Click here to view this article's online features:

ANNUAL Further

- Download figures as PPT slides
  Navigate linked references
- Navigate linked refere
   Download citations
- Explore related articles
- Search keywords

# Ice Surfaces

# Mary Jane Shultz

Laboratory for Water and Surface Studies, Department of Chemistry, Tufts University, Medford, Massachusetts 02155; email: mary.shultz@tufts.edu

Annu. Rev. Phys. Chem. 2017. 68:285-304

First published online as a Review in Advance on March 15, 2017

The Annual Review of Physical Chemistry is online at physchem.annualreviews.org

https://doi.org/10.1146/annurev-physchem-052516-044813

Copyright © 2017 by Annual Reviews. All rights reserved

# Keywords

hydrogen bonding, single crystal, cubic ice, hexagonal ice, surface melting, electron backscatter diffraction, sum frequency generation

## Abstract

Ice is a fundamental solid with important environmental, biological, geological, and extraterrestrial impact. The stable form of ice at atmospheric pressure is hexagonal ice,  $I_b$ . Despite its prevalence,  $I_b$  remains an enigmatic solid, in part due to challenges in preparing samples for fundamental studies. Surfaces of ice present even greater challenges. Recently developed methods for preparation of large single-crystal samples make it possible to reproducibly prepare any chosen face to address numerous fundamental questions. This review describes preparation methods along with results that firmly establish the connection between the macroscopic structure (observed in snowflakes, microcrystallites, or etch pits) and the molecular-level configuration (detected with X-ray or electron scattering techniques). Selected results of probing interactions at the ice surface, including growth from the melt, surface vibrations, and characterization of the quasi-liquid layer, are discussed.

#### **1. INTRODUCTION**

# *I<sub>b</sub>*: ice phase with ABAB stacking

Ice is arguably among the most fundamental and ubiquitous solids in the Universe (1–3). Consisting of two of the three most abundant elements, ice and its liquid form, water, not only shape Earth and our Solar System but also transport material throughout the Universe. Of the 18 or so crystalline phases of ice, hexagonal ice ( $I_b$ ) is the stable phase at atmospheric pressure. Given the importance of ice to Earth, it might be expected that  $I_b$ —hereafter referred to simply as ice—is well characterized. That it is not is a testament to the challenges, both theoretical and experimental, in divining ice's secrets.

Ice is challenging in part due to configurational flexibility exemplified by the famous residual entropy of ice at 0 K (4). The source of residual entropy lies in the tetrahedral coordination around the oxygen atom: Two coordinations are bonds to hydrogen atoms and two are lone pairs. Hence, water forms an extended network, but there is considerable flexibility for locating the hydrogen atoms to satisfy the "ice rules" (5): exactly one hydrogen atom must be located between any pair of oxygen atoms and every oxygen atom must be covalently bonded to exactly two hydrogen atoms. Surface termination leads to dangling valences. Dangling valences, even at the ideal surface, can be random or patterned (6-10). Finally, as is common with many solids, the ice surface can relax and/or reconstruct. Thus, it is not surprising that "research on the properties of the ice surface has a long and often controversial history" (11, p. 324).

Single-crystal surface studies revolutionized understanding of heterogeneous catalysts and nanoparticles ranging from pure metals to alloys to semiconductors. The global impact of this work was recognized with the 2007 Nobel Prize awarded to Gerhardt Ertl. Applying the single-crystal surface strategy to ice has been hindered by challenges both in substrate generation and in probe methodology. As a result, questions about molecular-level structure, dynamics, surface binding site patterns, and adsorbate interactions/transformations remain unanswered (12). Taking inspiration from catalyst studies, this review begins with a description of two key developments for substrate preparation: growth of high-quality single crystals and connection of surface-structure probe signals with surface molecular configuration.

The goal of this review is to highlight recent advances that promise to help unlock ice surface secrets, as well as to summarize important open questions. The emphasis is on experimental results. The first requirement for examining the surface is preparing it; Section 2 describes recently developed tools. The connection between the macroscopic shape and the crystal structure is discussed in Section 3. Interfacial interactions are described in Section 4.

# 2. GROWING AND ORIENTING

Several methods exist for growing single crystals and model ice surfaces in the laboratory, including deposition on a substrate (13–18) and growth from the melt in either a Bridgman (19, 20) or a Czochralski (21) apparatus.

#### 2.1. Bridgman Method

The oldest technique for growing single crystals was developed by Bridgman in 1925 (19). Somewhat modified by Stockbarger (20), this is the method of choice for growing large GaAs semiconductor crystals and other mixed-element semiconductor crystals, as well as very low–defect density Si crystals. In broad strokes, the technique consists of passing a crucible containing the melt and a single-crystal seed from a high-temperature region into a low-temperature one. The single-crystal seed both circumvents issues associated with kinetic growth due to supercooling and provides an



Schematic of a crucible used in a Bridgman apparatus (not drawn to scale). The crucible body is 2.5 cm in diameter and approximately 30 cm long. The capillary is approximately 4 mm long. The bulb provides a convenient way to flash-freeze a polycrystalline seed. The combined capillary and neck select a single domain to seed the growth tube.

oriented substrate for crystal growth. The Bridgman–Stockbarger method has been modified for single-crystal ice growth (**Figure 1**) (22, 23) in two significant ways. First, a polycrystalline seed is used rather than a single crystal because it is easier to generate a noncontaminated polycrystalline seed by simply flash-freezing water in the seed bulb, e.g., by touching the bulb to a dry ice pellet. The crucible narrows to a neck that spatially filters the multiple flash-frozen crystal domains to a single domain that seeds the remainder of the boule. The capillary connecting the seed bulb to the crucible is surprisingly effective at reducing the millions of exposed faces generated by flash-freezing to fewer than five exposed faces in the crucible (23). The few domains propagate through the crucible until they reach the neck. At the neck, domains that intersect the shoulders are quenched. Only domains aligned with the neck emerge to seed the remainder of the boule. In short, the capillary and neck select the single domain that generates the boule.

The second significant modification of the Bridgman–Stockbarger method concerns process parameters designed to keep a stable, near-equilibrium growth front. Temperature fluctuations are minimized via the viscosity of the surrounding thermal transfer fluid (ethylene glycol) and by further surrounding the growth apparatus with a temperature-stabilized bath. The temperature gradient in the growth zone is controlled both to minimize convective mixing and to ensure dissipation of the heat of fusion between steps. In the reported work, the temperature gradient is maintained at 0.015  $\pm$  0.001°C/mm using a proportional integral differential controller. Success is demonstrated by near-100%, optically perfect single crystal production.

The Bridgman ice-growth process yields a surprising result about the ice-water interface. Faces of the polycrystalline seed are presumably randomly oriented because the seed is generated by flash-freezing water in the bulb. As growth proceeds up the capillary, these numerous faces compete; the more stable faces occupy increasingly larger fractions of the ice-water interface **EBSD:** electron backscatter diffraction

**STM:** scanning tunneling microscopy

*d*-OH: OH bond lacking an acceptor

*d*-O: lone pair dangling valence

(24–27). The surprising result is that the most stable face—the face that seeds the larger boule—is never the basal face. Indeed, the faces that emerge are the primary prism face and the secondary prism face, with the secondary face being slightly more likely. This result, discussed further in Section 4.1.1, is attributed to slight differences in the balance between the surface entropy and surface enthalpy among the three major faces of ice.

The orientation of the crystal axes relative to the boule axes is not known a priori for boules grown with the Bridgman method. However, the orientation can be determined using several methods including X-ray diffraction, electron backscatter diffraction (EBSD), and etching. Of these, etching is the most convenient for laboratory work (28).

#### 2.2. Czochralski Method

The Czochralski method of single-crystal ice growth was first reported in 1975 (29). It consists of attaching an oriented, single crystal to a cold ( $\sim$ -20°C) pin and extracting it from a rapidly circulated melt. The major advantages of the Czochralski method are that it is fast and that the orientation of the crystal within the boule is known because growth is seeded by a single crystal. Czochralski-grown ice boules are typically 30 mm long, whereas Bridgman-grown crystals are limited only by the physical dimension of the crucible and growing chamber.

