Morphological Study of Ice Crystal Growth

Senior Thesis in Experimental Physics by

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Abstract

The morphologies and growth rates of ice crystals have been observed and documented using a novel experiment, with the goal of investigating the overarching principles of the molecular dynamics of ice crystal growth. The experimental set-up consists of two side-by-side temperature-regulated diffusion chambers. Thin ice needles, up to several millimeters in length and a few microns in diameter, are grown in the first chamber off of a metal wire through nucleation caused by the application of a high voltage. These electric needles are then transferred to the second chamber with a controllable internal water vapor supersaturation level, and subsequent growth of the ice crystals is observed. The crystal morphology is captured digitally via optical microscopy and is analyzed in the form of time-stamped images.

Varying the supersaturation and overall temperature affects the crystal morphology as well as growth rate and yields insights into the basic physical principles governing crystal growth. A theory that proposes to explain the resulting morphology of ice crystals due to variations in temperature and supersaturation conditions suggests that relative growth rates of the principal facets of a crystal depend on the current morphology of the crystal and on an instability. Computer simulations of this proposed theory called the *Structure-Dependent Attachment Kinetics* model are tested against real ice crystals to determine the accuracy of the proposed theory.

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1 Introduction

Formation of crystalline structures in freezing water yields a vast variety of morphologies and growth rates. Processes at the interface of non-equilibrium surfaces on the molecular level yield large morphological differences in the resulting crystal structure. Understanding the processes governing the formation of ice crystals may give insight into the crystal structures of other materials. Many questions about ice crystal growth remain unanswered [1]. For instance, there is no definitive explanation of why under some conditions the crystals are cylindrical and under others they are plate-like. It is also unknown what governs the pattern of the attachment of water vapor particles to a growing ice crystal.

Studies of ice crystal formation from water vapor dating as far back as the 1930's have yielded the Nakaya morphology diagram showing the complex behavior of crystal formation under varying temperature and saturation conditions [?]. However explanations of the morphological transitions seen in the diagram are not thorough.

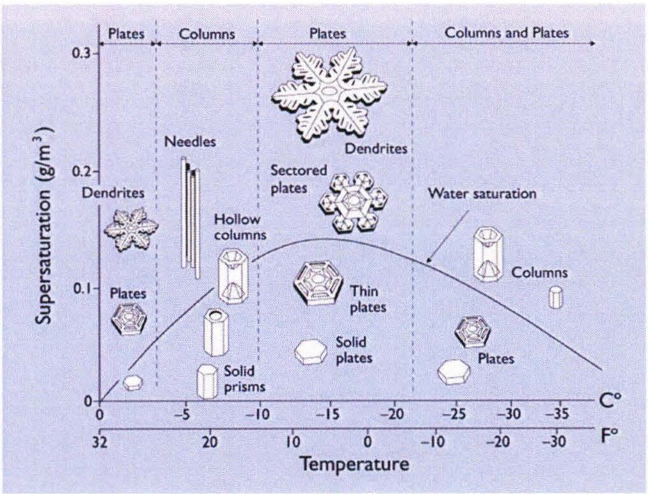

Figure 1: The Nakaya morphology diagram demonstrates the variation of ice crystal morphology with water vapor supersaturation and with temperature. The transitions between plate and column morphologies appear very apparent. These sharp transitions are indicative of an instability that may be very sensitive to specific physical conditions and may be related to more than the supersaturation and temperature.

For instance, there is a very short transition from columnar crystals to plate-like crystals at -10^{o}C [7, 3, 4, 5]. Such a radical morphological transition is indicative of an instability.

We endeavored to understand the governing physical principles that define the diagram by studying the resulting morphologies and growth rates. We focused on the region of -15^{o}C in the transition between the low and high supersaturation of the surrounding air.

2 SDAK Theory

2.1 Basic Intrinsic Growth

The basic unit of an ice crystal is a hexagonal pillbox shape pictured below. It has six prism faces and two basal faces, with the *c*-axis defined to be perpendicular to the basal faces.

A growing unit can grow in two directions: the basal direction perpendicular to the basal planes and the prism direction perpendicular to the prism planes. These two growth directions have their corresponding growth velocities which we call v_{basal} and v_{prism}. If $v_{basal} > v_{prism}$ then the resulting crystal shape with be columnar. If $v_{basal} < v_{prism}$ then the resulting shape will be plate-like.

