Physical Dynamics of Ice Crystal Growth

Kenneth G. Libbrecht

Department of Physics, California Institute of Technology, Pasadena, California 91125; email: kgl@caltech.edu

Keywords

Crystal growth, solidification, layer nucleation, diffusion-limited growth, ice, faceting, molecular dynamics

Abstract

We examine ice crystallization from liquid water and from water vapor, focusing on the underlying physical processes that determine growth rates and structure formation. Ice crystal growth is largely controlled by a combination of molecular attachment kinetics on faceted surfaces and large-scale diffusion processes, yielding a remarkably rich phenomenology of solidification behaviors under different conditions. Layer nucleation plays an especially important role, with nucleation rates determined primarily by step energies on faceted ice/water and ice/vapor interfaces. The measured step energies depend strongly on temperature and other factors, and it appears promising that molecular dynamics simulations could soon be used in conjunction with experiments to better understand the energetics of these terrace steps. On larger scales, computational techniques have recently demonstrated the ability to accurately model the diffusion-limited growth of complex structures that are both faceted and branched. Together with proper boundary conditions determined by surface attachment kinetics, this opens a path to fully reproducing the variety of complex structures that commonly arise during ice crystal growth.
1. A CASE STUDY IN SOLIDIFICATION DYNAMICS

Water ice is one of the most common solid materials on the earth’s surface, playing important roles in a broad spectrum of meteorological, biological, environmental, chemical, and physical processes. Although the material properties of ice have been known for many decades, our basic understanding of ice crystal growth remains surprisingly poor. A prime example can be found simply by observing the falling snow. The winter clouds produce a great diversity of snow-crystal forms, from slender columns to thin plates, at times branched, sectored, hollowed, and faceted, as shown in Figure 1. Yet extensive laboratory and theoretical investigations have still not determined why these varied structures appear under different growth conditions. For example, we do not yet possess even a qualitative understanding of why snow crystal growth alternates between plate-like and columnar forms as a function of temperature, as seen in Figure 1, although this behavior was first observed more than 75 years ago (1).

The focus of this review will be on single-crystal ice Ih growing near the triple point, including ice forming from liquid water and from water vapor. Although this confines our attention to just a small region of the water phase diagram, the phenomenology we encounter is already quite puzzling, driven by complex nonequilibrium molecular dynamics at the ice/water and ice/vapor interfaces together with large-scale heat- and particle-diffusion effects. We ignore isotopic effects here, as these appear to be relatively minor regarding all aspects of ice growth, at least insofar as they have been measured.

Figure 1
The formation of atmospheric snow crystals remains a largely unsolved problem. (a) The morphology diagram qualitatively describes the growth of snow crystals as a function of temperature and water vapor supersaturation. The water saturation line shows the supersaturation of liquid water relative to ice. (b) Photographs of the iconic snowflake shape—thin, flat, stellar-dendrite snow crystals, such as those in subpanels i and ii—are almost always taken in a narrow temperature range near −15°C. Slender columnar and needle-like crystals appear only when the temperature is near −28°C (iii). Composite snow crystal types, like the capped column (iv), form when growth conditions change as the crystal develops. The crystals shown range in size from 1 to 4 mm. Although morphological changes with temperature and supersaturation were first documented more than 75 years ago (1), the underlying physical mechanisms that drive these puzzling growth behaviors are not well known. Photos by the author (10).
Much has already been written about the mechanical, optical, electrical, and thermodynamic properties of bulk ice, as well as its numerous solid phases [for example, see 2–5, and references therein]. These works generally describe ice in thermal equilibrium, although growth is an intrinsically nonequilibrium, dynamical process. Reviews of ice crystal growth have been relatively infrequent, focusing mainly on the formation of atmospheric snow crystals (1, 6–8), and several popular-science books on that subject have recently appeared (9–11).

Our principal motivation in studying this subject is to better understand the physical dynamics of crystal growth more generally, using ice as an in-depth case study. Although general aspects of crystal-growth theory can be found in several texts (12–15), comprehensive comparisons between theory and experiment are somewhat rare, especially quantitative investigations of growth rates that examine molecular attachment kinetics over a broad range of conditions. Our hope is that a better understanding of the fundamental physical processes controlling ice solidification will contribute to materials science overall, and will facilitate the future creation of advanced materials in ways yet unknown.

2. PHENOMENOLOGY AND GROWTH MORPHOLOGIES

In broad brushstrokes, there are two primary physical effects that govern ice growth rates and the formation of complex structures during solidification. One is surface attachment kinetics, and the other is the diffusion of heat and/or particles. The interplay of these two processes, acting in concert over a range of length and time scales, leads to a fascinating phenomenology of observed ice growth behaviors, and we begin with brief descriptions of the ice/water and ice/vapor cases.

2.1. Ice Growth from Liquid Water

A key variable describing the solidification of ice from liquid water is the degree of supercooling, \( \Delta T_{\text{surf}} = T_m - T_{\text{surf}} \), where \( T_m \approx 0^\circ \text{C} \) is the temperature of the ice/water interface in equilibrium and \( T_{\text{surf}} \) is the temperature of the ice/water interface during growth. It is customary to write the growth velocity \( v_n \) (normal to the surface) in the Wilson-Frenkel form,

\[
v_n(\Delta T_{\text{surf}}) = K_T \Delta T_{\text{surf}},
\]

where \( K_T \) is the kinetic coefficient. This automatically gives the equilibrium condition \( v_n = 0 \) when \( \Delta T_{\text{surf}} = 0 \), although in general \( K_T \) is also temperature dependent. Other important variables may include the surface orientation relative to the crystal axes, solute concentrations, overall crystal morphology, the presence of container walls or other foreign materials, or simply the initial conditions and/or boundary conditions describing a particular system. Except where noted, in this review we focus primarily on ice growth in a pure water bath, unconstrained by the presence of solutes or other materials.

Another commonly used measure of supercooling is \( \Delta T_{\text{bath}} = T_m - T_\infty \), where \( T_\infty \) is the temperature of the supercooled water surrounding the crystal, far from the growing interface. Latent heat created at the ice/water interface is usually removed via diffusion, so generally \( T_{\text{surf}} > T_\infty \). Often \( \Delta T_{\text{surf}} \) and \( \Delta T_{\text{bath}} \) are used interchangeably in the literature, which can lead to some confusion. Because \( T_{\text{surf}} \) is often difficult to determine near a growing interface, \( \Delta T_{\text{bath}} \) is commonly used when describing experimental results.

For a small supercooling with \( \Delta T_{\text{bath}} < 1^\circ \text{C} \), a microscopic seed crystal tends to grow into the form of a simple, circular disk. The slow-growing basal surfaces form the two faceted faces of the disk, indicating growth limited by surface attachment kinetics. Meanwhile the outward growth of the edge of the disk is limited primarily by the diffusion of latent heat. As \( \Delta T_{\text{bath}} \) is increased, the disk growth becomes unstable via the Mullins-Sekerka instability (12, 16), resulting in the formation of dendritic branching, still mainly restricted to two dimensions by basal faceting.
When $\Delta T_{\text{bath}} < 2^\circ\text{C}$, ice tends to grow into thin, plate-like dendritic structures. (a) A photo showing an ice crystal sheet lifted from the surface of a lake. Similar pond crystals can be found when the temperature dips just below $T_m$ overnight, yielding slowly growing ice sheets. (b) Ice growing from liquid water held between two plastic plates as the plates were pulled at constant velocity toward a cold region. The growth morphologies transition from relatively simple plates (at low pull velocity, resulting in a low supercooling) to dendritic structures at higher pull velocities. Photos by the author.

In an open body of supercooled water, such as a quiet pond or lake, buoyancy forces often push the ice disk to the surface, aligning the $c$ axis of the crystal along the vertical. The disk then grows outward along the water’s surface to form large, often single-crystal, dendritic structures, such as the pond crystal shown in Figure 2. The process can easily be reproduced in the laboratory, yielding ice plates with thicknesses of 1 cm or more, with the $c$ axis conveniently oriented perpendicular to the faces of the plate. This is a simple method for preparing large, single-crystal ice specimens for use in laboratory experiments (17).

As a function of $\Delta T_{\text{bath}}$, the ice growth morphologies progress from circular disks to dendritic plates when $\Delta T_{\text{bath}} < 2^\circ\text{C}$, to unbranched needle-like structures when $\Delta T_{\text{bath}} \approx 4^\circ\text{C}$, to branched needle-like structures when $\Delta T_{\text{bath}} \approx 8^\circ\text{C}$, to platelets when $\Delta T_{\text{bath}}$ is in the range 10–30$^\circ\text{C}$, as described in (18). For all of these growth morphologies, one can measure the growth velocity $v_{\text{tip}}$ of an outermost structural point (for example, the tip of a growing dendrite), and doing this yields approximately a single function $v_{\text{tip}}(\Delta T_{\text{bath}})$ (19). Diffusion-limited dendrite growth theory reproduces this function reasonably well, confirming that ice growth from liquid water is largely limited by heat diffusion. However, little attention has been given to reproducing the observed ice growth morphologies in detail using numerical models, and the diversity of morphological structures suggests that this could be a fruitful area of research.

