Exploring the Curved Dendritic Growth of Frost on Glass

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ABSTRACT

The crystallization and growth of ice on surfaces has been a neglected area of research. Anyone who has visited or lived in a temperate or cold climate has noticed the remarkable frost growth that occurs on a glass surface. Frost forms on surfaces below the freezing point of water and in supersaturated conditions. In this exploration, an apparatus has been constructed to grow frost in controlled conditions. Experiments were run at different temperatures, supersaturations, and on different surfaces. The frost crystals, which were grown on glass or plastic slides, were photographed under a microscope and assumed a variety of unexplained forms. Among these forms, curved dendritic growth has been the main focus of this research. Frost that was grown on glass not washed with detergent showed less of this curved branching than thoroughly cleaned glass. Frost growing on plastic had even less curved dendritic growth than frost growing on glass (washed or not washed). Results have revealed consistent patterns of the orientation of crystal axes as they curve and bend within a single crystal. A crystal that is oriented at an angle with respect to the surface is likely to have a varied growth tip as its orientation changes. This changing growth tip will then affect the direction of growth of the crystal. These relationships between orientation and growth tips are crucial to a better understanding of crystal growth on a surface.

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I. Introduction

Although ice crystallization has been studied for many years now, very little research has been done to categorize, identify, and understand the nature of frost growth on surfaces. Previous studies which share some relation include Nakaya’s study (1954) examining the growth of crystals from vapor on a suspended rabbit hair. Another similar, although not directly related study, was a study by Hallet and Mason (1958). Their study relates to the influences that changes in temperature and supersaturation may have on a crystal grown from vapor. Although many studies have been done about crystal growth from vapor, nearly nothing exists in literature about crystal growth from vapor on a surface.

Initial curiosity for this study was sparked when Charles Knight noticed an irregular frost pattern on an overhead window made of glass. The crystals that formed on this glass were many centimeters in length and extraordinarily straight (Fig. 1A). Perhaps the most interesting observation was the unexpected nature of the frost. The straight lines of frost suddenly changed direction and then continued along a different straight path at an angle to the original orientation. This phenomenon prompted Erick Adame and Charles Knight to investigate this almost completely unexplored area of science.

When frost forms on surfaces, the surface temperature is below the freezing point of water, and the air is supersaturated with respect to ice. Supersaturation exists when the air contains more water vapor than the amount that would be in equilibrium with ice. Equilibrium occurs when the ice crystal is neither growing nor evaporating.

Figure 1A. Photograph showing very straight frost growth. Window that the frost grew on was at least one meter in length. Photograph by Charles Knight.

Figure 1B. A main focus of the research was curved dendritic growth. Notice the curved branches present in this frost sample.
The researchers developed a useful technique for growing frost in controlled conditions. This enabled observations to be made based on experiments to recognize differences in growth with variables including temperature, supersaturation, and the nature of the surface.

Although the initial curiosity can be attributed to the frost growth first photographed by Charles Knight, observing frost growth in the laboratory has driven this research to focus on dendritic frost growth. Dendritic is a term which describes branching. Figure 1B illustrates how this type of frost growth branched and curved unexpectedly. Studying this pattern and other types of frost crystal growth may be useful in areas of science where crystals are very important (e.g. areas of biology and computer technology).

II. METHODS

Apparatus

An apparatus (Fig. 2) was constructed to create frost at controlled conditions. This consisted of two 3/16 inch copper plates, one above the other, placed parallel to one another one inch apart. Pipes, also made of copper, were soldered to the top and bottom plates. These pipes were attached via tubing to cooling fluid circulators which kept the fluid at the desired temperatures and ultimately maintained the temperature of the copper plates. The high thermal conductivity of copper ensured uniform temperatures across the plate surfaces. Acrylic sides were placed around the perimeter of the plates. These acrylic sides were sealed tight and were about 3/4 inches thick and one inch tall.

Outside the main section of the apparatus, styrofoam was placed above and below the two plates to provide extra insulation. Insulation of the entire apparatus was necessary to maintain control of the temperatures and to avoid evaporation tendencies.

Diagram of Apparatus

![Diagram of Apparatus]

Figure 2. This is an illustration of the apparatus, drawn to scale, that was used to create the frost for this experiment. Thermistors (not included in drawing) were used to monitor temperatures.
Procedure

Within the apparatus, glass slides (12 slides, each 50x65mm) were placed on the bottom plate. Slides were used because they are easy to handle when viewing under microscopes and while photographing. To change the nature of the surface, these slides could be thoroughly cleaned. Initial runs of this experiment used glass that was simply rinsed and dried with a paper towel. Later runs involved boiling the slides in a strong detergent for 30 minutes, rinsing thoroughly in hot water, and air-drying the slides. The slides washed in detergent were only handled wearing latex gloves to avoid contact with skin oils.

