Ice-Phobic Surfaces That Are Wet

Howard A. Stone*

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, United States

ABSTRACT

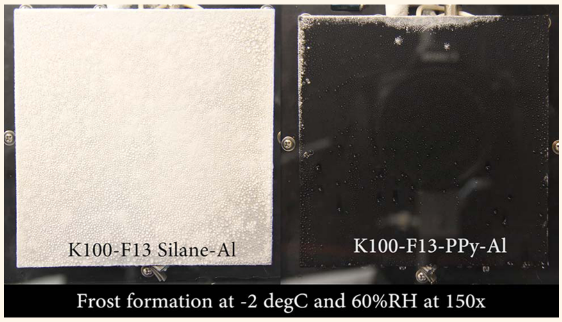

Image courtesy of Dr. Philseok Kim and Michael J. Kreder

Ice formation on surfaces and structures produces damage and inefficiencies that negatively impact all manners of activities. Not surprisingly, for a long time, an unmet challenge has been to design materials capable of minimizing or even eliminating the formation of ice on the surface of the material. In recent years, there were significant efforts to develop such ice-phobic surfaces by building on the advances made with superhydrophobic materials since these, by definition, tend to repel water. However, a robust response includes the ability to deter the formation of ice when a substrate colder than the freezing temperature is exposed either to impacting water droplets or water vapor (*i.e.*, frost formation). In the latter case, superhydrophobic surfaces in high humidity conditions were shown to allow significant ice accumulation. Consequently, a new design idea was needed. In this issue of *ACS Nano*, it is shown how a liquid-infiltrated porous solid, where the liquid strongly wets and is retained within the material, has many of the properties desired for an ice-phobic substrate. The composite material exhibits low contact angle hysteresis so only small forces are needed to provoke droplets to slide off of a cold substrate. This new slippery surface shows many characteristics required for ice-phobicity, and a method is demonstrated for applying this kind of material as a coating on aluminum. Ice may have met its match.

The formation of ice on surfaces negatively impacts many aspects of our lives, from the operation of cars, planes, trains, and ocean-going vessels, to roads, power lines, transmission towers, turbines, wind mills, and roofs of all types of structures. Thus, the problems caused by ice formation produce difficulties in most major sectors of society, spanning transportation, power generation and transmission, and home and office buildings. This situation has been recognized for decades, and studies of the properties of ice-covered surfaces date back at least to the late 1950s.[1,2] In spite of much research, ice-caused damage to materials remains a major problem.

In recent years, there had been optimism that a new solution might be at hand since the advances made in producing superhydrophobic materials heralded the possibility of surfaces that repelled water and thereby potentially limited the accumulation of ice. Indeed, in this very journal in 2010, an excellent Perspective summarized the interest and approaches toward "ice-phobic" surfaces,[3] while highlighting a recent publication documenting the potential of superhydrophobic surfaces to minimize the adhesion of ice during impact of droplets in situations of relatively low relative humidity.[4] Unfortunately, this optimism proved to be rather short-lived, especially in conditions of high humidity. A good and novel idea was thus needed! Such an idea was recently introduced by the group of Joanna Aizenberg at Harvard University.[5] In this Perspective, I briefly summarize properties of surfaces that are important to understanding liquids on solids and describe a liquid-infiltrated porous material that shows promise toward minimizing accumulation of ice on surfaces.

With respect to the formation of ice on surfaces, there are two main routes that are considered: the impact of water droplets on surfaces with temperatures below the freezing point and the formation of ice directly from the vapor phase of a supersaturated ambient (*i.e.*, frost formation). Both situations occur in common atmospheric conditions, so any robust and successful strategy to prevent ice formation must demonstrate the ability to mitigate ice accumulation from both vapor and liquid precursors.

Some Properties of Surfaces. In order to appreciate the main physical ideas and related challenges of ice-phobic substrates, I begin with a few remarks about the wetting of liquids on surfaces. It is well-known that liquids form a well-defined angle of contact when a drop is placed on a smooth

* Address correspondence to hastone@princeton.edu.

Published online August 09, 2012
10.1021/nn303372q

surface. This contact angle, θ_c, is often considered to characterize the wettability of the surface (but see the remarks about contact angle hysteresis below). Researchers speak of perfectly wettable surfaces, $\theta_c = 0°$, and partially wetting surfaces when the contact angle is finite. Hydrophobic surfaces have $\theta_c > 90°$. It is not easy to find common materials with contact angles over 120°.[6] However, with special chemical treatments, and most particularly, by introducing roughness, either by mechanically roughening the surface in more or less a random fashion, or by using nano- and microfabrication methods, it is often possible to achieve (effective) contact angles of about 150° or larger. This regime of nonwetting is referred to generally as superhydrophobicity. Two configurations with large contact angles are possible: the Cassie (or Cassie–Baxter) state, where droplets sit on top of the roughness and mostly experience an air cushion, and the Wenzel state, where the droplet liquid displaces the air to contact the substrate fully.

