

Crystal Growth in the Presence of Surface Melting and Impurities: An Explanation of Snow Crystal Growth Morphologies

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Abstract. We examine the molecular dynamics of crystal growth in the presence of surface melting and surface impurities, and from this propose a detailed microscopic model for the growth of ice from the vapor phase. Our model naturally accounts for many aspects of the experimental data that are otherwise difficult to explain, and it suggests a variety of measurements that can provide further confirmation. Although additional work is needed to refine these ideas, we believe that the combined influences of surface melting and impurities provide a viable solution to the 60-year-old mystery of why snow crystal morphologies vary so dramatically with temperature.

1 Introduction

The formation of complex structures during solidification often results from a subtle interplay of nonequilibrium, nonlinear processes, for which seemingly small changes in molecular dynamics at the nanoscale can produce large morphological changes at all scales. One popular example of this phenomenon is the formation of snow crystals, which are ice crystals that grow from water vapor in an inert background gas. Although this is a relatively simple physical system, snow crystals display a remarkable variety of columnar and plate-like forms, and much of the phenomenology of their growth remains poorly understood [1].

One of the most enduring puzzles surrounding snow crystal formation has to do with changes in the growth morphology with temperature. As shown in Figure 1, the overall structure of snow crystals grown in air alternates twice between plate-like and columnar forms as a function of temperature. This behavior was first observed in the early 1940s [2], and for over 60 years scientists have been unable to provide even a qualitative explanation for why snow crystal morphologies exhibit this temperature dependence [1]. Mason [3, 4] suggested that the basic habit is determined by variations in surface diffusion rates on the basal and prism facets, but did not provide an explanation of why the rates alternated with temperature in the proposed manner. Nelson and Knight [5, 6] suggested that morphologies are determined by variations in layer nucleation rates on the basal and prism facets, but again did not explain why the rates alternated with temperature. The Lacmann-Stranski-Kuroda (LSK) model [7, 8, 9] was perhaps the most ambitious attempt to create a microscopic model of ice crystal growth. In this model, the authors proposed that variations in growth rates on the two facet surfaces are brought about by temperature-dependent changes in the structure of the ice surface related to surface melting. As we will see below, however, the LSK model does not agree with recent ice growth data.

In this paper, we examine how surface melting and surface impurities can affect crystal growth, and from this propose a new microscopic model for ice crystal growth as a function of temperature. We also propose a new impurity-mediated growth instability that promotes the formation of thin plate-like crystals as well as slender columns or sheath-like structures. Our model suggests that impurities play an essential role in determining snow crystal growth morphologies under normal atmospheric conditions, and that growth in perfectly clean air would be markedly different from that shown in Figure 1. While the effects of surface impurities have been largely ignored in previous work, our model suggests that impurities have profoundly affected essentially all experimental observations to date.

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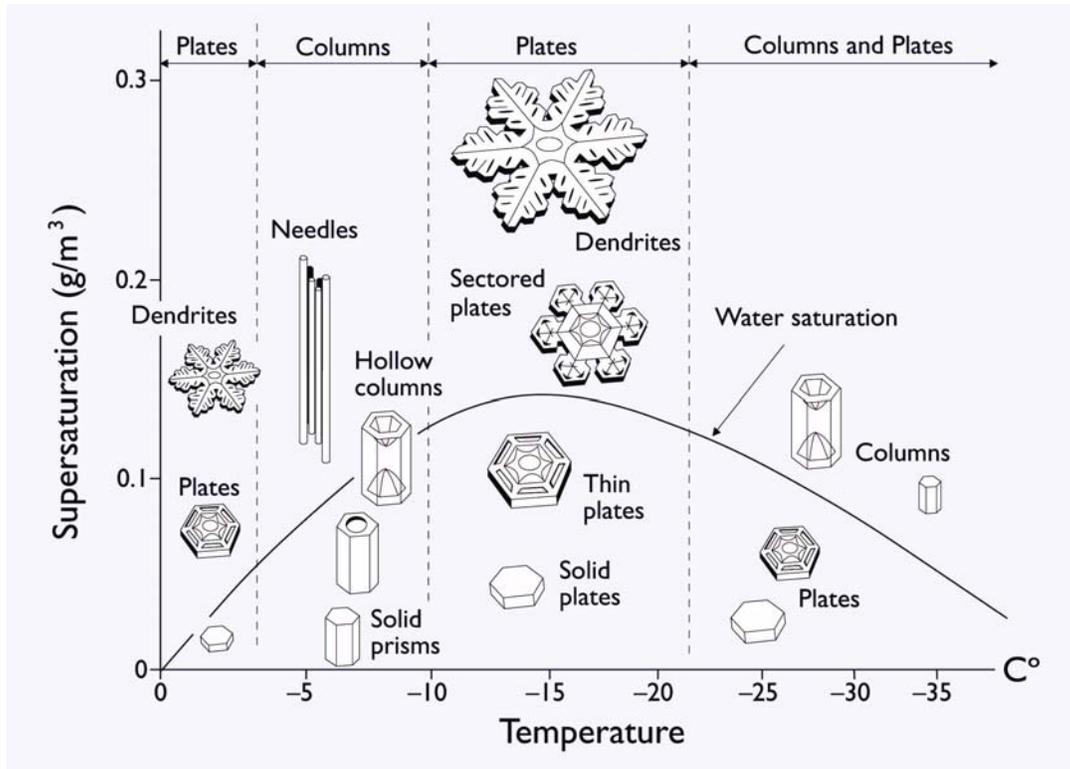


Figure 1. The *snow crystal morphology diagram*, showing how the morphology of ice crystals growing from water vapor in air at a pressure of one bar changes with temperature and supersaturation. The solid line indicates the supersaturation of supercooled water relative to ice. At high supersaturations, the overall structure alternates between plate-like and columnar forms as the temperature is reduced.

Finally, we comment on how snow crystal growth morphology should vary with impurity level, and we propose new experiments that can provide further insights into this phenomenon.

