out of the three pathways to ice formation involve a metastable liquid phase, we emphasize nucleation behavior of metastable liquids. In this spirit, we are reviewing, discussing, and proposing anti-icing concepts in the framework of the classical nucleation theory.

2.1. Classical nucleation theory

One of the most common approaches to describe ice nucleation is given by the classical nucleation theory (originally derived by Turnbull, Vonnegut and Fletcher[6]), which has been utilized and further elaborated on by a large number of research groups world-wide. Over the past decade, scientists shed new light upon the sometimes unexpected and unpredictable behavior of supercooled water droplet freezing on hydrophilic, hydrophobic, and superhydrophobic surfaces, varying in surface texture, curvature, and chemical composition.[7–9] The combination of the present nucleation theory—and specific thermodynamic properties of confined/interfacial water in contact with the surface—was employed in a thermodynamic framework for the rational design of robust icephobic surfaces for long freezing delays.[9] It was also used to predict an ideal icephobic surface texture for extremely low nucleation temperatures (the temperature at which spontaneous freezing takes place).

For a new phase to be initiated and grow, favorable conditions for stable nucleation must be fulfilled, *i.e.*, the free energy barrier for ice embryo formation must be overcome (**Figure 2a**). To understand the role of ice nucleation in crystallization events, such as the freezing of water droplets in contact with a solid surface, we consider the ice nucleation rate (J) for a water droplet on a surface, be expressed by[7,9]

$$J = K(T)\exp\left(\frac{-\Delta G(T)}{k_{\mathrm{B}}T}\right), \qquad \mathbf{1}$$

where K is a kinetic pre-factor representing the attraction (adsorption and integration) of free water molecules to a forming ice embryo, ΔG denotes the thermodynamically derived energy barrier for the formation of a critical ice embryo (the minimum stable size a nascent ice crystal needs to reach to initiate freezing), and k_{B} is the Boltzmann constant. As indicated in **Figure 2**a, ΔG can also be seen as maximum work W_{c} (combination of volumetric and surface work) required to form a nucleus of the crystalline phase in the bulk liquid (homogeneous nucleation) or at the interface between the bulk liquid and a solid phase (heterogeneous nucleation). The free energy barrier ΔG and factor K in **Equation 1** depend strongly on the degree of supercooling of the liquid, which will be further discussed. Clearly, theory and experiment show a strong bearing on temperature for the nucleation rate in homogeneous and heterogeneous nucleation as reported in the literature.[6,7,9]

The kinetic factor, $K_{,}$ describes the diffusion of the water molecules across the water-ice interface of the ice nucleus, including the water molecule number density at the ice nucleus-water interface and the diffusion activation energy for a water molecule to cross this interface. One can imagine that the diffusivity of water—expressed by the diffusion activation energy in the factor K— depends not only on temperature, as expressed by the empirical Vogel-Fulcher-Tammann equation,[6] but also on liquid composition, impurities, and thermodynamic boundary conditions. It was demonstrated in numerical simulations by Nistor *et al.*[10] that water molecules making contact with a concave ice-water interface (not solid-water interface) are more likely to be aligned with the ice cluster and freeze directly, while molecules in contact with regions of convex ice-water interfaces tend to move back into the liquid as molecules are unable to migrate into surface pockets (**Figure 2**d).

2.2. Heterogeneous nucleation: The role of surface curvature and the quasi-liquid layer

The change in Gibbs free energy, ΔG, which is the thermodynamic energy barrier for the formation of a critical ice embryo, is a function of temperature and ice-water interfacial energy. The classical nucleation theory shows that the free energy barrier for heterogeneous nucleation is lower than homogeneous nucleation at a given temperature, and this reduction is usually expressed as a ratio (less than unity),

$$f = \frac{\Delta G_{\mathrm{het}}}{\Delta G_{\mathrm{hom}}} \ . \qquad \mathbf{2}$$

This ratio (f) is a function of the roughness radius of curvature R (**Figure 2c**)—that is, not simply the RMS roughness—[9] and the ice-water contact angle (θ_{IW}) which forms at the substrate interface. From nucleation theory we know that at a given temperature, an ice nucleus must reach a critical stable radius (r_{c}) for freezing to initiate and propagate (**Figure 2**a),

$$r_{\mathrm{c}} = \frac{2\gamma_{\mathrm{IW}}}{\Delta G_{f,\mathrm{V}}}, \qquad \mathbf{3}$$

where γ_{IW} denotes the ice-water interfacial energy and $\Delta G_{f,\mathrm{V}}$ represents the difference in volumetric free energy between bulk solid (ice) and bulk liquid, which follows from the Gibbs-Helmholtz equation. For the case when the surface roughness curvature approaches the critical nucleus radius ($R / r_{\mathrm{c}} \approx 1$), the theory reveals a strong bearing of R on ice nucleation. **Figure 3a** shows plots of f for different ice-water contact angle values θ_{IW} on surfaces with convex ($f_{\cap}$) and concave ($f_{\cup}$) surface features as a function of x, where $x = R/r_{\mathrm{c}}$. For concave surface features with $x \approx 1$ and $\theta_{\mathrm{IW}} = 90^{\circ}$ (nanopits), we see that $f_{\cup} = 0.2$ and that nucleation should be well enhanced.

Contrary to the classical nucleation theory, experiments have shown that the freezing delay time and nucleation temperature are constant for a broad range of RMS roughness values (~0.1 to ~100 nm, over 3 orders of magnitude) at approximately -25°C ($r_{\mathrm{c}} = 1.7\,\mathrm{nm}$).[9] In order to account for this discrepancy, a reduced entropy and enhanced viscosity in the hydration layer (*i.e., quasi-liquid layer*) was postulated to exist between the forming ice nucleus and the solid surface, therefore affecting θ_{IW} and ultimately the nucleation rate of ice.[9,11,12] While it is reasonable to accept that the change of properties in this layer is gradual (property gradient between forming ice and solid surface), it is often convenient to employ the quasi-liquid layer presence in theoretical considerations in terms of its average properties taken over a so defined *effective* thickness. In a recent publication,[13] this hypothesis was also underscored by studying temperature-dependent nucleation rates of ice in contact with hydrophilic and hydrophobic surfaces. The nucleation rate calculations revealed the dominant role of interfacial water on the freezing delay. It is shown in the following that the presence of a quasi-liquid layer directly influences θ_{IW} and thus the freezing delay of the surface.

If we revisit **Figure 3a** (plot of $f_{\cup}$) we see that when $x < 10$, *concave* nanopits should promote nucleation, and should therefore dominate the freezing process. Since pits are an unavoidable byproduct of making bumps, one would expect all nanotextured surfaces to enhance nucleation, not suppress it. However, if a quasi-liquid layer forms at the interface between an ice embryo and a solid surface, this may counteract any ice nucleation promoting effects of concave nanopits (**Figure 3**a).[9] This is due to the fact that both the quasi-liquid layer thickness and the effective (through the presence of the quasi-liquid layer) ice-water contact angle θ_{IW} increase with decreasing R.[9] Therefore, the nucleation on "*flatter*" regions (radii of curvature above $10r_{\mathrm{c}}$, where nanopit curvature effects are not important) becomes the dominant mode, resulting in the constancy of the experimentally measured nucleation temperature.[9] Moreover, the presence of confined water in nanopits affects thermodynamic properties of water, *e.g.*, melting point, density, and excess entropy. Hence, since nanopits have been shown to not necessarily enhance nucleation due to the presence of a quasi-liquid layer,[9] they can then be utilized to affect the thermodynamic properties of water (*i.e.*, freezing point depression), accounting for *confinement effects*,[9,14] and attempt to maintain a robust liquid layer (confined liquid layer) on the substrate surface.

The discussion above sheds further light on the findings of Jung *et al*.[7] In contrast to Eberle *et al.*,[9] it was shown experimentally that surfaces with nanometer-scale roughness close or even smaller than the critical size of an ice nucleus (*e.g.*, $x \leq 1$ in **Figure 3a**) displayed freezing time delays at least one order of magnitude longer than surfaces with roughness values one or several orders of magnitude larger than the size of critical nucleus. However, if the relative difference of experimentally determined freezing delays (a factor of approximately 10 in Ref.[7]) is transformed into a temperature representation, the change in nucleation temperature turns out to be less than 1°C (*cf.* **Section 2.3**). Hence, in this context the effect of surface roughness can be seen as relatively small. We can conclude from the nanopit discussion that surfaces having only a fraction of the area occupied with nanoscale pits below $10r_c$—which is the case for most micro- and nanostructured surfaces—will result in a constant nucleation temperature with respect to nanoscale roughness variations.