Typical extraction rates are 5 mm/h (30), much faster than Bridgman parameters. The contrast between these two techniques likely lies in the mechanism for preventing incorporation of alternate-orientation crystallites into the growing boule. Alternate-orientation crystallites are out of register with the bulk ice orientation and hence form a grain boundary with the growing boule. Bridgman growth excludes these out-of-register crystallites via thermodynamic growth: Higher-energy crystallites either reorient into registry with the bulk or melt. Czochralski growth is kinetically controlled and uses a well-stirred melt. It is believed that the weak grain-boundary connection between nonregistered crystallites and the bulk crystal, in conjunction with fast stirring, sweeps misregistered crystallites off the growing surface (21).

#### 2.3. Growth on a Substrate

The molecular-level structure of the ice surface strongly influences interactions between ice and gas-phase molecules in the atmosphere (31–33). Hence, ice has been the subject of numerous ultrahigh vacuum techniques that image at the molecular level. Recent studies with scanning tunneling microscopy (STM) (9, 34–42) provide insights into the ice surface. For STM studies, ice is grown on a substrate: Cu (34, 40), Pt (35, 36, 41, 42), Pt/Ru (39), or BaF<sub>2</sub> (38). In what follows, we focus on the influence of the substrate on ice structure.

The Cu(111) surface has a hexagonal structure with lattice constants that closely match those of ice, and so is considered to be an excellent substrate for growing model hexagonal ice surfaces. At the surface, the ideal tetrahedral coordination of the oxygen atoms is disrupted, generating dangling OH bonds (*d*-OH) and dangling lone pairs (*d*-O). A naïve picture suggests that the surface is planar, tessellated with hexagonal rings that are decorated with dangling OH bonds orthogonal to the surface. STM data at low temperatures (<160 K) combined with modeling (34, 40) suggest a richer picture consisting of admolecules with little area covered by a simple hexagonal structure. Monomer admolecules are bonded to the surface via three strained hydrogen bonds that favor a donor–donor–acceptor configuration. As the adcluster grows, linear structures are more stable than hexagonal rings or star-like structures. Linear structures are reminiscent of a striped or Fletcher (6) phase that has strings of nearest-neighbor *d*-OH orientations. The STM images cannot distinguish *d*-OH from *d*-O, but clearly show a chain structure for the admolecules.

Annealing to 130 K generates one-hexagon-wide adrows growing along the [112] direction of cubic ice ( $I_c$ ) or the [1101] direction of hexagonal ice. Calculations (38) suggest that these adrows are either parallel to or form 60° angles with a Fletcher stripe. This configuration is consistent with faceting and observation of equilateral triangular islands on annealing to 149 K (34). Formation of linear structures gives rise to an effective local electric field (37) that directs the orientation of impinging polar molecules, affecting the adsorption energy. Modifying the adsorption energy likely also modifies the ice structure.

Modification of the ice structure is clearly observed on  $BaF_2(111)$ . Water on  $BaF_2(111)$  is imaged at room temperature with scanning polarization force microscopy (38), a method that produces coarser resolution than low-temperature images on metals. The results, however, provide insight into interaction between water and surfaces that have been proposed as excellent icenucleating agents. The (111) face of  $BaF_2$  consists of trilayers, with  $Ba^{2+}$  ions sandwiched between  $F^-$  layers. The lattice constant is 4.38 Å, comparable to that of ice (4.52 Å). Contrary to prediction,  $BaF_2$  is not a good ice-nucleating agent. The oxygen atoms nicely bind to the  $Ba^{2+}$  sites, but the hydrogen atoms bind to the adjacent  $F^-$  ions. This configuration inhibits formation of an ice bilayer and hence hinders ice growth. Water molecules accumulate at step edges, growing chains along the [ $\overline{1}10$ ] direction. Other directions are hydrophobic.

The influence of step edges is also seen for ice grown on Pt(111) (35, 39, 41, 43). Ice is usually deposited as an amorphous film at <120 K. After heating, ice crystallizes into a hexagonal array that is in register with the underlying metal atoms. First-layer water molecules, however, do not form an ideal hexagonal array: only *d*-O molecules are observed (44). The non-hydrogen-bonded OH group points to the metal to maximize interaction there. At 125 K, interaction with adsorbates can be sufficient to flip the water from OH down to OH up. The flip is accompanied by formation of hexagonal layers (39). This example illustrates both the flexibility of the water molecule and a source of challenge in obtaining molecular-level data on ice.

Combining experiment and theory, a series of papers examined the water layer structure as the film thickness increased (35, 36, 41). At low coverage, ice forms  $I_b$  patches on terraces. Growing the patches large enough to span across the step edges leads to a very interesting phenomenon involving hexagonal and cubic ice. We next discuss the subtle but important differences between these two crystal structures.

Ice is an insulator, so STM does not probe beyond the top bilayer. Thus, STM is not able to distinguish between hexagonal and cubic ice because these differ only in the bilayer stacking. Layers in hexagonal ice alternate as ABAB ..., whereas those in cubic ice are ABCABC .... This seemingly subtle packing difference has profound consequences. All hexagonal rings in cubic ice are chair-configuration hexagons, whereas those in hexagonal ice include boat-configuration hexagons. The only stable face of cubic ice is the (111) plane, whereas several faces of hexagonal ice have nearly identical energies. Specifically, the hexagonal basal face, the primary prism face (the rectangular sides of the hexagonal prism), and the secondary prism face (a cut across alternate hexagonal apices) are nearly isoenergetic. Pyramidal faces that cut across the sharp edge between the basal face and the prism faces are only slightly higher in energy. All of these faces are observed (45–47).

For ice grown on a substrate, the stacking difference between hexagonal and cubic ice interplays with the step height to determine which crystal forms. Flat substrates generate  $I_b$  ice, likely due to edge termination by prism faces. As two  $I_b$  patches meet, the step height is critically important. The substrates Pt(111) (35, 36, 41) and BaF<sub>2</sub>(111) (38) feature step heights corresponding to one ice bilayer, so two hexagonal patches can join smoothly across the step only if the bilayers are similarly oriented. The orientation can be visualized with the tetrahedral coordination around the oxygen atoms of the upper half bilayer (**Figure 2**). For cubic ice, the triangular bases of the tetrahedra in both bilayers face in the same direction. Two patches can thus smoothly join with *I<sub>c</sub>*: face-centered cubic ice; phase with ABC stacking



Ice crystal structure: top view of the basal face showing tetrahedral coordination around the oxygen atom. In the top bilayer, the upper atoms are colored red; in the lower bilayer, upper atoms are colored green. Remaining oxygen atoms are not shown for clarity. The O–O distances in hexagonal and cubic ice are the same. (*a*) In cubic ice ( $I_c$ ), the tetrahedral triangular bases are all oriented in the same direction. (*b*) In hexagonal ice ( $I_b$ ), tetrahedral triangular bases are rotated 180° from bilayer to bilayer. As a result,  $I_c$  lacks stable prism faces. In contrast, the energies of the prism faces of  $I_b$  ice are comparable to that of the basal face.  $I_c$  also lacks the open channels that are characteristic of  $I_b$ .

only a simple screw dislocation. In contrast, the hexagonal ice tetrahedra are rotated by 180° in alternate bilayers.  $I_b$  would thus form a high-energy grain boundary at the single bilayer step. The crystal structure thus shifts from hexagonal to cubic as the patches bridge the step edge (41).

As the ice film grows thicker to  $\sim 20$  nm (about 50 bilayers), it can support double spirals. Depending on orientation, double spirals can accommodate two step height shifts; that is, they negate the established single spiral (41). Thicker films thus support return to hexagonal ice. This example exquisitely illustrates the importance of the supporting substrate.

