**On the role of surface quasi-liquid in determining ice surface morphology**

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**Abstract**

*Current theories of dynamics at the ice-vapor interface do a poor job of explaining how ice surfaces at this interface choose among faceted, dendritic, or rounded morphologies. Here we explore the hypothesis that a key missing element is the quasi-liquid layer that forms at this interface at temperatures above . We do so by modeling the ice surface as a system of reaction-diffusion equations in which the time scales of freezing/thawing, horizontal diffusion, and exchanges with the vapor phase, are made explicit. Model parameterizations are informed by independent simulations of the vapor field around growing and ablating ice crystals, and by quantitative ice surface morphologies derived from scanning electron microscope experiments. The outcome is a more comprehensive, predictive, and experimentally grounded theory of ice crystal surface morphology 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 crystal’s lattice, this admolecule diffuses across the surface until it fills an unoccupied position in the crystal lattice, or else detaches from the surface and re-enters the gas phase.

As appealing as the BCF model is, we can identify two important shortcomings. One concerns the various morphologies adopted by a crystal in response to persistent inhomogeneities of the overlying vapor field. One such inhomogeneity is that experienced by an initially-faceted ice crystal, which, in a supersaturated vapor field, leads to persistently higher vapor pressures above facet corners compared to facet centers. Under some conditions, this results in faster growth at facet corners, eventually leading to indented crystal morphologies, and even dendritic forms (e.g., snowflakes). Under other conditions, however, faceted morphology is stubbornly maintained despite this inhomogeneity – an example being the faceted ice crystals commonly found in cirrus clouds. The maintenance of faceting under such conditions is especially puzzling when the crystal is large enough that admolecule surface diffusion is too slow to spread out the inhomogeneity over the entire length of the crystal. Similar comments apply to subsaturated conditions: under some conditions, an initially-faceted crystal responds to subsaturated conditions by adopting a rounded geometry, while under other conditions it maintains faceted geometry.

BCF theory offers little insight into what governs the above possibilities for ice at any temperature, but the situation is worse (at least conceptually) as the temperature of the ice approaches melting. Above , there are no lattice gaps available to an admolecule that has deposited on the ice surface, because the interface is entirely covered by a quasi-liquid layer (QLL) that thermalizes nearly every water vapor molecule that impacts the surface on a picosecond time scale.

The QLL thus appears to present insurmountable problems for the BCF model. Instead, we argue, a model is needed in which the QLL plays a central role in crystal growth (above ). Such a model was presented by some of the authors in 2016 (N2016), a quasi-liquid continuum model referred to here as QLC-1. Because that model forms the foundation for the revision presented here (“QLC-2”) with the idea that differences between the two can be made more transparent.

QLC-1 frames the problem of ice surface dynamics in terms of two mesoscale variables, and (see Fig. 1), which represent the total thickness of the ice surface and the thickness of its quasi-liquid part. Time evolution of these variables is governed by a pair of reaction-diffusion differential equations that represent the three processes indicated in Fig. 1, namely, (i) exchanges (deposition and ablation) with the vapor phase, (ii) horizontal diffusion of the QLL across the ice surface, and (iii) interconversion of QLL molecules to/from the underlying ice.

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| **Figure 1**. Visual representation of mesoscale variables , , and , and processes affecting them, in QLC-1 (as well as the present revision, QLC-2) model. Dashed arrows represent processes affecting how these variables evolve over time. |

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 termed “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. The difference in these volatilities is quantified in QLC-1 as a difference in equilibrium supersaturation, .
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 newly-formed ice layers is smaller at facet corners compared to facet centers. In this paper, we designate this distance as “”; in Fig. 2(a) we see that .

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

1. Horizontal diffusion moves quasi-liquid away from thicker, surface II-like regions, and toward thinner, surface I-like regions of the surface. 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, diffusion leads to an increase in the average volatility of the surface, causing the surface as a whole to experience a net “diffusive slowdown” in its growth rate. (The reader is referred to N2016 for a quantitative version of this argument.)

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 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.