It should also be remembered that ice and water coexist in equilibrium along a line in the water phase diagram. Our discussion in the preceding paragraphs treated $T_m$ as a single temperature, which is an approximation that holds at low pressures. A more general view is to examine ice growth as a function of $\Delta \mu_{\text{interface}}$, the change in chemical potential across the ice/water interface (equal to zero in equilibrium). For example, when $T_m < -16^\circ\text{C}$ (at pressures above 165 MPa), both the prism and basal surfaces exhibit faceting, so the basic growth morphology at low $\Delta \mu_{\text{interface}}$ becomes that of a fully faceted hexagonal prism (20, 21). In contrast, only basal faceting is observed.
at low pressures. Unfortunately, the high-pressure regions of the phase diagram are difficult to access experimentally, so we know very little about ice growth behavior far from the triple point.

Stepping away briefly from the pure-water case, the freezing of ice from water solutions has received considerable attention in the scientific literature. For dilute solutions, the presence of a solute typically yields a freezing point depression proportional to concentration (Blagden’s law), plus solvated molecules are not readily incorporated into the ice lattice. Thus both heat and solute diffusion should be included in a solidification model. At higher solute concentrations, complex 3D patterns can emerge in freeze casting (22, 23) and during lyophilization (also known as freeze drying) (24). There is typically little chemical interaction between solute molecules and growing ice surfaces, although this is not always the case (25, 26). A notable, and quite dramatic, exception is the case of antifreeze proteins, which bind strongly to certain ice surfaces and can halt growth altogether at low supercoolings (27, 28). As our understanding of ice growth from pure water improves, so too does the potential for realizing applications from these chemically more complex systems.

### 2.2. Ice Growth from Water Vapor

The growth of ice from water vapor is usually described in terms of two primary parameters: the growth temperature \( T_{\text{surf}} \) and the water vapor supersaturation \( \sigma_{\text{surf}} = (c_{\text{surf}} - c_{\text{satur}})/c_{\text{satur}} \), where \( c_{\text{surf}} \) is the volumetric number density of water vapor molecules just above the growing ice/vapor interface and \( c_{\text{satur}} = c_{\text{satur}}(T_{\text{surf}}) \) is the saturated number density above a flat ice surface in equilibrium. Unlike the ice/water case, much of the ice/vapor coexistence line is rather easily accessible experimentally, and a good sampling of \( (T, \sigma) \) parameter space can even be found in the earth’s atmosphere. Again one must distinguish \( \sigma_{\text{surf}} \) and \( T_{\text{surf}} \) from \( \sigma_{\infty} \) and \( T_{\infty} \), the latter referring to the boundary conditions far from the crystal. Typically \( \sigma_{\text{surf}} < \sigma_{\infty} \) because of particle diffusion if a background gas (such as air) is present, and \( \Delta T_{\text{surf}} > T_{\infty} \) because of latent heat considerations. Both particle and heat diffusion factor into ice growth from water vapor, plus the growth rates may be influenced by substrate interactions, surface chemical interactions, initial growth conditions, and other factors.

In the limit of infinitely fast surface attachment kinetics, the ice growth rate is determined simply by the net flux of water vapor molecules striking the ice/vapor interface, which can be calculated from ideal-gas statistical mechanics. This gives the Wilson-Frenkel form \( v_h = \alpha v_{\text{kin}} \sigma_{\text{surf}} \), where \( v_{\text{kin}} = (c_{\text{surf}}/c_{\text{ice}})(kT_{\text{surf}}/2\pi m_{\text{mol}})^{1/2} \) is a temperature-dependent kinetic velocity, the mass of a water molecule is \( m_{\text{mol}} \approx 3.0 \times 10^{-26} \, \text{kg} \), and \( c_{\text{ice}} = \rho_{\text{ice}}/m_{\text{mol}} \approx 3.1 \times 10^{28} \, \text{m}\text{⁻³} \) is the number density of ice (\( \rho_{\text{ice}} \approx 917 \, \text{kg/m}^3 \)). The dimensionless factor \( \alpha \), called the attachment coefficient, describes the deviation from fast kinetics. For an infinite planar surface, we must have \( 0 \leq \alpha \leq 1 \) on average (8), although nonlocal transport effects on finite crystals may yield violations of this rule (30).

Attachment kinetics is typically the dominant factor determining growth behavior when the supersaturation is low, or the crystal size is small, or there is little background gas pressure (31, 32). In any of these circumstances, ice crystals grow as simple hexagonal prisms, defined by faceted basal and prism surfaces. For large crystals growing at low background pressures, heat diffusion becomes an important factor as well (33). Evacuated voids in solid ice, known as negative crystals, also grow in the shape of hexagonal prisms (34).

As \( \sigma_{\infty} \) increases around ice crystals growing in air, both particle diffusion and attachment kinetics play large roles in structure formation. The morphology diagram provides only an oversimplified picture of the large menagerie of different types of atmospheric snow crystals that result (10). Observations down to \( T = -70^\circ\text{C} \) reveal additional behavioral changes at low temperatures (35). However, low-temperature ice growth is sensitive to the presence of chemical contaminants (36), and this may explain some of the variability seen when \( T < -20^\circ\text{C} \). Faceting generally diminishes as \( \sigma_{\infty} \) increases in air, yielding highly branched crystals like those shown in Figure 3.

www.annualreviews.org • Physical Dynamics of Ice Crystal Growth 275
Figure 3

Single-crystal dendritic structures like these arise during the diffusion-limited growth of ice from water vapor in air at high supersaturation levels, as seen in the snow-crystal morphology diagram (Figure 1). (a) At temperatures near $-15^\circ$C, slow basal growth yields nearly planar crystals with essentially two-dimensional branching. Each main branch features a roughly parabolic tip that grows outward with a tip velocity proportional to supersaturation, and sidebranches grow parallel to neighboring main branches. Note that the sidebranch spacing is both aperiodic and asymmetrical in these fast-growing dendrites. (b) Near $-5^\circ$C, ice dendrites exhibit a nonplanar shape, with prograde and retrograde sidebranches. The diagram next to the photo shows the orientation of the sidebranches relative to the crystal axes (29). Again the dendrite tip velocity at $-5^\circ$C is approximately proportional to supersaturation. Photos by the author.

Even with extensive branching, however, attachment kinetics strongly affects the overall structure. Ice growth morphologies generally become more complex with increasing crystal size, increasing $\sigma_\infty$, and increasing background gas pressure (37).

It is instructive at this point to examine the detailed formation of an iconic winter snowflake—a stellar-dendrite crystal with six-fold symmetry, for example, the photo shown in subpanel i of Figure 1b. Once a cloud droplet freezes to form a nascent snowflake, the crystal begins growing by absorbing water vapor from its surroundings. The basal and prism surfaces grow slowly (because of their attachment kinetics), so the small crystal initially takes the form of a faceted hexagonal plate near $T = -15^\circ$C. As it grows larger, the Mullins-Sekerka instability causes branches to sprout from the corners of the plate, where the near-surface supersaturation is highest. Subsequent development of the branches depends on the temperature and supersaturation surrounding the crystal, as the growth behavior is quite sensitive to these conditions. At times the branches sprout additional sidebranches, and at other times the branches grow more slowly and become faceted. During a typical 30-min lifetime of a growing snowflake, the growth conditions may change many times, yielding a final crystal with a complex, branched shape. However, the individual branches all experience nearly the same changing conditions as a function of time, so all six grow in synchrony, yielding a structure that is both complex and symmetrical on macroscopic scales. Snowflake photographers (including the author) tend to seek out specimens with near-perfect symmetry, but these are actually quite rare in nature; the vast majority of natural snow crystals are lopsided or malformed to varying degrees. The repeated application of induced sidebranching (38) tends to yield the most symmetrical crystals.

The morphology diagram describes the shapes of frost crystals as well, as these also grow from water vapor in the atmosphere. Frost crystals appearing on the ground overnight are typically quite small, but plate-like and needle-like morphologies can often be seen using a low-power
magnifier. Larger crystals are called hoarfrost, and centimeter-scale crystals are not uncommon, especially when crystals grow in undisturbed places for days or weeks. Window frost forms from water vapor as well, but its development is substantially influenced by the presence of the glass substrate, including microscopic scratches or chemical residues that often guide the formation of large-scale patterns (9).

3. EQUILIBRIUM PROPERTIES

3.1. Energetics

Although our focus in this review is ice crystal growth, it is useful to examine the limiting case in which the growth rate goes to zero, giving us ice/water or ice/vapor interfaces in equilibrium. Of particular importance are the equilibrium energies, including bulk (3D), surface (2D), and step (1D) energies.

