



MELTING BELOW ZERO

New research shows how a layer of water on the surface of ice—even at temperatures well below freezing—can influence everything from the slipperiness of a skating rink to the electrification of thunderclouds

by John S. Wettlaufer and J. Greg Dash

The first weather report of the year warning of a cold snap sets homeowners to the task of insulating their most vulnerable water pipes. They know that preventing the water from freezing inside the pipes will avert damage that could happen as the water turns solid and expands. But what many people do not know is that they are also guarding against an even greater pressure generated because the surface of the ice remains liquid.

The freezing of water and the melting of ice are among the most common and dramatic examples of matter changing phases, yet basic aspects of how these transformations occur have long puzzled the physicists and chemists who study them. In the past 15 years, researchers have discovered some answers in a thin layer of water, only a few molecules thick.

This quasiliquid film, a natural state of solid ice formed by a process called surface melting, bears some structural characteristics of the solid below it but has the mobility of a fluid. Despite its microscopic size, this film plays a central role in the basic principles of melting and freezing—and in their many environmental consequences. Working both as a path-

way for flowing water and as a carrier of electrical charge, this slick coating has the power to force boulders from the ground and to blast lightning bolts from the sky.

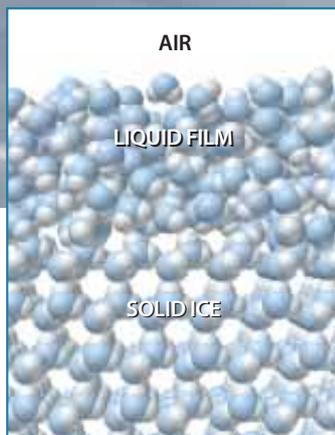
Snowballs and Ice Skates

On hearing the term “surface melting,” one’s first reaction might be to imagine how a solid melts from its surface inward as it is heated. A pat of butter on a stove or a lump of solder under a soldering iron begins to liquefy on its surface simply because the outside is hotter than the inside. But surface melting refers specifically to a less obvious effect: even if the solid is the same temperature inside and out, it develops a thin coating of its liquid phase at several tens of degrees Celsius below the overall melting point.

To understand the physics of surface melting, picture yourself deep inside an ice crystal, where the water molecules adopt a fixed and repeated pattern that builds a rigid lattice. As you move from the crystal’s center to its surface, you periodically encounter water molecules, each one neatly coordi-



FILMS OF WATER make ice surfaces slick for skaters, even at temperatures below freezing, because water molecules in the ice crystals lose their rigidity as they extend into the open air (*right*).



RICHARD HAMILTON SMITH Corbis; MICHAEL GOODMAN (inset)

nated with its four nearest neighbors. As you approach the crystal's surface, however, the lattice becomes distorted as the outermost molecules reach out into the unstructured environment of the air around them. These surface molecules have the fewest chemical bonds holding them in place, and as a result they vibrate more violently as the temperature warms than do the molecules in the interior of the crystal. At a sufficiently high temperature—but still below the normal melting point—the molecules begin to flow in a liquidlike layer [*see illustration above*].

The idea that a thin film of liquid exists on the surface of ice is not a new one, but for many years people misunderstood its origin. Anyone who has ever taken sides in a snow-

ball fight knows that to produce an effective projectile, the snow needs to be wet. Dry snow just does not stick together. And what about the futile attempt to manufacture a “sand-ball” at the beach? In the 1630s French scientist and philosopher René Descartes wrote down his observations of why ice sticks together. Some 200 years later musings over the same question challenged English physicist Michael Faraday to begin two decades of careful studies of snow and ice. “When wet snow is squeezed together, it freezes into a lump (with water between) and does not fall asunder as so much wetted sand or other kind of matter would do,” Faraday wrote in the fall of 1842. Excerpts from Faraday's diary record the first investigation into what we know today as surface melting. It seemed to him that a thin layer of water coating the snowflakes must freeze to glue them together. This layer, he concluded, is a natural phenomenon of ice just below its melting point.