2 Developing a Picture of Ice Crystal Growth

2.1 Basic Considerations

For an ice crystal growing from water vapor, we can write the growth velocity normal to the surface in terms of the Hertz-Knudsen formula [1, 10]

$$v_n = \alpha v_{kin} \sigma_{surf}$$

where v_{kin} is a temperature-dependent kinetic velocity derived from statistical mechanics, σ_{surf} is the water vapor supersaturation just above the growing surface, and α is the condensation coefficient, which contains the surface physics that governs how water molecules are incorporated into the ice lattice, collectively known as the attachment kinetics [1]. The attachment kinetics describing ice crystal growth is quite complex, so in general α will depend on T , σ_{surf} , the surface structure and geometry, surface chemistry, etc. If molecules striking the surface are immediately incorporated into it, then $\alpha = 1$; otherwise $\alpha \leq 1$.

If an ice crystal is growing in an inert background gas, then diffusion of water molecules to the ice surface often significantly impedes the growth [1], so that $\sigma_{surf} < \sigma_\infty$. The physics of the diffusion process is well known, and computer models can be used to calculate growth rates and morphologies from known attachment kinetics, or to extract α values from growth measurements [11, 12]. Laboratory measurements of the growth of small ice crystals in air at one bar, in conditions similar to those found in the atmosphere, allowed us to extract the typical values of

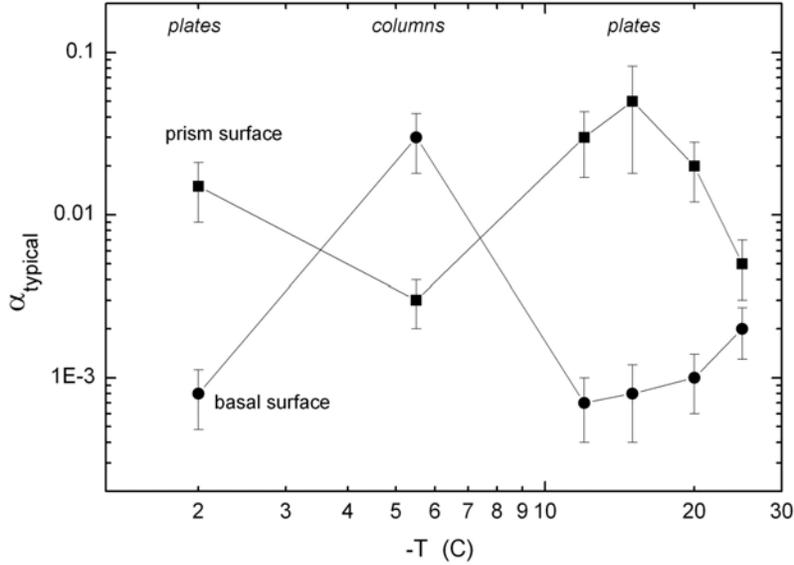


Figure 2. Ice growth measurements in ordinary laboratory air at one bar, for which diffusion modeling has produced α for the basal and prism facets [14]. Here we show data for supersaturations typical in our experiments, ranging from $\sigma_\infty \approx 1.5$ percent at $T = -2$ C to $\sigma_\infty \approx 3$ percent at $T = -20$ C. For the small crystals observed, σ_{surf} was typically no less than $\sigma_\infty/2$ over the entire crystal surface. Note that these data show a dependence with temperature that is expected from the morphology diagram.

α shown in Figure 2 [14]. Note that the changes in α_{basal} and α_{prism} with temperature in this figure agree with the temperature dependence seen in the morphology diagram, as one would expect.

In what follows we develop a microscope model for α under conditions that are typical for atmospheric ice growth and other conditions relevant for laboratory experiments.

2.2 Surface Melting

Surface melting refers to an equilibrium phenomenon in which a quasi-liquid layer (QLL) exists at the surface of a crystalline solid near the melting point. The thickness of the QLL is generally a strong function of temperature, diverging as the bulk melting point is approached. As the name suggests, both the structure and molecular dynamics of the QLL resemble that of a fully melted liquid, at least when the layer is sufficiently thick. Surface melting is present in most crystalline solids [13], and it has been especially well studied for ice [15, 16]. Because surface melting is central to our ice growth model, we summarize the basic concepts here.

One useful way to think about surface melting is from the perspective of the Lindemann criterion [17, 1]. This century-old idea states simply that a crystalline solid will melt when thermal motion of molecules in the crystal lattice produce excursions from equilibrium that are greater than approximately 10-15% of the normal lattice spacing. The Lindemann criterion works reasonably well for a wide range of bulk materials [18], and it has been directly verified both experimentally [19] and in molecular dynamics simulations [20].

If we assume a simple model in which a molecule is held in a harmonic potential, then thermal motion produces average oscillatory amplitudes of approximately

$$x = \left(\frac{kT}{\kappa} \right)^{1/2}$$

where κ is an effective spring constant. Near the solid surface the molecular binding is weaker than in the bulk, so we write

$$\kappa(d) = \kappa_0 - f(d)\Delta\kappa$$

where d is the distance from the surface, $0 < \Delta\kappa < \kappa_0$ is a constant, and $f(d)$ is a function with $f(0) = 1$ and $f(\infty) = 0$. For the simplest model in which half the restoring force is absent at the surface, we might expect $\Delta\kappa \approx \kappa_0/2$.

The Lindemann criterion states that the bulk will melt when x reaches some value $x_0 = (kT_m/\kappa_0)^{1/2}$, where T_m is the bulk melting temperature. Extending this, we expect that surface melting will occur down to a depth d at which

$$x(d) = \left(\frac{kT}{\kappa_0 - f(d)\Delta\kappa} \right)^{1/2} = x_0.$$

Expanding for small $\Delta\kappa/\kappa_0$ and for small $t = (T_m - T)/T_m$, this reduces to simply

$$t = f(d)\Delta\kappa/\kappa_0.$$

For the case of ice we assume $f(d) = \exp(-d/\lambda)$, where λ is a scaling length for the intermolecular interactions [13], and with this the thickness of the quasi-liquid layer becomes

$$d(T) \approx \lambda \log \left(\frac{\Delta\kappa}{t\kappa_0} \right)$$

which is valid for small t .