The bulk energies are the latent heats released during the formation of condensed phases at the relevant phase boundaries. For ice near the triple point, the latent heat of fusion (solid/liquid) is $L_f \approx 3.3 \times 10^3$ J/kg, the latent heat of deposition (solid/vapor) is $L_v \approx 2.8 \times 10^6$ J/kg, and for completeness we include the latent heat of condensation (liquid/vapor) $L_h \approx 2.5 \times 10^5$ J/kg. These quantities change with position on the phase boundary: $L_f$ drops to $L_f \approx 2.3 \times 10^3$ J/kg at $T \approx -22^\circ C$ (near the lowest-temperature, highest-pressure point on the ice/water phase boundary), and $L_v$ drops to $L_v \approx 2.6 \times 10^6$ J/kg near absolute zero (2).

Surface energies are more difficult to measure (or calculate) and are therefore not as well known. The liquid/vapor surface energy has been determined from observations of the oscillations of water droplets, giving $\gamma_v \approx 0.076$ J/m$^2$ near the triple point, dropping to $\gamma_v \approx 0.059$ J/m$^2$ at $T = 100^\circ C$. The solid/liquid surface energy is derived from the rates of homogeneous nucleation of water droplets, giving $\gamma_d \approx 0.033$ J/m$^2$ near the triple point, dropping to approximately $\gamma_d \approx 0.020$ J/m$^2$ at $T = -40^\circ C$ (44). The solid/vapor surface energy has proven quite difficult to measure, although surface wetting measurements suggest that Antonow’s relation is a reasonable approximation near the triple point: $\gamma_v \approx \gamma_d + \gamma_h \approx 0.109$ J/m$^2$ (2, 3). The ice surface energies are likely isotropic to a few percent (45), although anisotropies have not yet been measured.

Step free energies play an important role in ice crystal growth, factoring into the 2D nucleation of new terraces on faceted surfaces. The ice/water step energy on the basal facet near the triple point is $\beta_{basal,sv} \approx 5.6 \times 10^{-13}$ J/m (46–48), and $\beta_{prism,sv}$ is essentially zero, as the prism surface is not faceted except at high pressures. Measurements of step energies on the ice/vapor interface give $\beta_{basal,sv} \approx \beta_{basal,sl}$ near $T_m$ (48), and both $\beta_{basal,sv}$ and $\beta_{prism,sv}$ increase sharply at lower temperatures.

Considering a simple geometric picture of a faceted ice/vapor interface, an abrupt terrace step of height $a$ adds an additional surface area equal to $a \ell$, where $\ell$ is the length of the step, implying a step energy $\beta_{sv} \approx a \gamma_{sv}$. Surface relaxation essentially makes the step less abrupt, yielding $\beta_{sv} < \beta_{sv,0}$. If the terrace step is a gradual one of effective width $w$, we have $\beta_{sv} \approx (a/w)\beta_{sv,0}$ in the limit $a/w \ll 1$. Measurements of $\beta_{sv}/\beta_{sv,0}$ thus provide some indication of the effective width of a terrace step, which may be relevant for modeling terrace steps and computing step energies using molecular dynamics simulations, as is discussed below.

3.2. Surface Premelting

Water molecules near an ice/vapor interface are not as tightly bound to the crystal lattice as molecules below the surface, and this leads to a phenomenon called surface premelting (3, 49). As the temperature approaches the melting point for an ice surface in equilibrium, the top molecular layers form a quasi-liquid layer (QLL) that has a disordered structure with characteristics similar
to bulk liquid. The thickness of the QLL diverges as $T \rightarrow T_m$, making it impossible to superheat ice above $T_m$. One physically intuitive way to think about surface melting uses the Lindemann criterion, which states that a solid will melt if thermal fluctuations of the intermolecular distance become larger than approximately 10–15% of the average distance, and these fluctuations are larger near the surface than in the bulk (8, 50). Surface premelting is common in many other materials, and cluster premelting is a related phenomenon.

Physical models of ice premelting are fairly crude, and the overall thickness of the QLL as a function of temperature $d_{QLL}(T)$ is not well known, with different experiments yielding quite different estimates for $d_{QLL}(T)$. Very roughly, $d_{QLL}$ becomes comparable to the lattice spacing at $T \approx -10^2 \text{ C}$, and increases rapidly as $T \rightarrow T_m$ (49). Molecular dynamics simulations also indicate the presence of surface premelting (51–54). It has long been speculated that surface premelting affects the ice/vapor attachment kinetics (6, 55), but the importance of its role is not yet known.

3.3. The Gibbs-Thomson Effect

The Gibbs-Thomson effect refers to a difference in the thermodynamic properties of a curved interface relative to those of a flat interface. In liquid water, the equilibrium temperature of a sphere of ice with radius $R$ is $T_{eq} = T_m - T_\Delta d_{sl} \kappa$, where $\kappa = 2/R$ is the curvature of the spherical interface, $T_\Delta = L_\text{sl}/C_\text{water} \approx 78 \text{ K}$, $C_\text{water} \approx 4220 \text{ J/kg K}$ is the specific heat of water, and $d_{sl} = \gamma_{sl} C_\text{water} / \rho_\text{water} \approx 0.38 \text{ nm}$ is the capillary length (12). The Wilson-Frenkel law then becomes $v_m(\Delta T_{sat}) = K_1 (\Delta T_{sat} - T_\Delta d_{sl} \kappa)$.

In vapor, an ice sphere may possess an electrical charge as well, giving a more general form of the Gibbs-Thomson effect: $\epsilon_{eq} \approx \epsilon_{sat}(1 + d_m \kappa - R_{ms}^2 / R^2 + R_{pol}^2 / R^2)$, where $d_m = \gamma_{ms} / \epsilon_{sat} \kappa kT \approx 1 \text{ nm}$, $R_{ms} = \epsilon_\phi \phi_0 / 2 \epsilon_\kappa kT$, $R_{pol} = \xi \phi_0 / kT$, $\phi_0 = Q / 4 \pi \epsilon_0 R$ is the electrical potential of the sphere, and $\xi$ is the molecular polarizability. In the case of ice, $\xi \approx 3.4 \times 10^{-20} \text{ C}^2 / \text{m N}$ for a water molecule, so $R_{ms} \approx 0.2(\phi_0 / 1000 \text{ V}) \mu\text{m}$ and $R_{pol} \approx 1.0(\phi_0 / 1000 \text{ V}) \mu\text{m}$ (8, 56).

The time needed to relax to the ice equilibrium shape is $t_{eq, \text{vapor}} \approx R^2 / 2 d_m \alpha v_{kin}$ for ice in vapor (45) and $t_{eq, \text{liquid}} \approx R^2 / 2 d_m K_1 T_\Delta$ for ice in liquid water, where $R$ is the radius of the ice particle. These times are both quite long, and (to our knowledge) no ice growth experiments have yet been in a regime in which the equilibrium shape would have been observed. Theoretical considerations suggest that the equilibrium shape of an ice crystal is nearly spherical, with only slightly faceted basal and prism faces (45).

4. SURFACE ATTACHMENT KINETICS

Surface attachment kinetics refers to the interfacial dynamical processes governing how molecules from disordered liquid or vapor states attach to the crystal lattice. In general, the attachment kinetics can depend on the interface temperature, the degree of supercooling or supersaturation, and many other parameters. Because it is fairly easy to create essentially dislocation-free ice crystals, both from liquid water and from water vapor, we focus our attention here on the growth of perfect ice crystals as the more fundamental problem.

4.1. Nucleation Theory

On faceted surfaces, the attachment kinetics are often limited by the nucleation of new molecular terraces, as described by classical nucleation theory (12–15). For a simple monomolecular solid surface, crystal growth is driven by a chemical potential jump at the interface, such as a nonzero supercooling or supersaturation. A general polynuclear growth model gives the normal growth
velocity \( v_n \approx A \Delta \mu \exp \left( -\frac{S \beta^2 a^2}{\Delta \mu k T_{\text{surf}}} \right) \) (12, 48), where \( S \approx 1 \) is a geometrical factor, \( \beta \) is the step free energy at the crystal interface, \( a = \xi_1^{1/3} \approx 0.32 \, \text{nm} \) is the molecular size, \( \Delta \mu \) is the chemical potential jump at the interface, \( k \) is the Boltzmann factor and \( T_{\text{surf}} \) is the interface temperature. We prefer this particular functional form so that \( v_n \approx A \Delta \mu \) (the Wilson-Frenkel law) when \( \beta \to 0 \) and the exponential term goes to unity, although we expect that \( A \) may depend weakly on \( \Delta \mu \).

For growth from liquid water, \( \Delta \mu \approx a^4 \rho_{\text{ice}} L_{\text{sl}} \Delta T_{\text{surf}}/T_{\text{m}} \), giving
\[
v_n \approx K_T \Delta T_{\text{surf}} \approx A_{\Delta} \Delta T_{\text{surf}} \exp \left( -\frac{T_0}{\Delta T_{\text{surf}}} \right)
\]
with \( k T_0 = S \beta^2 a^4 / \rho_{\text{ice}} L_{\text{sl}} \) (12, 48). The prefactor \( A_{\Delta} \) is determined by how fast liquid molecules diffuse into position to join the solid lattice, which can be roughly estimated by the Einstein-Stokes relation
\[
A_{\Delta} \approx L_{\text{sl}} \rho_{\text{ice}} a^2 / 6 \pi \eta_{\text{eff}} T_{\text{m}}
\]
where \( \eta_{\text{eff}} \) is the dynamic viscosity for liquid near the surface. The kinetics of liquid water near an ice surface is nontrivial, and it is possible that \( \eta_{\text{eff}} \) may differ from the normal bulk viscosity.

