

Exploiting Topographical Texture To Impart Icephobicity

Adam J. Meuler,^{†,5} Gareth H. McKinley,[‡] and Robert E. Cohen^{†,*}

[†]Department of Chemical Engineering and [‡]Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States and ⁵Air Force Research Laboratory, Edwards Air Force Base, California 93524, United States

Frost is the greatest artist in our clime - He paints in nature and describes in rime.

Thomas Hood (1799–1845)

ABSTRACT Appropriately structured topographical features that are found in nature (e.g., the lotus leaf) or that are produced synthetically (e.g., via lithography) can impart superhydrophobic properties to surfaces. Water beads up and readily rolls off of such surfaces, making them self-cleaning. Within the past few years, scientists and engineers have begun exploring the utility of these surfaces in mitigating the icing problem prevalent in the operation of critical infrastructure such as airplanes, ships, power lines, and telecommunications equipment. An article in this issue advances our fundamental knowledge in this area by examining the dynamic impact of water droplets on both smooth and topographically structured supercooled substrates. The results illustrate that, under at least some environmental conditions, superhydrophobic surfaces can minimize or even eliminate ice formation by repelling impinging water drops before they can freeze. Subsequent research will build on these results, possibly leading to the fabrication of commercially viable and durable icephobic surfaces that mitigate the icing problem under all environmental conditions.

The formation and subsequent build up of ice hinders the operation of many components of modern infrastructure, including aircraft, ships, offshore oil platforms, wind turbines, dams, power lines, and telecommunications equipment. The strategies that are currently employed for combating icing are generally resource intensive (e.g., spraying aircraft with anti-freeze fluids) and/or prone to failure. A more appealing and universal strategy for mitigating the icing problem is to engineer surfaces that minimize both the quantity of ice that forms on a surface and the adhesion of the accreted ice. While research focused on the development of such icephobic surfaces dates to at least the late 1950s,^{2,3} well-established design principles for their fabrication have remained elusive.

A common strategy for minimizing ice formation and adhesion has been the application of chemical coatings to vulnerable surfaces. Such treatments can be classified as either sacrificial or permanent.⁴ Sacrificial coatings are, by design, removed from substrates over time, requiring periodic application to remain effective and potentially having adverse environmental consequences. Examples of such materials include greases that remove ice particulates as they are shed from protected surfaces⁵ and sol–gel materials that slowly release freezing point depressants.⁶ We speculate that the vulcanizing anti-icing coatings manufactured by NuSil Silicone Technology (www.nusil.com/whitepapers/index.aspx) operate at least in part *via* this sort of depletion mechanism, with unreacted oligomers being shed along with ice particulates.

Permanent coatings are conceptually more appealing than their sacrificial counterparts because they neither re-

quire periodic reapplication nor are detrimental to the environment. A substantial amount of research has focused on reducing the strength of ice adhesion by applying permanent hydrophobic coatings such as polymers to nominally smooth substrates.^{2–4,7–9} While it has long been known that such coatings could reduce the strength of ice adhesion,^{2,3} it was not clear how, if at all, this reduction correlated with various measures of the hydrophobicity of the surface. This uncertainty recently changed with the report of a strong, linear relationship between ice adhesion strength and the water wettability parameter $[1 + \cos \theta_{\text{rec}}]$, where θ_{rec} is the receding contact angle of water.⁹ This factor $[1 + \cos \theta_{\text{rec}}]$ scales with the *practical work of adhesion*¹⁰ required to remove a liquid water drop from a surface.¹¹ These ice adhesion data,⁹ reproduced in Figure 1, were acquired using a custom-built adhesion apparatus and test substrates comprising nominally smooth steel discs that were coated with 21 different polymers and polymer nanocomposites with a broad range of water wettability.

The correlation provided in Figure 1 has important implications for the design of icephobic surfaces because it suggests that further appreciable reductions in ice adhesion strength require surfaces with receding water contact angles θ_{rec} above 120° , corresponding to $[1 + \cos \theta_{\text{rec}}] \leq 0.5$. There are no known materials that exhibit receding water contact angles on smooth surfaces that are substantially above this value, however.^{12,13} The only known methodology for increasing the receding water contact angle above 120° and thus further reducing the ice adhesion strength is to incorporate topographical surface features

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*Address correspondence to recohen@mit.edu.

