**Abstract**

Existing theories of faceted ice crystal growth suffer significant limitations in terms of their representation of the quasi-liquid layer (QLL) that forms atop ice surfaces at temperatures above 240 K. Here we make progress toward filling that knowledge gap by revising a previously-introduced, micrometer-scale system of reaction-diffusion equations that specifies the time scale of freezing of quasi-liquid relative to other surface processes (such as surface diffusion). Solution of these revised equations allows examination of the consequences of a much broader range of environmental conditions (such as water vapor concentration above the ice surface) than previously possible. We also take advantage of recent advances techniques to reconstruct surface morphologies from scanning electron microscope experiments, with micrometer-scale resolution. The outcome is a more comprehensive, predictive, and experimentally vetted theory of ice crystal growth and ablation than has previously been possible.

1. **Prior theories of faceted ice crystal growth and ablation**

The qualitative picture provided by the Burton-Cabrera-Frank (BCF) model of crystal growth goes something like the following: a gas-phase molecule (e.g., water vapor) hitting a crystalline surface becomes attached to that surface as an “admolecule.” Not (yet) part of the ice lattice, this admolecule is able to diffuse across the surface, until it meets one of two fates: either it finds and fills an unoccupied gap in the crystalline lattice, or (failing to do so in time) it detaches from the surface and re-enters the gas phase.

As intuitively appealing as the BCF model may be, we can identify two main drawbacks. One is that it does not adequately explain how crystals maintain faceted surfaces in the presence of persistent inhomogeneities of the overlying vapor field. An example of a persistent inhomogeneity is that experienced by a faceted crystal growing within a vapor field in which facet corners experience higher vapor pressure than facet centers. Without some countervailing mechanism, such facets cannot persist over time, but rather must convert to dendritic, and possibly fractal growth geometries (e.g., snowflake-like geometries in the case of water ice).

A second drawback of the BCF model is specific to water ice at a temperature of 240 K and above. At 240 K, there are no unoccupied gaps in the crystalline lattice available to an admolecule, because of the existence of a quasi-liquid layer (QLL) between the ice and the gas phase. Rather, the QLL thermalizes nearly every incoming water molecule that impacts the surface, on a picosecond time scale.

The QLL thus poses insurmountable conceptual problems for the BCF model. Instead, a model is needed in which the QLL plays a central role. For example, some sections of a QLL-covered surface are expected to have thicker QLL than others (because, e.g., of the aforementioned inhomogeneities in the vapor field). That spatial variation in QLL thickness, in turn, may be expected to leads to variations in the volatility of water vapor, on a micrometer length scale, across a given surface.

The quasi-liquid continuum model introduced by some of the authors in 2016 (N2016) recasts the problem as an ice surface covered by a QLL, by designating two mesoscale variables, and (see Fig. 1), which represent the total thickness of the ice surface and the thickness of the quasi-liquid part of the surface, respectively.

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| **Figure 1**. Visual representation of mesoscale variables , , and , and processes affecting them, in the N2016 (and present) model. Dashed arrows represent processes affecting how these variables evolve over time. |

The time evolution of these two variables, according to N2016, is governed by a pair of reaction-diffusion differential equations that represent the three processes indicated in Fig. 1, namely, (i) vapor deposition and ablation to and from the QLL, (ii) horizontal surface diffusion of the QLL, and (iii) interconversion of QLL molecules to/from the underlying ice. The main insight afforded by N2016 is that it provides a mechanism by which faceted ice crystal growth occurs. At the heart of that mechanism is a process called “diffusive slowdown,” an emergent property of the reaction-diffusion system of equations in which the surface structures itself in a way that excess vapor that is deposited at corners of a growing facet are incorporated less efficiently into the ice lattice compared to facet centers, thus leading to faceted growth … steps are more tightly bunched together at facet boundaries compared to the facet center.

The model presented in N2016 suffered from several limitations, however, of which the most important for our present purpose is that the time scale of process (iii), the interconversion of quasi-liquid and ice, was fixed relative to processes (i) and (ii); in real crystal facets, these relative time scales may vary from facet to facet, or as a function of temperature. The revised model presented here corrects this deficiency.