For ice growth from water vapor, we have \( \Delta \mu \approx \sigma_{\text{surf}} k T \) for \( \sigma_{\text{surf}} \ll 1 \), giving
\[
v_n \approx A_{\text{basal}} \sqrt{\sigma_{\text{surf}} / \eta_{\text{eff}}} \approx A_{\text{basal}} \sqrt{\sigma_{\text{surf}} / \eta_{\text{eff}}} \exp \left( -\frac{\sigma_0}{\eta_{\text{eff}}} \right)
\]
with \( \sigma_0 = S \beta^2 a^4 / k^2 T_{\text{m}}^2 \) (48). For fast kinetics on rough surfaces, we expect \( A_{\text{basal}} \approx 1 \), although this may not be the case if nucleation is not the only factor that limits growth.

4.2. Ice/Water Kinetics

In many observations of ice growth from liquid water reported in the literature, the growth rates are strongly limited by the diffusion of latent heat generated at the growing crystal surface, and in this case the bath supercooling \( \Delta T_{\text{bath}} \) can be markedly different from \( \Delta T_{\text{surf}} \) at the interface. Because the interfacial temperature \( \Delta T_{\text{surf}} \) is the essential variable governing growth kinetics, for now we restrict our attention to experiments where heat-diffusion effects have been carefully considered and modeled to determine growth velocities \( v_n(\Delta T_{\text{surf}}) = K_T \Delta T_{\text{surf}} \).

Figure 4 shows an overview of \( K_T \) measurements for pure liquid water as a function of supercooling. Growth of the basal surface is generally well described by a 2D nucleation process at small supercoolings. By aligning the ice c axis parallel to the axis of a thin capillary tube, the effects of heat diffusion are relatively small and calculable, allowing the basal attachment kinetics to be extracted directly from growth data (46, 47). The basal kinetics line in Figure 4, given by \( K_T = 7.3 \times 10^{-4} \exp(-0.23 / \Delta T_{\text{surf}}) \), approximately describes experimental measurements after correcting for heat-diffusion effects. For \( \Delta T_{\text{surf}} > 0.1^\circ \text{C} \) the corrections become so large that extracting the basal attachment kinetics becomes unreliable for the measurements cited. Using nucleation theory, the basal kinetics curve yields a step free energy of \( \phi_{\text{basal}} \approx (5.6 \pm 0.7) \times 10^{-11} \, \text{J/m} \) for the basal ice/water interface (46, 47). This appears to be a robust result, as two independent experiments measured nearly identical \( T_0 \) values.

The curve labeled fast kinetics refers to measurements of fast-growing ice surfaces in capillary tubes (57–59). These data are of substantially poorer quality than the basal growth data, so this curve is only a rough approximation. The growth morphologies were likely needle-like crystals growing along the inner walls of (relatively large) capillary tubes, thus reducing heat-diffusion corrections to some degree. Modeling this process is problematic, however, so we cannot estimate systematic errors arising from residual diffusion effects, although they may be substantial.

We also plot \( K_T(\Delta T_{\text{surf}}) \) from the Einstein-Stokes model described above, assuming \( \eta_{\text{eff}} \) is equal to the measured bulk viscosity of water as a function of temperature. There are surprisingly few modern experiments on ice growth rates from which kinetic attachment coefficients can be extracted, leaving much opportunity for improvement in this area. At high growth rates, however, great care must be exercised to separate kinetics-limited growth from diffusion-limited growth, perhaps requiring novel experimental techniques to obtain reliable measurements.
The graph in Figure 4 suggests a relatively simple picture of ice/water growth kinetics, with a nucleation barrier on the basal surface accompanied by quite fast kinetics otherwise. However, the observed complex growth morphologies as a function of supercooling suggest that this picture is too simplistic. It is difficult to see how such basic surface kinetics, combined with a model of diffusion-limited growth, could reproduce the variety of morphologies described by Shibkov et al. (18, 19). It appears, therefore, that additional data and modeling of diffusion-limited ice growth from liquid water may yield important new results.

4.3. Ice/Vapor Kinetics

Ice and water vapor coexist over an easily accessible line on the water phase diagram, and there exists a substantial body of experimental and theoretical work exploring attachment kinetics at the ice/vapor interface. The preferred experimental method is to observe the growth of small ice prisms on a substrate in near-vacuum conditions, where the effects of heat and particle diffusion are minimal. Faceted basal and prism surfaces have received the most attention, as their low attachment coefficients ($\alpha_{\text{basal}}, \alpha_{\text{prism}} \ll 1$) often dominate the overall ice growth behavior. Nonfaceted surfaces (also called rough surfaces) generally have quite fast kinetics, suggesting $\alpha_{\text{rough}} \approx 1$.

Numerous experiments performed over several decades measured ice growth rates as a function of water vapor supersaturation over a variety of temperatures and background pressures [e.g., 33, 37, 55, 60–63], but their results were adversely affected by several significant systematic errors (64). The data from these experiments clearly revealed the presence of substantial nucleation barriers on both the basal and prism facets (31, 32), but the experimental accuracies were not sufficient to provide reliable determinations of the surface attachment coefficients. A careful
Figure 5

(a) An interferometric measurement of a small ice crystal plate with a thickness of 3 µm and a distance of 35 µm between opposing prism facets. A bright slit of light obscures the crystal (shown in the inset photo), and two reflections (from the substrate/ice and ice/air interfaces) interfere to give a series of fringes in the dispersed reflected light (top of photo, in true color). The fringe spacing determines the crystal thickness, and monitoring the phase of the fringe pattern can be used to measure growth velocities \( v_{\text{meas}} \) with <1 nm/s precision. (b) Measurements of the basal attachment coefficient \( \alpha_{\text{basal}} = \frac{v_{\text{meas}}}{v_{\text{kin}} \sigma_{\text{surf}}} \) as a function of the inverse supersaturation \( \frac{1}{\sigma_{\text{surf}}} \) at the ice surface, for several different temperatures. The data are well represented by \( \alpha_{\text{basal}}(\sigma_{\text{surf}}) = A_{\text{basal}} \exp\left(-\frac{\sigma_{0,\text{basal}}}{\sigma_{\text{surf}}}\right) \), where the parameters \( A_{\text{basal}} \) and \( \sigma_{0,\text{basal}} \) are extracted from fits to the data. For the data shown we see that \( \sigma_{0,\text{basal}} \) changes with temperature, but all the data are consistent with \( A_{\text{basal}} = 1 \) (65).

Elimination of systematic effects finally allowed suitable measurements of \( \alpha_{\text{basal}} \) and \( \alpha_{\text{prism}} \) over a broad range of conditions (65), and our current picture of ice/vapor kinetics is based largely on those measurements.

Figure 5 shows some example measurements of \( \alpha = \frac{v_{\text{meas}}}{v_{\text{kin}} \sigma_{\text{surf}}} \) as a function of \( \sigma_{\text{surf}} \), where \( \sigma_{\text{surf}} \) was determined from experimental parameters and \( v_{\text{meas}} \) was measured interferometrically. These data, along with similar data taken at other temperatures and on the prism facet, are well represented by the functional form \( \alpha(\sigma_{\text{surf}}) \approx A \exp(-\frac{\sigma_{0,i}}{\sigma_{\text{surf}}}) \), which is expected from the polynucleation model described above. Fitting the two-dimensional data \( \alpha(\sigma_{\text{surf}}, T) \) then eliminates \( \sigma_{\text{surf}} \) as a variable, leaving the fit parameters \( A(T) \) and \( \sigma_{0,i}(T) \) for the basal and prism surfaces, as shown in Figure 6.

Interpreting the measurements of \( A_i(T) \) and \( \sigma_{0,i}(T) \) shown in Figure 6 presents a significant challenge, as our understanding of the detailed molecular structure and dynamics of the ice surface is far from complete. Turning this around, we find that crystal growth measurements can be used as an effective experimental probe, combining with molecular dynamics simulations and other experimental and theoretical inputs to construct a better physical picture of the ice surface. We continue this line of reasoning in the discussion below, describing a comprehensive model of ice growth kinetics. But first we must examine some additional measurements that contribute significantly to this model.