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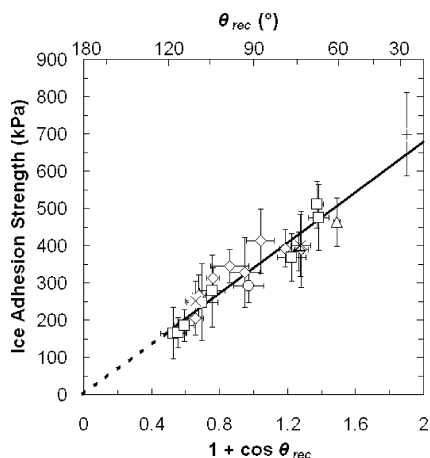


Figure 1. Average strengths of ice adhesion measured at $-10\text{ }^{\circ}\text{C}$ for bare steel and steel coated with 21 different polymeric materials plotted against the water contact angle parameter $[1 + \cos \theta_{\text{rec}}]$. The solid line is the linear best fit to the data that is required to pass through the origin ($\tau_{\text{ice}} = (340 \pm 40 \text{ kPa})(1 + \cos \theta_{\text{rec}})$, $R^2 = 0.92$), and the dashed line represents the extrapolation to the origin. The ice adhesion strength is reduced by a factor of 4.2 when the steel is coated with the optimized polymer nanocomposite. Figure reproduced from ref 9. Copyright 2010 American Chemical Society.

that allow surface-bound water droplets to exist in the composite Cassie–Baxter state¹⁴ before freezing occurs.

A schematic representation of a Cassie–Baxter droplet on a textured surface is shown in Figure 2a. Water droplets in this composite state are generally characterized by higher receding contact angles than are droplets on chemically equivalent smooth surfaces because they rest partially on solid surface features and partially on air.^{15–17} Surfaces that support composite state water droplets with both advancing and receding contact angles above 150° are commonly described as *superhydrophobic*; water droplets

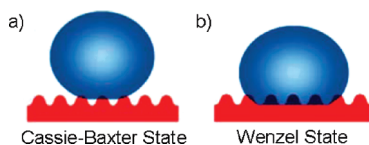


Figure 2. Schematic representations of liquid water droplets on textured surfaces that are in the (a) composite Cassie–Baxter and (b) fully wetted Wenzel states. The presence of air pockets underneath the Cassie–Baxter state droplets leads to higher receding water contact angles than are exhibited by a chemically equivalent smooth surface, while the increased area for solid–liquid interaction in the Wenzel state leads to a lower receding water contact angle and stronger drop adhesion than is observed on a chemically equivalent smooth surface.

readily bead up and roll off of such surfaces. Roughening a surface does not always lead to increased water repellency, however, and the equilibrium configuration of a liquid droplet on a surface depends on both the interfacial energies of the liquid and solid phases and the topography of the substrate.^{18,19} If it is energetically unfavorable for a three-phase contact line to be supported on the texture, then the water droplets may fully wet the surface and adopt the so-called Wenzel configuration that is illustrated in Figure 2b.²⁰ These fully wetted droplets have an increased area for solid–liquid interaction and are thus characterized by lower receding contact angles and stronger adhesion to the substrate than are droplets on smooth surfaces.^{15–17}

The different solid–liquid contact areas that are shown in Figure 2 have strong implications in the consideration of ice adhesion to structured surfaces. It is clear that water must freeze in the composite Cassie–Baxter state if the ice adhesion strength is to be reduced below that of a smooth substrate. A few groups have quantitatively measured the adhesion strength of composite state ice to textured superhydrophobic surfaces using a custom-built cen-

trifugal apparatus and climate chamber intended to mimic outdoor ice accretion.^{21,22} The measured ice adhesion strengths on these rough surfaces closely matched the predictions of the correlation reported⁹ in Figure 1, which is perhaps surprising given the sensitivity of adhesion measurements to the specific details of the test configuration and conditions.¹⁰ Several other groups have also reported reduced ice adhesion on superhydrophobic surfaces but do not provide quantitative values of ice adhesion strength and/or receding water contact angle needed for comparison with the correlation in Figure 1.^{23,24}

We note that fabricating effective textured icephobic surfaces is not as straightforward as preparing substrates that are superhydrophobic toward static water droplets at room temperature. Effective icephobic surfaces must resist transitions to the fully wetted state that may be brought about by the kinetic energy of impinging water droplets (e.g., freezing rain)²⁵ or by the condensation of moisture from the ambient atmosphere within the microtexture.^{26,27} The robustness of Cassie–Baxter liquid repellency with respect to these dynamic per-

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turbations has received little attention in the literature, particularly for the subzero temperatures associated with icing. Consequently, it is not clear if previously reported textured icephobic surfaces^{21–24} are effective over a broad range of environmental conditions, particularly those that would facilitate the condensation of water droplets or the desublimation of frost inside the topographical features.