Faraday and fellow British physicist John Tyndall conducted independent experiments that proved—at least to them—that a liquid film exists on the surface of ice at equilibrium, but some powerful contemporaries were unconvinced. In 1849 James Thompson and his brother William Thompson (who later became Lord Kelvin) countered with a suggestion that the thin layer of water results only from the temporary lowering of the melting point, which occurs when another object in contact with the ice increases the pressure against it. Molecules are packed more tightly in water than in ice, so squeezing ice under the sharp blade of a skate, for instance, takes the solid a step closer to its liquid form.

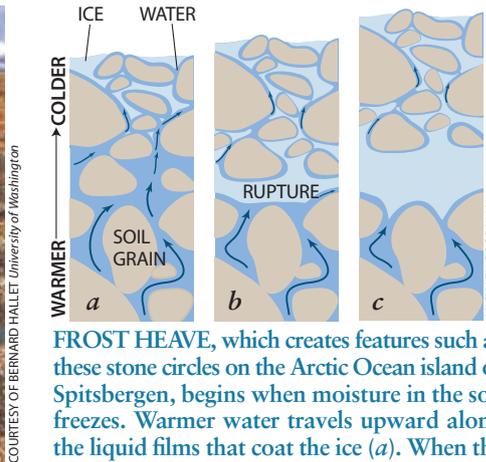
This phenomenon, called pressure melting, became the accepted explanation for the slipperiness of ice and is still found in many textbooks today. A simple calculation, however, shows that pressure melting cannot explain this slick surface except at temperatures close to ice's normal melting point. A person gliding across a frozen lake on a conventional skate lowers the melting point of the ice by no more than a couple of degrees C. So if pressure melting were the only factor, a skate would slide only when the temperature hovered around freezing, a rather unsafe time to be out on an ice-covered lake anyway. To account for this discrepancy, Frank P. Bowden and T. P. Hughes of the University of Cambridge argued in 1939 that a different factor dominates at lower temperatures: friction between the ice and the skate blade creates enough heat to form a thin layer of water.

Both pressure melting and frictional heating have held scientists' attention for more than 100 years, but neither explains why, as any skater could tell you, it is so tricky to stand still on skates. Nor do these theories explain the underlying dynamics of frost heave or the electrification of thunderclouds, two important environmental effects of ice [*see box on next two pages*]. For complete answers, we turn back to Faraday's observations of surface melting, a phenomenon intrinsic to virtually all solids.

Wet Surfaces

Although physicists in addition to Faraday had predicted the existence of surface melting by the 1950s, no one actually observed the microscopic layer of liquid on a melting surface until the mid-1980s. In 1985 Joost M. W. Frenken and J. Friso van der Veen of the Institute for Atomic and Molecular Physics in Amsterdam fired beams of ions at a crystal of lead as they heated it to near the metal's melting

Environmental Effects of Surface Melting



THE HARD, COLD GROUND

After a fall freeze, farmers in rock-ribbed regions such as New Hampshire may awaken to an upheaval of their previously cleared fields: stones stand on pedestals of ice needles, and soil bulges up around larger rocks. This occurrence—called frost heave—ranges from an agricultural annoyance to an industrial nightmare. Despite its dramatic effects, frost heave owes its strength to microscopic liquid films on the surface of ice.

Frost heave begins when chilly air cools the soil and freezes some of the water near the top of the ground, but the real damage is wrought after this initial freeze. Molecular forces and impurities on the ice surfaces can prevent the moisture from freezing solid until the temperature drops several tens of degrees below zero Celsius. Until then, a microscopic film of water coats the ice crystals, which grow between the tiny fragments of rock and clay that make up the soil.

Water from deeper soils feeds the growth of the ice crystals. Warm water contains more free energy than cold water, and like all compounds, it wants to reach a state of lowest free energy. In freezing soils this tendency trans-

lates into what scientists call thermomolecular pressure: warm water is drawn toward areas where it can lose some of its energy by forming ice. Conveniently, the water has a built-in roadway—the liquid films on the ice surfaces.