1. **A revised quasi-liquid reaction-diffusion model**

The present theory has much in common with that of N2016, beginning with its representation of an ice surface defined by the two mesoscale variables and three processes shown in Fig. 1. The governing reaction-diffusion equations are given by

(1a)

(1b)

Some notes about this model are as follows, with differences between it and N2016 noted:

1. represents the idea that surface diffusion depends on the thickness of the quasi-liquid only; the underlying ice is considered immobile on time scales considered here.
2. is the rate at which vapor-phase water molecules collide with the quasi-liquid; it is assumed that these stick, on a picosecond time scale, with 100% efficiency.
3. defines the thickness of quasi-liquid when it is in equilibrium with the underlying ice. Here (as in N2016) we use the sinusoidal form

(2)

It is evident from this equation that this thickness varies continuously from a thin state (“surface I”) with thickness , to a thick state (“surface II”) with thickness . These are indicated schematically in Fig. 1.

1. The model assumes that surface II is more volatile (has a higher equilibrium vapor pressure) than surface I. Therefore, the net surface supersaturation at a given point on the surface, designated as in Eq. 1a, is not simply a function of the overlying water vapor concentration, but also of the state of the QLL at any given point: a given concentration of water vapor will “look” more supersaturated over surface I, and less supersaturated to surface II.

To compute , we define a variable that quantifies the degree to which a given surface is similar to surface I or II,

(3)

With this definition, surface I will have , while surface II will have . We then express as

(4)

where is a measure of the difference in the equilibrium vapor pressure of surfaces I and II, and is the supersaturation relative to surface I. We will assume here that both (a scalar quantity) and are fixed parameters of a given trajectory. Forms of the latter are described in more detail below. Eq. 4 is at slight variance with, and simpler than, the corresponding expression in N2016.

1. is a first-order relaxation constant describing the time scale at which quasi-liquid/ice equilibrium is achieved. That is, if we imagine an initial situation having an amount of quasi-liquid given by , then equilibration after a time occurs according to

(5)

If one takes the time derivative of Eq. 5, and assumes that is small, the second term on the right-hand side of Eq. 1b results.

Equations 5 and 1b represent the primary departure of the present model from N2016. With this revision, we are able to specify the rate of quasi-liquid/ice equilibration relative to processes (i) and (ii). Specifying a small value for , for example, would represent the idea that quasi-liquid/ice equilibration is fast compared to diffusion and exchanges with the vapor phase, while large would mean the opposite. We do not have reliable independent guides for determining , but we do have a guidepost: because the “diffusive slowdown” mechanism for stabilization of faceted ice growth described in N2016 required that quasi-liquid/ice equilibration be slow compared to surface diffusion, we should not be surprised if we find that large leads to stable growth scenarios. We return to this topic below.

1. **SEM/GNBF surface morphologies**

Environmental SEM imaging of ice crystals has seen considerable activity in recent years. Those techniques offer “mesoscale” resolution of ice surfaces – i.e., as small as micrometers – with conditions that are adjustable in real time: one can use the technique to grow crystals, or ablate them, by manipulating the temperature and pressure inside the SEM chamber. In tandem with those developments is the development of computer codes that permit quantitative reconstruction of the surface morphology using a Gauss-Newton in a Bayesian Framework (GNBF) algorithm.

Together – in a process we will refer to as “SEM/GNBF retrieval” – we can examine not just the morphologies of static ice, but the changing structure of ice surfaces as they evolve over time in response to variations in temperature and water vapor concentration scenarios. SEM/GNBF retrieval therefore provides a unique opportunity for suggesting numerical experiments, and for evaluating predictions, of the quasi-liquid reaction-diffusion model. Questions we seek answers to here include:

1. *What is the effect of variation in time scales of ice-quasiliquid equilibration vis a vis other processes, as introduced in the present model (but absent in N2016)?*
2. *Existence of faceted ablation*. Is there such a thing as faceted ablation, and if so, what is the mechanism?
3. *Facet curvature*. What does concavity or convexity of a facet tell us about the conditions surrounding a crystal?
4. *Generalizations of surface morphology dependence on environmental conditions.* Is it possible to make general statements about how surface morphology varies as a function of supersaturation, diffusion coefficient, and other parameters?
5. *Facet resilience*. SEM observations show that faceting is resilient in the sense that a crystal with rough surface morphology can be restored to smooth morphology when exposed to highly inhomogeneous vapor fields. What resilience properties does the model exhibit?
6. *Does facet roughness have an intrinsic characteristic length scale*? More particularly, is there a difference between the roughness that appears under supersaturated conditions, vs subsaturated conditions?
7. *What about differences between facets*?
8. **Implementation details**