#### 3. MOLECULAR STRUCTURE-CRYSTAL STRUCTURE CONNECTION

One of the stunning features of the ice literature is the sheer volume of unanswered questions. Ice grows under rather mundane conditions and has been known for a very long time. The large number of unanswered questions is a testament to the challenges posed by the flexible nature of the hydrogen bond binding the solid. Among the only recently answered questions is the relationship between the macroscopic morphology and the molecular-level structure of ice. Microcrystallites, snowflakes, and etch pits all have a hexagonal structure long associated with the basal face. At the molecular level, there are two hexagons in the basal face (**Figure 3**). One is defined by the chair-configuration hexagonal structure, hereafter referred to as the molecular hexagon (**Figure 3**, green outline). The other hexagon is derived from the crystallographic unit cell. The unit cell is a right-angle, rhombohedral prism (**Figure 3**, blue outline). The crystallographic hexagon (**Figure 3**, black outline). Notice that the molecular and the crystallographic hexagons are orthogonal. In a hexagonal structure, *a* axes point to the hexagonal apices, so the molecular and crystallographic *a* axes are also orthogonal. The essence of the question is: Which



(*a*) Stick model looking down on the basal face of hexagonal ice. The molecular hexagon is the smaller hexagon, outlined in green. The crystallographic rhombohedral unit cell is shown in blue (and, in panel *b*, in three dimensions). The crystallographic hexagon includes the unit cell and is completed in black. Note that the molecular and crystallographic hexagons are rotated 90° to each other.

hexagon is reflected in the shape of snowflakes, the orientation of negative crystals, and the shape of microcrystallites?

The widespread assumption (18, 46, 48–57) is that the growth hexagon is the crystallographic hexagon. Until recently (58), experimental evidence for this assumption has been tenuous, based on a paper by Nakaya (56). The argument is that dendrites should grow in low-index directions. All angles in the dendrites corresponded to low indices if the prism apices corresponded to {1010}, but not if they corresponded to {1120} (59, 60). This conclusion appears to have propagated, being cited by Higuchi (51), who developed ice etching. Higuchi's method is widely used, particularly in glaciology research, and provides a readily applied laboratory method for determining crystal orientation (28, 51, 53, 61). Often the focus is on the *c* axis orientation between crystallites, so the *a* axis orientation has been less relevant. As focus shifts to fundamental issues such as face-specific ice growth kinetics (55, 62–67) and its dependence on molecular-level structure, *a* axis orientation between critical.

### 3.1. The Probes

Connecting the macroscopic structure to the underlying molecular-level configuration is greatly aided by large single crystals. Within a hexagonal structure, there are three *a* axes connecting opposing hexagonal points. Consequently, the *a* axes of the two molecular-level hexagons—the molecular hexagon and the crystallographic hexagon—are related by a mere  $30^{\circ}$  rotation. Thus, connecting the macroscopic hexagonal prism shape to either molecular-level hexagon requires that the microscopic and the macroscopic probes sample the same crystallite. Single crystals found in the environment typically exhibit numerous dislocations on the periphery of void hexagons (68). Dislocations can easily shift the *a* axis by tens of degrees. Thus, availability of large, low-defect single crystals enable compelling connection between the macroscopic shape and the microscopic configuration. Probes making this connection are described in this section.

**3.1.1. Etch and growth.** Etching was developed by Higuchi (51, 61) as an improvement over Tyndall flowers (56) to probe the ice macroscopic shape. Etch pits have the shape of negative hexagonal prisms truncated at the surface (**Figure 4***a*). Determining orientation of both the *c* and



Etch and growth of ice. (*a*) Example etch pits with truncated hexagonal prism submerged on the left side. The hexagonal point is rolled toward the bottom of the photo. (*b*) Scanning electron microscopy image of small crystallites showing hexagonal prism shape with chamfer between basal end cap and rectangular sides. Panel *b* reproduced from Reference 69 with permission. (*c*) Primary-face etch pits showing chamfered corners similar to those of microcrystallites.

*a* axes from the etch pit profile is a geometric exercise (28, 53). Success in generating any desired face (28) validates the negative crystal model for the etch pits.

Crystal growth is the inverse of etching. Microcrystallites can be imaged with scanning electron microscopy (45–47). As shown in **Figure 4b**, the overall crystallite shape is also that of a hexagonal prism. Note that the basal face meets the primary prism face at a 90° angle; the surface energy is lowered if the 90° corner is chamfered. **Figure 4c** shows that the larger etch pits from a primary prism face are also chamfered. Complementarity of etch pits and microcrystallites suggests that both growth and desorption reflect the same hexagonal structure. Generating a molecular-level picture for the water–water interactions that lead to the overall hexagonal shape or the specific chamfer morphology requires answering the question of which hexagon—the molecular or the crystallographic—is reflected in the macroscopic observed shapes. This connection is discussed below following description of the molecular-level probe EBSD.

**3.1.2. Electron backscatter diffraction.** EBSD is based on the well-known wave properties of electrons. Electrons reflect from the various crystal planes, interfering and creating a diffraction pattern. The first diffraction patterns, called Kikuchi patterns, were reported in 1928 (70). Because electrons are charged particles, penetration depth is shallow, typically  $\sim$ 20 nm, so EBSD is a surface technique (71). Application of EBSD to ice is more recent, just over a decade old (72–76).

EBSD data are typically displayed in pole figures (**Figure 5**). Three axes are imaged for ice: the *c* or optical axis, the crystallographic *a* axis, and a third mutually orthogonal axis in the basal plane labeled the *b* axis. Note that the hexagonal symmetry means that there are three *a* and three *b* axes. The data consist of scatter plots of axis orientations over the sampled area (**Figure 6***a*,*b*). A false-color pole plot of the *c* axis for a single-crystal sample is shown in **Figure 6***a*; note the tight spot indicating consistent *c* axis orientations for the >400 spots sampled. A similar plot for the *a* axis (**Figure 6***b*) shows multiple, tightly clustered spots consistent with the three *a* axes.

#### 3.2. The Connection Implications

The connection between the crystallographic and the etch hexagon is revealed by using large single crystals, so that both etch and EBSD data are obtained from the same surface (58). The hexagon connection is most clearly shown with a basal face sample. Note that the c axis hot spot



Schematic of pole figure data from electron backscatter diffraction (EBSD). Backscattered electrons impinge on a phosphor screen; phosphorescence is imaged on a charged-couple device array. Data are typically processed with software that accompanies the EBSD instrument. The crystal plane normal penetrates the reference sphere, the penetration point is connected to the south pole of the reference sphere, and the projection-plane crossing point is recorded. The projection-plane crossing points generate the pole projection plot.

(Figure 6*a*) is somewhat off-sphere north because the sample *c* axis is slightly tilted relative to the surface normal. The six ends of the three *a* axes (Figure 6*b*) also reveal the surface tilt; the three lower *a* axes' ends are slightly above the horizon, the 10-o'clock axis is on the horizon, and the remaining two are slightly below the horizon. A photomicrograph of etch pits on the same surface is shown in Figure 6*c*. An etch pit is outlined, magnified, and overlaid on the *a* axis EBSD image in Figure 6*d*. The merged figure clearly shows that the crystallographic *a* axes coincide with the etch pit apices; the etch pit hexagon coincides with the crystallographic hexagon. A similar experiment with X-ray (30) diffraction draws the same conclusion.

Armed with the correspondence between etch pit hexagonal prisms and the crystallographic hexagon, the molecular configuration on the various faces is clear. For example, a surface with the rectangular etch pattern of **Figure 4***c* is correctly labeled as a primary prism face of the crystallographic hexagonal prism. Surface termination consists of rows of water molecule pairs (**Figure 7***a*). The lower half bilayer features pairs in the unoccupied rows staggered between top-half bilayer pairs. Surfaces with V-bottom boat etch patterns (similar to **Figure 4***a*) are secondary prism faces and are terminated in water molecule chains (**Figure 7***b*). Both the chain and the pair axes are along the *c* axis.