4.4. An Edge-Sharpening Instability

Considering the low-pressure \( \alpha_{\text{basal}} \) and \( \alpha_{\text{prism}} \) measurements at \( T = -15^\circ C \) [given by \( \alpha_i = A_i \exp(-\sigma_{0,i}/\sigma_{\text{surf}}) \), with \( A_i(T) \) and \( \sigma_{0,i}(T) \) specified in Figure 6] quickly reveals that \( \alpha_{\text{prism}} < \alpha_{\text{basal}} \)
Recent measurements of ice growth rates reveal a rather complex picture of the structure and dynamics of the ice/vapor interface as a function of temperature and other conditions. The graph in panel a was derived from parameterizing the growth measurements described in Reference 65 using $\alpha_i(\sigma_{\text{surf}}) = A_i \exp\left(-\sigma_{0,i}/\sigma_{\text{surf}}\right)$, where $i = \text{basal}$ (dark blue, closed points) or $i = \text{prism}$ (light blue, open points). The additional red data points were obtained from additional measurements (41, 48, 67). The step energy on the two ice facets can be extracted from these data, yielding the results shown in panel b. Here the red point gives the step energy on the ice/water interface for $T \approx T_m$. The data suggest that the equilibrium structure of the basal ice/quasi-liquid layer interface approaches that of the ice/water interface, as indicated by similar step energies as $T \to T_m$.

A simple geometrical picture of surface reconstruction near a molecular step, where the step energy is determined by the additional surface area added by the step. Several features of this graph are discussed at length in the text.

at all supersaturations at this temperature. This inequality is inconsistent with the appearance of thin plate-like crystals at $-15^\circ C$ (as seen in the morphology diagram in Figure 1), which argues that the opposite inequality must be true. Our preferred explanation for this inconsistency is to postulate that $\sigma_{\text{prism}}$ depends on the width of a prism facet, specifically that $\sigma_{0,\text{prism}}$ drops precipitously as the terrace width approaches molecular dimensions. This effect yields a novel edge-sharpening instability (ESI) in the ice growth behavior in air (42, 66, 67), as described in Figure 7.

Although we can only speculate as to a molecular mechanism that would reduce $\sigma_{0,\text{prism}}$ on narrow prism terraces, the ESI model does make several predictions that are (so far) being confirmed in new experiments (42, 66, 67). Therefore, we add the ESI phenomenon to our overall picture of ice growth kinetics, giving the additional red point in the $\sigma_{0,\text{prism}}$ graph at $T = -15^\circ C$ in Figure 6. The ESI model suggests reductions in $\sigma_{0,\text{prism}}$ at temperatures near $-15^\circ C$ as well,
This drawing illustrates how an edge-sharpening instability (ESI) in diffusion-limited vapor growth can promote the formation of thin plates at −15°C. Beginning with a faceted ice prism (a), slow crystal growth in air results in slightly concave faceted surfaces (b). Because the supersaturation is highest near the corners (the Berg effect), steps on the basal and prism faces preferentially nucleate there (note that the corner is rounded at the molecular scale by the Gibbs-Thomson effect). If the crystal is growing sufficiently slowly, the steps propagate away from the corner, thus maintaining macroscopically faceted surfaces during growth. The width of the uppermost prism terrace decreases as the growth rate increases, however, and experimental data suggest that this in turn lowers the nucleation barrier on that terrace. The result is a runaway growth instability, as the lower $\sigma_{0,\text{prism}}$ brings about faster step nucleation, thus narrowing the prism facet further and reducing $\sigma_{0,\text{prism}}$ further (42, 66, 67). The ESI mechanism thus yields a plate-on-pedestal morphology (c), in which a thin plate-like crystal grows out from the top edge of the initial prism.

which we include as dashed arrows in Figure 6 at −10°C and −20°C. The reduction in $\sigma_{0,\text{prism}}$ may extend to temperatures above −10°C, as this is neither excluded or required by the existing data.

### 4.5. Air-Dependent Attachment Kinetics

It is well known that particle diffusion greatly limits the growth of ice crystals in air, but it is also possible that the presence of air could directly affect the surface attachment kinetics. This has been speculated for many decades (6, 55), but distinguishing between diffusion-limited growth and kinetics-limited growth requires a well-defined experimental system with an accurate diffusion model that allows one to understand the growth data in detail. Only recently have we produced measurements that cannot (in our opinion) be potentially explained by diffusion effects.

Observations of the growth of thin ice needles at $T = −5°C$ (41) indicate that $a_{\text{prism}} \approx 0.002$ in air, much smaller than $a_{\text{prism}}$ values measured at low pressures. Moreover, the data suggest that $\sigma_{0,\text{prism}}$ is not greatly changed by the presence of air at −5°C, while $A_{\text{prism}}$ is much lower. These new data lead us to include the two red points shown in the $A_{\text{prism}}$ graph in Figure 6.

Our preferred model to explain these data includes a pressure-dependent $A_{\text{prism}}(T)$ that fits both the high- and low-pressure data in Figure 6. This would explain both the deep dip in $A_{\text{prism}}(T)$ near −5°C, when the air pressure was near 1 bar, and the shallower dip in the low-pressure data, when the air pressure was roughly 0.01 bar. In this model we have $A_{\text{prism}} \approx 1$ at all temperatures for a pure ice/vapor environment with zero background gas, which is a prediction for future experiments.

Here again, our model is driven primarily by experimental measurements, and we can only speculate as to the molecular mechanisms involved. One possibility is some type of air-induced step erosion in which collisions with air molecules erode and eliminate small terraces before they grow to a sufficiently large size that they become stable to such perturbations (68). This mechanism
would effectively reduce the rate of 2D nucleation on faceted prism surfaces without changing the step energy. Why this phenomenon would display so prominently near \(-5^\circ\)C, and not at other temperatures, remains a mystery.

### 4.6. Molecular Dynamics Simulations

One approach for better understanding the many-body physics underlying surface attachment kinetics is through molecular dynamics simulations, and ice has been studied extensively using these methods since the 1980s (51, 69–71). The simulations have greatly improved over three decades, modeling ever larger numbers of particles for ever longer physical times, but connections between simulations and experimental measurements remain tenuous at best. For example, surface premelting is seen with much detail in simulations of the ice/vapor interface (51–54), but laboratory measurements of this phenomenon involve various averages over surface properties (3, 49), making quantitative comparisons difficult. As another example, anisotropic crystal growth at the ice/water interface has been observed in simulations (53, 72–74), revealing a drop in $K_T$ at high supercoolings arising from liquid diffusion effects that are different for the basal and prism facets. However, the simulations are done at high supercoolings that are not easily accessible in experiments. The possibility of making more meaningful comparisons between simulations and observations presents a motivation for pursuing improved ice-growth measurements and models.

A particularly exciting new development in molecular dynamics simulations is the direct extraction of step energies (75, 76). To our knowledge, such calculations have not yet been done on either the ice/water or ice/vapor interfaces, although we now have fairly accurate measurements of $\beta_{\text{basal}}$ on the ice/water basal surface near $T_m$, along with measurements of both $\beta_{\text{basal}}(T)$ and $\beta_{\text{prism}}(T)$ over a range of temperatures on the ice/vapor surfaces (Figure 6). Note, however, that the geometrical picture shown in Figure 6 suggests that effective step widths are quite large, with $w \gg a$, especially near $T_m$, so large sample sizes will likely be needed to accurately calculate $\beta_{sv}$ from molecular dynamics simulations.

In addition, the recent observation of single terrace steps (77) demonstrates a promising new experimental tool, making it possible to directly measure surface diffusion and perhaps other dynamical processes on faceted surfaces. As with other ice growth measurements, however, the presence of systematic errors from diffusion and other sources can substantially affect the desired measurements (78).

### 5. DIFFUSION-LIMITED GROWTH

In many circumstances, ice crystal growth rates and morphologies are determined by some combination of diffusion and attachment kinetics. It is instructive to first look at the case of spherically symmetrical growth, assuming angle-independent values of $\alpha$ or $K_T$. Although the spherical solution cannot include faceting or branching, it is instructive for determining which growth processes are dominant under which conditions.

#### 5.1. Spherical and Cylindrical Solutions

For growth from liquid water, we have the thermal diffusion equation $\partial T/\partial t = D_w \nabla^2 T$, where the thermal diffusivity of water is $D_w = \kappa_{\text{water}}/\rho_{\text{water}}C_{\text{water}} \approx 1.4 \times 10^{-5}$ m$^2$·s$^{-1}$, and $\kappa_{\text{water}} \approx 0.6$ W/m·K is the thermal conductivity of water. To this we add the attachment kinetics $v_0 = dR/dt = K_T \Delta T_{\text{surf}}$ and the Gibbs-Thomson effect $T_{eq} = T_m - T_{eq} \Delta T_{\text{surf}}$. The boundary conditions are $T(r = \infty) = T_m$, at the far-away boundary and $L_{\text{diff}} v_0 = -\kappa_{\text{water}}(\partial T/\partial r)_{\text{surf}}$ at $r = R$, describing the diffusion of
latent heat generated by growth of the sphere. (Note that we have made an implicit assumption that heat is only carried outward through the surrounding water. This is true for spherical growth, but may not be true in all circumstances. For example, for a small crystal growing on a substrate we would also have to include heat transfer through the ice, with \( \kappa_{\text{ice}} \approx 2.4 \text{ W/m·K} \) in addition to heat transfer through the water.)