The intrinsic growth velocity of a facet can be parameterized as

$$v = \alpha \cdot v_{kinetic} \cdot \sigma_{surface} \tag{1}$$

where $v_{kinetic}$ is the temperature-dependent velocity derived purely from statistical mechanics and $\sigma_{surface}$ is the water vapor supersaturation relative to the growing ice surface.

The attachment coefficient $\alpha(\sigma, T)$ encapsulates all other dependencies of the intrinsic growth velocity and accounts for the molecular dynamics governing crystal growth at the interface between the ice surface and the surrounding water vapor. We call this coefficient the *intrinsic* attachment coefficient. It is parameterized as

$$\alpha = Ae^{-\sigma_0/\sigma_{surface}}. \tag{2}$$

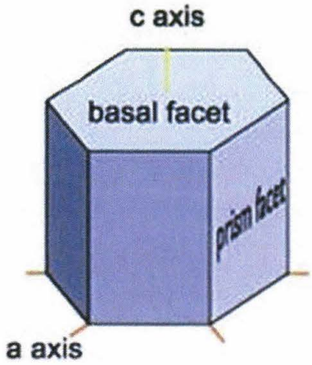

Figure 2: The basic unit of an ice crystal is a pillbox-like hexagonal unit. The c-axis is defined as the axis passing through the centers of the two opposite hexagonal facets. These facets are called the basal facets. The other six rectangular facets are called the prism facets. A crystal can grow in the basal direction (upwards, parallel to the c-axis), or in the prism direction (outwards, perpendicular to the c-axis). The direction in which the prism grows faster determines the final shape of the crystal (columnar if growth is greater in the basal direction and plate-like if growth is greater in the prism direction).

According to classical nucleation theory, σ_0 must be related to the step energy β which in turn is related to the edge of a molecule-thick terrace forming near the edge of a growing ice crystal. The coefficient A is likely related to surface melting effects which reflect the temperature T. Therefore, until now it has been accepted that the attachment coefficient α is a function only of supersaturation and temperature. Presently, no theory that exists is thorough enough to explain this dependence fully, so we must accept measured values of these parameters as given.

2.2 A Disagreement and a Resolution

Physical measurements of v_{basal} and v_{prism} on crystals grown in the laboratory have yielded measurements for α in terms of A and σ_0 in a temperature range from -2^oC to -40^oC, and the results are shown below.

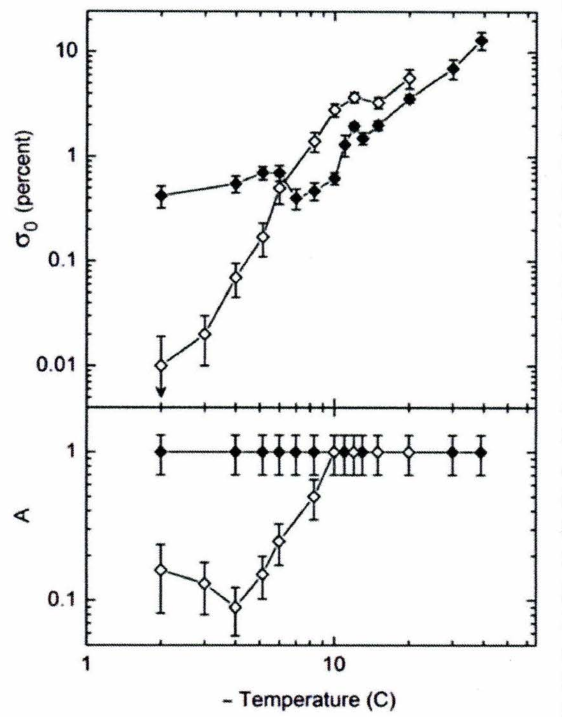

Figure 3: The measured intrinsic growth rates of the basal and prism facets of ice crystals have yielded values for σ_0 and A which parameterize the attachment coefficient $\alpha = Ae^{-\sigma_0/\sigma_{surface}}$ and the velocity of the growth of a facet is $v = \alpha v_{kinetic}\sigma_{surface}$. Solid points are values for the basal facets and the open points are for the prism facets.