Results of molecular-level surface probes can be interpreted in terms of both short- and longrange interactions. The next section contains discussion of interaction probes: growth from the melt (23, 77), spiral growth (18, 78), surface vibrations (79, 80), and premelting (30, 81, 82).



Correlation between crystallographic axes and etch axes. Electron backscatter diffraction (EBSD) pole figures are color coded: red indicates high-density crossing points, blue low density, and white no density. (*a*) The *c* axis pole figure tight clustering indicates a single crystal with axis slightly tilted relative to the surface. (*b*) The *a* axis pole figure shows six points corresponding to three  $\pm a$  axes. (*c*) Etch pit image of the surface used in EBSD. (*d*) Etch hexagon outlined, magnified, and laid over the *a* axis pole plot. The conclusion is that the etch hexagon coincides with the crystallographic hexagon.

#### 4. MOLECULAR-LEVEL INTERACTIONS

Connecting etches/growth and crystallographic hexagons is important for molecular-level models of growth and melting. We desribe two microscopic methods to monitor growth: reading the frozen front record and using laser confocal microscopy–differential interference microscopy (LCM-DIM). Interactions likely guide molecules and nanoscopic particles into registry with the growing interface (83). Vibrational spectroscopy has the potential to probe these interactions; results using surface-sensitive vibrational spectroscopy sum frequency generation (SFG) to probe interactions suggest that long-range interactions significantly affect vibrational energies. Section 4.3 discusses the old but unsettled issue of surface premelting, also known as formation of a quasi-liquid layer (QLL) on the ice surface.

# differential interference microscopy

LCM-DIM: laser

confocal microscopy-

**SFG:** sum frequency generation

**QLL:** quasi-liquid layer

## 4.1. Growth

Faces of ice are nearly isoenergetic. The close energy match challenges experimentalists to design experimental conditions capable of yielding a clear conclusion about which face is the most stable



Stick model of the two prism faces of ice. In both images the *c* axis is vertical, with surface terminating molecules shown in red, the next layer in green, and the remainder with reduced size. (*a*) Top view of the primary prism face showing hydrogen-bonded pairs aligned along the *c* axis. (*b*) Top view of the secondary prism face showing chains of hydrogen-bonded water molecules; the chain axes are aligned along the *c* axis.

or about the growth mechanism. As a fringe benefit of the equilibrium conditions supported by the Bridgman apparatus, a boule cross section contains a frozen record of the equilibrium growth. Section 4.1.1 describes the connection between the frozen record and face stability; the conclusion is that the secondary prism face is the most stable at the solid–liquid interface. The growth mechanism can be probed with differential interference microscopy (DIM). Results suggest that growth on a substrate occurs via a layer-by-layer spiral growth mechanism, as discussed in Section 4.1.2. Each of these is described in greater detail in the following paragraphs.

**4.1.1. Growth from the melt.** As indicated above,  $I_b$  has three major faces: the basal face and the primary and secondary prism faces. All have very similar energies. Small perturbations tip the balance of which is the most stable, and hence largest, face (26, 27). This delicate balance is thought to explain the dendritic shape of snowflakes (55, 62–65, 84). Although a comprehensive model is still lacking, it is likely that snowflake growth (growth at the solid–vapor interface) is kinetically controlled. In contrast, growth at the solid–liquid interface can be thermodynamically controlled because material transport to the interface is not an issue and slow growth ensures near-equilibrium thermal transport. On the basis of a Wulff model relating face energy and surface area (24, 26, 27, 85), Bridgman single-crystal ice growth yields evidence for the lowest-energy face at the ice–water interface. The boule slowly lowers from an above-freezing region to a subzero region, so once it is solidified, the frozen boule cross section contains a record of the growing front, much like tree rings reveal past climate. Relative face energy is revealed by prominence of a given face among multiple boules.

The growth face is determined through examination of the ice-crystal lattice orientation with respect to the boule cross section. If we classify the growing face as basal if the *c* axis is tilted  $<45^{\circ}$  from the boule axis and as prism if tilt  $> 45^{\circ}$ , the result is that basal face boules are never observed. Prism face growth is subdivided into primary and secondary according to the *a* axis orientation. Secondary prism boules outnumber primary boules by  $\sim3:2$ . Because the polycrystalline seed crystal contains a random face sampling, this predominance suggests that the secondary face is the most stable face at the solid–liquid interface, followed closely by the primary prism face.

Face	Primary prism	Secondary prism	Basal
Termination motif	Bonded pairs	Bridging chains	3-Coordinate
Successful docks	14/16	1/2	3/4
Entropy* (cm <sup>-2</sup> )	$8.07 \times 10^{14}$	$7.20 \times 10^{14}$	$6.94  imes 10^{14}$
Enthalpy ( $\mu J \times cm^{-2}$ )	5.94	6.90	5.57

Table 1	Configuration.	enthalpy, and	entropy	of ice	faces

\*Relative to bulk.

A simple model similar to Pauling's (4) model for the residual entropy of ice at 0 K suggests a source of stability of the two prism faces relative to the basal face. Formation of a hydrogen bond is exothermic, so faces with greater *d*-OH density release more heat on bonding the termination layer (**Table 1**). The other component of surface energy is entropy. Surface entropy is modeled relative to the residual entropy of ice. Because the liquid has greater entropy than the solid, faces with greater entropy—those with more flexibility in attaching the termination layer—are favored. Prism faces not only release more heat but also have greater entropy per unit area than the basal face. Thus, only prism faces are observed in the frozen record. Between the two prism faces, the primary prism face is favored by entropy and the secondary by enthalpy. Entropy and enthalpy are necessarily closely matched at the freezing point, so it is not surprising to observe both prism faces in nearly equal number among the frozen boules.

Note that this model for face determination also suggests the basis for kinetic growth favoring the basal face. The two prism faces release more heat per unit area than does the basal face. If thermal conduction is limited, as is expected for the thin dendrites in a snowflake and the poor thermal conductivity of the gas phase, then the greater exothermicity of the two prism faces results in greater evaporation from these faces, leading to accumulation on the basal face.

**4.1.2. Differential interference microscopy spiral growth.** One of the open questions concerning ice is that of the growth mechanism: Does ice grow layer by layer [Frank–van der Merwe (FM) growth] or by island growth [Vomer–Weber (VW) growth], perhaps by attachment of preformed crystallites (83)? To address this question, LCM-DIM (86) was used to probe the surface. LCM-DIM is capable of high spatial resolution. It probes the solid–air interface on a bilayer scale. Elementary, single spiral steps at the basal face were reported in 2010 (18); double spirals were reported in 2014 (78). In the reported work, the solid was grown from the vapor on a AgI crystal. In light of subsequent work (41), it seems likely that the first report was dominated by cubic ice, the second transition to hexagonal ice. Nonetheless, the consistent interpretation is that ice grows via an FM mechanism rather than nucleating at defects, which would lead to island formation.

FM: Frank–van der Merwe or layer-by-layer growth VW: Vomer–Weber or island growth

#### 4.2. Interactions and Vibrations (Sum Frequency Generation)

There are only two methods capable of probing either buried or high–vapor pressure interfaces at the molecular level: the two nonlinear spectroscopies, SFG and second harmonic generation (SHG) (87–90). Of these, only SFG is capable of detecting OH vibrations. The OH vibrational frequency is highly sensitive to the hydrogen bonding environment, redshifting by as much as 700 cm<sup>-1</sup> from the unperturbed OH stretch. This makes the OH vibration a prime candidate for probing interactions at the ice surface.