All these findings demonstrated the *crucial relevance* of *surface curvature* for *the physics of icing on surfaces* and can be exploited to analyze nucleation in the limit of a hypothetically ideal surface comprised of an array of nanoscale pits with infinitesimal small asperities,[9] as shown graphically by **Figure 3b**. The nucleation temperature of such a hypothetical surface was estimated by Eberle *et al.* and it was predicted that the nucleation could be depressed to very low temperatures for very small pit radii $r < O(10)$nm, *i.e.*, high confinement.[9] A more accurate and complex calculation of this kind should involve the effect of the substrate surface atoms on the ice nucleation temperature.[14] Such a surface may also be very efficient against ice adhesion were nucleation barriers to be overcome, since an interfacial liquid layer is expected to exist between ice and substrate, preventing strong substrate-ice bonding (**Figure 2c**).[15] Such liquid layers—when formed on hygroscopic surfaces—have already demonstrated a substantial reduction in ice-substrate adhesion.[16,17]

2.3. Freezing delays

The effects of substrate wettability and nucleation thermodynamics are intertwined, and studies have reported both delays in ice formation on superhydrophobic[18–20] surfaces as well as the opposite effect.[7,21]

Surface wettability with respect to water can be theoretically linked to surface wettability with respect to ice (ice-water contact angle) by combining the three Young's-type equations for the contact angles liquid-vapor-solid, ice-vapor-solid, and ice-liquid-solid, assuming the formation of a spherical segment of an ice nucleus immersed into a supercooled water droplet sitting on an ideally smooth (no surface roughness) solid surface.[7] Accordingly, surface chemistry controlled wettability should affect both water and ice-water contact angles and consequently the probability of freezing. This was not confirmed by nucleation experiments, where the ice-water contact angle seemed to be *unaffected* by surface wettability (liquid-vapor-solid contact angle) for the materials tested.[9] Instead, a clear correlation between ice-water contact angle variation and quasi-liquid layer formation due to a surface curvature related water confinement was shown.[9] This has important ramifications for strategies related to surface engineering, as intrinsic wettability modification—which works well for controlling the nucleation behavior in other phase change processes (*e.g.* boiling, condensation)—may not be a useful tool for controlling ice nucleation behavior.

Beyond the reported effect of an quasi-liquid layer formation on the freezing delay, Boinovich *et al.*[22] concluded that for long time scales of freezing delays the influence of substrate wettability on the nucleation kinetics is mainly determined by thermodynamically related effects on the energy barrier of embryo formation (exponential factor in **Equation 1**) while for short time scales, non-stationary effects such as adsorption and integration of water molecules to a growing and collapsing nucleus (pre-factor K in **Equation 1**) govern the freezing delay. This finding was compared with the classical heterogeneous nucleation theory assuming the formation of a fully immersed spherically shaped ice nucleus sitting on a substrate. The available surface area for collisions of water molecules and correspondingly the flux of water molecules onto a forming heterogeneous ice nucleus increases with the ice-water contact angle and reaches its maximum for the case of an homogeneous ice nucleus at a theoretical ice-water contact angle of 180°.[22] From this theoretical approach it can be concluded that for short time scales, when ice embryos of a critical radius are in the homogeneous or heterogeneous nucleation conditions, it is the former condition that would be more likely to freeze due to enhanced water molecule adsorption and integration.

However, for long time scales, as is the case when dealing with freezing delays on superhydrophobic surfaces, the contact area between the droplet and the solid (ϕ) has been shown to play an important role in the freezing process. From nucleation theory, a reduced contact area reduces the nucleation rate proportionally by the factor $\phi = \frac{J_\phi}{J}$. In Ref.,[9,22] experiments with varying solid fractions of the contact area while keeping the surface chemistry constant have shown that a reduction in contact area lowers the nucleation temperature and increases freezing delay times.

Freezing delays are often employed to quantify the icephobic character of a surface.[7,9,19] The rationale for using freezing delays comes from the fact that an icephobic surface should delay the freezing of a supercooled droplet as much as possible. Within the framework of nucleation theory, and by employing Poisson statistics, one can express the average freezing delay time required for ice to nucleate in a supercooled droplet as $\tau_{\mathrm{av}} \propto \frac{1}{J}$ (for constant temperature). Freezing delays are obviously a strong function of temperature, since delays are inversely proportional to the nucleation rate from above and **Equation 1**. Their strong relation on temperature is experimentally substantiated,[22] and delays have shown to increase up to two orders of magnitude per unit °C.[9] For example, by using a surface at a slightly elevated temperature above its representative ice nucleation temperature, a remarkable average ice nucleation delay of 25 hours at -21 °C could be measured.[9] The approach of rational icephobic surface design reduces to designing superhydrophobic surfaces with a low nucleation temperature through controlled nanostructuring guided by thermodynamic principles where such surfaces should be utilized at temperatures slightly above the ice nucleation temperatures for which they are designed.

2.4. Freezing locations

Another important consideration is the thermodynamically favored location for the critical ice nucleus formation (**Figure 2**b): *i.e.*, water-substrate interface; air-water interface; or air-water-substrate interface. Recent experiments and simulations[23,24] show evidence that ice nucleation rates are enhanced near the gas-liquid interface, supporting the previous hypothesis of free surface-induced nucleation in supercooled water droplets.[25] For example, experiments by Shaw *et al.*[24] have shown that for a dry particle, serving as nucleation site, contacting the free surface of a supercooled water droplet tends to trigger freezing at a higher temperature than in immersion mode where the same particle is fully immersed in the droplet. Moreover, theoretical calculations show the crucial role of free surfaces on the freezing process.[23] Molecular dynamics simulations on supercooled liquid silicon and germanium[23] have demonstrated that the presence of free surfaces, *i.e.*, gas-liquid interface, may enhance the nucleation rates by several orders of magnitude with respect to those in the bulk liquid, suggesting the transferability of surface induced nucleation also to other tetrahedrally coordinated materials showing a density decrease in solidification such as water.

As shown in **Figure 2**a, the free energy change for the formation of a critical ice cluster (expressed by the free energy barrier ΔG in **Equation 1**) is the sum of the ice-liquid interface contribution (ΔG_{S}) and the volumetric contribution (ΔG_{V}) of ΔG. Since in the case of surface-induced nucleation the forming ice clusters reside in the liquid close to the gas-liquid interface, the variation of the ice-liquid interface contribution of ΔG is expected not to vary significantly compared to bulk-induced nucleation.[23] However, ΔG_{V} is instead decreased as compared to the bulk due to the free surface energy-induced small lateral pressure ($p_{\mathrm{lat}} < 0$) close to the gas-liquid interface, adding a pressure-dependent term $\delta G_{\mathrm{V}}\left(p_{\mathrm{lat}}\right)$ to the volume free energy change[23]

$$\delta G_{\mathrm{V}} \sim p_{\mathrm{lat}}\left(\rho_{\mathrm{L}} - \rho_{\mathrm{I}}\right) / \rho_{\mathrm{L}} \rho_{\mathrm{I}} , \qquad \mathbf{4}$$

where ρ_{L} and ρ_{I} are the number densities of the liquid and the forming ice cluster, respectively. It then follows for $\rho_{\mathrm{I}} < \rho_{\mathrm{L}}$ that the formation of an ice nucleus near the air-liquid interface is more favored due to a slightly lowered energy barrier for nucleation, relative to that in the bulk where $p_{\mathrm{lat}} = 0$. The comparison of stationary and non-stationary nucleation rates of supercooled sessile water droplets also indicate favored nucleation on suspended nanoparticles located at the air-liquid interface with respect to nucleation on the substrate, decorated with the same nanoparticles.[22] The previous discussion provides an indication of how free surfaces, *i.e.*, at the gas-liquid interface, can trigger heterogeneous nucleation due to small lateral pressure reduction and thus slightly reduced energy barriers for nucleation compared to the bulk liquid. This leads to the question of how the enhanced free surface area of water droplets on superhydrophobic surfaces due to surface texture related air pockets can have an influence on lowering the energy barrier for nucleation. This may be a very interesting topic for future ice nucleation experiments on superhydrophobic surfaces.

2.5. The effect of environmental conditions

In the previous discussion, the effects of humidity and gas flow on nucleation of supercooled water were not taken into account. However, environmental humidity and gas flow, which are naturally present in many icing applications, can fundamentally alter the ice nucleation mechanism, thereby also drastically affecting their icephobic behavior and relevance. It was recently shown[8] that local evaporative cooling of the liquid free surface (see **Figure 2**b) exposed to external gas flow and reduced humidity can render homogeneous nucleation the thermodynamically preferred ice nucleation mechanism instead of commonly expected heterogeneous nucleation on water contacting solids. More specifically, Jung *et al.*[8] found that under unsaturated gas flow conditions, homogeneous nucleation (from the gas-water droplet interface, first image sequence in **Figure 3c**) took place. On the other hand, under saturated gas flow conditions heterogeneous nucleation (from the substrate, second image sequence in **Figure 3c**) was the favored mode, as widely accepted. The change in nucleation mode is explained using nucleation theory combined with the analysis of temperature variation and evaporation of the supercooled droplet under changing environmental conditions.[8] The investigation on the effect of environmental conditions on icing is worthwhile because the mode of nucleation determines the role of the substrate in nucleation events. As an example, consider the homogeneous nucleation case: the nucleation starts from the water-air interface, so the surface no longer solely controls the onset of freezing, and any surface engineering is also *restricted by environmental icing conditions*.