From these results we see that at -15^oC, $A_{basal} = A_{prism}$ and $\sigma_{0,\,basal} < \sigma_{0,\,prism}$. Therefore from (1) and (2),

$$\alpha_{prism} < \alpha_{basal} \quad \Rightarrow \quad v_{prism} < v_{basal} \tag{3}$$

from which we can infer that columns should form instead of plates. However, all experimental results indicate that plate-like crystals form at -15^oC, as seen in Figure1. Therefore, we are led to propose that α does not depend only on supersaturation and temperature, but on another parameter which would cause the relationship between α_{prism} and α_{basal} to invert under the same physical conditions so that $\alpha_{prism} > \alpha_{basal} \quad \Rightarrow \quad v_{prism} > v_{basal}$ and thus yield plate-like growth at -15^oC.

This disparity in expected crystal shape suggests that attachment kinetics depends on more than temperature and supersaturation. It may also depend on the morphology of the growing crystal: the current morphology may have an effect on the subsequent growth of its facets by affecting the attachment kinetics represented by the attachment coefficient α. This theory is called the *Structure-Dependent Attachment Kinetics* model, or "SDAK" for short [8].

2.3 Structure-Dependent Attachment Kinetics (SDAK)

The SDAK model predicts that relative facet growth rates are determined by an instability at the edge of a growing crystal. The growth at this edge is dominated by the nucleation of terraces of the basal and prism facets. If the basal nucleation rate increases as the prism rate decreases, then the crystal will grow into a columnar shape. If the prism nucleation rate increases as the basal rate decreases, then the crystal will grow into a plate-like shape. The nucleation rate depends on the water vapor supersaturation level at the surface of the crystal, as well as on other parameters. This surface supersaturation varies between the basal and prism facet, and this variation may lead to the strong differentiation between the two morphologies. Understanding what causes this distinct variation in supersaturation may explain the nature of the instability that determines the morphology of the growing crystal. The competition between the initial basal and prism growths may be due to an instability at the edge of an initially isometric crystal. This may explain the abrupt changes between morphology types seen in the morphology diagram.

The SDAK model suggests that the attachment coefficient α depends not only on supersaturation but also on the morphological structure of the ice crystal. At the temperature of -15^oC, the model suggests that for a thin plate, the actual attachment coefficient α_{prism} is larger than the intrinsic α_{prism} for a large faceted surface. This would reverse the relationship between the basal and prism coefficients so that $\alpha_{prism} > \alpha_{basal}$. This would explain the disagreement between the inequality (3) which implies that plates should form instead of columns, and the physical results which consistently yield plates at -15^oC.

Further, the SDAK model suggests that a reduction of the nucleation energy at the edge of a thin plate causes α_{prism} to increase. The reduction of the nucleation energy is directly related to the reduction of $\sigma_{0,prism}$. Therefore, the theory proposes that for a thin plate, the supersaturation $\sigma_{0,prism}$ decreases in correlation with the decrease of the width of the outermost molecular surface on the prism facet.

The same predictions apply for growth in the basal direction with the basal parameters. Therefore, the SDAK theory predicts a positive feedback: an initial plate-like shape will grow to become increasingly thin-plate-like and an initially columnar-like shape will grow to become increasingly columnar. The relative importance of the SDAK effect in the basal and prism directions depends on the specific surface dynamics [9].

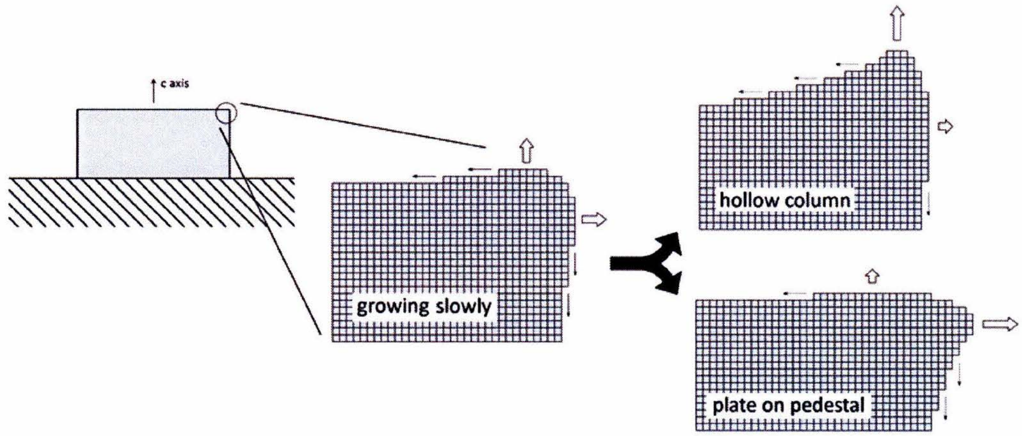

Figure 4: An illustration of the SDAK model instability. An instability is amplified through higher growth rates at sharper edges so the initial growth direction determines subsequent shape. the growth at a corner is dominated by the nucleation rate of terraces growing on the basal and prism facets, so the relative rate of nucleation at the two facets determines the overall direction of growth. As an edge grows in one direction, the edge gets sharper and grows yet faster, creating a positive feedback loop.