In summary, the corners of an initially flat facet exposed to supersaturated vapor will experience an enhancement in growth rate because of increased vapor concentration above it, but that same enhancement leads to a compensating increase in diffusive slowdown. When these effects are in dynamic balance, the result is a steady state characterized by equal growth rates of all regions of facet. That steady state, in turn, would be interpreted at the mesoscopic scale (e.g., in a high-resolution optical or scanning electron microscope) as 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 and vapor pressure. These time scales should therefore be adjustable quantities within the theory.

Our goal in this work is to evaluate strengths and weaknesses of a revised quasiliquid continuum model for ice crystal growth and ablation designed to address this deficiency. Section 2 presents such a model, referred to here as QLC-2. Section 3 (with details given in Appendix 1) summarizes scanning electron microscopy (SEM) image processing algorithms that can be used to construct quantitative ice surface morphologies. Section 4 (with details given in Appendix 2) summarizes results from independent gas-phase simulations that can be used to inform parameterizations of QLC-2 having to do with the structure of the vapor field in contact with growing ice crystals. Section 5 discusses implications of these results in other contexts, including cirrus ice crystal morphologies, ideas from nonlinear dynamics, and Turing’s pattern-formation theory.

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 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. prescribes the thickness of quasi-liquid when it is in equilibrium with the underlying ice, according to

(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 both the microstate and 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, as previously described, 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 those processes, while large would mean the opposite. We do not have reliable observational values of , 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 image actively growing and ablating crystals 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 vetting model predictions of surface morphology against experiment at resolutions that are not quite commensurate with one another, but approaching that level. Details are given in Appendix 1.

1. **Gas-phase simulations**

QLC-2 requires 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 of vapor-phase simulations to constrain properties of the vapor field overlying 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 focusing on a particular topic or question. ESEM/GNBF and gas-phase modeling results presented alongside, 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 concentrations, distributed as shown in Fig. 4(a). Figures 4(b) and 4(c) show that these conditions lead to steady state, “V”-shaped profiles, in which the surface is dominated by primarily surface I – like microstates. This scenario exhibits more tightly bunched (smaller ) at facet boundaries, which in turn (as described above in the summary of diffusive slowdown) leads to a net increase in volatility of the surface as a whole, hence faceted growth.

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), the surface is dominated by surface I – like microstates, and the layer bunching leads to *reduced* volatility of the surface near the corners, hence faceted ablation.

The model results shown in Fig. 4 also suggest the following general pattern: growing ice facets possesses concave curvature, whereas ablating ice facets possess convex curvature. 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 .

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

It is well-known that real ice crystals exhibit faceted growth, but are they also capable of 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. | |

Do real faceted ice crystals exhibit curvature like that indicated by the QLC-2 predictions of Fig. 4? Fig. 6(a) displays an ESEM image of a crystal and a GNBF construction of a portion of its basal facet. 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. The GNBF construction, displayed in Fig. 6(b), reveals a distinct concavity, on the order of 1000s of layers over the horizontal span analyzed () … which corresponds to .

Turning to ablation, Figs. 6(c-d) show an ESEM image of an ablating, faceted crystal, and its GNBF-constructed surface. *The GNBF reconstruction hopefully reveals convexity ….* .*]*

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|  | Need image |
|  | Need image |
| **Figure 6**. SEM image of a growing crystal (left) and an ablating crystal (right) …. | |

Thus, the pattern predicted by QLC-2 is borne out: growing ice facets do indeed exhibit facet concavity, while ablating ice facets exhibit facet convexity – although we hasten to point out that the values are far smaller in the observations than in the model.

*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 the ESEM images displayed in Fig. 5. …

Focusing next on the model, we show in Fig. 7 values of the mean horizontal layer separation, (introduced above), 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 , declining with yet more supersaturation. …. As supersaturation increases, further to the right in the figure, declines monotonically, ultimately leading (we surmise) to dendritic growth.

On the left-hand side of Fig. 7 are 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. We surmise that eventually, at sufficiently high subsaturation, ablation must cease to be faceted, and transition to rounded.

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| **Figure 7**. Mean horizontal layer separation () as a function of corner supersaturation . |

Figure 8 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 8**. 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, at sufficiently small , dendritic forms, such as snowflakes.