Python, accelerated with Numby. Surface morphology extraction using the GNBF formalism …

1. **Environmental conditions as model parameters**

Figure 2 displays examples of supersaturation profiles used to parameterize solutions to the model. Why do they have these shapes? Well, …

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| **Figure 2**. Supersaturation and subsaturation profiles. |

1. **Results**

*I. Effect of variation in the time scales of ice-quasiliquid equilibration vis a vis other processes*… [still working on this, preliminary work says that bigger stabilizes the formation of steady states, but otherwise has little effect on the shape of the steady-state profiles]

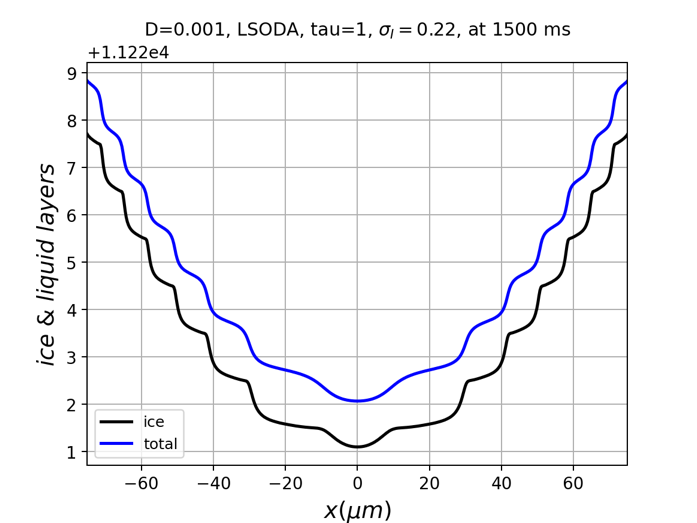
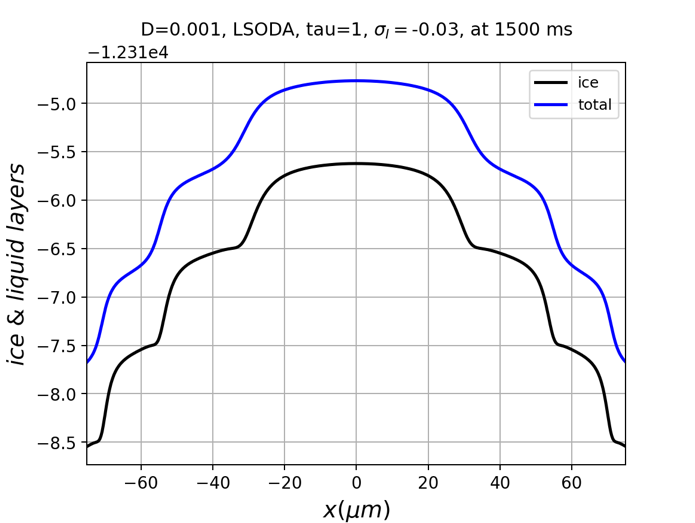
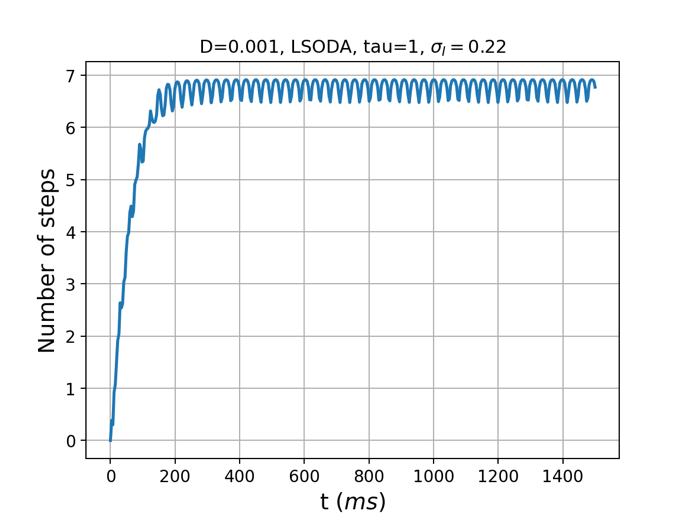
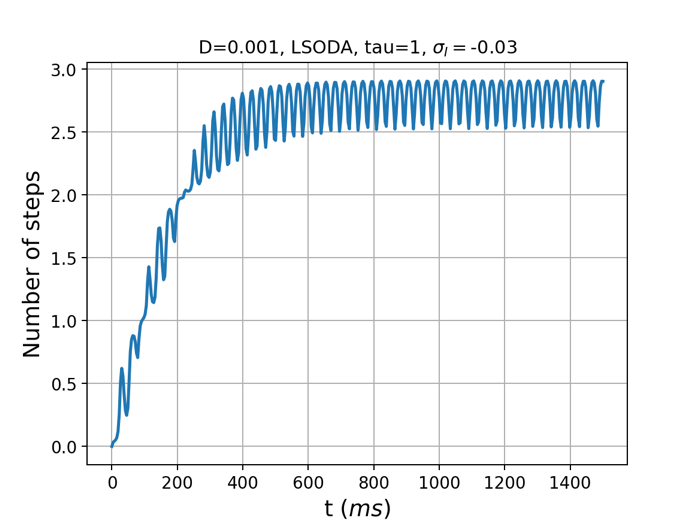
*II. Existence of faceted ablation*