Each experiment began with the bottom plate set near the freezing temperature of water to evaporate any excess ice from previous runs. As the supply of water vapor, filter paper containing 20 ml of water was frozen onto the top copper plate. Once the slides were placed on the bottom plate, the top plate was placed over the acrylic sides and covered by styrofoam. The researchers then waited for the top plate to reach its desired temperature before finally dropping the temperature of the bottom plate to a colder temperature than the top plate.

Once the frost crystals were formed, the top plate was removed and the glass slides with the most interesting frost crystals were selected. To prevent the crystals from evaporating in the cold room, each slide was placed in a plastic Petri dish filled with hexane which protected the crystals from exposure to dry air. Hexane was used as opposed to other liquids because hexane’s chemical properties do not allow it to mix with water or ice, thus preserving the frost.

The slides were then photographed using a Nikon F 35mm camera; first for survey pictures of the entire slide, then under a microscope to focus on more interesting crystal structures. The film used was Kodak Technicon Black and White film. These photographs were developed by the researchers and used as recorded data. This complete method was repeated changing the controls of temperature, duration of crystal growth, and the nature of the crystal growth surface.

Principles

A fundamental part of this apparatus is the temperature configuration of the two plates. Since warm air is less dense than cool air, the warmer air will rise above colder air. Upon beginning the experiment, the bottom plate is warmer than the top plate and causes convection. This convection allows water molecules to diffuse evenly within the apparatus therefore creating uniform vapor pressure throughout. A graph of equilibrium vapor pressure versus temperature (Fig. 3) shows how at different temperatures, the environment may be supersaturated with respect to either water or ice, or both. At temperatures below 0°C there is a noticeable difference between the equilibrium vapor pressures of ice and water. This difference in temperature dictates how much supersaturation exists with respect to ice or water - an important variable in this experiment. It is for this reason that temperature control of the apparatus was crucial. The temperature in a typical run varied within ±0.1°C with the accuracy of the thermistors off by +0.09°C for the bottom plate and +0.05°C for the top plate.
III. RESULTS

Variables

To understand and observe the many types of frost, experiments were run using different temperatures, supersaturations, and different surfaces. These three variables were manipulated separately to view their effects on frost growth.

Changing the nature of the surface on which the frost is growing resulted in a dramatic change in the mode of crystal growth. The earliest experiments were done using glass slides (50 x 65mm) that were washed in hot water and then dried with towels. The frost crystal growth observed was very straight and showed less branching. In contrast, taking those same slides and washing them in a strong detergent for 30 minutes and allowing them to air-dry, resulted in large amounts of curved dendritic growth. An even more drastic change was observed when using a polycarbonate slide. Frost growth on these slides was minimal and the crystals tended to grow more vertically towards the vapor source.

A majority of the research was conducted using a temperature of around -16.3°C for the top plate and a temperature of around -17.6°C, for the bottom plate. To observe the effects of warmer temperatures on frost growth the plates were controlled at temperatures near -8.2°C and -8.8°C. The observed frost crystals surprised the researchers. The overall slides contained fewer crystals. Another type of frost crystal that had not yet been seen in this exploration was observed. This strange new crystal contained a main stem with slightly curved branches along it. This growth type appeared particularly interesting when examined under cross polaroids. The orientation of the stem constantly changes. It also appeared to be a polycrystal even though it was obvious that there was a single stem. This type of frost was observed on two consecutive runs with these warmer temperatures. However, warmer temperatures do not seem to be the direct cause for this type of growth. At these warmer temperatures, it becomes more difficult to distinguish if it is supersaturated with ice or water, which may have a great influence on this type of growth as well. Another possible cause for this type of growth is the nature of the glass. The consistent parallel direction of this growth suggests that a pattern exist in

Figure 3. During this experiment temperatures were maintained above the saturation line of ice without going above the saturation line of water. www.cco.caltech.edu/~atomic/snowcrystals/ice/vapor2.gif
the glass that influences the growth. However, it was evident that there was an overall
decrease in the number of frost crystals at warmer temperatures.