At equilibrium, a small drop placed on a superhydrophobic surface will be near-spherical; in the Cassie state, it rests mostly on a cushion of air and has a small area of contact with the substrate. Moreover, drops that impact these surfaces are generally observed to bounce. These last two observations were suggestive to many that superhydrophobic surfaces provided a plausible route toward an ice-phobic material. Indeed, there remain creative attempts to combine micro- and nanostructuring to create surfaces that, at least in some situations, delay the onset of ice formation.[7] However, on the basis of additional ideas discussed below, I fear that such surface fabrication strategies alone will not yield a robust ice-phobic material for general applications.

Contact Angle Hysteresis. From the standpoint of whether a liquid will actually be retained on a surface, as is essential when seeking to understand whether a subcooled substrate can freeze any deposited liquid, contact angle hysteresis is also important. For example, if a drop is placed on an inclined plane, where the drop then experiences a component of the gravitational force tangent to the plane, the drop can maintain a static configuration if the leading (advancing) contact angle is larger than the trailing (receding) contact angle since this difference of contact angles exerts a net force on the drop that counters gravity.[8] The difference in contact angles is referred to as "contact angle hysteresis". Microscopically, this phenomenon is generally associated with "pinning" of the contact line at surface defects, so the hysteresis is typically large on rough surfaces and small on smooth surfaces. The larger the contact angle hysteresis, the larger the force tangent to the surface that is necessary to move the drop; conversely, the smaller the contact angle hysteresis, the smaller the force tangent to the surface that is needed to move the drop. Such forces can come from gravity, a fluid flow over the surface, *etc.* Hence, we have a conundrum: superhydrophobic surfaces, which are typically rough, should be expected to have low contact angle hysteresis in the Cassie state, but this state generally evolves irreversibly to the Wenzel state for which there is large contact angle hysteresis.[9] So even though liquids have a relatively low attraction to the substrate, eventually the drops themselves become difficult to dislodge once they are on the superhydrophobic surface.

For all practical purposes, this feature of contact angle hysteresis leads to the demise of the ice-phobic possibilities of typical superhydrophobic surfaces—it is difficult to remove small drops before they freeze. In contrast, on smooth surfaces with low contact angle hysteresis, drops readily slide (even those with low contact angles for which the liquid is viewed as wetting). It is for the above reasons associated with hysteresis of contact angles, and the associated sliding of drops that experience tangential forces, that the term "wettability" often has two distinct and somewhat opposing meanings: one associated with the contact surface area and the other associated with the ease of sliding drops on a surface.[10]

We should also note that characterizing a given surface for the work required to separate ice from the substrate is important. A comprehensive study of ice adhesion was reported by Meuler *et al.*, who found the magnitude of the ice adhesion strengths on smooth surfaces correlated with the liquid–solid adhesion energy based on the receding contact angle.[11]

Recent Approaches Based on Superhydrophobic Surfaces and Their Apparent Shortcomings. Reflecting on the literature, it seemed plausible only a few years ago that superhydrophobic surfaces could provide a means to limit ice formation on surfaces, if for no other reason than because these surfaces are energetically disposed to reduce the contact area with water. Some studies of drop impact supported this view, at least at low relative humidity. However, as documented by Varanasi *et al.*,[12] when model superhydrophobic surfaces were exposed to an ambient atmosphere of relatively high humidity, frost readily formed on the surfaces, which subsequently became much more ice-friendly. As a consequence, the formation of ice fundamentally changes the basic wettability of the surface: whereas the dry surface would typically cause impacting drops to bounce, with some frost, impacting droplets freeze on the surface. The important conclusion that results, which significantly changes the perspective of material design routes for ice-phobic materials, is that the superhydrophobic response is lost once ice forms. In fact, it even appears that the ice coating is more robust than it is on a smooth surface (Figure 1).