There have been numerous measurements of surface melting in ice [15], and there is general consensus that the QLL thickness $d(T)$ at least roughly follows the logarithmic relation described above. There is, however, great disparity between the different measurements, probably because most experiments do not measure $d(T)$ directly, but rather measure some quantity related to $d(T)$ in an uncertain way (see [21, 22] and references therein for a review of recent measurements). Molecular dynamics simulations are making progress toward understanding the surface structure of ice, including surface melting [23, 24, 25], although reliable quantitative results are elusive. As a result of both experimental and theoretical uncertainties, we do not yet fully understand the equilibrium structure of the ice surface in detail, or how this structure varies with temperature. Further, we do not know if surface melting is different on different crystal facets, or in general how the QLL varies with the surface orientation relative to the underlying ice lattice.

In spite of these problems, theory and experiment do give us a relatively simple qualitative picture of the development of surface melting in ice as a function of temperature. At very low temperatures, surface melting is largely absent, so there is relatively little disorder or time-dependent restructuring at the surface. As the temperature increases, surface melting begins turning on gradually, causing some disordered motion in the top few molecular layers, and this motion increases in extent with increasing temperature. Eventually this disordered motion starts to look like a fully developed QLL that sits atop the bulk crystal, and a somewhat distinct boundary appears between the two. Very close to the melting point, the QLL is thick enough that it becomes an essentially distinct layer with largely liquid-like properties. Finally, the layer thickness diverges as the melting temperature is approached.

As was pointed out in connection with the LSK model [7, 8, 9], it appears likely that surface melting plays an important role in ice crystal growth dynamics. The available data indicate that surface melting shows considerable variation over the temperature range $-20 \text{ C} < T < 0 \text{ C}$, coincident with the most pronounced variations in snow crystal morphology, and it is plausible that surface melting is substantially different on the two principal facets over this range. Unfortunately, we have little theoretical or experimental guidance as to how the structural changes associated with surface melting affect crystal growth dynamics [26].

2.3 The Role of Surface Impurities

It has long been known that high levels of gaseous impurities in air at one bar can dramatically affect snow crystal growth and morphologies ([1] and references therein). A wide range of chemical impurities, such as vapors from many alcohols, acids, hydrocarbons, etc., affect both ice crystal morphologies and growth rates. However, observations over many decades have shown that the morphology diagram is a robust feature of snow crystal growth in air, provided the air is fairly clean. Our own “rule of thumb” in the lab has been that growth morphologies are largely unaffected as long as one cannot smell anything in the air. Since impurity effects seen at high concentrations are not

seen in cleaner air, researchers were led to believe that the modest levels of residual impurities in ordinary laboratory air or in the atmosphere were probably not playing a significant role in ice growth dynamics.

These observations may be deceptive, however, because even a seemingly low concentration of surface-active impurities may not be negligible. Consider growth in air which contains a fraction f of some impurity that immediately attaches to the ice surface upon contact. Diffusion limits the transport of impurity molecules to the surface, and the time needed to form a single monolayer on a spherical crystal is

$$\tau_{mono} \approx \frac{R}{Da^2fn_{air}} \quad (1)$$

where R is the crystal radius, D is the diffusion constant ($D = 2 \times 10^{-5}$ m²/sec in air at one bar), n_{air} is the number density of the air ($n_{air} = 2.5 \times 10^{25}$ /m³ at one atmosphere), and a is the effective size of an impurity molecule (which we assume to be $a \approx 1$ nm). Equation 1 holds for times longer than the characteristic diffusion time $\tau_{diff} = R^2/D$. Note that $D \sim P^{-1}$ and $n_{air} \sim P$, where P is the air pressure, so τ_{mono} is independent of P to lowest order. This expression becomes

$$\tau_{mono} \approx 2 \left(\frac{R}{1 \mu\text{m}} \right) \left(\frac{1 \text{ ppm}}{f} \right) \text{ msec} \quad (2)$$

which is much shorter than typical snow crystal growth times. The growth velocities of micron-scale ice crystals in air are typically no higher than a few microns per second, so impurities may be playing a role even for very small ice crystals.

For times much longer than τ_{mono} we expect that the impurity density on the ice surface will reach some equilibrium value, assuming that thermal excitations are sufficient to remove adsorbed molecules from the surface at some rate. Gaseous impurities striking the surface will increase the surface density as $d\rho_{surf}/dt \sim fn_{air}$, while losses give $d\rho_{surf}/dt = \rho_{surf}/\tau_{loss}$, where τ_{loss} is the characteristic time for impurities to leave the surface. These rates are equal in equilibrium, giving $\rho_{surf} \sim fn_{air}\tau_{loss}$. Thus while τ_{mono} is independent of P , we see that reducing the pressure will reduce the equilibrium impurity surface density as $\rho_{surf} \sim P$ (assuming τ_{loss} is independent of P).

Experience with other condensed matter systems also suggests that impurity effects may be important. Creating atomically clean semiconductor surfaces often requires extensive baking, sputtering, or other types of surface cleaning, all of which must be done under ultrahigh vacuum conditions. The high vapor pressure of ice near the melting point precludes the use of ultrahigh vacuum techniques, and nearly all experiments with ice have not involved careful surface preparation to remove adsorbed impurities.

Figure 3 shows the typical composition of clean dry air. We expect that laboratory air, particularly inside closed chambers used for ice crystal growth experiments, would contain a long list of solvent vapors, volatile organic compounds and other chemical impurities near or above the ppm level.

With these simple considerations, we are led to suspect that even low levels of impurities in relatively clean air could strongly affect ice crystal growth. The remainder of this paper examines issues of impurity residence time, mobility, how these change in the presence of surface melting, and generally how impurities affect ice crystal growth rates and morphologies.