The SDAK theory can be tested against physical crystals by using a computer model that predicted the growth of an ice crystal, given initial parameters, by using an algorithm that simulated SDAK mechanisms. The model generated an image of the predicted profile of the resulting ice crystal and a set of data points specifying the predicted radius of tip of the crystal and the radius of the base of the crystal, 50μm from the tip at progressing time values.

In order to test the SDAK theory, we first needed to have real ice crystals to compare their growth rates with those predicted by the SDAK theory. We chose to focus on growing crystals at a fixed temperature of -15^oC and at varied water vapor supersaturations. All of these crystals had plate-like morphologies, as predicted by the morphology diagrams.

3 Experiment

The physical experiment set-up is worth a brief description. It is a dual-chamber construction. The chambers are thermally insulated and share one wall. This wall has a double sliding door to allow passage between the chambers with minimal perturbation to each chamber's conditions. The first chamber prepares in ice crystal base whose subsequent growth is studied in the second chamber.

3.1 Dual Chamber 1

The purpose of the first first chamber, "DC 1", is to create a very high water vapor supersaturation at the location where ice needles grow. The supersaturation needs to be high so that ice needles grow quickly (the ice grown here is not the structure to be studied).

The bottom wall and and lower parts of the side walls are made of aluminum while the top wall and top parts of the side walls are made of copper. Hanging off of the top walls is a copper well that contains water. The bottom of the chamber is cooled while the top is heated, so that water vapor comes off of the water well and travels downward to the colder temperature, creating a water supersaturation within the chamber.

There are several moving parts in DC 1. A horizontal shutter is connected at the top wall by a vertical rod with a handle on the outside of the chamber. This shutter can rotate and cover the central area of the chamber where the ice needles are growing. While the ice is growing, the shutter is kept to the side. However

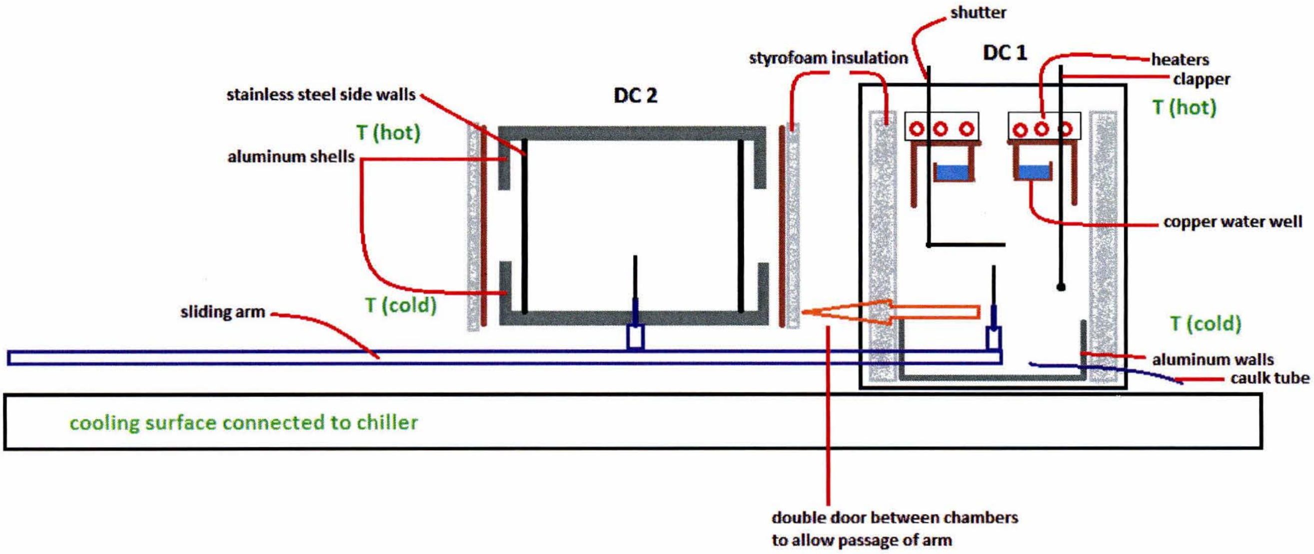

Figure 5: A schematic of the dual chamber experimental set-up. The first chamber DC1 has a very high water vapor superaturation in which ice needles grow rapidly along their c-axes. The temperature and supersaturation of the second chamber DC2 are controlled or observe the resulting crystal growth at the tips of the ice needles grown in DC1.

once the needles have reached a desired length, the shutter is useful in lowering the supersaturation around the ice to prevent it from growing further and shelters the ice as it is transferred to the next chamber.