The formation of a critical nucleus of ice in a supercooled sessile droplet inevitably leads to the explosive release of latent heat upon recalescent freezing, bringing the water from supercooled to equilibrium freezing temperature (~0°C), resulting in an ice-crystal scaffold (partially solidified liquid).[7] In a second, subsequent freezing stage, the remaining liquid in the interspace of this slushy phase freezes isothermally at a rate one to several orders of magnitude slower than the previous one, which is mainly controlled by the rate at which the heat released during freezing is conducted into the substrate and/or dissipated to the environment.[26] It was demonstrated in Ref.[26] that the freezing of individual droplets on a relatively low thermal conductivity substrate (polymeric) is associated with a concentric formation and propagation of a condensate *halo* and which ultimately freezes to form an annular frost layer on the substrate adjacent to the droplet (**Figure 3d**). This process is mainly governed by the low thermal conductivity of the substrate and the degree of supercooling. On the other hand, for a substrate with high thermal conductivity (*i.e.*, copper), under identical relative humidity of 30% and degree of supercooling (15 K), the condensate microdroplets evaporated completely before they could freeze.

This experimental and theoretical investigation of frost formation from supercooled individual droplets clearly indicates a highly effective path of minimization of frost layer formation and propagation for good thermal conductor substrates, unraveling the complex interplay of substrate, droplet and environment.[26] The presented process[26] involves multiple simultaneous phase transitions, showing ice spreading also by initiating sequential freezing of neighboring droplets in the form of a domino effect even under undersaturated environmental conditions.[26]

While frosting can occur from recalescent freezing of water droplets on low-thermal conductivity substrates in an undersaturated environment, it usually forms as a result of a supersaturated environment with respect to ice and/or water. Under these conditions and surface temperatures below 0°C, frost typically forms either directly from the vapor phase through desublimation (ablimation frosting) or via water vapor condensation, forming supercooled micron size-droplets which eventually freeze through nucleation (condensation freezing).

Frost formation can significantly increase ice adhesion on superhydrophobic surfaces, which poses a major challenge for many icephobicity strategies.[21,27] One of the main issues is that frost nucleation occurs without any spatial preference on superhydrophobic textures: this leads to an increase of the ice-substrate effective contact area, and thus leads to an increase of ice adhesion. In an alternative approach to superhydrophobic surfaces, ultra-smooth lubricant impregnated surfaces (LIS)[28,29] and slippery liquid-infused porous surfaces (SLIPS),[29,30] which exhibit remarkable droplet roll-off properties, have also been studied for anti-frosting. After a defrosting cycle (*i.e.*, heating), droplets easily slide off from lubricated surfaces, which keeps the surface free of water and reduces ice formation in the next frosting cycle. In fact, non-wetting surfaces have been utilized to reduce the overall heat consumption during active heating to remove ice as compared with untreated surfaces.[31] LIS and SLIPS may, however, be susceptible to irreversible damage during frost formation, and oil is likely to be depleted from them.[28] Designing icephobic surfaces capable of inhibiting frost formation can therefore be seen as a promising and challenging research path moving forward.

From the preceding discussions on nucleation and freezing delay we can highlight the following five aspects:

- First, for surface nanoroughness, the nucleation temperature is relatively insensitive to a broad range nanopit sizes (*i.e.*, radius of curvature).
- Second, an extraordinary heterogeneous nucleation delay can be theoretically achieved by designing a surface comprised of an array of nanoscale *pits* with infinitesimal small asperities, taking advantage of the presence of the quasiliquid layer and the freezing point depression of water.[9,14]
- Third, keeping the radius of curvature of the roughness *bumps* in contact with water smaller than the smallest stable ice nuclei formed increases the energy barrier for ice nucleus formation (retards icing).

- Fourth, the nucleation delay can be further reduced by minimizing the solid-air fraction of the surface, one instance where icephobicity and superhydrophobicity are linked.
- Fifth, using an icephobic surface that was designed according to the aforesaid principles, in a temperature range above its representative ice nucleation temperature, results in remarkable freezing delay times.

With this rational design framework, one can design robust icephobic surfaces for inhibiting heterogeneous nucleation and promoting freezing delay. From the discussion about freezing locations, and the effect of environmental conditions on freezing, we can conclude the following:

- Theoretical and experimental studies indicate a slightly elevated ice nucleation rate close to the free surface (gas-liquid interface) compared to the bulk liquid (surface induced nucleation). For droplets in contact with a solid surface, this may suggest a favored heterogeneous nucleation site at the water-solid-vapor interface (contact line).
- Under dry conditions with gas flow, ice nucleation may start from the free interface of the droplet (liquid-vapor); therefore, the substrate no longer solely controls the onset of freezing and may limit surface engineering capabilities.
- Evaporation from a freezing supercooled sessile droplet generates frost *halos* surrounding it even in a dry environment (undersaturated). The frost halo radius is inversely proportional to the thermal conductivity of the substrate. For low-thermal conductivity substrates, this frost formation may initiate freezing to neighboring droplets resulting in a *domino effect*, leading to frost propagation.
- Frost formation can have devastating consequences on icephobic surfaces designed to repel metastable liquid water, *e.g.*, superhydrophobicity. This is due to a lack of control over nucleation processes at the surface. Thus, environmental conditions where frosting is the preferred pathway to ice formation (*e.g.*, desublimation) can be seen as an important problem moving forward.

3. Transport: Droplet mobility

Of the three possible pathways to ice formation, vapor-to-solid (*i.e.*, desublimation or deposition), liquid-solid (*i.e.*, metastable liquid droplet freezing), or vapor-liquid-solid (*i.e.*, condensation freezing), it is the latter two categories that non-wetting surfaces are particularly well-suited for. Superhydrophobic surfaces—sometimes referred to as non-wetting surfaces—are characterized by extreme water *repellency*, as well as by enhanced droplet *mobility* thanks to a combination of high contact angles and low contact angle hysteresis. Superhydrophobicity is achieved when air/gas is trapped at the solid/liquid interface, *i.e.*, between the liquid and the solid substrate, leading to a reduced effective contact between the liquid and the solid substrate. For anti-icing applications focused on preventing the liquid-solid variety of freezing (*i.e.*, metastable liquids), superhydrophobicity can be beneficial by minimizing the contact area between the liquid and the substrate, as well as the contact time of an impacting drop, t_c, allowing surface de-wetting before the water can actually freeze and stick to the substrate. Rapid de-wetting can be achieved by enhancing rebound of an impacting drop through an increase of the receding contact angle,[32] and/or by shedding of sessile water drops through minimization of contact angle hysteresis.[8,33] Spontaneous drop removal without external forces was also observed on superhydrophobic surfaces, due to the jumping motion of the coalesced drops in dropwise condensation regime.[34] For anti-icing applications, it is essential that superhydrophobic surfaces preserve their non-wetting properties under realistic conditions, at sub-freezing temperatures and under dynamic conditions (*e.g.*, repelling falling water droplet). Particularly, drop impact is a critical aspect for superhydrophobic surfaces, since the liquid meniscus may penetrate into the surface texture, displacing the entrapped gas/air. This engenders the loss of superhydrophobicity causing the drop to stick (be fully or partially impaled) on the surface.

3.1. Droplet Impalement in Textured Surfaces

Minimizing the contact time between an impinging droplet and a non-wetting substrate is inherently beneficial to icephobicity, as prolonged contact may increase the probability of a nucleation event. The contact time (t_c) is proportional to the inertial-capillary timescale

$$\tau = \left(\rho_\mathrm{l} D^3 / 8\gamma_\mathrm{lv}\right)^{0.5}, \qquad \mathbf{5}$$

where ρ_l, γ_lv, and D are the liquid droplet density, liquid-vapor interfacial tension, and initial drop diameter. This time scale is practically constant for a large range of impacting velocities and was also shown to be affected by drop break-up[35] and by the value of the receding contact angle.[32] To this end, it is worth noting that phenomena such as liquid penetration into the surface texture and resulting impalement can dramatically affect solid-liquid contact[36] and cannot be predicted by the simple physics of the above contact time scale.