2.4 Growth of a Clean Ice Surface

Crystal growth involves complex dynamical processes at the molecular level, and the task of modeling this phenomenon is certainly made more difficult with the addition of surface melting and surface impurities. Our relatively poor theoretical understanding of crystal growth in these circumstances makes it difficult to develop an accurate *a priori* model, so we use experimental observations as much as possible to guide our thinking. For our baseline model of the growth of a clean ice surface, we rely mainly on growth measurements taken at low background pressure [28, 29]. Not only is ρ_{surf} expected to be lower for low-pressure measurements, as described above, but we also believe getting from the ice reservoir in our growth chamber reduces the impurity fraction f as well, which in turn reduces ρ_{surf} . As we discuss further in the next section, we believe these two factors greatly decrease the impurity effects on

<u>Constituent</u>	<u>Fraction</u>
Nitrogen	78%
Oxygen	21%
Argon	~1%
Carbon dioxide	380 ppmv
Neon	18 ppmv
Helium	5 ppmv
Methane	2 ppmv
Krypton	1 ppmv
Hydrogen	0.5 ppmv
...	

Figure 3. Constituents of clean dry air under typical atmospheric conditions. Laboratory air, particularly in chambers used for ice crystal growth experiments, is likely to contain substantial concentrations of additional chemical impurities from a variety of sources.

our growth measurements. Based mainly on these low-pressure growth measurements, we propose a model for the growth of an impurity-free ice surface that includes the following properties:

The surface attachment kinetics are described by 2D nucleation-limited growth. Crystal growth via 2D nucleation has been well studied, and for such growth we can write $\alpha \approx A \exp(-\sigma_0/\sigma_{surf})$ [10, 1], where the surface diffusion parameter A and the critical supersaturation σ_0 are both functions of T , surface orientation, and potentially other parameters. Our low-pressure measurements generally fit this functional form well over the full range of our measurements [28, 29]. In some cases we observed faster-growing crystals with $\alpha \sim \sigma_{surf}$, indicating growth in the presence of spiral dislocations [10], but these cases were relatively rare [29].

The critical supersaturation σ_0 decreases smoothly and monotonically with increasing temperature, and is essentially the same for both the prism and basal facets. The justification for this statement comes mainly from [28], in which this behavior was observed for $-40 \text{ C} < T < -10 \text{ C}$. From the theoretical side we expect that surface melting will decrease the edge free energy β of an atomic step on the vapor/solid interface as the QLL thickens, until it eventually becomes equal to β for a step at the liquid/solid interface. Given the gradual onset of surface melting described above, we expect that β (and thus σ_0) would decrease smoothly and monotonically with increasing temperature, as we observed [28]. This behavior is in contrast to the LSK model, which predicts large, nonmonotonic changes in σ_0 with temperature.

The A factor is large for clean surfaces, with little temperature dependence. Recent observations [30] suggest that the measurements of A in [28] were contaminated to some degree by surface impurities, which reduced the measured growth even at low pressure. We now believe that A is generally quite large for impurity-free surfaces [29, 30], with only a weak, monotonic dependence on temperature, but this hypothesis is not well tested.

It appears that essentially all ice growth experiments to date have been contaminated by surface impurities to some degree, so our clean-ice model is quite uncertain. For considering the morphology diagram, however, the exact growth behavior of a clean surface is less important than the fact that the growth is fast. Our model suggests that ice growth in air under normal atmospheric conditions is predominantly limited by surface impurity effects, as we describe next.

2.5 Growth in the Presence of Surface Impurities

The most basic and important feature of our new ice growth model is the role of surface impurities. Whereas this factor has been largely ignored in earlier models, we believe surface impurities can reduce growth rates by orders of magnitude compared to growth of a clean surface, even in normal, reasonably clean atmospheric conditions.

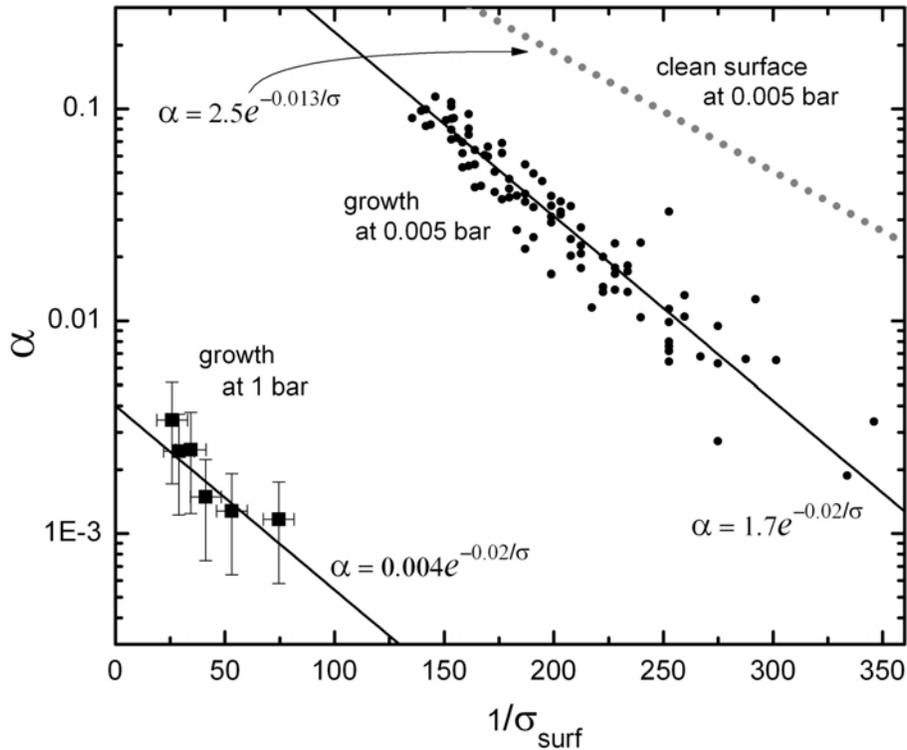


Figure 4. Measurements of the attachment coefficient α as a function of inverse surface supersaturation σ_{surf}^{-1} for basal surfaces at -15 C, comparing data taken at different background air pressures [29, 30, 14]. The top dotted line shows the rough locus of our highest measured growth rates for ice surfaces that have been cleaned as described in the text [30], which we interpret as growth of an impurity-free surface.

Furthermore, we believe that the temperature-dependent interplay of surface impurities with surface melting is largely responsible for the most enigmatic features seen in the snow crystal morphology diagram.