An SFG spectrum is generated by overlapping a visible and an infrared laser beam on the surface. The intensity is the square of the nonlinear polarizability,

$$I(\omega) = \frac{32\pi^3\omega^2 \sec^2 \eta_{\rm SF}}{c^3 n_1(\omega_{\rm SF})n_1(\omega_1)n_1(\omega_2)} \left| \tilde{E}(\omega_{\rm SF}) \cdot \tilde{\tilde{\chi}}^{(2)} : \tilde{E}(\omega_{\rm vis})\tilde{E}(\omega_{\rm IR}) \right|^2,$$

where  $\eta_{\rm SF}$  is the sum frequency angle,  $\tilde{E}$  is the electric field vector for the  $\omega_j$  beam,  $n_i(\omega_j)$  is the index of refraction in medium *i* at frequency  $\omega_j$  [1 = visible, 2 = IR (infrared)], *c* is the speed of light, and  $\tilde{\tilde{\chi}}^{(2)}$  is the second-order hyperpolarizability (third-order tensor) for the surface. SFG thus provides two experimental handles—the polarization of the visible and the infrared beams—and reports on surface composition via  $\tilde{\tilde{\chi}}^{(2)}$ . Both the polarization and the directional properties of  $\tilde{\tilde{\chi}}^{(2)}$  have been used to delve into the structure of ice surfaces.

The directional properties of  $\tilde{\tilde{\chi}}^{(2)}$  are probed by using a visible excitation polarized 45° to the input plane, defined as the plane formed by the surface normal and the impinging light propagation direction. With 45° incident polarization, the electric field excites both tangential and longitudinal polarizations. The emitted sum frequency polarization is thus not limited to either polarization. Instead, the tangential and longitudinal responses interfere, generating an amplitude ( $A_{\Theta 45p}$ ) response

$$A_{\Theta 45p} = \left[ (\cos \Theta_{\rm SF} \cos \eta_{\rm SF} L_X K_X^{\rm vis} \pm \sin \Theta_{\rm SF} \cos \eta_{\rm SF} L_Y K_Y^{\rm vis}) \chi_{XXZ} + \cos \Theta_{\rm SF} \sin \eta_{\rm SF} L_Z K_Z \chi_{ZZZ} \right] \\ \times \cos 45^\circ K_Z^{\rm IR} e_{45}^{\rm vis} e_p^{\rm IR},$$

where  $\Theta_{SF}$  is the experimentally determined sum frequency polarization angle, *L* and *K* are optical and Fresnel factors, and  $\chi_{IJK}$  are the elements of the hyperpolarizability tensor. Measuring the SF polarization reveals the balance between the longitudinal,  $\chi_{XXZ}$ , and the transverse,  $\chi_{ZZZ}$ , surface polarizations.

The ice 3,100-cm<sup>-1</sup> peak shows an unusual response: It is not a simple dipole (80, 91, 92). Interpretation of this result is not yet complete (93–95), but it appears that the peak consists of two uncorrelated dipole responses. Why the two dipole responses are uncorrelated is an open question. Theory suggests that one of the dipole responses is due to bilayer stitching bonds (94). This represents the first assignment of a distinct bonding motif in the broad hydrogen-bonded region. Assignment of the origin of the second dipole awaits further experimental and theoretical developments.

The  $3,100\text{-cm}^{-1}$  peak is nearly the most redshifted of the OH stretches in the ice surface. On the other end are the nearly isolated resonances at about  $3,400 \text{ cm}^{-1}$ . Being on the blue end of the hydrogen-bonded resonances, the  $3,400\text{-cm}^{-1}$  peak originates from weak hydrogen-bonded oscillators. Theory indicates (96, 97) that weak hydrogen bonding is associated with 3-coordinate, *d*-O surface-termination water molecules. On the secondary prism face, surface termination consists of chains of water molecules (**Figure 7**). This chain consists of water molecule pairs along the *c* axis connected by pairs nearly orthogonal to it. This configuration provides an additional experimental variable: The surface can be oriented with the *c* axis in the plane of incidence or orthogonal to it.

The hydrogen bond between a bonded pair is parallel to the surface. Due to this orientation the pair bond is SFG-silent. Thus, SFG-observed resonances in the hydrogen-bonded region report on OH oscillators pointing into the surface. The strength of the hydrogen bond to the surface is nonetheless sensitive to the bonding partner. Consider a molecule with a d-O: Its bonding partner can have either a d-O or a d-OH. If the partner configuration affects the surface-donating OH bond strength, the SFG spectrum will show distinct resonances for these two configurations. In addition, the pair aligned with the c axis is in a different polarization environment than the

pair nearly orthogonal to it; the SFG spectrum should show distinct resonances for these two environments. Thus, there are four potential resonances in the weak hydrogen-bonded region: d-O, d-O parallel to c; d-O, d-OH parallel to c; d-O, d-OH parallel to c; d-O, d-OH orthogonal to c; and d-O, d-OH orthogonal to c. All four are observed (79, 98). Peaks are assigned on the basis of polarization: longitudinal if d-O, d-O; transverse if d-O, d-OH. The two pairs aligned along the c axis form weaker hydrogen bonds to the surface (shifts to 3,390 cm<sup>-1</sup> and 3,425 cm<sup>-1</sup>) than the two orthogonal to the c axis (shifts to 3,385 cm<sup>-1</sup> and 3,372 cm<sup>-1</sup>). The two longitudinal pairs form surface bonds of nearly identical strength (3,385 cm<sup>-1</sup> and 3,390 cm<sup>-1</sup>).

On the basal face, all dangling bonds are perpendicular to the surface and are isolated from other dangling bond molecules. Thus, there is only one *d*-O configuration. The donor to the surface bond resonance is at 3,385 cm<sup>-1</sup>, the same frequency as the two longitudinal configurations on the secondary prism face.

The hydrogen-bond strength variation among the four weak hydrogen bond configurations is significant: nearly 70 cm<sup>-1</sup>. The level of detail of these experimental results presents a challenge to theorists trying to model hydrogen bond strength at the solid surface, but may also give insight into hydrogen bonds at the liquid interface.

#### 4.3. Premelting and the Quasi-Liquid Layer

Among the open questions about ice surfaces are: What is the temperature for formation of the QLL? For a given temperature, how thick is the QLL? What is the nature of the QLL? These questions have received intense scrutiny since the QLL was postulated by Faraday in 1859 (99). (For a review, see 100; for a discussion of efforts through 2006–7, see 101.) In sum, techniques as diverse as glancing angle X-ray (102, 103), SFG (82), He atom scattering (104), atomic force microscopy (105, 106), ellipsometry (107), photoelectron spectroscopy (108), nuclear magnetic resonance (NMR) (109, 110), theory (111–114), and differential interference contrast (57, 115, 116) conclude that the QLL exists. There is wide discrepancy among the techniques concerning the formation temperature, from as low as 200 K to as high as 260 K. The discrepancy has been attributed to various causes, from contamination to differing probe depths. There is also disagreement about the nature of the QLL. Theory indicates that it is ordinary supercooled water (117), whereas recent interfacial force microscopy (105) suggests that the QLL is neither ice nor water but rather a new viscoelastic phase.

There is evidence that probe depth influences conclusions about QLL onset temperature. Two SFG studies illustrate the probe depth issue. The shallowest probe depth is provided by the free-OH signature. On the ideal basal surface, terminating OH bonds are orthogonal to the surface. Using deviation from orthogonality as a signature of QLL formation leads to the conclusion that the QLL forms at  $\sim$ 200 K (81, 82, 118), the coldest temperature reported. More recent work (30) examined the hydrogen-bonded region, which probes deeper into the surface. As the temperature is lowered there is a step-by-step redshift. The shift, together with modeling, suggests that the transition consists of bilayer-by-bilayer melting and begins at 255 K, nearly the warmest temperature reported. These two reports not only probe different depths, but also probe different characteristics. The free OH is sensitive to the termination-layer configuration, whereas the hydrogen-bonded region is sensitive to four-coordinate bonding extending deeper in the lattice.

Considering these results together, it is clear that even the definition of the QLL is not agreed upon. Absent such a definition, it is not clear what signature to examine. We know that the technique used, probe depth, and characteristic measured affect conclusions. Much more effort is needed.