A Bio-Inspired Idea. So if well-studied superhydrophobic surfaces, which tend to "repel" water, fail to provide a robust ice-phobic response, is there a materials idea that

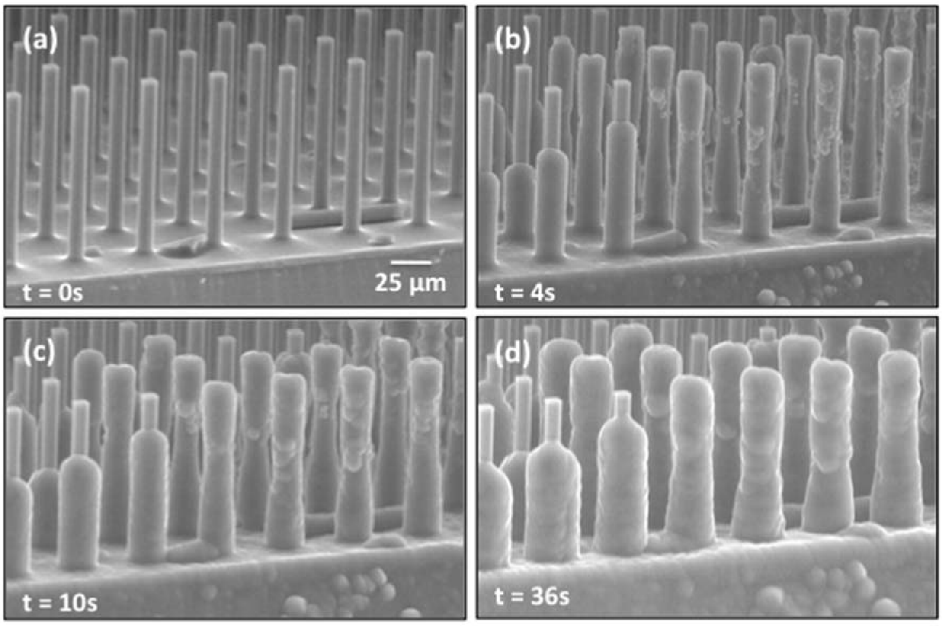

Figure 1. Frost formation on a microfabricated superhydrophobic surface. (a) Dry surface with a contact angle (for the flat material) of about 110°. The surface is maintained at −13 °C, and after the start of the experiment, the relative humidity is increased. (b−d) Frost formation is observed and occurs everywhere, including the top of the posts, the valleys, and the sides of the posts. Reprinted with permission from ref 12. Copyright 2012 American Institute of Physics.

might be more successful? To address this question, the Aizenberg group took inspiration from plant biology and recognized that minimizing contact angle hysteresis was likely the significant design approach.[13] For the latter, a smooth surface is desired, so that contact line pinning is minimized, and the smoothest surface available is that of a liquid. The authors were aware that the pitcher plant, a carnivorous species that traps and devours insects, has a slippery boundary that it uses to ensnare unsuspecting visitors. With this bio-inspiration, the authors designed their own liquid-infiltrated slippery substrate.

Thus, we turn to a new type of composite material, which is a slippery, liquid-infused porous surface, or SLIPS (Figure 2). From the standpoint of "liquid repellency", the most important ingredient is that the infused liquid must preferentially wet the substrate relative to an immiscible ambient fluid. In the examples studied to date, the substrate is textured either naturally or by fabrication at the nano- and/or micrometer scales and is completely wet by the infused liquid; the

From the standpoint of "liquid repellency", the most important ingredient is that the infused liquid must preferentially wet the substrate relative to an immiscible ambient fluid.

nanostructuring helps to retain the infused liquid. With icing conditions in mind, the infused liquid should have a freezing point well below the temperature expected in applications. Most significantly, the boundary of the substrate is now effectively a liquid interface, whose surface guarantees minimal contact line pinning, so low contact angle hysteresis is expected. Any deposited liquid droplets readily slide on the surface given the smallest tangential forces, and thus, this approach offers the potential for a substrate that minimizes ice accumulation.

An Anti-Icing Design. In order to apply SLIPS for potential anti-icing applications, it is important to adapt the technology to relevant and widely used engineering materials, in particular, metals. Aluminum is a common material that is widely used for structural applications such as industrial construction, marine vessels, airplanes, and heat exchangers, for which ice- and frost-free surfaces would improve and extend many applications. Consequently, as described in this issue of *ACS Nano*, the authors developed an electrodeposition technique of a textured conducting polymer to give the metal surface a nanostructured coating.[5] This step was followed by a chemical treatment (fluorination) and then infiltration of a low freezing point fluorinated liquid into the porous coating. To demonstrate the ice-phobic character of the SLIPS-coated aluminum, the authors studied contact angle hysteresis since, as explained above, this property is crucial to rapid and easy removal of water droplets. They also investigated frost formation on the surfaces.