Figure 3 shows a modeled ice crystal surface under ablating (left) and growing (right) conditions. The ablating scenario was parameterized by subsaturation conditions of the kind shown by the dashed line in Fig. 2, having more extreme subsaturation at corners than at facet center. We see in Fig. 3 that the facet achieves a steady-state profile – i.e., faceted ablation – after about , at which time a facet profile having about three more molecular layers than at facet boundaries persists indefinitely.

The growth scenario shown on the right of Fig. 3 is a result of parameterizing the water vapor amount in the pattern shown in the solid blue line of Fig. 2. We see that this facet also achieves steady state, although in this case the facet center is about seven molecular layers *thinner* than at facet boundaries.

Both scenarios exhibit signs of diffusive slow-down described in N2016: steps are more tightly bunched together at facet boundaries compared to the facet center. As described in N2016, this bunching is a spontaneous, emergent property of the facet, a result of the fact that, in the case of the growing crystal, supersaturation is most extreme at the corners, hence the rate of new layer formation is greatest there. That bunching at the corners, in turn, reduces the efficiency with which the surface is able to retain deposited water vapor, compared to facet center; eventually, result is that retention is uniform across the facet, and the surface locks into a steady-state profile (i.e. faceted growth).

This “diffusive slowdown” mechanism was first described in N2016, where only growth conditions were considered. Here, we see that a similar mechanism describes the process of ablation, with layer bunching now reducing the volatility of the surface near the corners.



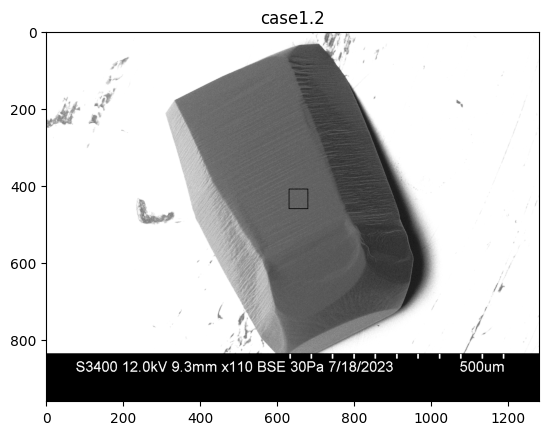
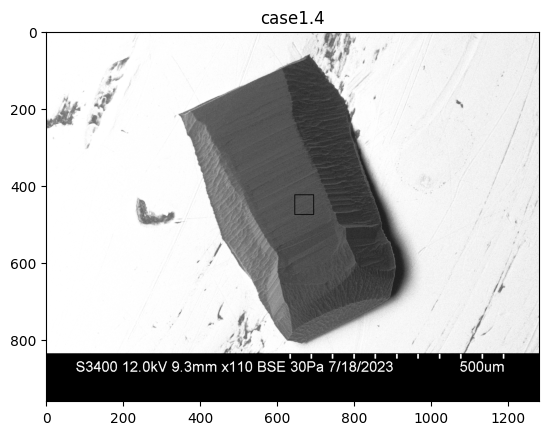
**Figure 3**. Stabilization of faceted ablation (left panels) and faceted growth (right panels).