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 an initially faceted surface, after it is roughened by some perturbation (e.g., by higher temperature or a lower supersaturation), can usually be restored to its initial smooth faceted state after the initial conditions are restored. An example is shown in Fig. 9

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| **Figure 9**. SEM image of a rough facet restored to smoothness. |

What resilience, if any, is exhibited by modeled facets? Figure 10 is an examination of this question.

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| **Figure 10**. Examination of model facet resilience. Curves in the upper-left graph show timelines of that characterize the surface when subjected to the supersaturation curves shown in the upper-right insets, over the indicated time intervals. |

The sequence of images in Fig. 10 begins with an initially-flat profile, which is then subjected to the following sequence:

1. From to , the surface is been exposed to the supersaturated water vapor curve shown in the inset located in the upper right part of the figure. By , the profile has evolved to the faceted, steady-state profile labeled “A”.
2. From to , a perturbation is introduced in the form of the subsaturated water vapor curve shown in the inset located in the middle-right part of the figure. During this time, the surface evolves into the highly perturbed state labeled “B”.
3. From to , the initial supersaturated water vapor regime is restored. During this time, the surface recovers its pre-perturbation faceted profile labeled “C”.

Conclusion … qualitatively, QLC-2 exhibits resilience analogous to that of a real crystal facet, such as the one shown in Fig. 9. We should hasten to add, however, the perturbed states exhibit vastly different vertical scales. That is, in Fig. 10, the perturbed profile seen at , caused by the perturbation begun at , is non-faceted (i.e., “rough”) only on the order of a few dozen monolayers of ice, whereas the actual crystal shown in Fig. 9 exhibits ridge-to-valley distances on the order of thousands of monolayers.

1. **Discussion**

The QLC-2 model presented here represents significant improvements over the QLC-1 reported in N2016. Its equations of motion embody a more faithful representation of ice/QLL freeze/thaw equilibration, and its numerical solutions are more stable. Parameterizations of QLC-2 are better constrained by microscopy (ESEM/GNBF), and by independent numerical simulations of the overlying vapor field. But what novel insights does it provide?

1. *A single, unified framework explains faceted growth and ablation*

QLC-2 provides a unified mechanism that explains not only faceted growth (how crystals resist dendritic geometries when subjected to supersaturation conditions), but also faceted ablation (how they resist rounding when subjected to subsaturation conditions).

A second observation along these lines is that, 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 thickness of a single “layer” of ice has shown that a proportional increase in results. Preliminary numerical experiments varying and have shown that …

1. *The evolution of surface morphology of descending cirrus cloud crystals is dominated by changes in atmospheric pressure (rather than temperature)*

The framework presented here allows us to anticipate the effects on cirrus cloud particles as they 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 . When the effect of increased pressure dominates, we can expect more greater enhancements in growth at facet corners. When the effect of increased temperature dominates, however, we can expect greater persistence of smooth facets.

Although there is no single observational datum that would help us resolve these different predictions, we can comment that in exceptionally cold regions (such as the Antarctic Plateau), or even in mid-latitudes where high-altitude cryo-capture of ice crystals on ground-launched balloons is possible, observations have shown that cirrus clouds are frequently hollowed and roughened, suggesting dominance of increased pressure as cirrus cloud particles descend through the atmosphere.

1. *Ice crystal surface morphologies possess intrinsic distances*

Wehave presented data here – as in Fig. 8 – that the characteristic distance between adjacent layers of ice () increases in proportion to the same as Turing patterns. In part, this is no surprise, since Turing’s theory, like QLC-2, is couched in the context of a reaction-diffusion equation. Differences include the fact that Turing’s analysis proceeds from an analysis of perturbations to an initially homogeneous distribution of chemical species, whereas the patterns in QLC-2 steady states emerge as steady states of the equations of motion.

It is also noteworthy that both QLC-2 and experimentally-observed roughening of ice facets exhibit a distinct asymmetry in characteristic distances, both being greater on the ablation side than on the growth side (see Figs. 5 and 7). [Not sure what to do with though.]

**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>