A few previous publications have examined the dynamic wetting behavior of supercooled liquid droplets and the subsequent accretion of ice (or lack thereof) on textured substrates.^{23,28} The relevant dimensionless parameter that should be used for reporting impact data in an unambiguous way is the Weber number, $We = \rho V^2 R / \gamma_{LV}$, which is the ratio of the incoming kinetic energy per unit volume of a liquid drop ($\sim \rho V^2 / 2$) to the capillary pressure ($\sim \gamma_{LV} / R$).^{29,30} Because most dynamic tests are performed in the laboratory using drops released from rest under gravity at a height h , the energy of the impacting droplet can also be readily evaluated in terms of the initial gravitational potential energy to give $We = \rho ghR / \gamma_{LV}$. Additional dimensionless groups can also be developed that suitably quantify the degree of subcooling, the relative magnitude of the water hammer impulse pressure,²⁵ and the effects of fluid viscosity on the impact dynamics.

Cao *et al.* prepared superhydrophobic nanoparticle–polymer composites with a range of particle sizes and investigated the dynamic impact of supercooled water droplets in the laboratory ($-20\text{ }^\circ\text{C}$ from a height of 5 cm, corresponding to $We \sim 40$) and in freezing rain in Pittsburgh, PA.²³ The water always rolled off of the substrates prior to freezing when the radii of the constituent nanoparticles were below 100 nm but regularly froze to surface coatings composed of nanoparticles with larger dimensions. Cao *et al.* argued, using a model de-

rived from classical nucleation theory, that these larger particles reduce the free energy barrier and catalyze the nucleation of ice. The smaller particles, in contrast, enable a textured superhydrophobic state without promoting ice nucleation and allow water to roll off the surface prior to freezing, minimizing the accretion of ice.²³ Wang *et al.* reported a related investigation of water drops impacting three test substrates at $-6\text{ }^\circ\text{C}$ ($100 < We < 250$): smooth aluminum, flat silicone rubber, and superhydrophobic aluminum prepared by acid etching and stearic acid passivation.²⁸ The ice buildup on the superhydrophobic surface was substantially lower than it was on either of the smooth substrates because the sprayed water droplets were able to bounce or to roll off the superhydrophobic substrate prior to freezing.

The research reported by Mishchenko *et al.* in this issue further advances our understanding of the dynamic wetting of supercooled water droplets and subsequent ice accretion by combining high speed imaging with modeling of nucleation, heat transfer, and wetting dynamics.¹ The high speed imaging reveals that water droplets released from a height of 10 cm ($We \sim 20$) deformed and then completely retracted from tested superhydrophobic surfaces when the substrate temperature was greater than about $-20\text{ }^\circ\text{C}$. Colder surface temperatures led to freezing of the impinging water during the deformation or retraction processes that are associated with surface impact. The complementary modeling of the retraction force on the droplets predicts that this force has an exponential dependence on the interfacial temperature, accounting for the sharp transition from complete repulsion to pinning and freezing over a narrow temperature range. Furthermore, the authors note that, when water does freeze to the superhydrophobic substrates, the adhesion of the accreted ice was lower than it was on chemically equiva-

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lent smooth surfaces, a result in agreement with previous literature reports.^{21–24} The research reported by Mishchenko *et al.* in this issue further advances our understanding of the dynamic wetting of supercooled water droplets and subsequent ice accretion by combining high speed imaging with modeling of nucleation, heat transfer, and wetting dynamics.