Kim *et al.* report a series of experiments demonstrating that a SLIPS-coated aluminum surface has

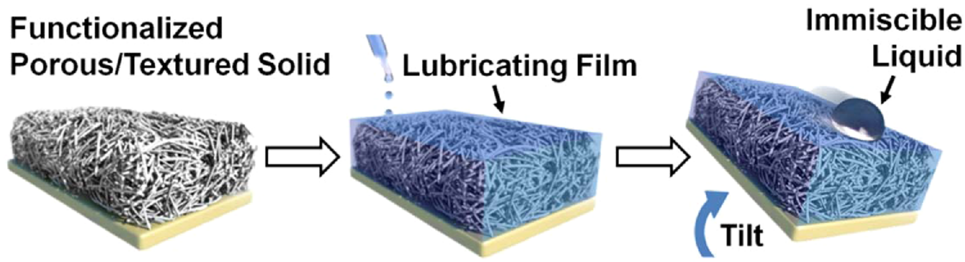

Figure 2. Design features of a slippery, liquid-infused porous surface, or SLIPS. A liquid is infiltrated into a functionalized porous or textured solid. The liquid should perfectly wet the solid and have a more favorable wettability for the solid than the ambient fluid. In this way, the surface of the substrate is actually a liquid interface, which typically exhibits very low contact angle hysteresis. Droplets readily slide along the surface given a small tangential force, *e.g.*, from the slight tilting of a plane (private communication: T.-S. Wong and J. Aizenberg).

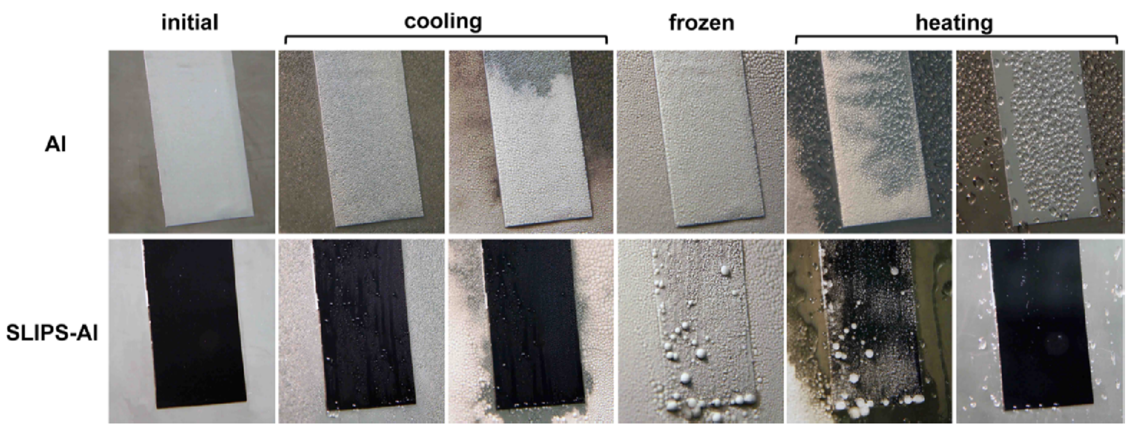

Figure 3. Contrasting ice formation from a high humidity environment to a plain aluminum surface (top) and a SLIPS-Al-coated surface (bottom). Following the cooling and freezing conditions, the materials are deiced by heating. The samples are approximately 3 cm in width and inclined 75°. The details of the experiments are described in ref 5. The SLIPS-Al substrate performs better during cooling since the water droplets have a much reduced chance of sticking and freezing and upon heating since the SLIPS-Al more rapidly sheds the drops from the melted ice. Reprinted from ref 5. Copyright 2012 American Chemical Society.

significantly reduced ice accumulation.[5] The main physical reason for the observations is the ability of the condensed or melted water droplets to slide easily off of the surface before freezing of the droplets occurs, which is to be contrasted with droplets on typical superhydrophobic surfaces that remain pinned and eventually freeze. An excellent demonstration of this property is presented in Figure 3, which compares a plain aluminum surface with a SLIPS-coated aluminum surface in conditions of high humidity that lead eventually to ice freezing on the surface. The SLIPS-coated surface is more resistant to freezing, and no ice is formed down to −2 °C, but ice does eventually form at lower temperatures. However, as the surface is then heated, the SLIPS-coated surface more readily sheds the melted water drops or entire ice sheets since the infiltrated liquid does not freeze and the surface has low contact angle hysteresis. In addition, the authors measured the adhesion of ice to these surfaces to be almost 2 orders of magnitude lower than state-of-the-art materials that show the lowest ice adhesion. Consequently, there is strong evidence that the SLIPS approach provides an effective strategy for a next generation ice-phobic material.