There is also a clapper hanging from the top wall. It is a small weight, hanging so that it can hit the metal wire off of which the ice needles grow. When the clapper hits the wire, it not only cleans the wire of any accumulated ice, but it also lowers the wire's temperature.

A narrow tube enters the chamber near its bottom. This tube is what caulk vapor is passed through.

Finally, the arm which holds the base off of which the ice needles grow enters DC 1 from the bottom left. This arm is mobile and goes through both cold chambers. The walls shared by DC1 and DC2 are connected by a double door that can open to let the base attached to the arm fit through when the arm is being entered and retracted from the chambers.

3.2 Dual Chamber 2

The second cold chamber, "DC 2", requires more precision because this is where the growth of ice crystals is observed under specific physical conditions. The bottom and top "caps" of the chamber are make of aluminum. During crystal growth, the bottom is cooled and the top is heated to create a temperature gradient throughout the chamber. These temperatures are controlled with high precision. To restrict the temperature gradient to the vertical direction, stainless steel plates connect the top and bottom aluminum faces of DC 2. If the temperature also varies horizontally, then convection currents arise and this creates a non-uniform supersaturation in the chamber.

Thus the only significant perturbation to the supersaturation is the stem of the arm off of which the ice is growing, as well as the ice itself. It occur several times that a taller ice crystal shielded a shorter one, creating an area of lower supersaturation for the lower crystal and the effects were noticeable in the morphology differences between the two crystals.

4 Experimental Preparation

4.1 Preparing the Ice

In the first chamber, ice needles were grown off of a metal wire by turning on a voltage which caused nucleation. Needles that grew along their c-axis produced a well-defined perpendicular surface at their tip were called *electric needle*, or *e-needles* for short. Such needles were desirable for the experiment. If transferred to an environment with a different supersaturation and in the absence of an applied voltage, most of the subsequent crystal growth took place on the tips of the e-needles and the geometries of these tip growths were based on the e-needle's c-axis. It is these growths on the tips of the e-needles that we studied for comparison with the predictions of the SDAK theory.

4.2 Recording Ice Growth

The e-needles were transferred to the adjacent second chamber along with the wire that they were growing off of. There the subsequent growth off the ice crystals on the ends of the e-needles were observed.

Time-stamped images of the growing crystals were recorded by a camera aimed into the second chamber for analysis. The temperatures of both chambers were controlled by setting their top and bottom faces to desired temperatures. This created a temperature gradient within the chambers, which affected the supersaturation level. The supersaturation of the chamber was measured in terms of the temperature difference ΔT between the chamber's top and bottom faces.

4.3 System Adjustments and Fine Tuning

By taking a temperature profile using a thermistor, we verified that along the central vertical axis of the chamber, the temperature changed linearly with height. The greater ΔT, the greater the supersaturation. Finding the exact relation between ΔT and the supersaturation remains a challenge that involves modeling of the temperature distribution within the chamber.

It was crucial to perfect the experimental set-up and data processing procedures in order to have more authoritative results. The images had to be made clearer so that morphological measurements would be more accurate. Here, the first issue was that the exposure time was long enough to catch shakes and vibrations in the ice crystals. To eliminate this problem, the exposure time had to be decreased. To compensate for this, we installed a very bright lamp that looks into the second chamber and provides a strong backlight for the ice crystal.

The next problem was that the lamp was so strong that it slightly affected the crystal growth as the ice absorbed the light. To solve this problem, we installed a switch to turn the light on only long enough to capture an image of the crystal.

Next, to ensure that the electric needles were dependably c-axis, we adjusted vapor levels in the first chamber. It was observed that letting caulk vapor into the first chamber improved the quality of e-needles. However, the system turned out to be fairly sensitive to the amount of caulk vapor and through trial and error, we found that we needed many times less caulk vapor in the chamber than what we had been using. We've found the minimum amount of vapor needed to grow good needles and used only that amount, to prevent pollution within the chamber.

