**Abstract**

Existing theories of ice crystal growth offer little insight into the persistence of faceted crystal geometries under supersaturated conditions, especially at temperatures at which a quasi-liquid layer (QLL) lies between the crystal lattice and the overlying gas phase. Here we report progress toward filling that knowledge gap by revising a previously-introduced, micrometer-scale system of reaction-diffusion equations, in which the time scales of freezing and thawing of the QLL relative to other surface processes (QLL diffusion, and exchanges with the gas phase), are specified. Model parameterization is facilitated by separate simulations of the vapor field surrounding the ice crystal, which provides information about surface vapor concentrations, and by reconstructed ice surface morphologies obtained from scanning electron microscope experiments. The outcome is a more comprehensive, predictive, and experimentally vetted theory of ice crystal growth and ablation than has previously been presented.

1. **Introduction**

The qualitative picture provided by the Burton-Cabrera-Frank (BCF) model of crystal growth goes something like the following: when a gas-phase molecule (e.g., a water molecule) encounters a crystalline surface, it initially becomes attached to that surface as an “admolecule.” Not (yet) part of the ice lattice, this admolecule diffuses across the surface until it meets one of two fates: it may find and fill an unoccupied gap in the crystal lattice, or (failing to do so in time) it may detach from the surface and re-enter the gas phase.

As 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 water ice crystal situated in a supersaturated vapor field, in which facet corners experience higher vapor pressure compared to mid-facet (the typical situation). Because admolecule surface diffusion is not fast enough to even out that inhomogeneity, the expected consequence is that such crystals would grow faster at corners compared to mid-facet, leading to indented, and eventually dendritic, crystal geometries. Although such geometries are observed under some conditions (e.g., snowflakes), it is common to find stable faceted growth under other conditions (e.g., the faceted ice crystals in cirrus clouds). BCF offers no insight into how the latter occurs.

A second drawback of the BCF model is specific to water ice at temperatures 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. The first such model to be presented is a quasi-liquid continuum model (referred to here as QLC-1), introduced by some of the authors in 2016 (N2016). The QLC-1 model recasts the problem as an ice surface covered by a QLL characterized by 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 QLCM-1 (as well as the present revision, QLCM-2) model. Dashed arrows represent processes affecting how these variables evolve over time. |

The time evolution of these two variables, according to QLC-1 (as well as the revised, QCL-2 model introduced in this paper), 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 QLC-1 is that it provides a mechanism by which faceted ice crystal growth occurs. At the heart of that mechanism is a process N2016 called “diffusive slowdown,” which can be summarized as follows:

1. At the micrometer level, the QLL can be thought of as consisting of a continuum of microstates ranging from a thin, less-volatile microstate labeled surface I, to a thick, more-volatile one labeled surface II.
2. In a growing ice crystal, each time a new layer forms, a new pair of these microstates appears on the surface. Since new layers typically form at facet corners, where the water vapor concentration is highest, it is also the case that the horizontal distance between adjacent layers (which we designate here as “”) is small at facet corners compared to facet center. In Fig. 2(a), for example, we see that .

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| **Figure 2**. An ice surface covered by QLL, as simulated by QLCM-2. |

1. Of course, horizontal diffusion tends to even out the thickness of QLL. However, because surface I accounts for a smaller fraction of the total surface area (as seen in Fig. 2(b)), diffusion has a greater proportional effect on it. As a consequence, the average volatility of the surface is increased, and the surface as a whole experiences a net “diffusive slowdown” in its growth rate.

A second process identified in N2016 is that diffusive slowdown is not homogeneous across a facet. Instead, in a growing ice crystal, more diffusive slowdown can be expected to occur at the facet corners. The reason is as follows:

1. In regions where is small, QLL thickness gradients are large. In Fig. 2(b), for example, it is clear that the gradient in QLL thickness at I’ is greater than at I. It follows that, in a growing ice crystal, we would expect more diffusive slowdown at facet corners.

Thus, the QLC-1 explanation of faceted growth goes as follows: an initially flat facet exposed to supersaturated vapor begins to add layers of ice preferentially at its corners, because the supersaturation is greatest there. This eventually leads to smaller (layers closer together) at facet corners, hence more diffusive slowdown there. When this excess diffusive slowdown catches up with the faster deposition at facet corners, growth becomes homogeneous across the entire surface, which is synonymous with faceted growth.

QLC-1 suffered from several structural deficiencies, however, of which the most important for our present purpose is that the time scale of process (iii) illustrated in Fig. 1, the interconversion of quasi-liquid and ice, was fixed relative to processes (i) and (ii). In real crystal facets, these time scales may vary from facet to facet, or as a function of temperature, therefore they should be a parameterizable quantity.