A useful metric for describing the morphology of steady state profiles such as those appearing in Fig. 3 is the horizontal distance between successive molecular layers. Here we define a mean value of that distance as

(6)

For example, the ablating facet profile on the left of Fig. 3 is characterized by , whereas the growing facet profile on the right is characterized by . We will return to this growth/ablation asymmetry in in a later section.

Do real ice crystals exhibit faceted ablation? Figure 4 displays SEM images of an ice crystal under ablating and growing conditions. Since the ablating crystal retains its flat surface, we can conclude that faceted ablation has indeed occurred. The figure shows, moreover, that faceted ablation occurs even when the surface is rough (e.g., the prismatic facets in the figure). In fact, we observe faceted ablation quite frequently in SEM images of ablating ice crystals.



**Figure 4**. An ice crystal under ablating (left) and growing (right) conditions.

*III. Facet curvature*

The model results shown in Fig. 3 suggest the following general pattern: growing ice facets will exhibit facet concavity, whereas ablating ice facets will exhibit facet convexity. Is this pattern borne out by observations?

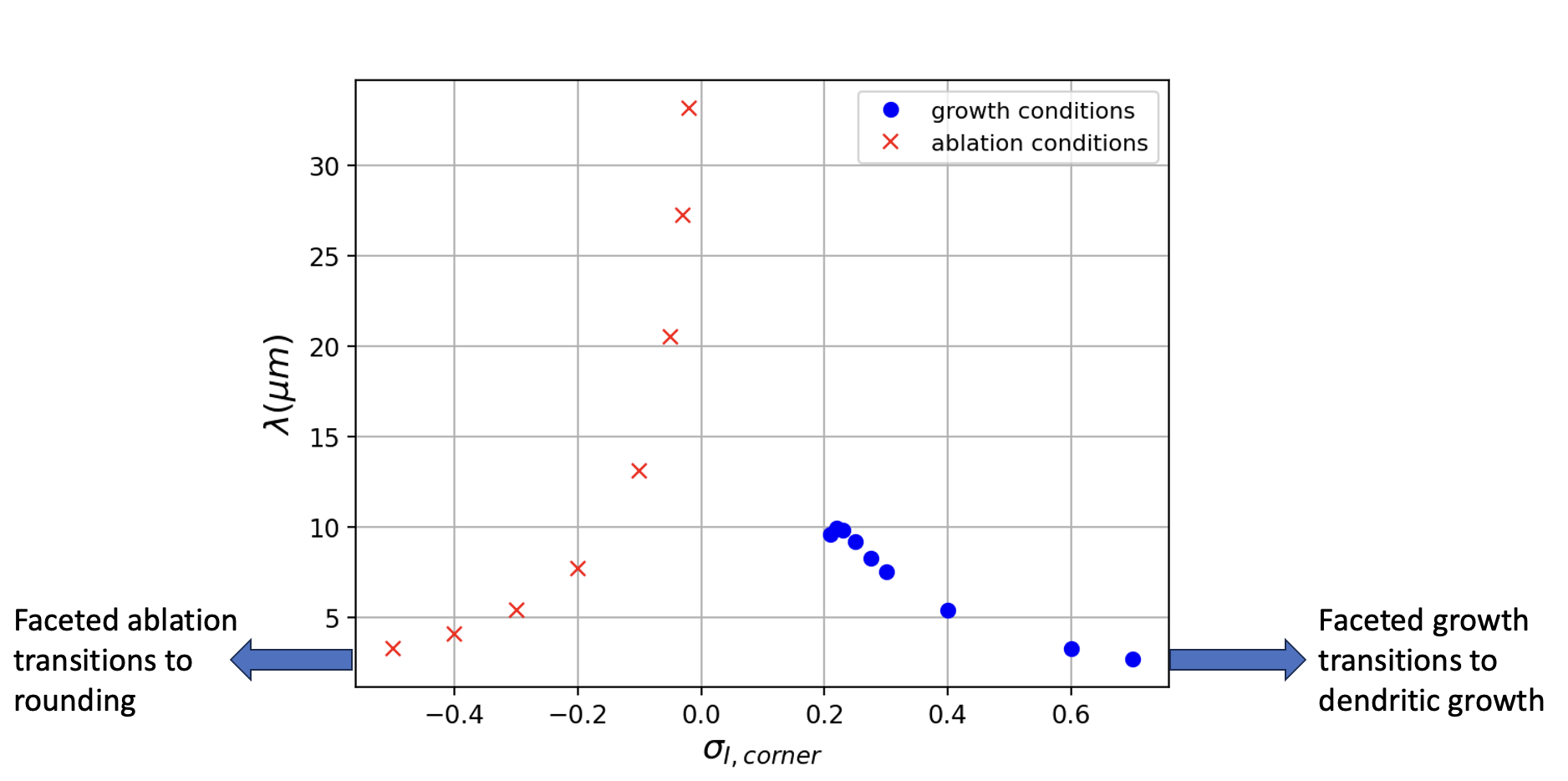
An SEM image of a growing crystal, and a GNBF reconstruction of a portion of its basal facet, are shown in Fig. 5. The GNBF reconstruction reveals a distinct concavity, on the order of 1000s of layers over the horizontal span analyzed (). The crystal is known to be growing, since subsequent images taken of this crystal revealed expanding boundaries against the metal substrate to which the crystal is attached. Thus, the pattern is borne out: growing ice facets do indeed exhibit facet concavity, whereas ablating ice facets will exhibit facet convexity, in agreement with the model prediction.