2.5.1 Low Pressure versus High Pressure

A major piece of evidence pointing to the importance of surface impurities comes from a comparison of ice crystal growth rates in air at high and low pressure, for which we show an example in Figure 4. These data show the condensation coefficient α for the basal surface at -15 C, but data at other temperatures and for the prism facet show similar trends. For growth at a pressure of one bar, the effects of diffusion have been subtracted by modeling [12], giving α as a function of σ_{surf} , the supersaturation at the growing surface. (For the small crystals measured, σ_{surf} and σ_{∞} typically differed by no more than a factor of two, so modeling uncertainties do not significantly affect the results shown.) Effects of diffusion are negligible for growth at 0.005 bar.

Looking first at the two data sets in Figure 4, we see that the growth rate (as parameterized by α) at one bar is 2-3 orders of magnitude smaller than at 0.005 bar. This behavior is inconsistent with all the previous ice growth models described above, which predict no substantial changes in α with pressure. Since diffusion has already been accounted for in Figure 4, we must ask what other physical effects could cause such a large difference in growth with pressure.

We feel it is unlikely that simple pressure forces can explain these data, since the air density is low enough that pressure effects should add a negligible perturbation to the surface molecular forces that determine the attachment kinetics. We examined whether the major chemical constituents in air could be responsible by measuring crystal growth rates in air, nitrogen, and argon at one bar [14]. To the accuracy of our data (better than a factor of two), all three gases yielded growth rates identical to those shown in Figure 4. These data suggest that the major atmospheric

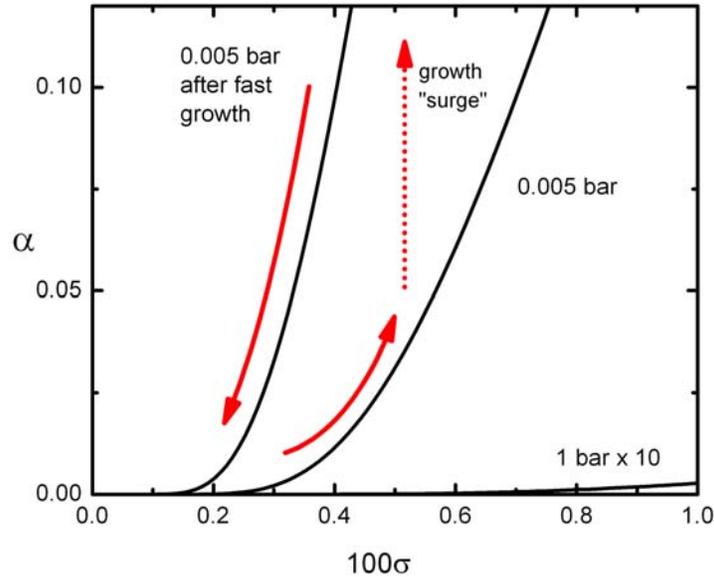


Figure 5. Schematic view of an unusual hysteresis behavior seen in ice growth [30], shown here for the example of the basal surface at -15 C. Initial growth at a background pressure of 0.005 bar is relatively slow (curve labeled 0.005 bar). As the supersaturation is slowly increased (lower arrow), the growth suddenly exhibits a “surge”, in which α can suddenly increase by a factor of four or more. We believe this event occurs because growth drives off or buries impurities on the ice surface. Once the impurities have been removed, they do not reappear quickly at low pressure, so $\alpha(\sigma)$ remains high (upper curve) as σ is varied. If the surface impurity density is allowed to build up again (by letting the crystal rest with $\sigma = 0$ for a few minutes), then the growth reverts to a lower $\alpha(\sigma)$. At 1 bar, the surface impurity density is always high, so α is always very low (the lowest curve shows 10α for typical growth at 1 bar).

components (see Figure 3), especially nitrogen and oxygen, can be treated as inert gases that do not strongly affect attachment kinetics. If nitrogen, oxygen, and the noble gases are all effectively inert, then we are left with the hypothesis that trace active impurities are likely responsible for the large dependence of α on background gas pressure. Assuming that an equilibrium is established between gaseous and surface impurities, we saw above that the surface impurity density is expected to scale as $\rho_{surf} \sim P$. Since P spans a factor of 200 in our measurements, we believe that impurities could account for the observations shown in Figure 4.

2.5.2 Hysteresis Effects

Our suspicions regarding surface impurities were strengthened with the further discovery of hysteresis effects in ice growth at 0.005 bar [30], as shown schematically in Figure 5. In these measurements we found that slowly increasing the growth of an ice crystal (by slowly increasing the supersaturation) often resulted in a sudden growth “surge” that would suddenly increase α by a factor of four or more. After such a growth increase, $\alpha(\sigma)$ remained large as long as the crystal continued growing, as shown in Figure 5. If the growth was halted for approximately 5-10 minutes ($\sigma \rightarrow 0$), then $\alpha(\sigma)$ was reduced to lower values.

The most reasonable explanation of this hysteresis phenomenon is that a period of rapid growth drives off many of the impurities on an ice surface. Assuming that impurities decrease α , removing impurities can result in an instability that explains the growth surge [30]. The growth remains rapid as long as impurities are not allowed to build up again on the surface. Halting the growth allows the surface impurity density to increase, which then reduces $\alpha(\sigma)$ to that of a dirty surface. Rapid growth in near vacuum is then seen as a method for cleaning the ice surface, after which one can measure $\alpha(\sigma)$ for an uncontaminated surface. The top curve in Figure 4 represents the approximate locus of the maximum “post-surge” growth rates we measured [30], which we interpret as being the normal growth of a clean