Our goal in this work is to evaluate the strengths and weaknesses of a revised quasiliquid continuum model for ice crystal growth and ablation (here referred to as QLC-2). Section 2 presents a revised model that addresses the deficiencies identified above. Section 3 summarizes recent advances associated with scanning electron microscopy that will help constrain and interpret model predictions, with details given in Appendix 1. In Section 4 we summarize assumptions built into gas-phase simulations used to inform parameterizations needed by QLC-2, such as the shape of supersaturation and subsaturation fields above the surface of ice; details are given in Appendix 2. Section 5 discusses these results in other contexts, including ideas from nonlinear dynamics and the theory of Turing patterns.

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

The present model, QLC-2, has much in common with QLC-1, 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

(1a)

(1b)

Some notes about this model are as follows, with differences between it and QLC-1 noted where relevant:

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 with 100% efficiency, and thermalize on a picosecond time scale.
3. defines the thickness of quasi-liquid when it is in equilibrium with the underlying ice. QLC-2 (like QLC-1) assumes the sinusoidal form

(2)

This formulation ensures that the QLL thickness varies continuously from the thin microstate (“surface I”) with thickness , to the thick microstate (“surface II”) with thickness .

1. The surface supersaturation at a given point on the surface, designated as in Eq. 1a, is a function of the microstate of the surface at that point and of the water vapor concentration above it. 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. Eq. 4 is at slight variance with, and simpler than, the corresponding expression in QLC-1.

1. is a first-order relaxation constant describing the time scale at which quasi-liquid/ice equilibrium is achieved. That is, if we imagine a surface with quasi-liquid amount , 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 QLC-2 from QLC-1. 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 above requires 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 dynamics. We return to this topic below.

1. **ESEM/GNBF retrievals**

Environmental SEM of imaging of ice crystals has seen considerable activity in recent years, including the ability to grow crystals, or ablate them, by manipulating the temperature and pressure inside an SEM chamber. In tandem with those developments is the development of computer codes for generating quantitative surface morphologies using a Gauss-Newton in a Bayesian Framework (GNBF) algorithm. The combination – a process we will refer to here as “ESEM/GNBF retrieval” – provides opportunities for comparing predictions of the QLC-2 model that have not, as yet, been exploited. Details are given in Appendix 1.

1. **Gas-phase simulations**

The QLC-2 and QLC-1 models require numerous parameterizations. Some of these were provided, in N2016, by molecular dynamics simulations, and some by experimental observations. Unexploited in N2016, however, is the power vapor-phase simulations to constrain properties of the vapor field lying over a given ice surface. Details are given in Appendix 2, of which the main conclusions may be summarized as follows …

1. **Results**

Here we describe the results of five lines of investigation we have pursued, each focused on a particular topic or question, with ESEM/GNBF and gas-phase modeling results presented as relevant.

*I. Effect of variation in the time scale of modeled ice-quasiliquid equilibration*

[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] … See Fig. 3 …

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| **Figure 3**. Effect of varying the ice-QLL equilibration timescale |

*II. Curvature of faceted surfaces undergoing growth and ablation*

Figure 4 shows a modeled ice crystal surface under growing and ablating conditions. The growth scenario on the left of the figure resulted from supersaturated water vapor amounts, distributed as shown in Fig. 4(a). Figures 4(b) and 4(c) show that these conditions lead to steady state, with the expected “V” profile. This scenario exhibits signs of diffusive slowdown already described in N2016, in that steps are more tightly bunched at facet boundaries, leading to a net increase in volatility of the surface as a whole, hence slower growth than if diffusion were not occurring.

The ablating scenario on the right of Fig. 4 resulted from subsaturated water vapor amounts, distributed as shown in Fig. 4(d). Figures 4(e) and 4(f) show that these conditions also lead to steady state, although in this case the profile is “” shaped (i.e., rounded), and the layer bunching now exposes primarily surface I to the gas phase, thus *reducing* the volatility of the surface near the corners, and therefore reducing the rate of ablation [more explanation needed here]

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| **Figure 4**. Stabilization of growing (left panels) and ablating facets (right panels). | |

Do real ice crystals exhibit faceted ablation? Figure 5 displays ESEM images of an ice crystal observed under growing and ablating 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 ESEM images of ablating ice crystals.

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| **Figure 5**. An ice crystal under growing (left) and ablating (right) conditions. | |

The model results shown in Fig. 4 suggest the following general pattern: growing ice facets possesses concave curvature, whereas ablating ice facets possess convex curvature. Is this pattern borne out by observations?

A useful metric for describing the curvature of steady state profiles such as those appearing in Fig. 4 is the local slope of the surface. Here we quantify that slope as a mean horizontal distance between successive molecular layers, defined as

(6)

For example, the growing facet profile on the left of Fig. 4 is characterized by , whereas the ablating facet profile on the right is characterized by .