# 5. OPEN ISSUES AND FUTURE DIRECTIONS

Ice remains an enigmatic solid. Enumerating all the open questions is well beyond the scope of this review; only those questions related to topics already discussed are addressed here. Recently developed methods for growing large, single-crystal samples and for generating any desired face are expected to significantly advance efforts to address these questions.

Several questions relate to ice growth: Does ice grow from the melt in the same manner as it does from the vapor? Is that growth layer-by-layer (an FM mechanism) or island growth (a VW mechanism)? If the latter, do nanocrystallites form and land on the developing face or do islands nucleate on the surface, perhaps because of near-surface defects? If ice is grown on a substrate, how does the substrate affect ice properties? What substrate is suitable as a model for the prism faces of ice?

Armed with the connection between the molecular-level structure and the surface termination, can we address fundamental questions about the impact of termination pairs (primary face) or chains (secondary face) on interactions between ice and impinging molecules? Nearly every question about the QLL remains unresolved. Progress requires an agreed-upon definition. Then we can address questions such as: What is the onset temperature? What is the nature of the QLL?

# **SUMMARY POINTS**

- 1. Methods are now available to grow large single-crystal ice samples, enabling fundamental studies similar to those that revolutionized understanding and optimization of catalysts.
- 2. The connection between the macroscopic hexagonal shape and etch pit profile and the crystallographic lattice is experimentally established.
- 3. The molecular configuration of various faces is determined. The primary face terminates in water molecule pairs and a bilayer structure. The secondary prism face consists of chains and a nonbilayer structure.
- 4. Hexagonal ice and cubic ice differ in oxygen atom tetrahedral orientation, resulting in channels in  $I_b$  but not in  $I_c$ . Interactions in ice are long range, so interactions with impinging molecules are expected to differ for these two forms of ice.
- 5. The structure of ice grown on a substrate is significantly altered by interactions with the substrate.
- 6. Numerous open questions include: What is the growth mechanism? Relative energies of various faces are not well understood. What is the impact of face termination on ice surface energy and reactivity? What definition is relevant for the QLL? At what temperature does the QLL form? What is the nature of the QLL?

# **DISCLOSURE STATEMENT**

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

# ACKNOWLEDGMENT

Partial support of this work from the US National Science Foundation (grant numbers CHE1565772 and CHE0844986) is gratefully acknowledged.



#### LITERATURE CITED

- 1. Stern SA, Bagenal F, Ennico K, Gladstone GR, Grundy WM, et al. 2015. The Pluto system: initial results from its exploration by New Horizons. *Science* 350:aad1815
- 2. Hand E. 2015. Late harvest from Pluto reveals a complex world. Science 350:260-61
- NASA. 2015. The Milky Way and Universe is awash in water. The Daily Galaxy, April 7. http://www. dailygalaxy.com/my\_weblog/2015/04/nasa-the-milky-way-and-universe-is-awash-in-water.html
- Pauling L. 1935. The structure and entropy of ice and other crystals with some randomness of atomic arrangement. J. Am. Chem. Soc. 57:2680–84
- Bernal JD, Fowler RH. 1933. A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions. *J. Chem. Phys.* 1:515–48
- 6. Fletcher NH. 1992. Reconstruction of ice crystal surfaces at low temperatures. Philos. Mag. B 66:109-15
- Buch V, Groenzin H, Li I, Shultz MJ, Tosatti E. 2008. Proton order in the ice crystal surface. PNAS 105:5969–74
- Pan D, Liu L-M, Tribello GA, Slater B, Michaelides A, Wang E. 2008. Surface energy and surface proton order of ice *I<sub>b</sub>*. *Phys. Rev. Lett.* 101:155703
- 9. Pan D, Liu L-M, Tribello GA, Slater B, Michaelides A, Wang E. 2010. Surface energy and surface proton order of the ice *I<sub>b</sub>* basal and prism surfaces. *J. Phys. Condens. Matter* 22:074209
- Materer N, Starke U, Barbieri A, Hove MAV, Somorjai GA, et al. 1995. Molecular surface structure of a low-temperature ice I<sub>b</sub>(0001) crystal. *J. Phys. Chem.* 99:6267–69
- Paesani F, Voth GA. 2007. Quantum effects strongly influence the surface premelting of ice. *J. Phys. Chem. C* 112:324–27
- Pedersen A, Wikfeldt KT, Karssemeijer L, Cuppen H, Jónsson H. 2014. Molecular reordering processes on ice (0001) surfaces from long timescale simulations. *J. Chem. Phys.* 141:234706
- Bluhm H, Salmeron M. 1999. Growth of nanometer thin ice films from water vapor studied using scanning polarization force microscopy. *J. Chem. Phys.* 111:6947–54
- Kaya S, Weissenrieder J, Stacchiola D, Shaikhutdinov S, Freund H-J. 2007. Formation of an ordered ice layer on a thin silica film. *J. Phys. Chem. C* 111:759–64
- 15. Kimmel GA, Petrik NG, Dohnalek Z, Kay BD. 2007. Crystalline ice growth on Pt(111) and Pd(111): nonwetting growth on a hydrophobic water monolayer. *J. Chem. Phys.* 126:114702
- Döppenschmidt A, Kappl M, Butt H-J. 1998. Surface properties of ice studied by atomic force microscopy. *7. Phys. Chem. B* 102:7813–19
- Sadtchenko V, Giese CF, Gentry WR. 2000. Interaction of hydrogen chloride with thin ice films: the effect of ice morphology and evidence for unique surface species on crystalline vapor-deposited ice. *J. Phys. Chem. B* 104:9421–29
- Sazaki G, Zepeda S, Nakatsubo S, Yokoyama E, Furukawa Y. 2010. Elementary steps at the surface of ice crystals visualized by advanced optical microscopy. *PNAS* 107:19702–7
- 19. Bridgman PW. 1925. Certain physical properties of single crystals of tungsten, antimony, bismuth, tellurium, cadmium, zinc, and tin. Proc. Am. Acad. Arts Sci. 60:305-83
- 20. Stockbarger DC. 1936. The production of large single crystals of lithium fluoride. *Rev. Sci. Instrum.* 7:133-36
- Czochralski J. 1918. Ein neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle. Z. Phys. Chem. 92:219–21
- 22. Bisson P, Groenzin H, Barnett IL, Shultz MJ. 2016. High yield, single crystal ice via the Bridgman method. *Rev. Sci. Instrum.* 87:034103
- Shultz MJ, Bisson PJ, Brumberg A. 2014. Best face forward: crystal-face competition at the ice-water interface. *J. Phys. Chem. B* 118:7972–80
- Wulff G. 1901. On the question of speed of growth and dissolution of crystal surfaces. Z. Krist. Mineral. 34:449–530
- Sundquist BE. 1964. A direct determination of the anisotropy of the surface free energy of solid gold, silver, copper, nickel, and alpha and gamma iron. *Acta Metall.* 12:67–86
- Degawa M, Szalma R, Williams ED. 2005. Nano-scale equilibrium crystal shapes. Surf. Sci. 583:126– 38