> Kim *et al.* report a series of experiments demonstrating that a SLIPS-coated aluminum surface has significantly reduced ice accumulation.

OUTLOOK AND FUTURE CHALLENGES

In this Perspective, I have described a recent study highlighting the potential of SLIPS as an ice-phobic material. In particular, the material performed well in high-humidity conditions involving freezing and melting cycles. As with any new idea, more studies are needed and over a broader range of conditions, but as the idea for the composite material/surface takes advantage of very low contact angle hysteresis, there should be optimism that the future of SLIPS for ice-phobicity is as bright as it is cold.

Of course, in many, if not most, applications, there is motion of the surface relative to the ambient. How will the associated fluid flows affect

SLIPS, and are there limits to the performance of the material when such surface (shear) stresses are applied? Will the materials work well in both laminar (low Reynolds number) flows and turbulent (high Reynolds number) flows? In addition, in many applications, two surfaces come into contact. How will SLIPS behave in such situations, especially if two surfaces coated with SLIPS are brought into contact? Finally, it is worth thinking about applications that take advantage of the design of SLIPS, which has an internal space through which liquid can flow. Are there possibilities to use the movement of the infiltrated liquid in applications such that SLIPS acts as a sensor or detector? Such multifunctionality would take a promising idea into new directions.

Conflict of Interest: The authors declare no competing financial interest.

REFERENCES AND NOTES

1. Raraty, L. E.; Tabor, D. The Adhesion and Strength Properties of Ice. *Proc. R. Soc.* **1958**, *A245*, 184–201.
2. Jellinek, H. H. G. Adhesive Properties of Ice. *J. Colloid Sci.* **1959**, *14*, 268–280.
3. Meuler, A. J.; McKinley, G. H.; Cohen, R. E. Exploiting Topographical Texture To Impart Icephobicity. *ACS Nano* **2010**, *4*, 7048–7052.
4. Mishchenko, L.; Hatton, B.; Bahadur, V.; Taylor, J. A.; Krupenkin, T.; Aizenberg, J. Design of Ice-Free Nanostructured Surfaces Based on Repulsion of Impacting Water Droplets. *ACS Nano* **2010**, *4*, 7699–7707.
5. Kim, P.; Wong, T.-S.; Alvarenga, J.; Kreder, M. J.; Adorno-Martinez, W. E.; Aizenberg, J. Liquid-Infused Nanostructured Surfaces with Extreme Anti-Ice and Anti-Frost Performance. *ACS Nano* **2012**, 10.1021/nn302310q.
6. Nishino, T.; Meguro, M.; Nakamae, K.; Matsushita, M.; Ueda, Y. The Lowest Surface Free Energy Based on $-CF_3$ Alignment. *Langmuir* **1999**, *15*, 4321–4323.
7. Guo, P.; Zheng, Y.; Wen, M.; Song, C.; Lin, Y.; Jiang, L. Icephobic/Anti-Icing Properties of Micro/Nanostructured Surfaces. *Adv. Mater.* **2012**, *24*, 2642–2648.
8. Furmidge, C. G. Studies at Phase Interfaces. 1. Sliding of Liquid Drops on Solid Surfaces and a Theory for Spray Retention. *J. Colloid Sci.* **1962**, *17*, 309–324.
9. Lafuma, A.; Quéré, D. Superhydrophobic States. *Nat. Mater.* **2003**, *2*, 457–460.
10. Gao, L.; McCarthy, T. J. Teflon Is Hydrophilic. Comments on Definitions of Hydrophobic, Shear *versus* Tensile Hydrophobicity, and Wettability Characterization. *Langmuir* **2007**, *24*, 9183–9188.
11. Meuler, A. J.; Smith, D.; Varanasi, K. K.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. Relationships between Water Wettability and Ice Adhesion. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3100–3110.
12. Varanasi, K. K.; Deng, T.; Smith, J. D.; Hsu, M.; Bhate, N. Frost Formation and Ice Adhesion on Superhydrophobic Surfaces. *Appl. Phys. Lett.* **2010**, *97*, 234102.
13. Wong, T.-S.; Kang, S. H.; Tang, S. K. Y.; Smythe, E. J.; Hatton, B. J.; Grinthal, A.; Aizenberg, J. Bioinspired Self-Repairing Slippery Surfaces with Pressure-Stable Omniphobicity. *Nature* **2011**, *477*, 443–447.