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| **Figure 5**. SEM image of a growing crystal (left) with its basal surface retrieved (right) | |

*IV. Generalizations of surface morphology dependence on environmental conditions.*

Values of the surface layer separation metric, (introduced in Eq. 6), are shown in Fig. 6. These values based on a series of simulations in which the supersaturation at the corner of the crystal () was varied, and all other parameters fixed. Focusing first on the right-hand side, we see that when conditions are just barely supersaturated (relative to surface II, the most volatile microsurface the quasi-liquid is capable of), this distance first appears with . As supersaturation increases to the right, becomes declines monotonically. We surmise that eventually, at high enough supersaturation, growth must cease to be faceted, and transition to dendritic.

On the left-hand side of Fig. 6 are displayed results when conditions are subsaturated relative to the least volatile microsurface of the model (surface I). We see that under these conditions, steady-state spatial wavelengths first appear much higher – over – and decrease for more extreme subsaturations farther to the left. We surmise that eventually, at extreme enough subsaturation, ablation must cease to be faceted, and transition to rounded.

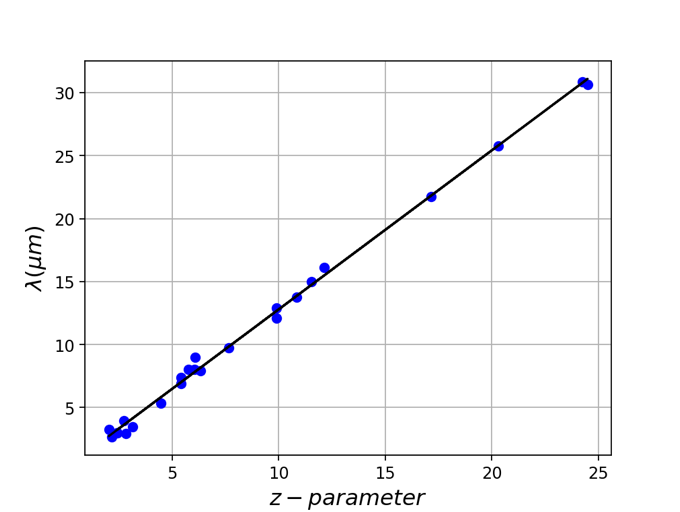


**Figure 6**. Spatial wavelength () as a function of corner supersaturation .

Figure 7 shows the dependence of on a parameter , defined by

(7)

where (as described above) is the surface diffusion coefficient, is the edge length of the crystal, and is the kinetic deposition velocity. We see that … The observation that is proportional to is noteworthy because of the connection to Turing patterns ….