Water continues to invade the spaces between the grains of icy soil until the buildup of water pressure there can counteract the pressure of the incoming water. This force between the ice and soil grains can grow to about 160 pounds per square inch for every degree below zero C, until the ice freezes completely. (For comparison, a service station's typical hydraulic lift needs only 21 pounds per square inch to raise a 3,000-pound car.) Most often, the soil ruptures underground long before this pressure is reached. Water then flows into the void, where it freezes into a solid layer of ice. The ice layer widens as more water flows in and freezes, forcing the ground above to heave.

In a recent study at the University of Washington, Larry A. Wilen, now at Ohio University, designed a simple apparatus that enabled him to make the first direct measurement of a microscopic equivalent of frost heave. Wilen fashioned a dime-shaped chamber, which enclosed an ice crystal encircled by water. A

FROST HEAVE, which creates features such as these stone circles on the Arctic Ocean island of Spitsbergen, begins when moisture in the soil freezes. Warmer water travels upward along the liquid films that coat the ice (a). When the water pressure between the ice and soil grains overcomes that of the incoming water, the soil ruptures (b). Water rushes in and freezes, and the ground heaves in response (c).

glass plate served as one face of the chamber, and a sheet of plastic formed the other. Between zero and -1 degree C, a film of water formed where the ice touched the plastic.

Wilen cooled the disk's surface so that its center was the coldest. The water at the disk's warmer edge, driven by the resulting thermomolecular pressure, flowed toward the center of the ice crystal along the liquid film. Some of the water froze along this path and raised the plastic cover, just as growing layers of ice underground pushed soil apart. With Grae Worster of the University of Cambridge, we have since developed a theory explaining the microscopic motion of this liquid film that drives frost heave.

ELECTRIFYING COLLISIONS

On a hot summer day we may dream of cooler times—and of ice, perhaps. And then, with a crash of lightning, ice falls as a downpour of hailstones. Ice is also there in the thunderhead, actively involved in the genera-

point, 328 degrees C. From the way the ions bounced back, the two researchers deduced that the rigid lattice of atoms at the crystal's surface became increasingly disordered—and began to resemble atoms in a fluid—at only 318 degrees C. The film thickened gradually as the temperature continued to rise, eventually melting the crystal from the surface inward. In 1986 Da-Ming Zhu, then a doctoral student at the University of Washington, and one of us (Dash) found that thin films of argon and neon undergo gradual phase changes below their normal melting points. Since then, researchers have shown that virtually all solids undergo surface melting.

So it is with ice. Several investigators have monitored the surface melting of ice in the laboratory, but their conclusions about the thickness of the film and its dependence on temper-

ature are not always consistent. The variability may stem partly from difficulties interpreting results of multiple techniques. Optical techniques, for example, record the density difference between the liquid film and the solid ice by the way each reflects light. Another method examines the structure of the crystal surface by measuring the way it scatters x-rays.

An additional factor that can widen the gap between the results of experiments using the same instrument is the great sensitivity of the liquid film to impurities dissolved in the water. Airborne impurities, most notably salts and carbon dioxide, can make their way into the instrument and build up on ice surfaces during freezing. We are just beginning to explore their influence on surface melting, but recent theoretical work by one of us (Wetlaufer) suggests that impurities enhance surface

tion of lightning. One of the most spectacular phenomena in everyday life, lightning was once explained as the thunderbolts of angry gods; in a later age it stimulated research on the basic nature of electricity. As it turns out, the microphysics of ice holds the key to how charge develops in clouds. The electrification involves a liquid film—only a few molecules thick—that coats the surface of ice crystals blowing through the clouds.