The droplet impact event is often characterized by Weber number (We), defined as, $We = \rho_\mathrm{l} U^2 D / \gamma_\mathrm{lv}$, where U denotes the velocity of impact, and is a measure of the ratio between fluid inertia and surface tension forces. The velocity of the water droplet that causes the liquid meniscus to penetrate the surface texture is defined as the critical velocity, U_c. If the impacting velocity (U) is greater than U_c, the impacting drop does not fully rebound from the surface and remains partially or entirely attached to the surface. This impalement phenomenon is often referred to as Cassie-to-Wenzel wetting transition and occurs when the impacting pressure of the water droplet overcomes the resistive capillary pressure, p_γ. This pressure is proportional to the surface tension of the water-air interface, γ_lv, and the advancing contact angle on the corresponding smooth surface (θ_a). p_γ is also inversely proportional to the characteristic cavity (*e.g.*, pore) size (r) based on the relation[37]

$$p_\gamma \propto \frac{\gamma_{\mathrm{lv}} \cos\theta_{\mathrm{a}}}{r_{\mathrm{pore}}}, \qquad \textbf{6}$$

where r_{pore} solely depends on the surface topography, and can be thought of as an effective pore size. By varying the surface texture, one can increase the capillary pressure to augment the water meniscus impalement stability under impact conditions. It is clear that as the water droplet impact velocity (U) increases, so does the associated dynamic pressure ($p_\rho \propto \rho_{\mathrm{l}} U^2$). However, when $U = U_{\mathrm{c}}$, $p_\rho \approx 0.1 p_\gamma$;[38] therefore, the pressure which causes droplet impalement must be of a different origin. Deng *et al.*[39] proposed that the water hammer pressure (p_{wh}) plays a key role in determining the impalement condition. Due to the water hammer pressure, caused by the impacting drop incompressibility, a shock wave is generated at the impact point and propagates at the speed of sound. In their work Deng *et al.* proposed an *effective* water hammer pressure (p_{ewh}) equal to a fraction of p_{wh} (pre-factor ~0.2). More recently, Dash *et al.*[40] found that the pre-factor should be modified significantly in accordance to the topography (texture) of the surface and should be $O(10^{-3})$. Note that the pre-factor of p_{wh} is an adjustable parameter which is used to fit the sum of the p_ρ and p_{wh} to the surface capillary pressure p_γ at the critical velocity, *i.e.*, when transition from rebound to stick droplet occurs, and is not derived from physical principles.

The physics behind the impalement mechanism, however, is still not completely understood. In this context, Mandre *et al.*[41] studied theoretically droplet impact events on a smooth surface, showing that the compressibility of the air layer between approaching droplet and substrate is a key feature guiding the first stages of drop impact dynamics. The air layer must be drained from underneath the droplet in order for the liquid to reach the substrate. The compressed air drainage can slow the droplet down, leading to regions of high pressure near the impact zone with a characteristic maximum pressure rise ($p_{\max}$). Ultimately, this high pressure deforms the liquid-air interface and forms a dimple: the cusp formation at the dimple periphery leads to the liquid pressure rises, as a consequence of the increased Laplace pressure, thus leading to a characteristic ring-like meniscus penetration, with a centrally trapped air bubble surrounded by an impaled ring, as visualized, *e.g.*, by X-ray imaging.[42]

Recently, the aforementioned ring-like penetration of the liquid meniscus into the substrate was also reported by Maitra *et al.*,[36] who systematically studied drop impact behavior on different micro, nano, and micro/nano multitier surfaces at varying substrate temperatures (~20 to -30 °C) aiming at understanding the behavior of water droplet impact on severely undercooled surfaces. In this context, the interplay between intervening air layer and the impact velocity of water drop is shown in **Figure 4**. At low impact speed, no penetration occurs and the drop can rebound from the surface. By increasing impact speed, the partial impalement regime is reached, when liquid starts to penetrate partially into the texture upon impact without touching the bottom of the surface; as a result, the drop is still capable of rebounding from the surface but the contact time increases at low temperatures due to viscous effects. For $U > U_c$, the liquid meniscus penetrates the surface texture fully and touches the bottom of the surface (full penetration regime) leading to a ring-like region around the impact point: in this area, recoil does not occur and a part of the drop remains attached to the surface.

In particular, it was recently found[36] that a linear trend exist between the characteristic maximum pressure developed in the air layer, $p_{\max}$, as found in Ref.[41], which rises with impact velocity as $\propto U^{28/9}$, and surface capillary pressure, p_{γ}, at the velocity of full impalement. Interestingly, $p_{\max}$ depends not only on liquid properties and impact velocity, but also on surrounding air conditions.[41] Stated succinctly: *environmental conditions are important to the impalement process*.

In order to reduce impalement (promote liquid meniscus stability), p_γ should clearly be maximized by optimizing surface chemistry and surface morphology. Surface chemistry can be modified to maximize the $\cos\theta_\mathrm{a}$ term in **Equation 6**. Given that the most hydrophobic materials we know (including alkyl, alkoxy and perfluorinates silanes, having end-groups with gradually reducing surface energies such as -CH_2, -CH_3, -CF_2 , -CF_2H, and -CF_3) would provide maximum contact angles of ~120°, the only remaining parameter that can be tuned is surface morphology, as expressed by the term r_pore in **Equation 6**. This term can be defined for the general case as the ratio between the cavity area (A_C) and its perimeter (L_C). As mentioned above, for well-defined surface geometry (micropillar based superhydrophobic surface), one can calculate the characteristic pore size as:

$$r_\mathrm{pore} = \frac{A_\mathrm{C}}{L_\mathrm{C}} = \frac{a_0(1-\phi)}{4\phi}, \qquad \mathbf{7}$$

where a_0 is the diameter of the micropillar and ϕ is the solid area fraction ($\phi < 1$).

3.2. Drop impact in freezing conditions

For droplet impact on substrates which are at low temperatures (substrate temperature down to -30°C; liquid droplet at ambient conditions), the impact event can be greatly affected by the viscous dissipation, and therefore the contact time rises accordingly.[36] In case of no impalement, viscous effects on superhydrophobic surfaces can be smaller than on hydrophilic surfaces.[43] However, since the viscous dissipation—which increases due to five-fold increase of water viscosity at -30°C compared to room temperature—is proportional to the surface area in contact with the droplet, strong viscous effects can be observed in case of liquid meniscus partial penetration into the textures. Particularly, the penetration occurring near to the impact point causes the liquid-solid contact area to locally increase. The viscous dissipation would be identical on the surfaces having same solid-liquid wetting area fraction (ϕ). For pillared surfaces, by reducing the pillar pitch (center-to-center spacing)—which is representative of surface characteristic cavity size—the capillary pressure would increase, aiding against water meniscus penetration. As the partial impalement decreases, the region of solid-water contact area would be less affected by viscous dissipation.[36] This highlights the importance of controlling the cavity size on the surface, for effectively resisting droplet impalement at low temperature.

The effect of water viscosity at low temperatures on the receding dynamics of a drop during impact is supported by other researchers.[44] Khedir *et al.*[44] investigated the water rebound mechanism from a superhydrophobic surface when both the drop and the surface were below the liquid freezing temperature. They reported that for very low impact speed (0.54 m s^{-1}) no variations of the contact time were observed, confirming that at low impact speed no partial penetration occurs (see **Figure 4**), and contact time is not affected by viscous effects; however, they reported that viscous effects led to a decrease of the drop restitution coefficient with decreasing temperatures.[44]

Since the actual task of icephobic surfaces is repelling droplets in a metastable liquid condition, the study of the impact behavior of supercooled drops on cold substrates is required. What is truly important from an engineering standpoint is to know whether or not a metastable liquid is going to solidify during contact with the solid surface. Mishchenko *et al.*[45] studied the effect of wettability on the freezing transition of a supercooled water droplet upon impact, identifying a threshold between -25°C to -30°C for drop to freeze and adhere to superhydrophobic surfaces. However, the critical role played by environmental conditions may have been overlooked: tests were performed in dry air room temperatures with a relative humidity of 5%. For air temperature at 20°C, the corresponding dew point is -21°C, remarkably close to the reported rebound-to-stick transition temperature. A hypothesis that was not considered is that, for surface temperatures lower than the dew point, frost may start to deposit on the surface, so that the surface is no longer clean and dry and the ice nucleation sites on the surface cause a change in surface wetting and act as nucleation sites for the drop. Indeed, in a different study Varanasi *et al.*[21] showed that frost formation on superhydrophobic surfaces can significantly affect their performance. The study showed that ice nucleates over the entire superhydrophobic surface (indiscriminately), and that superhydrophobic surfaces in this case had also significantly higher ice adhesion values compared to smooth hydrophobic surfaces.[21] Similar results were also reported by Kulinich *et al.*,[27] who observed a decrease an increase of ice adhesion strength in a humid environment.

Bahadur *et al.*[46] presented a model for predicting the nucleation time during the retraction phase after drop impact onto a superhydrophobic surface. The underlying idea of the model is that the retraction force—which is a function of the apparent receding contact angle—facilitates drop recoil, and thus rebound, after maximum spread is reached. Changes in the receding contact angle, resulting from ice nucleation, reduce the retraction force responsible for de-wetting, thus delaying or preventing drop recoil and rebound. Increased viscosity of water at low temperature also opposes to drop retraction, slowing down the receding phase of droplet dynamics. The model relies on one empirical parameter, the contact angle of ice on a flat surface in liquid water, *i.e.*, the contact angle formed between the liquid water-ice nuclei interface and the solid substrate: it was found that values that were equal to 90° led to the best fitting of experimental data.