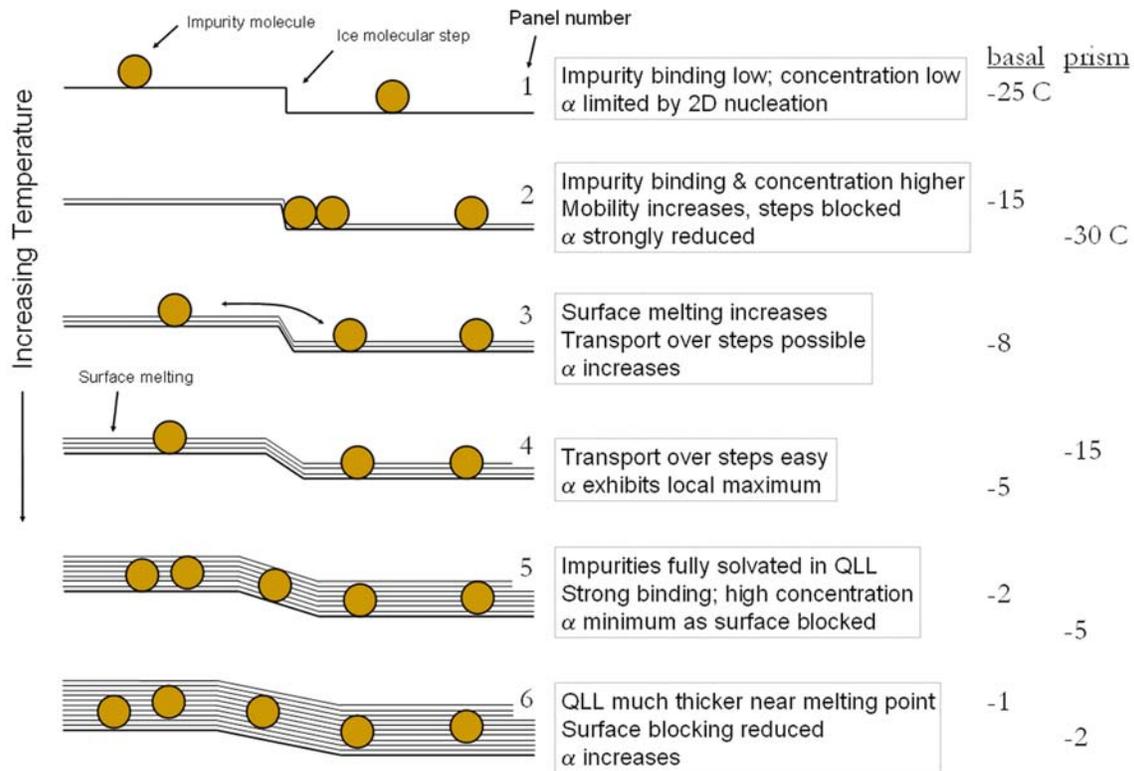


Figure 6. Our model for ice crystal growth in the presence of surface melting and surface impurities. Different panels refer to different temperatures, with colder temperatures at the top. The columns on the right show temperatures for each growth behavior on the basal and prism facets. See text for details.

ice surface.

With all these observations, our hypothesis of surface impurities reducing the ice growth rate provides a natural interpretation for the most striking features in our data, whereas we can find no other ready explanation.

2.5.3 Impurities and Surface Melting

To better understand the ice growth data, it is necessary to develop a molecular model that describes how the impurity effects vary with temperature and with facet surface. As a first step in this direction, we have constructed the model shown in Figure 6. Referring to the panels in this figure, starting at the top, our model has the following features:

Panel 1) At low temperatures, surface melting is negligible, so the ice surface is essentially rigid and static. There is little “smoothing” of molecular steps by surface melting, so the edge free energy β is relatively high [28]. Impurity molecules have a relatively weak binding to the rigid ice surface, so the equilibrium impurity surface density ρ_{surf} is low. In this regime, impurities have relatively little effect on the crystal growth rates, which are then mainly limited by 2D nucleation as on a clean ice surface.

Panel 2) As the temperature increases, surface melting begins to produce some disorder at the interface, represented by thin lines in the Figure. This disorder begins to smooth the molecular steps and reduce β , which is represented by a sloped molecular step in the Figure. The increased mobility of water molecules also results in a partial solvation of impurity molecules, which increases their binding to the surface, thus increasing ρ_{surf} . The impurity molecules exhibit increased mobility on the partially melted ice surface, and they bind more readily to steps than to the molecularly flat faceted regions. When an ice island forms via 2D nucleation and grows in extent, the moving step pushes impurity molecules along so they build up at the step edge, where they block subsequent growth. As a result, α is strongly reduced.

Panel 3) At still higher temperatures, surface melting increases and β is reduced. The increased agitation and disorder of water molecules on the surface increases the mobility of impurity molecules, which can now sometimes hop over the smoothed steps. This tends to reduce the buildup of impurities at the steps, so they do not block so completely the growth of islands. Thus α increases in comparison to Panel 2.

Panel 4) Again, increased surface melting leads to greater impurity mobility and an effectively reduced step height, so impurities now readily move over steps. Island growth is not blocked and α exhibits a local maximum.

Panel 5) The QLL now becomes thick enough that impurity molecules are essentially completely solvated, which greatly increases their binding to the surface. The impurity density increases to the point that the surface is now coated with a dense impurity layer. This blocks access to the underlying ice, which reduces α .

Panel 6) Surface melting diverges rapidly near the melting point, so now impurity molecules are essentially “floating” in the QLL. The layer is so thick that it takes a time much greater than τ_{mono} for the impurity concentration to build up to where it will substantially block ice growth. As the blocking timescale becomes comparable to or longer than the growth time, α increases.

On the right side of Figure 6, we have indicated temperatures at which the different growth behaviors are exhibited by the basal and prism facet surfaces in our model. There is a systematic offset in the temperature behavior of the two facets, which stems from an assumption that surface melting is generally more pronounced on the prism facet in comparison to the basal facet at a given temperature. A similar assumption was made in the LSK model, but it is neither excluded nor supported by our existing knowledge of surface melting in ice. It is also possible that there are differences in impurity binding and impurity mobility on the two facet surfaces, and these may also contribute to differences in the growth behavior with temperature.

This model is both complex and quite speculative, with only modest theoretical and experimental backing. We expect that some details will require modification and further refinement, but we believe that the overarching concepts are sound. In particular, we believe that surface impurities strongly reduce ice growth in comparison to that of an impurity-free surface, and that the complex interplay of surface melting and surface impurities is largely responsible for determining ice growth rates. Before examining some of the testable predictions this model makes, we first examine some of its features and describe how it can explain the snow crystal morphology diagram.