Lightning typically originates from the base of the cloud, where it is cold enough to freeze droplets of moisture. As these tiny ice crystals rise in updrafts, they bump into large clumps of hail falling to the ground. The smaller ice crystals tend to ricochet upward from the collision with a positive charge, leaving an equal negative charge on the falling hail. As a result, the cloud builds up electrical charge—positive charges near the top of the cloud and negative charges near the bottom.

Researchers gathered this information from observations and laboratory simulations, but they have struggled to account for the amount or sign of the clouds' electrical charge. In 1984 Greg J. Turner and C. David Stow of the University of Auckland in New Zealand proposed that the thin films of water that coat the surfaces of the ice crystals and the hailstones might be involved in the charging process. Five years later our University of Washington colleague Marcia Baker and one of us (Dash) explained how this might work: electrical charge is carried along with water that moves from the hailstones to the ice crystals when they collide.

Brian Mason tested this theory in our laboratory as part of his doctoral research, which he completed in 1998. Mason weighed grains of ice before and after a collision using two quartz-crystal microbalances, which can detect changes in mass on the order of a few ten-billionths of a gram—sensitive enough to detect the

minuscule mass of a few layers of water molecules. He also measured the electric currents that flowed during the collisions to determine whether charge moved with mass.

As Baker and Dash's theory had predicted, a transfer of mass was always associated with the movement of charge. The growing ice crystal—which gained a layer of water only

hundreds of molecules thick over an area of one hundredth of a square millimeter—adopted a positive charge after the collision.

In a surprising and significant result, Mason found that the amount of mass transferred was far greater than the basic theory of surface melting, which depends on temperature and the size of the crystal, could explain. This discrepancy was one of the essential clues that led us to develop a more rigorous model of the collisions that electrify clouds. At the heart of our theory is a mechanism

that increases the tendency of ice to liquefy even below its melting point: a forceful collision can create enough damage in the ice's solid molecular lattice to melt additional liquid, even at 10 or more degrees below its melting point.

Together with impurities, such as carbon dioxide, that are commonly present on ice, collisions lead to an increasingly thick film of water. The thickness of the film is important because it liberates more liquid mass and charge that can then move from one icy surface to another.

The formation of a liquid after such an impact also liberates negatively charged ions that had accumulated near the surface of the ice crystal as it grew. During a collision, ice crystals and hailstones share a melted layer, and the growing crystals lose some of their negative ions. That is how we suspect that hailstones falling through the base of the cloud gather the negative charge from which lightning originates.

Further experiments and calculations will test these new ideas, but there seems little doubt that the charging mechanism that leads to spectacular lightning displays and the forces that drive frost heave lie in a layer of water only a few molecules thick. —J.S.W. and J.G.D.



LIGHTNING typically originates from the base of thunderclouds, where falling hailstones accumulate a negative charge during collisions with ice crystals blowing in updrafts (inset).

melting. As it turns out, the solid ice efficiently rejects impurities that build up in the liquid films because they do not fit into its crystal lattice. Dissolved salts, for example, can thereby increase the thickness of the film by lowering both the melting point of the ice and the free energy of the liquid.

More than 150 years after Faraday's first observations of thin liquid layers on the surface of ice, we are only starting to tease out the underlying physical mechanisms responsible for its slipperiness, adhesive properties and outright destructive power. Many questions remain. What we do know is that a better grasp of the microphysics of ice will lead us closer to understanding its environmental effects. Delving into the molecular origins of frost heave and cloud electrification are but two possible avenues of research. SA

The Authors

JOHN S. WETTLAUER and J. GREG DASH, both physicists at the University of Washington, collaborate frequently. Their joint research has focused on how microscopic properties of ice surfaces and phase transitions drive large-scale phenomena in the environment.

Further Information

ICE PHYSICS AND THE NATURAL ENVIRONMENT. Edited by J. S. Wettlaufer, J. G. Dash and N. Untersteiner. NATO ASI Series I: Global Environmental Change, Vol. 56. Springer-Verlag, 1999. For additional references, visit Furio Ercolessi's Surface Physics Web site at <http://www.sissa.it/cm/sp/course/refs.html>