We believe that there are still a number of issues that must be understood and addressed before nanotextured surfaces will find widespread use in anti-icing applications. First, impinging supercooled water with higher Weber numbers (*i.e.*, higher kinetic energies) must be investigated on chilled superhydrophobic surfaces. Mishchenko *et al.* report complete repulsion of water dropped from a height of 10 cm ($We \sim 20$),¹ but it is possible that water droplets with higher kinetic energy could be impaled on the textured substrate, fully wet the surface, freeze in the Wenzel state, and consequently ad-

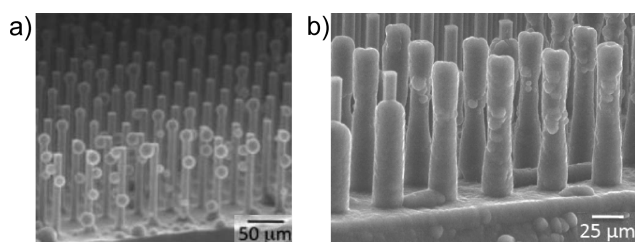


Figure 3. Environmental scanning electron micrographs of (a) liquid water condensing and (b) frost desubliming indiscriminately on superhydrophobic post surfaces. Both substrates are characterized by spatially uniform intrinsic surface energies with a smooth surface equilibrium water contact angle of 110° . Panel a is reproduced with permission from ref 27. Copyright 2009 American Institute of Physics. Panel b is reproduced with permission from ref 31. Copyright 2010 American Institute of Physics.

here more strongly to the rough substrate. Optimistically, Mishchenko *et al.* note that some of their closed-cell geometries (*e.g.*, honeycombs) are able to resist wetting by static drops in test chambers with pressures as high as 60 atm. This result suggests that such surfaces should also resist dynamic wetting, although such work has not yet been reported.

A second and likely more difficult challenge will be designing superhydrophobic surfaces that retain their water repellency when condensation and/or frosting are present. The experiments of Mischenko *et al.*, for example, were performed at low humidity ($<5\%$); it is not clear that water will still bounce off of the same surfaces when they are equilibrated in more humid environmental conditions. Some surfaces that are superhydrophobic at room temperature exhibit sharp and unfavorable decreases in the receding water contact angle as the temperature is lowered.²⁶ This class of surfaces includes HIREC-100, a sprayable nanoparticle blend that is available from NTT Advanced Technology Corporation (www.ntt-at.com). The likely mechanism for this decrease in liquid repellency is the capillary condensation of liquid water in the crevices of the surface texture that drives a transition from the Cassie–Baxter to the Wenzel configuration.^{26,27} An environmental scanning electron micrograph of such water condensation on a superhydrophobic surface composed of lithographically patterned posts is

reproduced in Figure 3a.²⁷ Other superhydrophobic surfaces are, in contrast, reported to be able to support composite state water droplets at subzero temperatures and moderate humidity.²⁸ This varied behavior is not yet well understood.

Water vapor does not always form a liquid condensate when it undergoes a phase transition on a supercooled surface. The water may also desublime onto a surface and form small ice crystals, a process that is commonly referred to as frosting.³¹ The image reproduced in Figure 3b illustrates that frost will form indiscriminately on superhydrophobic surfaces that are characterized by spatially uniform intrinsic interfacial energies, compromising their liquid repellency.³¹ Ice on frosted superhydrophobic surfaces can adhere more strongly than it does on chemically equivalent smooth surfaces³¹ because this “Wenzel ice” has a larger interfacial area of interaction with the substrate. One possible strategy for combating this frost-driven transition to the Wenzel state is to control the condensate nucleation spatially.²⁷ If the nucleation is constrained to the top portions of the surface texture, it might be possible to facilitate the formation of weakly adhered composite³¹ or “Cassie ice” and prevent the formation of the strongly adhered Wenzel ice.

A final challenge that must be overcome before textured superhydrophobic surfaces gain widespread use in anti-icing applications

is the development of commercially viable fabrication processes. Mischenko *et al.* have proposed using soft lithography protocols to prepare textured polymeric films that can be applied to surfaces in need of protection from icing.¹ Another appealing and universal approach is to use spray coating to readily deposit anti-icing materials on any arbitrary surface. Protocols designed to modify existing materials (*e.g.*, acid etching of metals) have also received attention in the literature,²⁸ although such processes are less universal than applying coatings. Any successful anti-icing protection must not only be readily applied to surfaces, but it must also be durable and long lasting, a particular challenge given the harsh environmental conditions associated with icing.

Ice accretion and adhesion are topics that are appearing in the scientific literature with increasing frequency.^{9,21–24,28,31} These recent reports have advanced our understanding of the icing phenomenon and shed light on some promising strategies for employing liquid water repellent materials as anti-icing surfaces. The work described in this issue by Mischenko *et al.* furthers our understanding of the efficacy of superhydrophobic surfaces in reducing ice formation and brings us one step closer to deploying such materials in commercial applications, and defeating Nature’s artist at its own craft.

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