The second chamber also seemed to be getting slightly polluted so we created a clean air flow through it. Clean nitrogen gas entered at a slow enough rate to not physically affect the ice crystals growing inside but substantial enough to keep the chamber clean.

5 Analysis

In order to test the proposed SDAK Theory, we compared physical ice crystals that we grew in the laboratory with the results of a computer model written in agreement with SDAK predictions.

5.1 Procedure

We grew ice crystals in the dual-chamber setting described in detail above. We observed the ice crystals through an optical lens and recorded time-stamped high-resolution images. The conditions of the chamber in which we were observing the crystal growth were two-dimensional: we controlled the temperature and the water vapor supersaturation level in the atmosphere surrounding the crystals. After growing the crystals, we analyzed the images and recorded the growing crystals' dimensions along with the time at which each image was taken. In this way, we was able to identify the geometry of the crystals and to quantify the crystal dimensions and the growth rates of each dimension, all as functions of the temperature and water vapor supersaturations of the immediate surroundings.

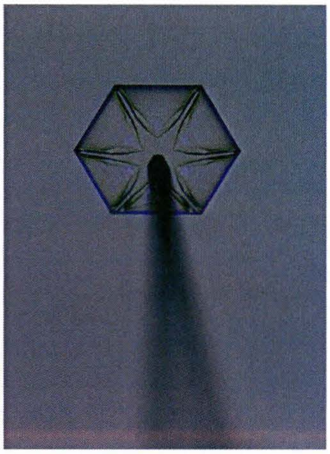

Figure 6: A photo taken of a plate grown in DC2. The view is from below with a sharp focus on the plate, so the base needle is out of focus.

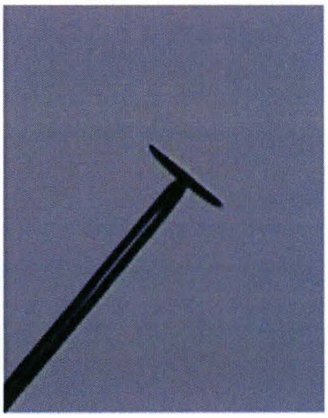

Figure 7: Anoth photo taken of a plate grown in DC2. This time the view is from the side and shows the same profile as the one generated by the SDAK computer simulation.

We then modeled crystal growth at -15^oC using the computer model. This model took the temperature and the water vapor supersaturations at the prism and basal faces as its primary parameters and modeled the resulting ice crystal shape in a step-wise fashion.

5.2 Modeling

With each timestep, the computer model generated a data entry of the crystal dimensions and updated a profile image of the crystal being modeled. Below is a composite image of the progression of the best fit model.

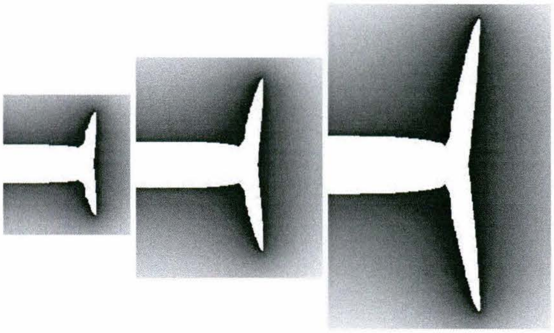

Figure 8: A composite image of the images generated by the SDAK simulation at different points in time. This is the image generated by the best fit model and the growth rates indeed match physical measurements closely.

Using the intrinsic values of $\sigma_{0,prism}$ and $\sigma_{0,basal}$ as guides for the actual values of the parameters, we found a good fit of the model predictions to experimental data that we had obtained. We compared the growth of the plate radius and of the base needle radius, located roughly 50 microns below the plate.

The supersaturations for this model were $\sigma_{0,prism} = 3\%$ and $\sigma_{0,basal} = 2\%$. These are of the same order as the measured intrinsic values of roughly $\sigma_{prism} \cong 7\%$ and $\sigma_{basal} \cong 4\%$, according to figure 3.