2.5.4 2D Nucleation

One of the principal effects of impurities in our model is to reduce the surface transport of water molecules to the edges of growing 2D islands, for example in Panel 2 of Figure 6. We believe that surface impurities do not act as nucleation centers to initiate the growth of islands, nor do they substantially change the step free energy. Thus impurities do not greatly affect the 2D nucleation process in general. If we parameterize the attachment coefficient as $\alpha = A \exp(-\sigma_0/\sigma)$, which is characteristic for 2D nucleation-limited growth [1], then our model suggests that the addition of surface impurities would change A a great deal while having little effect on σ_0 . Indeed, we have observed in all our low-pressure growth data [28, 29, 30] that σ_0 is remarkably insensitive to experimental parameters at a fixed temperature, in agreement with our model.

At the higher temperatures shown in Figure 6, we believe that σ_0 is small enough that 2D nucleation no longer limits growth to a great extent. Instead, we believe that the dominant growth-limiting factor is from impurities directly blocking the growing surface, as described above.

2.5.5 Kinetic Surface Melting

At high growth rates we expect that the effective thickness of the QLL would increase relative to its equilibrium value, which we refer to as *kinetic surface melting*, corresponding to the more familiar kinetic roughening [10]. Changes in the QLL thickness will in turn affect the surface dynamics in Figure 6, which will alter growth rates. The various effects of kinetic surface melting may be observable as changes in growth behavior with supersaturation.

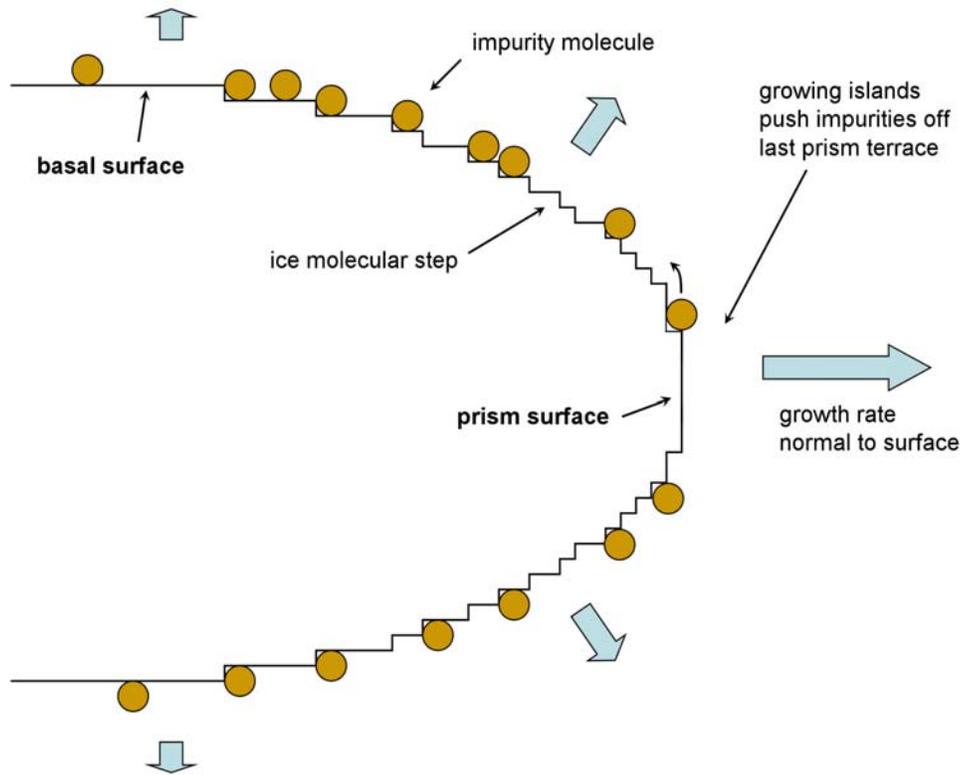


Figure 7. An edge-sharpening growth instability (ESGI), as demonstrated for the growth of a thin plate-like crystal (shown here in cross section near a growing edge). Because the plate is thin, the width of the last ice terrace can be of order 100 molecular diameters (see text). The growth of islands on this narrow terrace tends to push impurity molecules to the side, thus cleaning the terrace. With fewer impurities, α increases on the prism surface, and so does the growth rate. This effect results in a growth instability that sharpens the edges of growing plate-like crystals.

2.5.6 An Edge-sharpening Growth Instability

We believe that the intrinsic changes in α described above are effectively amplified by an additional edge-sharpening growth instability (ESGI), which is necessary to explain the growth of thin plates and other features in the morphology diagram [31]. In the model presented here, this instability comes about through impurity migration away from narrow terraces, as shown schematically in Figure 7. For growth at -15 C , the radius of curvature at the edge of a thin plate is of order $R \approx 1\ \mu\text{m}$. The width of the last molecular terrace on the prism surface is then $w \approx \sqrt{8aR} \approx 100a$, where a is the size of a water molecule. As new islands form via 2D nucleation on top of this terrace, they will tend to push impurity molecules laterally, removing impurities from the terrace, which increases α_{prism} as shown in Figure 7.

This behavior produces an edge-sharpening growth instability because the resulting α_{prism} depends on R . If we begin with a broad terrace (at the edge of a thick plate crystal), then impurity migration will clean the terrace somewhat, which will enhance the edge growth and result in a slightly smaller R . This reduces w , leading to more efficient cleaning of the terrace, and thus still higher α . In addition, the faster prism growth will give impurities less time to build up from the surrounding gas. Both effects result in a positive feedback that leads to thinner plates with faster edge growth. Kinetic surface melting may also play a role in this instability when the supersaturation is high.

In our diffusion modeling of thin plate growth, we extract α_{prism} from the growth velocity of the prism surface, which is determined by the growth rate on the last terrace. We believe that the high α_{prism} shown in Figure 2 at -15 C results mainly because the prism surface has been cleaned by the ESGI. For a large prism facet at this same temperature, there would be no cleaning of the surface, so α_{prism} would be much lower. The ESGI can greatly

amplify small intrinsic differences in α between the two facets to produce the much larger differences seen in Figure 2. As we pointed out earlier [31], this factor must be taken into consideration when comparing growth models for large, flat surfaces (Figure 6) with numbers extracted from the growth of plate-like or needle-like crystals (Figure 2). Amplification via the ESGI is most substantial for the growth of thin plates (near -15 C and -2 C) and slender needles and sheaths (near -5 C and below -30 C [32, 33]).