**Figure 7**. Surface layer wavelength () as a function of parameter for a range of values of , , and . The corner supersaturation is fixed at for all points.

*V. Facet resilience*

Facet resilience is defined here as the ability of a facet to recover from a perturbation. In SEM experiments, facets exhibit resilience in that after being roughened by some perturbation (e.g., by higher temperature) they are commonly observed to be restored to smoothness within less than a minute after the perturbation is removed. An example is shown in Fig. 8

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| **Figure 8**. SEM image of a rough facet restored to smoothness. |

What resilience, if any, is exhibited by modeled facets? Figure 9 is an examination of this question, beginning with an initially-flat profile, then subjected to the following sequence:

1. The blue curve is a timeline of that form on the surface when subjected to the inverse parabolic supersaturation curve indicated by the solid blue line in Fig. 2. After , it has evolved to the steady-state profile shown, characterized by .
2. At , a perturbation is introduced in the form of a new ambient water vapor regime, given by the solid, gray-colored sinusoidal subsaturation curve in Fig. 2. At , the surface has evolved into a nearly-flat profile. By , it has evolved into a highly rounded profile with a depression at facet center.
3. At , the original ambient water vapor regime (solid blue line in Fig. 2) is again imposed. By , the surface has recovered its pre-perturbation, steady state.

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| **Figure 9**. Examination of model facet resilience. |

Conclusion … qualitatively, the model exhibits resilience analogous to that of a real crystal facet, such as the one shown in Fig. 8. We should hasten to add, however, these perturbations occur on a vastly different vertical scale, compared to experiment. That is, the dip at the center of the facet in seen in Fig. 9 is only a few monolayers of ice, whereas ridge-to-valley distances seen in the real crystal in Fig. 8 amounts to thousands of monolayers of ice.

*VI. Does facet roughness have an intrinsic characteristic length scale*?

We have mentioned previously that a distinct growth/ablation asymmetry in is visible in SEM experiments, an example of which is shown in Fig. 4. Does the model have anything to contribute to this observation?

The model presented here is, unfortunately, not capable of the extreme depth variations that mesoscopic roughening represents: the vertical relief is too great to resolve in our model. There is, however, a hint at a growth/ablation asymmetry in experiments is an intrinsic property of the crystal, rather than the result of some imposed variability (e.g., a repeating variability in the overlying vapor field). That hint lies the fact that the model predicts a substantial asymmetry in growth vs ablation values (as shown in Fig. 5) … [Anything else to say about this, Jake?]

*VII. What about differences between facets?* Because facets have distinct underlying crystal cell structures, we can expect that their quasi-liquid properties will also be distinctive. Exploratory numerical studies varying the the thickness of a single “layer” of ice has shown that a proportional increase in results. Numerical experiments varying and have shown that …

Appendix

Simulation of the water vapor partial pressure, , in the space surrounding a square-shaped crystal shown in Fig. A1(a), was achieved by integrating the two-dimensional diffusion equation

(A1)

where is the diffusion coefficient of water vapor through air, which is computed by (based on a fit to data given in the Engineering Toolbox),

(A2)

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| (a) | (b) |
|  |  |
| **Figure A1**. (a) Simulation of vapor partial pressures, , in units , around a growing ice crystal. The black-outlined box at the center indicates the surface of the crystal, in this case spanning . Contours outside the crystal show values of at steady state. The entire simulation space spans in both dimensions. At , far-field partial pressures are fixed at . (b) along the surface of the crystal. | |

The last term on the right of Eq. A1 implements Neumann boundary conditions that represent depletion of water vapor in the layer adjacent to the crystal surface, due to crystal growth. Variables figuring in this term are:

* + except at the surface of the ice crystal, where it equals ;
  + is the mass density of ice;
  + is the mass density of water vapor (computed using the ideal gas law and the molar mass of water, ); and
  + is the specified growth rate of the ice surface.