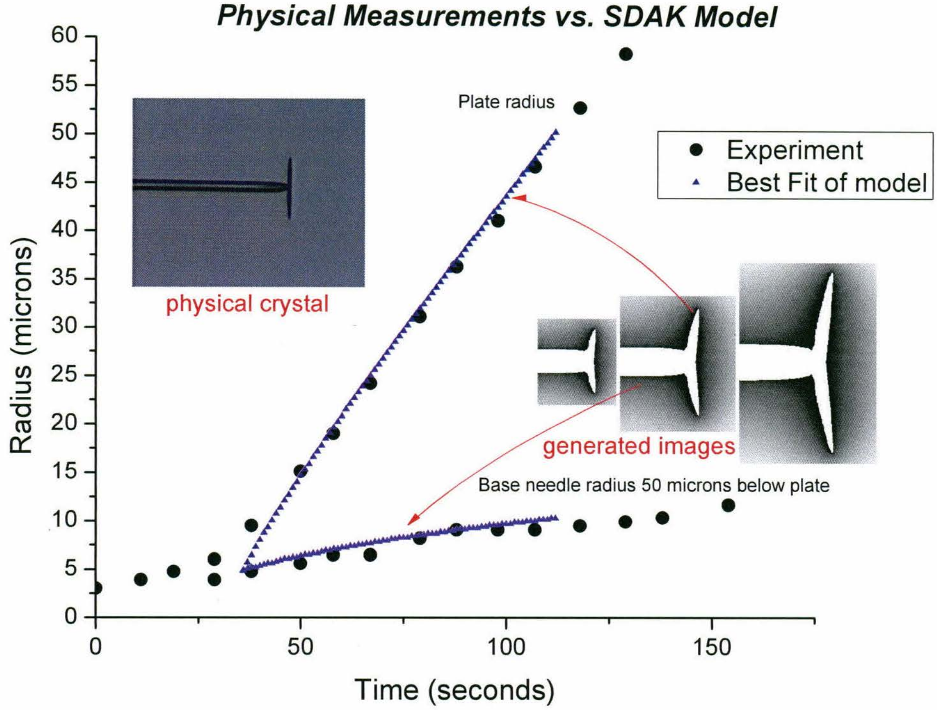

Figure 9: A plot of the SDAK model simulation and physical measurements of a crystal grown in the laboratory. For $\sigma_{0,prism} = 3\%$ and $\sigma_{0,basal} = 2\%$, the model fits the experimental data well. The two dimensions plotted are the plate radius and the base needle radius 50 microns below the plate tip.

In order to get a sense of the sensitivity to the supersaturations and thus an idea of the variance of the parameters, we've plotted the experimental results against model with various inputs. In each comparison, we varied either the basal or the prism supersaturation and kept all other parameters the same as in the best fit model. From the resulting plots, we see that the growth of the base is very insensitive to changes in the supersaturations because the plots almost completely overlap. The high sensitivity to $\sigma_{0,prism}$ corresponds to the SDAK effect of the prism parameters having a greater effect than the basal parameter sat -15^oC and therefore causing plates to form instead of columns at this temperature.

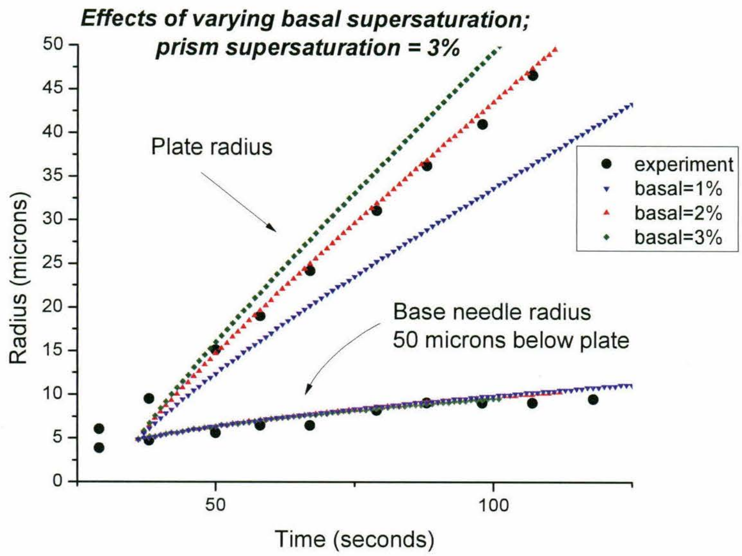

Figure 10: Variation of $\sigma_{0,basal}$ with $\sigma_{0,prism} = 3\%$. Plate growth is sensitive to changes in $\sigma_{0,basal}$.