Recently, we were able to investigate the impact behavior of extremely supercooled drops down to -17°C onto superhydrophobic surfaces,[47] and found out that increased viscous effects significantly influence all stages of impact dynamics, including meniscus impalement behavior. In addition to the viscous effects on reducing maximum spreading and increasing the contact time in case of partial meniscus penetration, we observed that meniscus penetration upon drop impact occurs with full penetration at the center, instead of ring shape, common to room temperature drop impact. This leads to an unobserved mechanism for superhydrophobicity breakdown: for room temperature drops, transition from bouncing to sticky (impaled) behavior occurs sharply at the condition of full texture penetration; differently, under supercooled conditions, the full-penetration velocity threshold was increased markedly (increasing by ~25% for the tested surface), without bubble entrapment. However, failure to completely de-wet due to viscous effects can still prohibit complete supercooled drop rebound, even though only partial texture penetration takes place.

3.3. Role of the gas layer: Sublimating surfaces

The presence and sustainability of a gas layer between a solid surface and an impacting water droplet plays a critical role in realizing dewetting, especially at low temperatures.[36] This was particularly evident in a recent study by Antonini *et al* [48] employing a sublimating surface. This study showed that sustaining a vapor layer on a surface can be beneficial in avoiding ice formation even in extreme freezing conditions, down to cryogenic temperatures. When a drop impacts on a sublimating substrate, such as solid carbon dioxide (commonly known as dry ice), a vapor layer due to substrate sublimation is generated at the solid-liquid interface. This vapor layer brings a double benefit, acting both as an air cushion and as thermal insulator. It allows the drop to hover over the surface in a contactless manner, rebounding or rolling away before it can freeze, despite the sublimating substrate being at extremely low temperature (-79°C), well below the water freezing point. In the same paper, the same phenomenon of floating drops was also demonstrated taking advantage of evaporation of a liquid nitrogen film on the substrate, at temperatures as low as -196°C.[48]

3.4. Superhydrophobic surfaces: De-frosting

Superhydrophobic surfaces may also present additional strengths, *e.g.*, by facilitating the cleaning of frosted surfaces during de-icing cycles. Along this line, Boreyko *et al.*[49] investigated the ability of a surface to restore a superhydrophobic wetting state after condensation freezing occurred on the substrate. Since the condensate drops and ice typically form on the entire surface and not only on the top of surface asperities,[49] one would expect that after de-icing the liquid water on the surface would be in Wenzel wetting state, thus pinned to the surface. However, the authors showed that on a nanostructured superhydrophobic surface, after the ice sheet is partially melted into a mixture of water and ice by heating up the surface above 0°C, the ice-water slush has a good mobility and can de-wet the surface spontaneously even at low surface tilt. This ability to de-wet during a de-icing cycle was attributed to the nanostructuring, on the basis of previous works, such as Ref.[50], where it was shown that nanoscale roughness minimizes the nucleation density of condensate relative to the density of surface features, enabling the majority of nucleating condensate to grow over the roughness in the energetically favorable Cassie-Baxter wetting state before coalescing with other drops. However, Jung *et al.*[8] showed that under shear gas flow in supersaturated conditions, superhydrophobic surfaces containing condensate in their surface texture asperities required relatively high shear gas velocities to cause droplet rolling and removal. Such findings are important in order to understand the freezing behavior of water, specifically on non-wetting surfaces, and to define the limits of functionality and applicability of such surfaces with respect to environmental conditions.

From the previous section on droplet transport, we can make the following conclusions:

- For droplet impact, minimizing substrate-supercooled water contact time reduces the probability of droplet freezing.
- At low temperatures, the viscosity of water is increased and affects the recoil dynamics of droplets impacting on surfaces, specifically the substrate-water contact time. This affect becomes dramatic when the impact velocity is sufficient to cause the liquid meniscus to partially penetrate the surface texture.
- By reducing the gap between surface features—towards nanotextured, closed cell geometries—one can minimize the potential for partial impalement of the water meniscus during drop impact.
- The performance of superhydrophobic surfaces can be severely degraded in an environment where frost can form, something future icephobic surfaces may need to address.
- The intervening gas layer between a substrate and an impacting water drop plays a very important role in drop dynamics and whether a drop will impale the surface texture (Cassie-Baxter to Wenzel transitions). To this end, such gas layers can be readily generated by sublimating surfaces and are capable of shedding droplets even at cryogenic temperatures.

4. Surface engineering considerations: Fabrication, durability, and scalability

The preceding sections gave us a roadmap for guiding the construction of ideal icephobic surfaces. A significant aspect that should be addressed regarding anti-icing strategies is the consideration of important issues associated with the stability, mechanical robustness, and scalability of the relevant techniques employed. Specifically, innovative materials developed within a lab may lack of longevity while being exposed to realistic conditions. Additionally, some anti-icing approaches seem to fail when used in industrial applications and other techniques are not eligible to be implemented for commercial exploitation due to their fabrication complexity and expensiveness.

4.1. Fabrication

The focus here will be a high-level overview of issues associated with synthesizing said structures and their use in industrial or commercial application (durability, scalability, *etc*.). **Table 1** presents a list of state-of-the-art ice repellent surfaces, which were guided by the aforesaid theories. **Figure 5** presents a categorical description of textured surfaces: single-tier texture (top) and multi-tier texture (bottom). It also presents a series of images for the nanostructures utilized to enhance a specific aspect of ice repellency: 1) drop impalement resistance; 2) quasi-liquid layer formation. The structures can be pores, cones, pillars, wires, pits, *etc*. For nanopore production, anodization techniques are now capable of producing high-aspect ratio (>1,000) structures on metallic substrates by similar techniques already used in industry for high-speed production of mechanically robust coatings (*i.e.*, hard anodization).[51] Similar structures have already demonstrated drop impalement resistance; however, the performance may not be sufficient for more intense anti-icing applications.[39] Since metallic surfaces (and their oxides) are natively hydrophilic, hydrophobic thin-film uniform coating treatments are necessary. The durability of such films is an important consideration for long-term performance as degradation leads to loss of the icephobic property.[52,53] Long-term stability of thin hydrophobic coating treatments is a problem other multiphase mass transfer applications have had long-standing issues with and have limited their industrial implementation (*e.g.*, condensation).[54–56] Durable multitier superhydrophobic surfaces—either polymeric or metallic-based—are now capable of being generating by single (or few)-step, large-area techniques; however, for icephobic applications, such surfaces suffer from similar problems as those mentioned above.[57–60] So while strategies and design exist for the construction of icephobic surfaces, and while much progress has been made on scalable techniques for generation of said surfaces, the icephobic performance is still not at a level that is acceptable for many desired applications (*cf.* Section 4.2).[61]

4.2. Durability (Utility)

Various criteria have been set to evaluate the performance of materials and demonstrate their anti-icing functionality. Ice nucleation delay, ice adhesion, and drop mobility are the most common features that qualify the icephobic behavior of surfaces. All these aforementioned criteria are necessary to be integrated with the practical application-oriented issues mentioned previously. In this section prospective anti-icing strategies will be presented and their sustainability towards real applications will be highlighted. **Table 2** also presents some of the best achievements in anti-icing surface technologies. We will refer to these throughout the following section.

The discussion in **Section 2** emphasized the need for a rational approach and design of surfaces based on thermodynamics principles and controlled surface structuring to avoid ice formation for a wide range of temperatures. Utilizing this approach, Eberle *et al.*[9] reported that for a rationally structured icephobic surface a very large freezing delay (as large as ~25 hours at -21°C) can be achieved.

For practical applications, such surfaces should be able to withstand realistic conditions, *e.g.*, prolonged exposure to freezing rain, abrasion, *etc*. Boinovich *et al.*[52] reported a highly durable, stainless steel-based superhydrophobic surface capable of demonstrating freezing delay capabilities even under prolonged exposure to freezing rain conditions. Also, for the case where icing did occur, the coating was able to maintain its non-wetting property after de-icing.

Furthermore, the coating demonstrated the ability to retain its non-wetting property even after 100 icing/deicing cycles. While the icing/deicing test is not relevant for ice nucleation delay tests, it does assess chemical stability (*i.e.*, tendency to resist hydrolysis) and mechanical durability (due to thermal fluctuations and volume expansion associated with phase transitions); therefore, such a surface can be considered well performing from an anti-icing application perspective.

It is clear that the requirement of design of an icephobic surface exhibiting long ice nucleation delay must be complemented by the requirement of mechanical and chemical robustness and stability. For a much more extensive discussion of the effect of repeat icing/deicing cycles on icephobic behavior, we refer readers to the following review articles.[1,2]

Water droplet impact on supercooled superhydrophobic surfaces is the topic of a number of recent studies. As discussed in **Sections 2** and **3**, the contact time of the metstable liquid droplet with a solid substrate (t_c) is a crucial parameter governing water droplet freezing. However, there is a theoretical minimum limit to t_c for bouncing droplets on superhydrophobic surfaces which do not break-up or *splash*.