The time needed to relax the diffusion field around the growing crystal is approximately \( \tau_{\text{diff}} = R^2/D_w \), the time needed for significant crystal growth is \( \tau_{\text{grow}} = R/v_w \), and half the ratio of these times is called the Peclet number \( P = \tau_{\text{diff}}/2 \tau_{\text{grow}} = Rv_w/2D_w \). When \( P \ll 1 \) we can ignore \( \partial T/\partial t \) to obtain the much simpler Laplacian equation \( \nabla^2 T = 0 \). With this assumption we solve the above equations to give the growth velocity of the sphere

\[
v_n = \frac{D_w}{X_w + R} \left( \frac{\Delta T_{\text{bath}}}{T_\Delta} - \frac{2d_w}{R} \right)
\]

for spherical growth from liquid water  

\[
\approx \frac{D_w}{R} \left( \frac{\Delta T_{\text{bath}}}{T_\Delta} - \frac{2d_w}{R} \frac{X_w}{\eta R T_\Delta} \right)
\]

when \( R \gg X_w \)

where \( X_w = D_w/K_T T_\Delta \) is a characteristic diffusion length for ice growth in liquid water. Note that when the growth is mainly diffusion limited \((R \gg X_w)\) we have \( v_n \approx D_w \Delta T_{\text{bath}}/RT_\Delta \), giving the Peclet number \( P \approx \Delta T_{\text{bath}}/(156 \text{ K}) \), verifying that \( P \ll 1 \) for typical supercoolings.

The spherical solution suggests that the \( d_w \) term in Equation 1 is negligible except at exceedingly low supercoolings. Specifically, the inequality \( 2d_w \ll D_w \Delta \Delta /K \) can be rewritten as \( \Delta T_{\text{bath}} \gg 2K_T X d_w/D_w \), which holds for all ice-growth measurements that have been done to date (to our knowledge). Put another way, any consequences of the Gibbs-Thomson effect on ice growth from liquid water are dwarfed by similar effects arising from finite surface attachment kinetics. (An exception to this statement would be the growth of disk-shaped crystals when \( \Delta T_{\text{bath}} \rightarrow 0 \). In this case a model with \( d_w \rightarrow 0 \) would yield a very thin disk, and the actual disk thickness would be limited by the Gibbs-Thomson effect.)

For growth from water vapor, one is faced with a double diffusion problem, as water molecules diffuse inward though the background gas to reach the growing interface, while latent heat diffuses outward. Because \( \sigma_{\text{sat}}/\sigma_{\text{ice}} \ll 1 \), the Peclet number is exceedingly small. Including finite surface attachment kinetics and the Gibbs-Thomson effect, the spherical growth problem can be solved analytically to give (8)

\[
v_n \approx \frac{\alpha}{\alpha H + \alpha_{\text{diff}} \epsilon_{\text{ice}}} \left( \frac{\sigma_{\text{sat}} - 2d_{sw}}{R} \right)
\]

for spherical growth from water vapor  

\[
\approx \frac{D_v \epsilon_{\text{sat}}}{\sigma_{\text{ice}} R} \left( \frac{\sigma_{\text{sat}} - 2d_{sw}}{R} - \frac{X_0 \sigma_{\text{sat}}}{\alpha R} \right)
\]

when \( H \rightarrow 1, \alpha_{\text{diff}} \ll \alpha \)

where \( H = 1 + \chi_0, \chi_0 = \eta D_v L_{\text{sat}} \rho_{\text{sat}} \epsilon_{\text{sat}} / \kappa_{\text{sat}} \epsilon_{\text{ice}} > 0, \eta = d (\log \epsilon_{\text{sat}}) / dT, D_v \) is the particle diffusion constant \((D_v \approx 2 \times 10^{-5} \text{ m}^2/\text{s} \text{ for air at 1 bar, scaling roughly with inverse background gas pressure}), \kappa_{\text{sat}} \) is the thermal conductivity of the surrounding gas \((\kappa_{\text{sat}} \approx 0.025 \text{ W/m·K} \text{ for air at 1 bar, roughly independent of pressure until the mean free path of gas molecules becomes comparable to the crystal size}) \) and \( \alpha_{\text{diff}} = X_{\text{sat}} / R \) with \( X_{\text{sat}} = \epsilon_{\text{sat}} D_v / \epsilon_{\text{ice}} v_{\text{kin}} \). In air, \( \chi_0 \) varies from about 0.08 at \(-30^\circ\text{C}\) to 0.79 at \(-1^\circ\text{C}\) (8).

Several limiting cases of Equation 2 were discussed in Reference 8, indicating that: (a) For ice growth from water vapor in air at a pressure near 1 bar, it is quite difficult to obtain useful information about \( \alpha \) unless \( \alpha \ll \alpha_{\text{diff}} \), which is typically only true only if \( \alpha \ll 1 \) and micron-scale crystals are observed (for example, \( X_{\text{sat}} \approx 0.15 \mu\text{m} \) in air at \(-15^\circ\text{C}\)); (b) in air, heat diffusion can be approximately modeled by a rescaling of \( \sigma_{\text{sat}} \) to \( \sigma_{\text{sat}} / \alpha \), and this behavior was confirmed...
in Reference 79; (c) at low background pressures, $D_v$ and $\alpha_{\text{diff}}$ are increased, allowing better measurements of $\alpha$; however heat diffusion becomes more important at low pressures.

When the sphere growth is limited primarily by particle diffusion ($\alpha_{\text{diff}} \ll \alpha$), Equation 2 again reveals that the $d_{\text{sv}}$ term is usually negligible compared with the kinetic term, except when $\sigma_\infty$ is quite small. We reached this same conclusion when using numerical methods to analyze ice growth data (43). Specifically, near $-15^\circ$C, our models produced unphysically thin ice plates as $\sigma_\infty \to 0$ unless the Gibbs-Thomson effect was included.

We have also found it useful to consider analytic models describing the growth of infinitely long ice cylinders of radius $R$ (43). The cylindrical solutions look much like the spherical solutions, except with additional factors of $B = \log(R_{\text{out}}/R)$, where $R_{\text{out}}$ is the outer boundary at which the supersaturation (or supercooling) is constant. The cylindrical case describes the growth of thin ice needles (79), plus both the spherical and cylindrical analytic models can be used to validate numerical models (43).

5.2. Parabolic Growth and Solvability Theory

Although dendritic ice growth exhibits complex branching and sidebranching behaviors, as shown in Figure 3, often the tip of a growing dendrite can be solved analytically to a good approximation. Over a broad range of conditions, the tip shape is well described as a paraboloid of revolution (or a simple parabola for 2D growth), with a constant tip radius of curvature $R_{\text{tip}}$ and tip growth velocity $v_{\text{tip}}$. Complex branching occurs below the tip, but the tip itself is essentially defined by just these two constant parameters, $R_{\text{tip}}$ and $v_{\text{tip}}$.

The overall parabolic shape is obtained from an analytic parabolic solution to the diffusion equation, analogous to the spherical and cylindrical solutions described above. The derivation is somewhat difficult, involving transformation into parabolic coordinates, and the result is known as the Ivantsov solution (12, 80). For the case of ice growth from vapor, the Peclet number is small and the Ivantsov solution becomes

$$v_{\text{tip}} \approx \frac{2D_v}{R_{\text{tip}}B} \frac{\sigma_{\text{sat}}}{c_{\text{ice}}} \left( \frac{2d_{\text{sv}}}{R_{\text{tip}}} \frac{v_{\text{tip}}}{\alpha_{\text{kin}}} \right)$$

with $B = \log(\eta_{\text{far}}/R_{\text{tip}})$ and $\sigma_{\text{sat}}$ is the supersaturation at the far boundary (at $\eta = \eta_{\text{far}}$ in parabolic coordinates). Note that this equation is quite similar to the spherical solution in Equation 2, with $H = 1$ as we are ignoring heat diffusion in the Ivantsov solution.

Although the Ivantsov solution is mathematically similar to the spherical and cylindrical solutions, an important physical difference is that $R_{\text{tip}}$ and $v_{\text{tip}}$ remain constant as the parabolic crystal grows. The diffusion equation alone will specify $v_{\text{tip}}$ for a given $R_{\text{tip}}$ (the other parameters being fixed by the boundary conditions), but diffusion alone does not specify $R_{\text{tip}}$. Producing a physical derivation of $R_{\text{tip}}$ became known as the dendrite selection problem during the 1980s, when it was studied extensively (81, 82).