2.5.7 The Morphology Diagram

Having laid out the characteristics of our molecular growth model, we can now examine ice growth at different temperatures to explain the macroscopic characteristics of the snow crystal morphology diagram. We consider different temperature regions separately.

Near -15 C. At this temperature the growth of the basal facet in air is strongly suppressed (Panel 2 in Figure 6), giving $\alpha_{basal} \approx 0.001$ when $\sigma_{surface}$ is a few percent. This must be a robust feature in any ice growth model, as thin, plate-like growth is a well-established feature of snow crystal growth in air (and other inert gases) at one bar. For growth at low pressures, however, the impurity surface density is much lower, so α_{basal} is much higher, explaining the data in Figure 4.

The intrinsic α_{prism} for a large, flat surface is higher than α_{basal} in air at -15 C, but it is not a great deal higher (Panel 4). Because α_{basal} is so low, however, the edge-sharpening growth instability described above quickly takes effect on the prism facet. The ESGI cleans the prism surface and greatly increases α_{prism} relative to what it would be on a large, flat surface, again explaining the α_{prism} data in Figure 2 at -15 C.

At temperatures somewhat above or below -15 C, α_{basal} is higher than the value at -15 C (panels 1 and 3), yielding a local minimum in α_{basal} around -15 C, as seen in Figure 2. The ESGI is then less effective at cleaning the prism facet, which yields a local maximum in α_{prism} near -15 C. Note that the growth of very thin plates in air, and the large effective α_{prism} values needed, results mainly from the removal of impurities from the prism facet by the ESGI.

Near -5 C. At this temperature the growth of the prism surface is suppressed by strong binding in the QLL (Panel 5), while the basal facet growth is substantially less suppressed (Panel 4), resulting in columnar growth. Under growth conditions with fairly low σ , the ESGI is not present, so columns grow with blunt ends. At sufficiently high σ , however, the ESGI can take effect on the basal facets, resulting in the growth of sheath-like crystals [32, 33].

Near -2 C. Here basal growth is suppressed by strong binding in the QLL (Panel 5), while the QLL is so thick on the prism facet that its growth is increased relative to that at -5 C. Because α_{basal} is low, the ESGI can take effect to increase α_{prism} to the value shown in Figure 2 and produce thin, plate-like crystals. At still higher temperatures, the growth of both facet surfaces is at some intermediate value (Panel 6), so the ESGI is no longer present, resulting in a more isometric morphology.

Below -30 C. Our model is most uncertain at low temperatures, but we expect growth of the prism surface will be suppressed (Panel 2), leading to the growth of columnar crystals. The ESGI will then lead to the growth of sheath-like crystals at high supersaturations, as observed [32, 33].

3 Discussion

We are enthusiastic about this new ice growth model for a number of reasons. First, it fairly naturally explains many previously puzzling features in our ice growth data, especially the substantial variation in the attachment coefficient with background gas pressure. Second, the model provides a viable explanation of the snow crystal morphology diagram, which has baffled researchers for over 60 years. Third, the influence of low levels of impurities is likely responsible for some of the disparity seen in previous ice growth experiments [27]. Fourth, the model is easily testable with additional growth experiments. And finally, the notion of impurities playing an essential role in normal ice growth has been largely ignored to date, so our model opens up new avenues for exploring impurity-dependent growth behavior.

Verifying all the microscope details outlined in Figure 6 will be an extremely difficult task, involving precise measurements of the characteristics of ice surface melting, impurity attachment kinetics, as well as impurity binding and mobility, all as a function of temperature. In addition, we would need to understand how these surface characteristics affect the molecular dynamics of crystal growth if we wish to determine growth rates and morphologies. Direct molecular-scale imaging of the ice surface, such as with scanning probe microscopy, is of limited use because the molecular motions are extremely rapid and the equilibrium vapor pressure is high, making the ice surface too unstable for most molecular-scale imaging techniques. Molecular dynamics simulations are also challenging for such complex surfaces.

Fortunately, one can use crystal growth itself as a diagnostic tool for exploring the molecular dynamics of the ice surface. By making additional, relatively straightforward measurements of crystal growth rates and morphologies as a function of temperature, supersaturation, background gas pressure, gas constituents, and surface orientation relative to the lattice, one should be able to examine a great many characteristics of our model in considerable detail. Although our model is quite speculative at present, it provides a useful guide for additional experiments that will no doubt lead to modifications and additional refinements.

Some potentially interesting directions include:

1) In extremely clean air (or other inert gases) at one bar, the growth rates should be very high because the ice surface would be free from impurities. The ESGI would not be present, and the morphology diagram would look very different from Figure 1. This would provide a dramatic “smoking gun” verification of the most important feature in our model, namely that even low levels of impurities substantially reduce ice growth rates. Unfortunately, creating an impurity-free gas is an experimental impossibility, and we cannot accurately estimate at present what impurity levels are necessary to produce growth rates that approach that of a clean ice surface. It appears likely, however, that even modest cleaning efforts will yield some measurable changes.

2) Even if one can only increase impurity levels relative to those found in ordinary laboratory air, measuring growth rates as a function of impurity density should provide many valuable insights into our model. High impurity levels would change many of the details in Figure 6 and would significantly alter the behavior of the ESGI. Experiments of this nature have not yet been done, but many should be quite straightforward.

3) We have little knowledge at present about which impurities have the greatest effect on ice growth, and which are most important under normal atmospheric conditions. Exploring the chemistry of impurity-mediated ice crystal growth should shed considerable light on the microscopic mechanisms involved.

Although snow crystal growth is a seemingly simple process, a closer look reveals that the underlying physics and chemistry are remarkably subtle and interesting. The observed morphological diversity of snow crystals results from a complex interplay of molecular dynamical processes occurring at the ice surface. There is much yet to be learned by investigating this fascinating phenomenon.

4 References

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