Bird *et al.*[35] implemented a strategy which induced droplet break-up—under conditions which it normally would not—by creating macroscale patterns on a superhydrophobic surface (see **Table 1**). When the drop impinges on the macroscale ridges, it splits into smaller water fractions, which rebound from the surface in a shorter time as compared with the non-splitting condition. The result is a 37% reduction in overall droplet-solid contact time (see **Table 2**). Additionally, they showed that the contact time—which was non-dimensionalized by the inertial-capillary time (t_c / τ; **Equation 5**)—was 1.4, which at that time was 46% lower than the best reported in the existing literature ($t_c / \tau = 2.6$).[62] Recently, Liu *et al.*[63] reported a fourfold reduction in t_c for droplet impact on a multitier superhydrophobic surface (macro pillars, nanotextured) as compared with conventional rebound on a nanostructured superhydrophobic surface ($t_c / \tau = 0.53$). Their strategy was to convert droplet kinetic energy into capillary energy stored as a meniscus penetrated into surface texture; if this energy was rectified into vertical motion at a sufficiently fast time-scale, so-called pancake bouncing could occur, resulting in a substantial reduction in contact time. In both studies, the maximum droplet impact velocities and Weber numbers utilized were limited to conditions which severely limit their applications: $U = 1.2$ m s^{-1} and $We = 53$;[35] $We = 58.5$.[63] To the former case, in many applications velocities higher than this We value are relevant and break-up may occur naturally without the need for special surface textures. To the latter case, if impact velocities are increased sufficiently high, full penetration—as opposed to partial penetration—of the liquid meniscus may occur resulting in a full loss of droplet mobility (impaled droplet). Therefore, such macro-scale texturing approaches are likely to be utilized for niche applications.

Towards enhancement of impalement resistance, McCarthy *et al.*[64] fabricated multitier superhydrophobic surfaces that were able to resist droplets impacting at velocities of 4.3 m s^{-1} ($We = 854$). To put that in perspective, a surface with a critical impact velocity of 5 m s^{-1} would be able to repel 70-75% of the total rainfall in West Bengal, India—a natural habitat of the superhydrophobic Lotus (*i.e.*, Lotus effect).[64] By employing nanocones alone, Checco *et al.*[65] succeeded in reaching even higher impacting velocities without impalement: 10 m s^{-1}. Regarding high-performance surfaces capable of resisting impalement from relatively fast moving droplets (>100 m s^{-1}), Mishchenko *et al.*[45] suggested that by changing the surface architecture from opened to closed cell geometries (*i.e.*, honeycomb-like, brick-like structures) the mechanical robustness of the superhydrophobic surface can be enhanced. High pressure experiments led them to conclude that such geometries should be capable of repelling droplets impacting with velocities up to 90-135 m s^{-1}. However, this hypothesis is yet to be verified experimentally.

It should be noted that the results of the aforementioned studies were restricted to ambient temperature and conditions. In order to apply these surfaces to real icephobic applications, it is necessary to consider drop impact experiments under realistic icing conditions (*i.e.*, low-temperatures of liquids and/or surfaces). Towards this direction, Alizadeh *et al.* studied droplet impact on surfaces down to -25°C.[43,66] Similarly, Maitra *et al.*[36] demonstrated that for lower substrate temperature such as -30°C the critical velocity was remarkably 2.6 m s^{-1} (We = 227).

Another issue that is of importance is the mechanical stability of the surfaces that undergo the process of drop impact (*i.e.*, coating integrity), since mechanical stability is closely connected to the viability of the surface for real applications. While such testing is necessary, a limited number of research works investigated the performance of superhydrophobic surfaces after repeat impact events, where loss of liquid repellency or erosion may occur. Towards this, Davis *et al.*[67] exposed a superhydrophobic nanocomposite coating to an air-water spray with varying impinging speeds, 14.5 m s^{-1}, 4.5 m s^{-1} and 3.4 m s^{-1}, in order to simulate fog impact. They observed that the anti-wetting property of the substrate degraded after sufficiently long exposure. In this instance the wetting property loss was attributed to penetration of water into the asperities of the sample microstructure. At higher impact speeds, one would expect erosion to become a dominate factor in property loss, and it is clear that more work on erosion and impact of high-speed fog onto superhydrophobic surfaces is necessary to elucidate the mechanical limits of these surfaces.

While this article does not address strategies towards reducing ice adhesion, from a durability perspective, especially as it relates to icephobicity, ice removal tests are effective at assessing coating durability.

Over the past several years superhydrophobic surfaces were regarded as a prospective strategy for reducing ice adhesion. A model to justify this implementation was presented by Kulinich *et al.*[27] according to which water in Cassie-Baxter state freezes and the entrapped air below the water reduces the contact area between the finally formed ice and the solid. The same researchers showed a mechanism of surface degradation after icing-deicing cycle exposure due to the roughness of a superhydrophobic surface. After 20 icing/deicing cycles the ice adhesion strength of ice was enhanced by 3 times verifying their surface degradation model. This outcome indicated that the tested superhydrophobic surfaces were not sustainable effective materials for anti-icing processes and may have limited applications. The capability of superhydrophobic surfaces to reduce ice adhesion was also tested on helicopter blades.[68] A decrease in the adhesion load on superhydrophobic surfaces ranging from the 16% to the 70% with respect to baseline metal material was reported. Superhydrophobic surfaces performed best in rime ice conditions, occurring typically at temperatures lower than -10°C.

In the search of a more prospective strategy for minimizing ice adhesion, the use of lubricated surfaces may have promise (see **Table 2** for ice adhesion performance). To this end, a water-immiscible organic liquid with low surface tension was used to impregnate a solid interface (*i.e.*, LIS, SLIPS) to significantly reduce droplet adhesion.[28,69,70] The great advantage of this technique is that the trapped organic liquid acts as a barrier layer that may prevent the penetration of the condensed water (prior to freezing) or the formed ice and reduces ice adhesion. Wilson *et al.*[30] exposed SLIPS to repeat freeze-thaw cycles and demonstrated that after 150 cycles it performed satisfactorily. Rykaczewski *et al.*[28] observed that LIS was quite unstable, and after a few frosting-defrosting cycles it lost its self-healing characteristics and was damaged irreversibly. One possible resolution is a honeycomb-like surface texture, proposed by Vogel *et al.*[69], which enabled interlocking of the lubricant improving stability.

Towards the same direction, Chen *et al.*[16] and Dou *et al.*[17] developed a robust anti-icing surface by employing the solid-liquid concept with the water acting as the lubricant. In one technique, a hygroscopic polymer was grafted on a microporous silicon wafer enabling the depression of the freezing point of the formed lubricating water layer; in the other, polymers with ionizable pendent groups were employed, which were more advantageous due to their substrate independence. In this way, a lubricating water layer was maintained between the ice and the substrate eliminating the direct contact of ice with the solid interface. This process decreases the ice adhesion significantly in comparison to conventional anti-icing surfaces. Its mechanical stability was also verified by measuring the ice adhesion with a number of abrasion cycles proving its self-healing ability and stability after 80 cycles (**Table 2**). This technique can provide longer term-solutions to anti-icing applications, since the water layer can be replenished by humidity or even melted ice.

The following are the conclusions that can be drawn from the previous section:

- By utilizing multitier superhydrophobic surfaces, one can obtain a surface which has a nucleation delay time in sessile droplets of ~25 hours at -21°C and a robust nucleation temperature of -24°C.
- While a great deal of drop impact work has been executed, to-date, no surface has shown the ability to maintain its non-wetting state under conditions which are relevant to aerospace applications (~100 m s^{-1}), and studies of the erosion behavior of such surfaces are lacking.

- While certain fabrication methods may be considered large-area, many performance issues (drop impalement resistances, mechanical durability, chemical stability) need to be addressed before icephobic surfaces will be realized in practice.[61]
- Macro-texturing to create favorable fluid transport behavior for reducing droplet-solid contact time during impact is limited to specific operating conditions ($We < 60$). Under more realistic operating conditions (high We), droplet splash or break-up occur naturally, therefore the liquid will be removed quickly irrespective of the surface macrotexture.

5. Conclusions and Perspective

This article presented the logic, fabrication techniques, and challenges associated with the realization of supericephobic surfaces. Depending on the application, the strategies that were outlined aimed at not allowing ice to form, *i.e.*, through enhancement of liquid drop mobility and removal, freezing temperature depression, and freezing delay enhancement; therefore, the emphasis was not on reducing ice adhesion once it formed. It is the opinion of the authors that from the fundamental thermofluids standpoint, an optimum icephobic surface should have the following qualities:

1) A surface chemistry/material with a minimum ice nucleation temperature. Such surfaces can be successfully operated even at a few degrees above this temperature allowing extended freezing delay time.