The additional physics needed to select a specific $R_{\text{tip}}$ comes from the second and third terms in Equation 4. Both terms are proportional to $R_{\text{tip}}^{-1}$ (because $v_{\text{tip}} \sim R_{\text{tip}}^{-1}$ to lowest order), and either term will suffice to select $R_{\text{tip}}$. Dendrite theory (also known as solvability theory) yields a second expression between $R_{\text{tip}}$ and $v_{\text{tip}}$, which in the vapor case becomes

$$v_{\text{tip}} R_{\text{tip}}^{3} = \frac{1}{\sigma_{\text{sat}}B} \left( \frac{2D_v \sigma_{\text{sat}}}{\alpha c_{\text{ice}}} \right)^{2}$$

where $s$ is a dimensionless constant known as the solvability parameter. To our knowledge, this seemingly simple result can only be obtained through a rather long and complex derivation (82, 83).
Importantly, the value of \( s \) depends on the anisotropy of \( \alpha \) (or the anisotropy of \( d \), if that were the dominant term). For a purely isotropic \( \alpha \) (or \( d \)), there would be no stable dendritic solution to the growth problem. Computer simulations reveal that the dendrite tip frequently splits for the isotropic case, yielding a branched seaweed-like structure that fills space randomly with branches. Anisotropy is necessary to produce dendrites that grow stably with constant \( R_{\text{tip}} \) and \( v_{\text{tip}} \), as are commonly observed in solidification experiments.

Combining the solvability relation with the Ivantsov solution for ice growth from water vapor and assuming a mildly anisotropic \( \alpha \approx 1 \) yields a tip radius that is independent of \( \sigma_{\text{far}} \), and thus a tip velocity that increases linearly with \( \sigma_{\text{far}} \) (8). Indeed, experiments indicate \( v_{\text{tip}} \approx (10 \, \mu\text{m/s}) \sigma_{\text{far}} \) for fishbone dendrites grown near \( T = -5^\circ\text{C} \), and \( v_{\text{tip}} \approx (5 \, \mu\text{m/s}) \sigma_{\text{far}} \) for stellar dendrites grown near \( T = -15^\circ\text{C} \), implying \( s \approx 0.2 \) and \( R_{\text{tip}} \approx 1.3 \, \mu\text{m} \) for both these cases (56).

Dendrite growth from liquid water is a more difficult problem, in part because the Peclet number is larger, but more importantly because \( K_T(\Delta T_{\text{surf}}) \) is only quite poorly known, as discussed with Figure 4 above. Interestingly, ignoring attachment kinetics entirely \((K_T \to \infty)\) and using the capillary \((d)\) term in Equation 1 to stabilize the tip growth yields a functional form for \( v_{\text{tip}}(\Delta T_{\text{bath}}) \) that reproduces the data in Figure 4 quite well. The unusually good fit to the data is discussed in (19), but the numerical estimates discussed above suggest that the capillary-only model is not physically correct for describing the growth of ice dendrites from liquid water.

5.3. Electrically Enhanced Needle Growth

The addition of electrical effects to the diffusion-limited growth of ice needles from water vapor adds an interesting twist to the solvability problem. In a nutshell, applying a high voltage to a growing ice needle changes the normal diffusion equation to the Smoluchowski equation, which describes diffusion in the presence of an additional external force. Electric fields near the needle tip also change the boundary conditions, specifically the equilibrium vapor pressure surrounding a charged sphere, as described above. The net effect is an additional \( \sim R^{-2} \) term within the parentheses in Equation 4, and this additional term tends to destabilize the needle growth (8, 56).

When the applied voltage is low, the tip velocity increases with increasing voltage without altering the overall dendritic growth behavior. Above a critical voltage, however, the normal tip growth becomes destabilized, resulting in a sudden jump in \( v_{\text{tip}} \). With the addition of certain chemical additives (56), the needle growth at \( T = -5^\circ\text{C} \) is directed along the c axis (which does not happen in clean air), yielding the electric needles shown in Figure 8. This phenomenon was first described by Mason and collaborators in 1963 (40), and the electric growth theory was developed in (8, 56, 84–86). Experimental details describing techniques for growing electric ice needles can be found in (39). The observed chemical effects, along with how the electric needle growth is ultimately stabilized, have yet to be explained.

5.4. Numerical Methods

The analytical theories of solidification described above are useful for examining general trends and the relative contributions of competing physical processes, but numerical modeling is necessary to address the full morphological complexity of diffusion-limited ice crystal growth. And although solving the diffusion equation for heat or particle diffusion is straightforward, incorporating the correct boundary conditions and reproducing realistic growth morphologies remains a nontrivial endeavor.

Numerical modeling of diffusion-limited growth is quite a rich and mature field, and we only provide a brief summary here. From the perspective of modeling ice growth, numerical methods...
Electric ice needles can be useful for obtaining quantitative measurements of the growth rates of complex ice crystals from water vapor (39, 40). (a) Several thin, c-axis ice needles (~2 mm in length) growing out from a frost-covered wire, obtained using the electrochemical technique described in Reference 39. (b) Ice crystals growing under different conditions on the needle tips, exhibiting several of the morphologies seen in the morphology diagram (Figure 1). Observing single-crystal structures growing out from the tips of ice needles allows for careful determinations of ice growth rates over a broad range of conditions (41, 42). For example, the composite image on the right shows measurements of a growing thin plate (c) together with a cylindrically symmetric numerical growth model (d) and a comparison of growth rates (e), from Reference 43.

Figure 8

can be broadly categorized by the form and degree of anisotropy of their surface boundary conditions. Weakly anisotropic systems, including both the surface tension and attachment kinetics terms in Equation 1, have been well studied using phase-field models, typically yielding nonfaceted or weakly faceted dendritic structures (87–90). These methods should apply well to the growth of ice from liquid water, but to our knowledge there are very few examples where realistic ice disk and dendritic structures have been investigated (91). It appears that quantitative comparisons between numerical models and improved ice growth measurements from liquid water could go far in elucidating the role of attachment kinetics as a function of supercooling, thus yielding improved measurements of $K_T(\Delta T_{\text{surf}})$.

As a general rule, we have found that the growth of highly anisometric structures (e.g., thin disks or slender needles) requires highly anisotropic attachment kinetics. Diffusion-limited growth with only mildly anisotropic attachment kinetics does not produce such structures. Thus the growth of a thin ice plate, be it a simple plate or a heavily branched plate, either from liquid water or from water vapor, indicates slow growth of the basal surfaces arising from strongly anisotropic attachment kinetics. Diffusion-limited growth yields branching and other small-scale structural features, but anisotropic kinetics are necessary for large-scale structural asymmetries. Adding highly anisotropic surface tension will also produce faceted ice structures (92), but the evidence
Figure 9
High-quality synthetic snow crystals can be grown using the plate-on-pedestal technique described in Figure 7. The small central forms seen in these two crystals outline their initial seed prisms. The outer branched plates grew entirely above the substrate, supported only by these central pedestals. Symmetrical structures were created via induced sidebranching, cycling the growth conditions between faceting and branching. Because these two crystals grew side-by-side and experienced the same changing growth conditions, their final forms are nearly identical. The crystals are surrounded by a field of supercooled water droplets that condensed on the substrate. Note that this is a single photograph by the author (38), not a composite image, unaltered except for overall color and brightness levels. Each of the two stellar snow crystals has a tip-to-tip diameter of 1.9 mm.

suggests that the ice surface tension is not highly anisotropic (45). Extending the technique in (92) to include highly anisotropic attachment kinetics appears to be a promising route (93).

Cellular automata methods on a fixed grid have been the most successful for modeling ice growth from water vapor (43, 94–99). The cellular automata method was the first to produce realistic snow-crystal structures that are both faceted and dendritic in 3D, exhibiting many observed morphological features. To date, however, these models have used parameterized surface boundary conditions that are physically incorrect, so the model structures could not be directly compared with quantitative experimental observations. Nevertheless, good progress is being made toward incorporating the correct attachment kinetics, and it may soon be possible to model even complex ice growth behaviors created in the laboratory, for example shown in Figure 9 (42, 43, 97).

6. TOWARD A COMPREHENSIVE MODEL OF ICE CRYSTAL GROWTH

In recent years, we have seen a resurgence of precise, quantitative ice growth experiments that are being paired with improved numerical modeling tools for dealing with effects from diffusion-limited growth and other systematic effects. These experiments are yielding new insights into ice growth dynamics, especially our physical picture of surface attachment kinetics at both the ice/water and ice/vapor interfaces.

As the picture becomes clearer, an underlying complexity is beginning to emerge. We are finding that a variety of physical phenomena are involved at different temperatures, on different
ice surfaces, and on different length scales. All of these contribute to the rich phenomenology of ice growth behaviors, and it is a continuing challenge to disentangle the different growth processes.

To better organize thinking on this subject, we have been developing a comprehensive model of ice growth kinetics that strives to include all the relevant physics (42, 48, 100, 101). This model is very much a work in progress, and additional experimental and theoretical developments are needed to push it forward. Nevertheless, some parts of the model are fitting into place, and we have found that it provides a useful framework for examining ice growth physics.