- 27. Sehgal RM, Maroudas D. 2015. Equilibrium shape of colloidal crystals. Langmuir 31:11428-37
- Shultz MJ, Brumberg A, Bisson P, Shultz R. 2015. Producing desired ice faces. PNAS 112:E6096– 100
- 29. Roos DvdS. 1975. Rapid production of single crystals of ice. J. Glaciol. 14:325-29
- Sánchez MA, Kling T, Ishiyama T, van Zadel M-J, Bisson PJ, et al. 2017. Experimental and theoretical evidence for bilayer-by-bilayer surface melting of crystalline ice. *PNAS* 114:227–32
- Girardet C, Toubin C. 2001. Molecular atmospheric pollutant adsorption on ice: a theoretical survey. Surf. Sci. Rep. 44:159–238
- Abbatt JPD. 2003. Interactions of atmospheric trace gases with ice surfaces: adsorption and reaction. Chem. Rev. 103:4783–800
- 33. Huthwelker T, Ammann M, Peter T. 2006. The uptake of acidic gases on ice. Chem. Rev. 106:1375-444
- Mehlhorn M, Morgenstern K. 2007. Faceting during the transformation of amorphous to crystalline ice. *Phys. Rev. Let.* 99:246101
- Thürmer K, Bartelt NC. 2008. Growth of multilayer ice films and the formation of cubic ice imaged with STM. *Phys. Rev. B* 77:195425
- Nie S, Bartelt NC, Thürmer K. 2009. Observation of surface self-diffusion on ice. *Phys. Rev. Let.* 102:136101
- Sun Z, Pan D, Xu L, Wang E. 2012. Role of proton ordering in adsorption preference of polar molecule on ice surface. PNAS 109:13177–81
- Cardellach M, Verdaguer A, Santiso J, Fraxedas J. 2010. Two-dimensional wetting: the role of atomic steps on the nucleation of thin water films on BaF<sub>2</sub>(111) at ambient conditions. *7. Chem. Phys.* 132:234708
- Maier S, Lechner BAJ, Somorjai GA, Salmeron M. 2016. Growth and structure of the first layers of ice on Ru(0001) and Pt(111). *7. Am. Chem. Soc.* 138:3145–51
- Bockstedte M, Michl A, Kolb M, Mehlhorn M, Morgenstern K. 2016. Incomplete bilayer termination of the ice (0001) surface. *7. Phys. Chem. C* 120:1097–109
- Thürmer K, Nie S. 2013. Formation of hexagonal and cubic ice during low-temperature growth. PNAS 110:11757–62
- 42. Badan C, Heyrich Y, Koper MTM, Juurlink LBF. 2016. Surface structure dependence in desorption and crystallization of thin interfacial water films on platinum. *J. Phys. Chem. Lett.* 7:1682–86
- Zaragoza A, Conde MM, Espinosa JR, Valeriani C, Vega C, Eduardo Sanche L. 2015. Competition between ices Ih and Ic in homogeneous water freezing. *J. Chem. Phys.* 143:134504
- 44. Kimmel GA, Zubkov T, Smith RS, Petrik NG, Kay BD. 2014. Turning things downside up: adsorbate induced water flipping on Pt(111). *J. Chem. Phys.* 141:18C515
- Pfalzgraff WC, Hulscher RM, Neshyba SP. 2010. Scanning electron miscroscopy and molecular dynamics of surfaces of growing and ablating hexagonal ice crystals. *Atmos. Chem. Phys.* 10:2927–35
- Pfalzgraff W, Neshyba S, Roeselova M. 2011. Comparative molecular dynamics study of vapor-exposed basal, prismatic, and pyramidal surfaces of ice. J. Phys. Chem. A 115:6184–93
- Neshyba SP, Lowen B, Benning M, Lawson A, Rowe PM. 2013. Roughness metrics of prismatic facets of ice. *J. Geophys. Res. Atmos.* 118:3309–18
- Aufdermaur VAN, List R, Mayes WC, DeQuervain MR. 1963. Kristallachsenlagen in Hagelkörnern. Z. Angew. Math. Phys. 14:574–89
- Barrette PD, Sinha NK. 1996. Lattice rotation in a deformed ice crystal: a study by chemical etching and replication. *Mater. Chem. Phys.* 44:251–54
- Furukawa Y, Nada H. 1997. Anisotropic surface melting of an ice crystal and its relationship to growth forms. *J. Phys. Chem. B* 101:6167–70
- 51. Higuchi K. 1958. The etching of ice crystals. Acta Metall. 6:636-42
- 52. Knight C, Knight N. 1965. "Negative" crystals in ice: a method for growth. Science 150:1819-21
- Matsuda M. 1979. Instruments and methods: determination of *a*-axis orientations of polycrystalline ice. *J. Glaciol.* 22:165–69
- Knight C. 1996. A simple technique for growing large, optically "perfect" ice crystals. J. Glaciol. 42:585– 87
- Libbrecht KG, Rickerby ME. 2013. Measurements of surface attachment kinetics for faceted ice crystal growth. J. Cryst. Growth 377:1–8

28. This paper describes a procedure for generating any desired ice face from a single crystal.

41. Experiment and modeling show substrate control of cubic versus hexagonal ice.

- 56. Nakaya U. 1956. Properties of single crystals of ice, revealed by internal melting. Res. Pap. 13, Snow Ice Permafr. Res. Establ., Wilmette, IL
- Sazaki G, Zepeda S, Nakatsubo S, Yokomine M, Furukawa Y. 2012. Quasi-liquid layers on ice crystal surfaces are made up of two different phases. *Proc. Am. Acad. Arts Sci.* 109:1052–55
- Brumberg A, Hammonds K, Baker I, Backus E, Bisson P, et al. 2017. Single crystal I<sub>b</sub> ice surface: connecting macroscopic etch pits and molecular structure. Unpublished research
- 59. Bader H. 1950. The significance of air bubbles in glacier ice. J. Glaciol. 1:443-51
- 60. Bader H. 1939. Der Schnee und Seine Metamorphose. Bern, Switz.: Kümmerly & Frey
- 61. Higuchi K. 1957. A new method for recording the grain-structure of ice. J. Glaciol. 3:131-32
- Libbrecht KG. 2014. Toward a comprehensive model of snow crystal growth: 3. The correspondence between ice growth from water vapor and ice growth from liquid water. arXiv:1407.0740 [cond-mat.mtrlsci]
- Libbrecht KG. 2013. Toward a comprehensive model of snow crystal growth dynamics: 2. structure dependent attachment kinetics near -5 C. arXiv:1302.1231 [cond-mat.mtrl-sci]
- 64. Libbrecht KG. 2012. On the equilibrium shape of an ice crystal. arXiv:1205.1452v1 [cond-mat.mtrl-sci]
- Libbrecht KG. 2012. Toward a comprehensive model of snow crystal growth dynamics: 1. Overarching features and physical origins. arXiv:1211.5555 [cond-mat.mtrl-sci]
- Libbrecht KG. 2003. Explaining the formation of thin ice crystal plates with structure-dependent attachment kinetics. J. Cryst. Growth 258:168–75
- Libbrecht K. 2003. Growth rates of the principal facets of ice between -10°C and -40°C. J. Cryst. Growth 247:530-40
- Mizuno Y. 1978. Studies of crystal imperfections in ice with reference to the growth process by the use of X-ray diffraction topography and divergent Laue method. 7. *Glaciol.* 21:409–418
- 69. Butterfield N, Neshyba S. 2016. SEM images: ice crystallites. Personal communication
- 70. Nishikawa S, Kikuchi S. 1928. The diffraction of cathode rays by calcite. Proc. Imp. Acad. 4:175-477
- Schwartz A, Kumar M, Adams B, Field D, eds. 2009. *Electron Backscatter Diffraction in Materials Science*. New York: Springer Science
- Iliescu D, Baker I, Chang H. 2004. Determining the orientations of ice crystals using electron backscatter patterns. *Microsc. Res. Tech.* 63:183–87
- 73. Prior DJ, Diebold S, Obbard R, Daghlian C, Goldsby DL, et al. 2012. Insight into the phase transformations between ice Ih and ice II from electron backscatter diffraction data. *Scripta Mater.* 66:69–72
- Baker I, Sieg K, Spaulding N, Meese D. 2007. Advanced electron microscopy techniques for studying ice and firn cores. Ext. Abstr. 185, USGS OF-2007-1047, US Geol. Surv., Reston, VA
- 75. Obbard R, Baker I, Sieg K. 2006. Using electron backscatter diffraction patterns to examine recrystallization in polar ice sheets. *J. Glaciol.* 52:546–57
- Weikusat I, DeWinter DAM, Pennock GM, Hayles M, Schneijdenberg CTWM, Drury MR. 2010. Cryogenic EBSD on ice: preserving a stable surface in a low pressure SEM. *7. Microsc.* 242:295–310
- 77. Shultz MJ, Bisson PJ, Brumberg A. 2016. Correction to "Best face forward: crystal-face competition at the ice-water interface." *7. Phys. Chem. B.* 120:10420
- Sazaki G, Asakawa H, Nagashima K, Nakatsubo S, Furukawa Y. 2014. Double spiral steps on *I<sub>b</sub>* ice crystal surfaces grown from water vapor just below the melting point. *Cryst. Growth Des.* 14:2133–37
- Bisson P, Shultz MJ. 2013. Hydrogen bonding in the prism face of ice *I<sub>b</sub>* via sum frequency vibrational spectroscopy. *J. Phys. Chem. A* 117:6116–25
- Groenzin H, Li I, Buch V, Shultz MJ. 2007. The single crystal, basal face of ice *I<sub>b</sub>* investigated with sum frequency generation. *J. Chem. Phys.* 127:214502
- 81. Wei X, Shen YR. 2002. Vibrational spectroscopy of ice interfaces. Appl. Phys. B 74:617–20
- Wei X, Miranda PB, Shen YR. 2001. Surface vibrational spectroscopic study of surface melting of ice. *Phys. Rev. Lett.* 86:1554–57
- De Yoreo JJ, Gilbert PUPA, Sommerdijk NAJM, Penn RL, Whitelam S, et al. 2015. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science* 349:aaa6760
- Libbrecht KG. 2007. The formation of snow crystals: Subtle molecular processes govern the growth of a remarkable variety of elaborate ice structures. *Am. Sci.* 95:52–59