2) The surface texture should have multi-tier structuring, designed also accounting for heterogeneous nucleation thermodynamics, to simultaneously reduce and optimize the liquid-solid contact area (lower nucleation temperature) and to enhance droplet mobility (reduce contact time, avoid impalement) of metastable liquid phases at the corresponding thermophysical properties. Note that the corollary, self-cleaning effect of superhydrophobicity also decreases the presence of ice-nucleation promoting impurities.

3) Such surfaces should be designed and utilized for the proper environmental conditions (pressure, humidity, *etc*.). Particularly adverse environment must be targeted with dedicated surface designs.

From the utility standpoint, aforesaid surfaces must also have a good degree of *robustness/durability* (mechanical, chemical, *etc*.) and *fabrication scalability* (large-area, cost, *etc*.). These last topics have received less attention in the literature to date and we deem it necessary that they become a research priority, hand-in-hand with exploring the associated exciting physics of icephobicity and functional surface sculpturing, if the findings of the significant research efforts of the community are to be harvested through broadly used applications.

In terms of additional—little explored research directions and the associated physics—we feel that investigating the effect of *thermodynamic properties beyond temperature* and *departing from atmospheric conditions*, carry both fundamental importance and application relevance (for example high/low pressure, velocity and humidity environments bring into play exciting physics and materials challenges). The same is true in terms of pursuing research on the, by comparison, ignored *"third kind" of phase transition*, *i.e.*, developing optimum icephobic surfaces for inhibiting desublimation processes (ablimation, deposition, *etc*.).

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Notes

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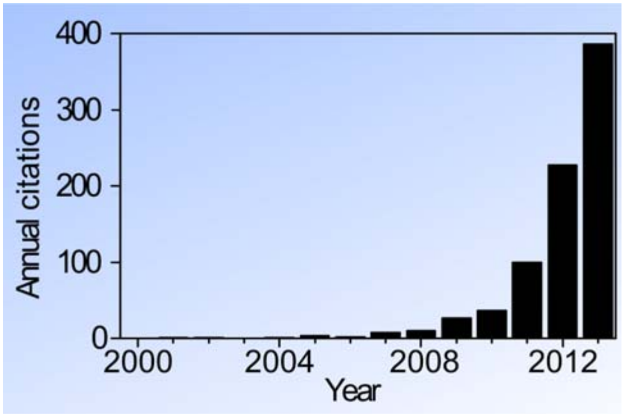


Figure 1. Number of citations by year for the following topics: icephobic or antiicing (excluding patents and review papers). Searches done on Web of Science.

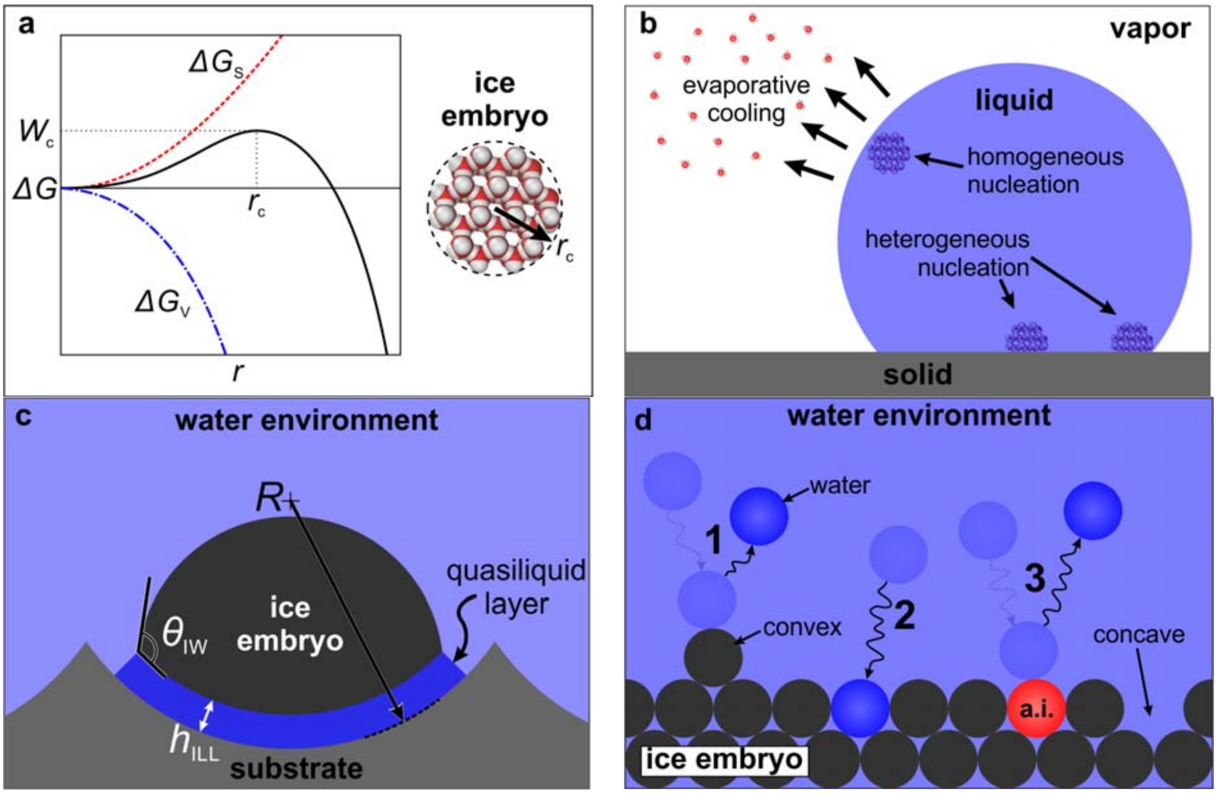
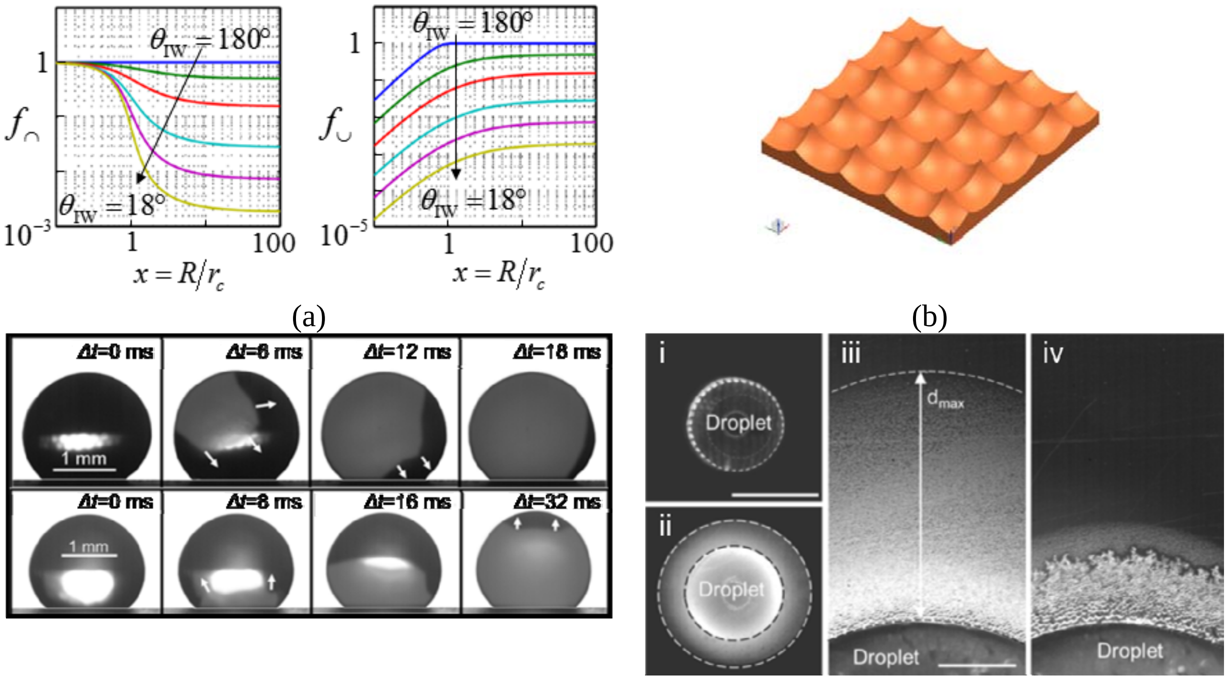


Figure 2. Schematics illustrating important aspects of nucleation: (a) *Homogeneous nucleation*: Plot of ΔG vs. embryo radius (r), showing that beyond a critical value, r_c, growth of the ice embryo is energetically favorable (homogeneous nucleation). Inset image is a schematic of an ice embryo of critical size; (b) *Nucleation*: Schematic depicting the regions within a water droplet where ice can nucleate and potential influences (*e.g.*, evaporation). (c) *Effect of curvature*: Ice embryo formation on a solid surface with concave surface features that have a radius of curvature R with $R \approx r_c$. A quasi-liquid layer of effective thickness h_{ILL} ($h_{\mathrm{ILL}} \propto R^{-1}$) is depicted and affects the resulting θ_{IW} value. (d) *Adsorption inhibition*: Ice clusters/embryos/crystals have both concave and convex surface features, and water molecules tend to migrate away from the convex regions (**1**), and towards the concave regions (**2**), and adsorption inhibitors (a.i.'s) adsorb to the embryo/nucleus surface and disrupt further growth of the ice embryo/nucleus (**3**). Please

note that the ice embryos, water molecules and the quasiliquid layer appear disproportionately to facilitate the aspects of nucleation. The size of an ice embryo is in the order of 1 nm while the quasiliquid layer thickness is in the order of a few atomic layers.