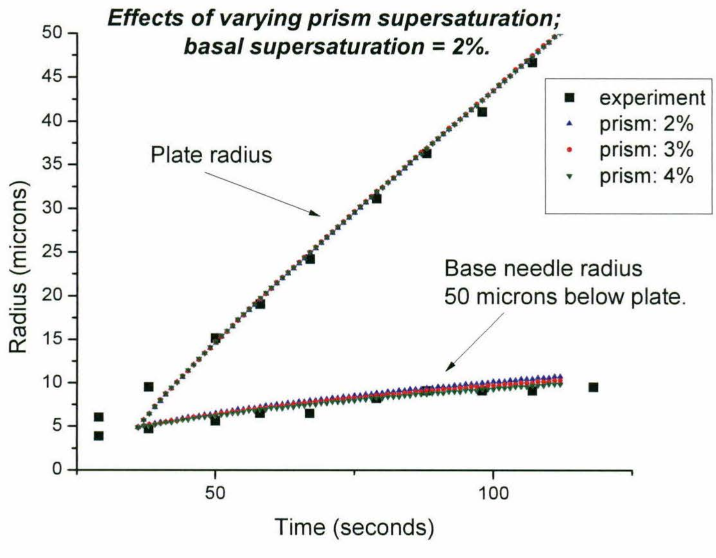

Figure 11: Variation of $\sigma_{0,prism}$ with $\sigma_{0,basal} = 2\%$. Plate growth is barely sensitive to changes in $\sigma_{0,prism}$.

The close agreement of the experimental measurements and those predicted by the model suggests that the SDAK Theory is valid. Not only did the overall thin plate morphology agree with experimental measurements, but the dimensions and growth rates also agreed.

The supersaturations used in the model were of the same order as the measured intrinsic values which suggests that the SDAK model is indeed valid and the relation between the intrinsic values and the modeled values is a direct result of the SDAK effect. Just as the SDAK model proposes, the intrinsic value of $\sigma_{0,prism}$ is decreased from 7% to 3% which would increase α_{prism}. The basal supersaturation also decreased from 4% to 2% so α_{basal} also increased. However, the prism supersaturation decreased more than the basal supersaturation, so the prism attachment coefficient was greater and therefore the prism growth dominated at this temperature, leading to a plate morphology.

At -15^{o}C where all physical experiments yield plates but pre-SDAK theory predicts columns, the SDAK effect on the prism facet is greater than that on the basal facet and this explains the prism morphology.

The close agreement of experiment with the SDAK model using the modified supersaturation parameters is a strong indicator that the SDAK theory is correct. The amount by which the supersaturations had to be altered in order to yield a good fit reflects the SDAK proposal that due to an edge instability, the supersaturations at the principal facets of a crystal are altered from their intrinsic values and the supersaturation of one facet is favored to drive the subsequent crystal growth.

References

[1] Libbrecht, K., 2005 *The Physics of Snow Crystals*, Reports on Progress in Physics, 69, 855-895.

[2] Beckmann, W., 1982 *Growth Rates and Habits of Ice Crystals Grown from the Vapor Phase*, Institut für Physikalische Chemie der TU, D 33 Braunschweig, West Germany.

[3] Bailey, M. et al, 2003 *Growth Rates and Habits of Ice Crystals between* $22^o C$ *and* $27^o C$, Journal of Atmospheric Sciences, 61, 514-544.

[4] Bailey, M. et al, 2008 *A Comprehensive Habit Diagram for Atmospheric Ice Crystals: Confirmation from the Laboratory, AIRS II, and Other Field Studies*, Journal of Atmospheric Sciences, 66, 2888-2898.

[5] Hallett, J. et al, 2009 *High resolution measurement of ice - supercooled water cloud interfaces*, Desert Research Institute, Reno, Nevada

[6] Libbrecht, K. 2012 *An Edge-Enhancing Crystal Growth Instability Caused by Structure-Dependent Attachment Kinetics*, Department of Physics, California Institute of Technology, Pasadena, California

[7] Nakaya, U. 1954 *Snow crystals: Natural and Artificial*, Harvard University Press

[8] Libbrecht, K. G., 2012 *Explaining the formation of thin ice crystal plates with structure-dependent attachment kinetics*, J. Cryst. Growth 258, 168-175 (2003)

[9] Libbrecht, K. 2012 *Toward a Comprehensive Model of Snow Crystal Growth Dynamics: 1. Overarching Features and Physical Origins*, Cornell University Library, arXiv:1211.5555 [cond-mat.mtrl-sci]