Dirichlet conditions, representing a far-field vapor concentration (), are imposed at the outside boundary of the simulation space.

Integration over time was performed using Euler’s method, i.e., with time steps , and distance intervals (which equals ). That is, at each time step, changes in were computed by

(A3)

Parameters for the integration are given in Table A1. The resulting vapor concentration contours shown in Fig. A1(a) are seen to decrease with proximity to the crystal, as expected since the growing crystal is drawing water vapor out of the surrounding air. This reduction is greater at facet center compared to facet corners, in a roughly parabolic fashion, as shown in the profile in Fig. A1(b).

It will be of interest to quantify this reduction in relative terms, as the “center reduction”,

(A4)

For example, in A1(b), .

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| **Table A1. Parameters for simulation of the vapor field around a growing, square-shaped ice crystal** | |
| Simulation space dimensions |  |
| Time step for integration |  |
| Time interval for integration |  |
| Spatial discretization |  |
| Diffusion coefficient at , |  |
| Ambient temperature |  |
| Ambient pressure |  |
| Diffusion Temperature-correction exponent |  |
| Diffusion coefficient under ambient conditions |  |
| Far-field water vapor partial pressure |  |
| Far-field water vapor supersaturation |  |
| Mass density of ice |  |
| Mass density of water vapor |  |
| Growth rate of ice surface |  |
| Parameters for under ambient conditions: |  |
|  |  |
|  |  |

Other simulation results (not shown) exhibit the expected property that higher far-field vapor concentrations, , lead to higher . The consequence of this should be that crystals would grow faster under such conditions, and therefore offset some of the increased , but that (negative) feedback is not built into Eq. A1, because is a fixed parameter.

According to Eq. A2, lower ambient temperatures and higher ambient pressures are both associated with smaller vapor diffusion coefficients, . Smaller , in turn, manifests as a more steeply curved profile across the crystal surface, compared to the example shown in Fig. A1(b): it is harder for water vapor to diffuse across the facet surface when is small. The expected consequence is that lower ambient temperatures and higher ambient pressures will increase the tendency for excess growth at facet corners, ultimately leading to highly indented, hollowed crystal morphologies, and even (in extreme conditions) dendritic forms, such as snowflakes.

The foregoing observation leads us to anticipate competing effects as cirrus ice particles fall through Earth’s atmosphere. Such crystals will encounter increased pressure, hence smaller , but also increased temperatures (unless there is an atmospheric inversion), hence larger . Eventually, falling ice particles pass through layers of the atmosphere that are dry enough to sublimate the crystals altogether. However, in exceptionally cold regions with high elevation (such as the Antarctic Plateau), or even in mid-latitudes where cryo-capture of ice crystals on ground-launched balloons is possible, observations have shown that cirrus clouds are frequently hollowed. Thus, as a cirrus ice crystal falls through the atmosphere, the effect of increasing pressure appears to win out over that of increasing temperature, enough to promote hollowing, although not so much that dendritic forms develop.

Figure A2 shows simulation results as a function of the crystal edge length. Fig. A2(a) shows that the steady-state concentration of water vapor at crystal corners declines with increasing crystal size. This is expected, since a larger growing crystal means there is more crystal surface area drawing water vapor out of the air.

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| (a) | (b) |
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| **Figure A2**. (a) Steady-state supersaturation, , at crystal corners, as a function of crystal size. (b) Reduction in at facet center as compared to at crystal corner (Eq. A4). | |

Fig. A2(b) shows the percent reduction in surface vapor concentration at facet center relative to facet corner (see the definition of in Eq. A4). is seen to be a smoothly increasing function of crystal size, well-described by

(A5)

Other simulation results (not shown) show that higher far-field vapor concentrations () do *not* alter this parameterization. Because of this invariance, is more useful than for describing the concentration of water vapor over a growing ice crystal facet.

References:

The temperature dependence of the diffusion coefficient was based on data from <https://www.engineeringtoolbox.com/air-diffusion-coefficient-gas-mixture-temperature-d_2010.html>