(a) (b)

(c) (d)

Figure 3. Ice nucleation and formation. (a) The geometrical factor f is plotted against the ratio $x = R/r_c$ for $f_\cap$ (convex roughness) and $f_\cup$ (concave roughness) for varying values of θ_{IW} (180°, 90°, 60°, 36.9°, 25.8°, 18.2°; Ref.[9] - Reproduced by permission of The Royal Society of Chemistry). (b) Hypothetical surface of an array of nanoscale pits with infinitesimal small asperities for extremely low nucleation temperatures (see main text for details). (c) Origin of homogeneous nucleation at the gas-liquid interface followed by ice front propagation in a supercooled sessile droplet (top row), origin of heterogeneous nucleation at the liquid-solid interface followed by ice front propagation in a supercooled sessile droplet (bottom row); Ref.[8] - reproduced by permission of Nature Publishing Group. (d) Top-view of: (i) water droplet on a poly(methyl methacrylate) (PMMA) substrate, (ii) concentric water condensation *halo*, and (iii)-(iv) frost formation from a freezing supercooled sessile droplet on a PMMA substrate; Ref.[26] -

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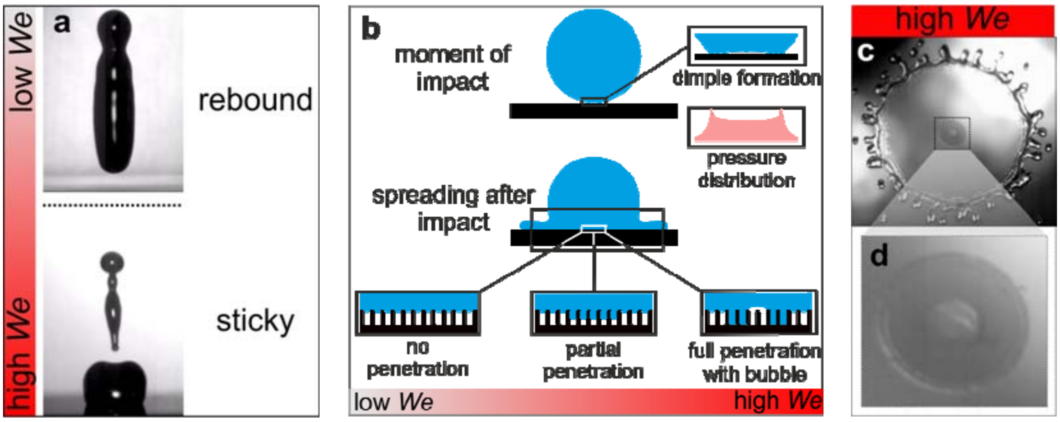

Figure 4. (a) Side-view high-speed images showing the restitution dynamics of a liquid droplet impacting on a superhydrophobic surface for low (We ~150) and high (We ~420) Weber numbers; the sticky situation is a result of liquid penetrating surface texture. (b) Mechanism of liquid meniscus penetration with increasing We. High values of We are associated with the formation of a dimple on the impacting droplet and an entrapped air bubble. (c)-(d) High-speed images showing an impacting droplet (U =3.8 m s^{-1} and We =461) on a superhydrophobic surface with meniscus penetration (dark region) and the formation of an air bubble (seen in **d**). Reprinted (adapted) with permission from Ref.[36]. Copyright 2014 American Chemical Society.

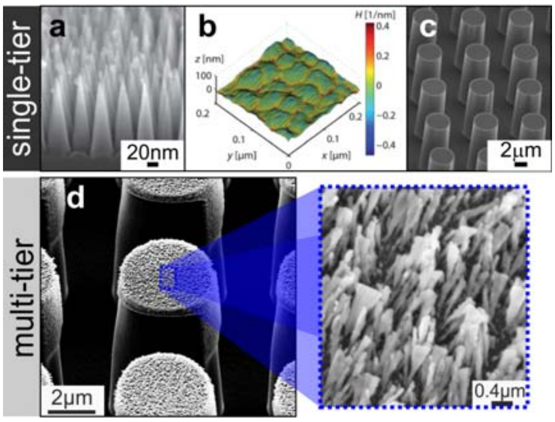

Figure 5. Micrographs depicting the relevant length scales and structures utilized in single-tier and multi-tier structures for icephobicity: (a) nanocones; (b) nanopits; (c) micropillars; (d) nanocone/micropillar. The materials are: (a) Etched silicon nanocones;[65] (b) etched SiO_2 nanopits;[9] (c) etched SiO_2 micropillars;[36] (d) etched silicon micropillar/nanotexture (nanotexture is shown with inset image).[36] (a) Ref.[65] - Reproduced by permission of John Wiley and Sons. (b)-(c) Ref.[9] - Reproduced by permission of The Royal Society of Chemistry. (d) Reprinted (adapted) with permission from Ref.[36]. Copyright 2014 American Chemical Society.

Icephobic surfaces	Description	Advantages	Disadvantages
Untextured	Surfaces exhibiting relatively high receding contact angles.	Reduce ice adhesion; relatively non-susceptible to damage from shear. Reduce condensation nucleation rate (*i.e.*, reduce condensation frosting).	No clear ice nucleation strategy; therefore, ice will form. External forces must be used to remove ice.
Single-tier texture	Nanotexture: Hydrophobic surfaces exhibiting high resistance to drop impalement or promoting quasi-liquid layers/confinement effects	Can resist droplet impalement. Can also promote quasi-liquid layers and confinement effects. Can maintain non-wetting states during condensation.	May have an increased nucleation temperature (compared with multi-tier case).
	Microtexture: Hydrophobic surfaces exhibiting high apparent contact angle values and low liquid adhesion	Low-droplet adhesion, so it can repel supercooled droplets. Lower nucleation temperature due to reduced solid-liquid contact area.	Cannot control condensation; susceptible to flooding. May not reduce ice adhesion, surface is damaged during ice removal.
Multi-tier texture	Hydrophobic surfaces consisting of a combination of macro-, micro-, nano-scale features, with each scale affecting/addressing an important process during transport and phase change.	Microscale texture can reduce droplet adhesion and nucleation temperature by promoting an air layer underneath it.	Currently, drop impact resistance and contact time reduction applies to speeds <10 m s^{-1}. Contact time reduction through macrotexturing only applies to $We < 60$.
		Micro/nanoscale texture can resist droplet impalement during dynamic impact and has a low nucleation temperature. It may also promote spontaneous droplet jumping.	
		Macro/micro/nano-scale texture can resist drop impalement, have a low nucleation temperature, and reduce droplet impact contact time.	

Table 1 Icephobic surfaces and their associated advantages and disadvantages.

Property	Test	(dimension)	Performance	References
ice adhesion	adhesion strength	(kPa)	~60	Subramanyam et al.[70]
			55	Chen et al.[16]
			40	Kulinich et al.[27]
			27	Dou et al.[17]
			15.6	Kim et al.[29]
	icing/deicing cycles	(number of cycles)	100	Boinovich et al.[52]
			80	Chen et al.[16]
ice nucleation delay	nucleation temperature	(°C)	-24	Eberle et al.[9]
	nucleation delay	τ_{av} (h)	25	Eberle et al[9]
drop mobility	droplet impact contact time	$t_{\mathrm{c}}\ \tau^{-1}$	2.6*	Li et al. [62]
			1.4*	Bird et al. [35]
			0.53*	Liu et al.[63]
	droplet impact impalement resistance	U (m s^{-1})	10*	Checco et al. [65]
			4.3*	McCarthy et al.[64]
			2.6 (T=-30°C)	Maitra et al. [36]
		We	826*	McCarthy et al. [64]
			227 (T=-30°C)	Maitra et al.[36]

Table 2. A brief overview of recent achievements in icephobic performance. Asterisks (*) indicate that the test was done under ambient conditions. As was noted in the text, the dimensionless time and Weber numbers are defined as $\tau = \left(\rho_{\mathrm{l}} D^3 / 8\gamma_{\mathrm{lv}}\right)^{0.5}$ and $We = \rho_{\mathrm{l}} U^2 D / \gamma_{\mathrm{lv}}$, respectively.

TOC GRAPHIC

On the Physics of Icing and the Rational Design of Surfaces with Extraordinary Icephobicity

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