75. This paper describes substrate handling procedures for successful electron backscatter diffraction from ice surfaces.

78. This research detects spiral growth and demonstrates LCM-DIM on ice.

- 85. Barnard AS, Zapol P. 2004. A model for the phase stability of arbitrary nanoparticles as a function of size and shape. *J. Chem. Phys.* 121:4276–83
- Sazaki G, Matsui T, Tsukamoto K, Usami N, Ujihara T, et al. 2004. In situ observation of elementary growth steps on the surface of protein crystals by laser confocal microscopy. *J. Cryst. Growth* 262:536– 42
- 87. Shen YR. 2016. Fundamentals of Sum Frequency Spectroscopy. Cambridge, UK: Cambridge Univ. Press
- Shen YR, Ostroverkhov V. 2006. Sum-frequency vibrational spectroscopy on water interfaces: polar orientation of water molecules at interfaces. *Chem. Rev.* 106:1140–54
- 89. Shen YR. 2002. Principles of Nonlinear Optics. New York: John Wiley & Sons
- Shultz MJ. 2008. Sum frequency generation: an introduction plus recent developments and current issues. In *Advances in Multi-Photon Processes and Spectroscopy*, ed. SH Lin, AA Villaeys, Y Fujimura, pp. 133–200. Singapore: World Sci.
- Shultz MJ, Bisson P, Groenzin H, Li I. 2010. Multiplexed polarization spectroscopy: measuring surface hyperpolarizability orientation. *J. Chem. Phys.* 133:054702
- 92. Groenzin H, Li I, Shultz MJ. 2008. Sum-frequency generation: polarization surface spectroscopy analysis of the vibrational surface modes on the basal face of ice *I*<sub>b</sub>. *7. Chem. Phys.* 128:214510
- Ishiyama T, Morita A. 2014. A direct evidence of vibrationally delocalized response at ice surface. *J. Chem. Phys.* 141:18C503
- Ishiyama T, Takahashi H, Morita A. 2012. Origin of vibrational spectroscopic response at ice surface. *J. Phys. Chem. Lett.* 3:3001–6
- Yamaguchi S, Shiratori K, Morita A, Tahara T. 2011. Electric quadrupole contribution to the nonresonant background of sum frequency generation at air/liquid interfaces. J. Chem. Phys. 134:184705
- Buch V, Tarbuck T, Richmond GL, Groenzin H, Li I, Shultz MJ. 2007. Sum frequency generation surface spectra of ice, water and acid solution investigated by an exciton model. *7. Chem. Phys.* 127:204710
- 97. Buch V. 2005. Molecular structure and OH-stretch spectra of liquid water surface. J. Phys. Chem. B 109:17771-74
- Shultz MJ, Bisson P, Vu TH. 2014. Insights into hydrogen bonding via ice interfaces and isolated water. *7. Chem. Phys.* 141:18C521
- 99. Faraday M. 1859. On regelation, and the conservation of force. Philos. Mag. 17:162-69
- Dash JG, Fu H, Wettlaufer JS. 1995. The premelting of ice and its environmental consequences. *Rep. Prog. Phys.* 58:115–67
- 101. Li Y, Somorjai GA. 2007. Surface premelting of ice. J. Phys. Chem. C 111:9631-37
- Lied A, Dosch H, Bilgram JH. 1994. Surface melting of ice I<sub>b</sub> single crystals revealed by glancing angle X-ray scattering. *Phys. Rev. Lett.* 72:3554–57
- Dosch H, Lied A, Bilgram JH. 1995. Glancing-angle X-ray scattering studies of the premelting of ice surfaces. Surf. Sci. 327:145–64
- Suter MT, Andersson PU, Pettersson JBC. 2006. Surface properties of water ice at 150–191 K studied by elastic helium scattering. *J. Chem. Phys.* 125:174704
- 105. Goertz MP, Zhu X-Y, Houston JE. 2009. Exploring the liquid-like layer on the ice surface. *Langmuir* 25:6905–8
- Döppenschmidt A, Butt H-J. 2000. Measuring the thickness of the liquid-like layer on ice surfaces with atomic force microscopy. *Langmuir* 16:6709–14
- 107. Furukawa Y, Yamamoto M, Kuroda T. 1987. Ellipsometric study of the transition layer on the surface of an ice crystal. *J. Cryst. Growth* 82:665–77
- Bluhm H, Ogletree DF, Fadley CS, Hussain Z, Salmeron M. 2002. The premelting of ice studied with photoelectron spectroscopy. *J. Phys. Condens. Matter* 14:L227–33
- 109. Dec SF. 2009. Clathrate hydrate formation: dependence on aqueous hydration number. J. Phys. Chem. C 113:12355–61
- 110. Dec SF. 2012. Surface transformation of methane–ethane sI and sII clathrate hydrates. *J. Phys. Chem. C* 116:9660–65
- 111. Park S-C, Moon E-S, Kang H. 2010. Some fundamental properties and reactions of ice surfaces at low temperatures. *Phys. Chem. Chem. Phys.* 12:12000–11

85. This paper delineates the thermodynamics that determine nano- and microscopic particle morphology.

87. This is a description of sum frequency generation by the founder of the technique.

- 112. Shepherd TD, Koc MA, Molinero V. 2012. The quasi-liquid layer of ice under conditions of methane clathrate formation. *J. Phys. Chem. C* 116:12172–80
- Limmer DT, Chandler D. 2014. Premelting, fluctuations, and coarse-graining of water-ice interfaces. *J. Chem. Phys.* 141:18C505
- Persson BNJ. 2015. Ice friction: role of non-uniform frictional heating and ice premelting. J. Chem. Phys. 143:224701
- 115. Asakawa H, Sazaki G, Nagashima K, Nakatsubo S, Furukawa Y. 2016. Two types of quasi-liquid layers on ice crystals are formed kinetically. *Proc. Am. Acad. Arts Sci.* 113:1749–53
- 116. Sazaki G, Asakawa H, Nagashima K, Nakatsubo S, Furukawa Y. 2013. How do quasi-liquid layers emerge from ice crystal surfaces? *Cryst. Growth Des.* 13:1761–66
- Henson BF, Voss LF, Wilson KR, Robinson JM. 2005. Thermodynamic model of quasiliquid formation on H<sub>2</sub>O ice: comparison with experiment. *J. Chem. Phys.* 123:144707
- 118. Wei X, Miranda PB, Zhang C, Shen YR. 2002. Sum-frequency spectroscopic studies of ice interfaces. *Phys. Rev. B* 66:085401