Fig. 6(a) displays an ESEM image of a growing crystal, and a GNBF construction of a portion of its basal facet. The GNBF construction reveals a distinct concavity, on the order of 1000s of layers over the horizontal span analyzed () … which corresponds to . 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.

*[Figure 6(b) shows an ESEM image of an ablating, faceted crystal, and a GNBF reconstruction of its surface. The GNBF reconstruction hopefully reveals convexity ….* .*]*

Thus, the pattern is borne out: growing ice facets do indeed exhibit facet concavity, while ablating ice facets will exhibit facet convexity, in agreement with the model prediction – although we hasten to point out that the values are far smaller in the observations than in the model.

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| **Figure 5**. SEM image of a growing crystal (left) and an ablating crystal (right) …. | |

*III. Characteristic length scales of growing and ablating surfaces*

Here we investigate the possibility that growing and ablating ice crystals possess intrinsic length scales. Focusing first on observations, we note that a distinct growth/ablation asymmetry appears in the roughening evident in ESEM experiments, an example of which is shown in Fig. 5. …

Focusing next on the model, we show in Fig. 6 values of the mean horizontal layer separation, (introduced in Eq. 6), for a range of corner supersaturations (). On the right-hand side, we see that when conditions begin to become supersaturated, the maximum distance that appears . On the left-hand side of Fig. 6 are displayed results when conditions are subsaturated. We see that under these conditions, the first values that appear are over – much higher than on the supersaturated side of the figure. values are seen to decrease with greater subsaturation to the left.

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| **Figure 6**. Mean horizontal layer separation () 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 …

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| **Figure 7**. Mean horizontal layer separation () as a function of parameter for a range of values of , , and . The corner supersaturation is fixed at for all simulation runs. |  |

It is of interest to note at this point a few broader implications of Figs. 6 and 7. According to the vapor modeling results described in Appendix 2, 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.

…. As supersaturation increases, further to the right in the figure, declines monotonically, ultimately leading (we surmise) to dendritic growth. We surmise that eventually, at sufficiently high subsaturation, ablation must cease to be faceted, and transition to rounded.

The observation that is proportional to in QLC-2 is noteworthy because of the connection to Turing patterns, a topic to which we return below. It is also

Thus, both theory and experiment support the existence of characteristic length scales as a function of super/subsaturation. We hasten to add that the scale of these phenomena is vastly different ….

*IV. Resilience of steady states*

In ESEM experiments, facets exhibit a certain resilience, in that after being roughened by some perturbation (e.g., by higher temperature or a lower supersaturation), 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 characterize the surface when subjected to the supersaturation curve shown in the upper-right inset. After , it has evolved to the steady-state growth profile labeled “A”.
2. From to , a perturbation is introduced in the form of the subsaturated water vapor curve shown in the second inset, during which time the surface evolves into the highly perturbed profile labeled “B”.
3. At , the first, supersaturated water vapor regime is restored. By , the surface has recovered its pre-perturbation steady state, labeled “C”.

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

Conclusion … qualitatively, QLC-2 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 vastly different vertical scales. That is, in Fig. 9, the reversal in the shape of the profile seen at , caused by the perturbation begun at , still has a net effect on the order of a few dozen monolayers of ice, whereas ridge-to-valley distances seen in the real crystal in Fig. 8 amounts to thousands of monolayers.

1. **Discussion**

The work presented here, while similar to that of N2016, is novel in several respects. The equations of the QLC-2 embody a more faithful representation of ice/QLL equilibration, and its numerical solution is more stable. Parameterizations of the model are better constrained by observations (ESEM/GNBF), and by independent numerical simulations of the overlying vapor field. But what benefits does the model provide?

*A unified mechanism for faceted growth and ablation*

The model provides a unified mechanism that explains not only how crystals resist dendritic geometries when subjected to supersaturation conditions, but also how they resist rounding when subjected to subsaturation conditions.

*Implications for cirrus clouds*

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.

*Faceted growth as a nonlinear attractor*

The larger significance of the resilience studies presented in *Section IV* here, is that QLC-2 resilience extends to starting conditions other than an initially flat surface ….

*Insights into 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. Preliminary numerical experiments varying and have shown that …

*Insights regarding facet roughening*

**Appendix 1 – ESEM/GNBF retrieval**

Here is a summary of key equations and constraints in the ESEM/GNBF retrieval …

**Appendix 2 – Vapor phase simulations**

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) |
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| **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 appearing 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: |  |
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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.

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.

**Appendix 3 – Numerical considerations**

Python, accelerated with Numby. Code and data are available on Github.

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>