6.1. Basal Facet Growth Kinetics

Growth of the basal facet from water vapor is well described by \( v_{\text{basal}}(\sigma_{\text{surf}}) \approx A_{\text{basal}} \exp(-\sigma_{\text{surf}}/\sigma_{0,\text{basal}}) \mu_{\text{basal}} \sigma_{\text{surf}} \), with \( A_{\text{basal}}(T) \approx 1 \) and the measured \( \sigma_{0,\text{basal}}(T_{\text{surf}}) \) shown in Figure 6, indicating growth limited essentially entirely by terrace nucleation, with the step energy \( \beta_{\text{basal,v}}(T) \) also shown in Figure 6. At the lowest temperatures measured, the terrace edge becomes sharper (in the sense of the geometrical picture in Figure 6), increasing \( \beta_{\text{basal,v}} \). We might expect \( \beta_{\text{basal,v}} \to \beta_{\text{basal,v,0}} \) at still lower temperatures, and this low-temperature behavior might be most amenable to calculation by molecular dynamics simulations.

As temperature increases, the terrace edge becomes less sharp, yielding \( \beta_{\text{basal,v}} < \beta_{\text{basal,v,0}} \). Between \( T = -13^\circ\text{C} \) and \( T = -5^\circ\text{C} \), surface premelting gradually changes the general character of the basal surface, from an ice/vapor interface to a more complex ice/QLL/vapor interface. Above \( T = -5^\circ\text{C} \), the nucleation barrier becomes localized essentially at the ice/QLL interface, and \( \beta_{\text{basal,v}} \) tends toward \( \beta_{\text{basal,d}} \), the basal step energy at the normal ice/water interface.

Thus we find a rather satisfying picture of the basal surface, where the measured \( \beta_{\text{basal}}(T) \) from vapor growth measurements describe the gradual influence of surface premelting on the equilibrium structure of a terrace step. And as \( T \to T_{\text{us}} \), nucleation at the ice/QLL interface becomes essentially indistinguishable from nucleation at the ice/water interface, yielding a correspondence between ice growth from water vapor and from liquid water (48).

To complete this picture of basal growth, we need additional measurements of \( K_{T,\text{basal}}(\Delta T_{\text{surf}}) \), especially at high supercoolings, to confirm and extend the measurements shown in Figure 4. If molecular dynamics simulations could also determine \( K_{T,\text{basal}}(\Delta T_{\text{surf}}) \) and \( \beta_{\text{basal,v}}(T) \) by using ab initio molecular models, in agreement with experimental measurements, then we could claim a reasonably complete understanding of the growth of basal ice surfaces (at least near the triple point). We are not there yet, but this goal looks achievable in the near future.

6.2. Prism Facet Growth Kinetics

If we consider the growth of large prism facets from pure water vapor, then again we find \( v_{\text{prism}}(\sigma_{\text{surf}}) \approx A_{\text{prism}} \exp(-\sigma_{\text{surf}}/\sigma_{0,\text{prism}}) \mu_{\text{prism}} \sigma_{\text{surf}} \), with \( A_{\text{prism}}(T) \approx 1 \) and the measured \( \sigma_{0,\text{prism}}(T_{\text{surf}}) \) shown in Figure 6. The low-temperature behavior is similar to the basal case, but this time \( \beta_{\text{prism}}(T) \) describes a gradual roughening of the prism surface, and apparently \( \beta_{\text{prism}} \to 0 \) as \( T \to T_{\text{us}} \). This fits with the fact that prism facets do not form when ice is grown from liquid water, even at low supercoolings. Note that roughening of the ice/vapor prism surface does not occur at an abrupt roughening transition at a specific temperature, as has been reported in the literature (102). Instead the roughening transition is gradual, quantified by the measured \( \beta_{\text{prism,v}}(T) \). This is another feature to look for in molecular dynamics simulations of the ice/vapor interface.

In contrast to basal kinetics, however, prism kinetics must include two significant complications: (a) the ESI described above, suggesting that the nucleation barrier is much smaller on narrow prism terraces near \( T = -15^\circ\text{C} \) than on larger terraces, and (b) \( A_{\text{prism,v}} \ll 1 \) in the presence of air near \( T = -5^\circ\text{C} \). These features appear to be required by observations, but we have no ready
explanation for their origin. Thus we find that prism facet growth is quite complex compared with basal growth, and its overall behavior remains quite puzzling.

6.3. Numerical Modeling

Progress toward understanding ice growth kinetics requires complementary advances in numerical modeling of diffusion-limited growth, as essentially all experimental measurements are affected by diffusion effects to some extent. Fortunately, the cellular automata methods mentioned above have been evolving rapidly and should soon be capable of full 3D quantitative modeling of experimental systems, at least for relatively simple geometries. The ability to reproduce complex growth structures will thus facilitate improved measurements of molecular kinetics, allowing progress in modeling and experiments to proceed hand in hand. Fully characterizing the attachment kinetics of ice/vapor and ice/water surfaces appears to be possible with continued effort.

The problem then moves to using molecular dynamics simulations to reproduce the various parameters that define the attachment kinetics, for example the step energies and $A_i$ values. This presents a substantial challenge, but we are encouraged by recent progress in these simulations, especially the ability to compute step energies on crystalline surfaces.

Over time it should be possible to construct a full chain of understanding of the phenomenon of ice crystal growth, spanning all the way from fundamental quantum theory describing the structure of H$_2$O molecules and their intermolecular interactions, to fully ab initio molecular dynamics simulations describing ice crystal growth kinetics in detail, to complete numerical models of structure formation in diffusion-limited growth. When that day arrives, we will finally comprehend the enigmatic snowflake.

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.

LITERATURE CITED


Contents

Novel Functionality Through Metamaterials (Venkatraman Gopalan, Don Lipkin & Simon Phillpot, Editors)

Control of Localized Surface Plasmon Resonances in Metal Oxide Nanocrystals
Ankit Agrawal, Robert W. Johns, and Delia J. Milliron ........................................ 1

DNA-Driven Assembly: From Polyhedral Nanoparticles to Proteins
Martin Girard, Jaime A. Millan, and Monica Olvera de la Cruz ............................. 33

Harnessing Instabilities to Design Tunable Architected Cellular Materials
Katia Bertoldi ........................................................................................................... 51

Negative-Poisson’s-Ratio Materials: Auxetic Solids
Roderic S. Lakes ...................................................................................................... 63

Sound Absorption Structures: From Porous Media to Acoustic Metamaterials
Min Yang and Ping Sheng ...................................................................................... 83

Structured X-Ray Optics for Laboratory-Based Materials Analysis
Carolyn A. MacDonald ........................................................................................... 115

Synchrotron X-Ray Optics
Albert T. Macrander and XianRong Huang .......................................................... 135

Current Interest

Active Crystal Growth Techniques for Quantum Materials
Julian L. Schmehr and Stephen D. Wilson .............................................................. 153

Atomic-Scale Structure-Property Relationships in Lithium Ion Battery Electrode Materials
Zhenzhong Yang, Lin Gu, Yong-Sheng Hu, and Hong Li ........................................ 175

Atomistic Simulations of Activated Processes in Materials
G. Henkelman ......................................................................................................... 199
Deformation of Crystals: Connections with Statistical Physics
James P. Sethna, Matthew K. Bierbaum, Karin A. Dahmen, Carl P. Goodrich,
Julia R. Greer, Lorien X. Hayden, Jaron P. Kent-Dobias, Edward D. Lee,
Danilo B. Liarte, Xiaoyue Ni, Katherine N. Quinn, Archibishman Raju,
D. Zeb Rocklin, Ashichern Shchekhawat, and Stefano Zapperi .................................. 217

Heusler 4.0: Tunable Materials
Lukas Wollmann, Ajaya K. Nayak, Stuart S.P. Parkin, and Claudia Felser ............. 247

Physical Dynamics of Ice Crystal Growth
Kenneth G. Libbrecht ..................................................................................................... 271

Silicate Deposit Degradation of Engineered Coatings in Gas Turbines:
Progress Toward Models and Materials Solutions
David L. Poerschke, R. Wesley Jackson, and Carlos G. Levi .............................. 297

Structural and Functional Fibers
Huibin Chang, Jeffrey Luo, Prabhakar V. Gulgunje, and Satis Kumar .............. 331

Synthetic Two-Dimensional Polymers
Marco Servalli and A. Dieter Schlüter ................................................................. 361

Transparent Perovskite Barium Stannate with High Electron Mobility
and Thermal Stability
Woong-Jhae Lee, Hyung Joon Kim, Jeonghun Kang, Dong Hyun Jang,
Tai Hoon Kim, Jeong Hyuk Lee, and Kee Hoon Kim ........................................... 391

Visualization of Atomic-Scale Motions in Materials via Femtosecond
X-Ray Scattering Techniques
Aaron M. Lindenberg, Steven L. Johnson, and David A. Reis ......................... 425

X-Ray Tomography for Lithium Ion Battery Research: A Practical Guide
Patrick Pietsch and Vanessa Wood ................................................................. 451

Indexes
Cumulative Index of Contributing Authors, Volumes 43–47 ...................... 481

Errata
An online log of corrections to Annual Review of Materials Research articles may be
found at http://www.annualreviews.org/errata/matsci

vi Contents