Changing the supersaturation was very easily done. Referring back to figure 3, it
is clear that supersaturation is a function of the temperature difference. Increasing the
temperature difference between the two plates (the upper plate always warmer than the
lower), increased supersaturation on the lower plate. Experiments were run at various
temperature differences. The top plate was maintained at a temperature of about -16.3°C,
while the bottom plate was adjusted cooler by increments of 0.7°C starting near -17.3°C.
Increasing the saturation was found not to have any major effect on the type of frost
growth. However, the researchers did notice a large increase in the number of crystals as
the supersaturation approached and exceeded saturation with respect to liquid water. In
contrast to lower supersaturations, the higher saturation runs tended to show crystal
growth that suggests more rapid crystal growth. This assumption is reasonable because
increases in growth rate occur with increased supply of moisture with snow flakes. “The
amount of moisture in the air affects the shape of the snow crystal”, (Charles and Nancy
Knight, 1973).

Observations

One of the first observations made was the curved dendritic frost growth on which
a great deal of this projects’ time was focused. However, this was not the only type of
frost growth that was observed. Changing the above variables allowed for a variety of
crystals to be photographed. Photographs provide a better understanding of the variety of
frost crystals than any description using words might do. The following series of figures
(4A, 4B and 4C) show the variety of frost crystals that were observed. Particular attention
was paid to the branching, curving, and numbers of crystals per unit area.

Figure 4A. This type of frost growth shows typical curved branching seen more prominently on
the thoroughly cleaned glass (washed using a strong detergent).
**Figure 4B.** The photo on the left shows frost growing on glass not washed with strong detergent. Experiments using this less clean glass tended to yield less curved crystals. The photo on the right is a crystal growing on polycarbonate. Crystals on this surface have a tendency to grow more vertically from the surface towards the vapor source.

**Figure 4C.** Frost growing on a clean glass surface. The mode of growth along the surface is very different across the three photographs. Similar frost patterns to these were seen in many of the experiments.
Question of Orientation

One very critical observation was how the orientation of the crystal related to the surface. This was seen in a photograph (fig. 5) of the curved dendritic growth that had been the main focus throughout this project. The photograph clearly revealed that in curving branches, the flat faces (a-axes) of the crystal tilt toward the outside of the curve. This gives some idea of the orientation of the crystal which will be useful in constructing a hypothetical explanation of the curvature itself.

![Figure 5. The flat faces that show the a-axis (known as basal faces), are evident in this photo and slant away from the inside of the curve. This is easily seen by the shadows in the pictures.](image)

IV. DISCUSSION AND CONCLUSION

A Comparison

A comparison of these frost crystals to typical snow flakes formed from vapor shows why the observed frost growth was unexpected (fig. 6). Figure 6B is a photograph of a snow crystal formed from vapor. The most “perfect” snowflakes have an amazing amount of symmetry. They usually take on the characteristic of a hexagon and have three main axes, each parallel to a hexagonal face. These axes are referred to as the a-axes. There is also one c-axis which in figure 6B would be perpendicular with the paper as well as all 3 a-axes. These same axes (both a and c) exist in frost crystals but are not as easily observed as they are in these more regular snowflakes as described in more detail by Hallet (1984).

Prior to observing the frost grown in the apparatus, one possible expectation was to see frost crystals that appeared to be truncated snowflakes. However these expectations were pushed aside with observations yielding unexplained growth patterns (fig 6A).
Crystal Orientation

These distinct differences, and even some similarities, in crystal growth may be very dependent on the crystal orientation (fig. 6). The many different possibilities of crystal orientation can cause changes in the way the tip of a frost crystal grows. A changing growth tip of a crystal can bring about a change in growth direction - specifically, curving. Macklin and Ryan briefly mention the significance of growth tips and their contribution to “non-rational growth” in crystals growing from aqueous solutions (Oct 1966). Although the present experiment grows crystals from vapor, similarities may exist. These crystals may have a different orientation throughout its growth because it is actually a single bent crystal. Viewing these crystals under cross polaroids has verified that these crystals are single crystals that seem to be bending and therefore having a constant change in orientation. To completely understand why curving occurs, a method is needed to measure the exact angle the crystal makes with the surface that it is growing on.
**Outstanding Questions**

This exploration of curved dendritic frost crystal growth on glass has brought about many questions for the researchers to answer in order to completely understand the growth of crystals on a surface. To continue this exploration further, one must create a method to measure the crystal orientation with the surface and relate this measurement with the bending of the crystal. This information would lead one to then discover a relationship between orientation and the mode of crystal growth. Finally, one would then need to examine the reproducibility of the many different types of frost growth in relationship with the initial orientation as well as the nature of the tips of growth as they frost grows.
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